Polysaccharides in drug delivery: An overview

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Technologies designed to target delivery or control drug release are known as ‘drug delivery systems’. Over the past twenty years there has been a vast amount of research utilizing polysaccharides to develop novel formulations designed to control drug delivery / release. In honor of Kevin Edgar, a former Eastman Chemical Company colleague, an introduction and overview of the use of polysaccharides in drug delivery will be presented.

Polysaccharides in drug delivery: Applications of cellulose derivatives for oral drug delivery

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Polysaccharides represent an important group of excipients. Particularly, cellulose and its derivatives are commonly used excipients for oral route of drug delivery. For oral delivery, cellulose derivatives are used to meet different requirements such as fillers, solubility and bioavailability enhancers of active pharmaceutical ingredients, ease manufacturing of dosage forms or to achieve certain release profile from formulations. Of particular interest is the use of cellulose derivatives to improve solubility and bioavailability of poorly water soluble drugs. It is estimated that approximately 40% of active substances currently in development fail because of low efficacy which can result from poor bioavailability arising from ineffective intestinal absorption and/or undesirable metabolic activity. To improve drug delivery, the amorphous form of a poorly water-soluble drug compound is often used to generate supersaturated solutions. The supersaturated solutions generated from the dissolution of amorphous solids may lead to an increase in absorption compared to that of a saturated solution if supersaturation can be maintained for a physiologically-relevant type period. However, to maintain supersaturation, crystallization (nucleation and crystal growth) must be prevented and polymeric additives, especially cellulose derivatives are used for this purpose. In addition, it has also been demonstrated that supersaturating bioactive delivery systems, consisting of amorphous solid dispersions of the poorly-water soluble compound with a water soluble polymer are capable of generating colloidal dispersions (nanosuspensions) when dissolved in aqueous solution and these dispersions are important to the bioavailability enhancement often seen with amorphous solid dispersions.
In this presentation, an overview with case studies, of the different uses of cellulose derivatives in formulations for oral drug delivery in drug development will be discussed. The underlying factors that affect the ability of polymeric additives to inhibit nucleation and crystal growth for a given drug compound will be presented. In addition, we will also report on the use of cellulose derivatives to improve nanosuspension yield of amorphous solid disperions in aqueous solution thus improving bioavailability in preclinical studies.

CELL 3

From computational modelling towards mechanistic design of polymers for oral drug delivery

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Amorphous solid dispersions can be used to improve the bioavailability of a high percentage of poorly water soluble drugs. However, amorphous solids are highly unstable, and the drug will crystallize over time, causing a decrease in solubility. Polymers are commonly employed to stabilize amorphous formulations and sustain high drug concentrations in solution for prolonged periods of time. Nevertheless, the molecular mechanism of stabilization is unclear, which makes the rational design of polymers challenging. This study combined experimental results and computational modelling to provide molecular insight into key structural and chemical features important for preventing nucleation of a model drug, helping us in the rational selection of a group of chemically diverse novel cellulose polymers. Two sets of polymers were studied. The first, included cellulose esters with diverse substituents including carboxylic acids, esters, ethers, hydroxyls, amides, amines, and sulfides. The second, included cellulose ethers with various degrees of substitution of side-chains ending with a carboxylic acid; and branched polymers including sulfides and carboxylic acid groups. Nucleation induction times showed that effective polymers contain carboxylate groups in combination with an optimal hydrocarbon chain length. There is an optimal degree of substitution of carboxylic acids, and it is essential to find the right hydrophobicity balance to create effective materials. As is made clear by quantum chemical calculations, the effectiveness of polymers containing carboxylate groups can be attributed to a more favorable solvation free energy, in comparison to non-charged groups. Moreover, molecular dynamics simulations of oligomers showed that polymers with long hydrocarbon chains tend to self-aggregate exhibiting shorter radii of gyration and solvent accessible surface area per atom.

CELL 4

Polysaccharides: Ubiquitous platform for controlled delivery of bioactive molecules

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Polysaccharides are ubiquitous natural occurring polymers widely used for a variety of biomedical applications including drug delivery and tissue regeneration. These polymers due to their biochemical similarity with human extracellular matrix components are readily recognized and accepted by the body. Natural polymers inherit numerous advantages including natural abundance, relative ease of isolation, and room for chemical modification to meet varying technological needs. The term “drug delivery” refers to approaches or systems for administering a pharmaceutical active ingredient to achieve a therapeutic effect in humans or animals. These approaches or systems aim to improve treatment efficacy, safety and/or patient compliance and may involve the use of different medical devices, administration routes and drug formulations. Polysaccharides are commonly used materials in the design of drug delivery systems because they are generally regarded as biocompatible and biodegradable, and can possess other desired properties, such as the ability to adhere to the body's mucosal linings. Polysaccharide based
nanoparticles may hold the positive features of both nanoparticles and polysaccharides, and are suitable for both parenteral and mucosal administration of drugs. In certain particular applications, the need for the polysaccharide functionalization become compulsory to achieve the desired reactive sites for the immobilization of the active principles. This presentation gives an overview of the most recent achievements made by the researchers from “Petru Poni” Institute of Macromolecular Chemistry Iasi, in the field of using polysaccharides (both unmodified and chemically functionalized) as efficient platform for drug delivery.

CELL 5

Cellulose nanocrystal conjugates for drug delivery and bioimaging applications

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Nanoparticles hold great promise for technological advances in the early detection and treatment of diseases. Many types of nanoparticles, including lipid-based micelles and liposomes, polymeric micelles and dendrimers, carbon nanomaterials, and inorganic and metallic nanoparticles, are being investigated for a great number of potential applications, such as site-specific drug delivery, biosensors for in-vitro and in-vivo diagnostics, and contrast agents for medical imaging. The shortcomings of many of these systems include low stability in the bloodstream, systemic or cellular toxicity, generation of toxic degradation products, and accumulation over time in certain organs such as the kidneys, liver, or spleen. For the past decade, in collaboration with biologists and biomedical engineers, we have investigated the potential of cellulose nanocrystals in biomedical applications. Cellulose nanocrystals are oblong nanoparticles obtained by partial degradation of a cellulose starting material. Their elongated shape and abundant surface hydroxyl groups distinguish cellulose nanocrystals from many of the above mentioned nanomaterials. This presentation reviews our current knowledge of the toxicity of cellulose nanocrystals and our studies of cellulose nanocrystal conjugates for targeted drug delivery and bioimaging applications.

CELL 6

Supramolecular design of cellulose hydrogel microspheres

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Cellulose microspheres are spherical particles with diameter above 10 μm and surface area of several hundred m²g⁻¹. They are prepared using cellulose solutions and different methods of coagulation in anti-solvents. Cellulose is the main component of the spheres and hybrid spheres can be prepared in combination with synthetic polymers or inorganic particles. Cellulose microspheres can be largely used in biomedical applications such as drug delivery, protein immobilisation, tissue regeneration and separation of isomers in pharmaceuticals. In the present study, we report the supramolecular design of cellulose-sulfonate hydrogel beads by blending water soluble sodium cellulose ethyl sulfonate (CES) with the pretreated cellulose in sodium hydroxide-urea- water solvent system at -6 °C followed by coagulation in the 2M sulfuric acid system. The increasing of CES amount from 10 to 90% had a substantial effect on the storage (G')- loss (G'') moduli and viscosity of the blended solutions. The CES concentration up to 50% in blends lead to the formation of physically stable hydrogels after coagulation in acidic medium at pH 1 and have shown the retention of near about same CES concentration at pH 6 after continuous water washings. The increased sulfonate content also enhanced the water holding capacity and internal porosity of the beads. The ATR-FTIR, RAMAN spectrometry was used for the qualitative determination of
sulfonate groups and SEM-EDX for the quantitative estimation in dried beads. In this research, we have established a correlation between the presence of anionic charge in the polysaccharide blend and stability of the prepared hydrogel bead. Hence our research provides a systematic methodology to design functional, highly porous cellulose hydrogels having the potential to be used as drug carriers in regenerative medicine and pharmaceuticals.

CELL 7

**Immunosensor based on cellulose nanofibrils for C-reactive protein detection**

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C-reactive protein (CRP) is an acute phase protein which has been widely used as a predictor of cardiovascular disease. We report herein the generation of cellulose nanofibrils (CNF) based immunosensors for CRP detection using quartz crystal microgravimetry (QCM). Ultrathin film of carboxylated CNF on the QCM chip was prepared via two methods: (i) CNF was firstly spin coated to QCM sensor, and then carboxylated using 2,2,6,6-tetramethyl-piperidine 1-oxyl (TEMPO)-oxidation method to convert the hydroxyl groups on CNF to carboxyl groups or (ii) the pre-carboxymethylated CNF suspension was spin coated directly on QCM chip. A ligand, protein A was conjugated to carboxylated CNF via 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride/N-hydroxysuccinimide (EDS/NHS) coupling chemistry for the further oriented immobilization of anti-human C-reactive protein (anti-CRP). The two methods give different surface density of carboxyl groups, which further influence the binding amount of protein A and anti-CRP. The detection efficiency for CRP of surfaces with oriented and randomly immobilized anti-CRP was compared. The specificity of CNF immunosensor for CRP detection and detection range was also investigated.

CELL 8

**Self assembly of *A. Tequilana* fructans and encapsulation of ibuprofen for targeting oral drugs to the colon**


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The fructans from *Agave tequilana Weber var. azul* (ATF) have a great potential as carriers of drugs to the colon due to their chemical structure, which contains β 2-1 linkages and make them non digestible in upper digestive tract. Additionally, ATFs have β 2-6 branches, which make them more readily soluble for further chemical modifications. ATFs are enzymatically degradable in the colon. The design of new drugs requires better transport and delivery systems. ATF derivatives (esters such as acetates, succinates or alkylates) have a great potential for designing technologies for controlled release. ATF esters can be tailored to meet different partition coefficients that promote their self-association thus enabling encapsulation capacity. In this work we esterified ATF with acetate, succinate, lauryl and mirystoyl esters, studied their solution and association behavior (critical micelle concentration, rheology and density of the solutions) and their capacity to encapsulate ibuprofen as model drug.
CELL 9

Effect of ethylene glycol-water mixed solvent on the synthesis of iron oxide/carbon nanocomposites and their adsorption performance

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We synthesized the high ferromagnetism iron oxide/carbon nanocomposites by the simple precursor and thermal calcination method. And the precursor was prepared by a microwave-assisted hydrothermal method in ethylene glycol (EG) and water mixed solvent. Furthermore, we discussed the different morphologies, phases, and magnetic properties of iron oxide crystals by changing the volume ratio of EG and water solvent. The features of nanostructure iron oxide were characterized by X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), and magnetic properties. Meanwhile, the investigation of dye adsorption revealed that iron oxide/carbon nanocomposites exhibited excellent dye absorbability and substantial reusability. These results indicate that the synthesis of iron oxide/carbon nanocomposites have great potential application in effective treating wastewater.

CELL 10

Solvent-exchanged porous bacterial cellulose nanopaper as reinforcement for polymers

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Bacterial cellulose (BC) is frequently regarded as an excellent candidate to produce green composite materials due to its outstanding mechanical performance and its renewable origin. The method of resin impregnation of BC nanopapers has often been used to produce composites with a high fibre volume fraction. In order to exploit the mechanical properties of BC, good resin impregnation of the fibres is key to achieving strong composites. However, traditional water dried BC nanopapers are difficult to impregnate due to their low porosity and permeability.

In this study, BC nanopapers with different bulk and surface properties have been prepared by solvent exchange from water to ethanol or acetone before drying. Water dried BC nanopapers exhibited a porosity of 33.6% whereas ethanol and acetone dried nanopapers had a porosity of 49.7% and 56.8%, respectively. The surface area and permeability of the nanopapers also increased when using a solvent with lower surface tension and lower polarity and hydrogen bonding capability. In this work, it is hypothesized that these solvent properties had an effect on the capillary forces during the drying of the wet BC cakes that led to the pore collapsing of the cellulose fibrous network. The degree of pore collapsing of the BC fibrous networks also had an effect on the morphology, thermal stability and mechanical properties of the nanopapers. The reinforcing ability of the BC nanopapers in polymer composites was also investigated. The composites were prepared by impregnating the BC nanopapers with acrylated epoxidised soybean oil (AESO). The mechanical properties and architecture of the composites varied depending on the porosity degree of the nanopapers.
**CELL 11**

**Water-based dissolution of wood cellulose and design of novel cellulose-based nanocomposite materials**

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Cellulose dissolution and regeneration have had important applications for a long time, mainly for textile fibres and for the preparation of cellulose derivatives. Cellulose can be dissolved in water at extreme pHs, in particular if a cosolute of intermediate polarity is added. We argue that cellulose is significantly amphiphilic. Cellulose has a strong tendency to re-assemble when dissolved; this process is strongly affected by surfactants and other additives decreasing hydrophobic interactions. In this work we have explored cellulose dissolution under aqueous alkaline conditions with urea as a solution-promoting cosolute of intermediate polarity. We have considered the co-regeneration of cellulose with another polysaccharide to prepare novel renewable materials. The behaviour of cellulose and chitosan polymer solutions and their mixtures was studied by rheology measurements. The dynamic rheology and the influence of time and temperature on the gelation of cellulose-chitosan solutions mixed at different ratios were investigated. Cellulose-chitosan nanocomposite particles and films were successfully prepared for the first time. Via mixing of the biopolymer solutions, emulsification (w/o) and regeneration by temperature induced sol-gel transition followed by addition of an antisolvent, spherical microparticles were obtained. Films were cast and regenerated. Using tuned protocols, different particle sizes, biopolymer distribution, porosity and mechanical performance could be obtained. Furthermore, a facile one-pot synthesis of spherical polycrystalline copper nanoparticles templated by regenerated cellulose in aqueous alkaline solution was demonstrated. The antibacterial properties were investigated for all the novel cellulose materials prepared.

**Figure.** From left to right; images of spherical cellulose-chitosan nanocomposite particles, transparent cellulose-chitosan films, and copper nanoparticles prepared *in situ* in a cellulose matrix.

**CELL 12**

**Facile Method for the Suspension, Dispersion, and Fabrication of Cellulose-based Plastics**

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Cellulose is one of the most abundant natural resources on this earth, and it is an important structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Cellulose history dates back to as early as the 1860s, when the first rayon fibers were commercialized by Courtaulds. Cellulose is a long chain of linked sugar molecules and due to the strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in common solvents. To date, limited successes made on the invention of new solvents to directly dissolve (or suspend) cellulose for commercialization usage and the increased toxicity associated with the current dissolution techniques has lessen the attractiveness of cellulose for use in the plastic industry. But, Tuskegee University researchers have discovered a new method that can be used to suspended tiny particles of cellulose “micro- and nanocellulose” without any modification of the backbone structure in an organic solvent that is commonly used in the plastic industry, which will remove the current limitations and allow for the creation of a new kind of biodegradable cellulose-based plastic. This product can be used in the formation of items ranging from packaging materials to plastic covers used as enclosures for electronics. As of date, under our method, we have successfully fabricated both biodegradable and non-biodegradable plastics with superior mechanical and thermal properties.

**CELL 13**

**Cellulose/vaterite nanocomposites: Sonochemical synthesis, and their applications in drug delivery and protein adsorption**

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Vaterite is one of the anhydrous polymorphs of calcium carbonate (CaCO₃), which is recognized as an important biomedical material due to its features such as high specific surface area, high solubility, high dispersion, and small specific gravity. However, the synthesis of vaterite with controllable size and morphology in the absence of any chemicals such as surfactant is still remaining a challenge. Herein, we report a facile, fast, surfactant-free and green sonochemical method to prepare vaterite by using cellulose as substrate and structure-directing agent in ethylene glycol at ambient condition. Experimental results showed that the phase of CaCO₃ can be regulated by adjusting the cellulose concentration in the reaction system, and porous vaterite nanospheres (assembled from rice-shaped vaterite nanoparticles) with average diameter of 206~246 nm can be obtained. The important role of cellulose and the formation mechanism of vaterite are explored and discussed in detail. Furthermore, the as-prepared cellulose/vaterite nanocomposites can be used as anticancer drug nanocarriers, and exhibit a high ability to damage cancer cells after loading docetaxel. The weight percentage of docetaxel in the cellulose/vaterite nanocomposites drug-delivery system was estimated to be approximately 29.37% and the docetaxel-loading capacity of the nanocomposites was about 416 mg g⁻¹ (mg drug per gram carrier). The as-prepared nanocomposites are also explored for protein adsorption using hemoglobin as model protein and showed relatively high protein adsorption ability (248 mg g⁻¹). These results indicate that the as-prepared cellulose/vaterite nanocomposites are promising for applications in biomedical fields, such as drug delivery and protein adsorption.

**CELL 14**

**Simple synthesis method towards amino-functionalized carbon dots: Carbonization of chitosan**

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Carbon dots (CDs) as a new series of fluorescent nanomaterials have drawn great attention in recent years owing to their unique properties and shown promising prospects as benign candidates for various potential application. However, many of the synthesis methods involve expensive or toxic starting materials, high temperature, long reaction time and further surface-passivation. Therefore, exploring
alternative route and starting materials for the synthesis of CDs are highly needed. Chitosan is the N-deacetylated derivative of chitin (a naturally abundant mucopolysaccharide), containing high amount of amino (-NH$_2$) and hydroxyl (-OH) functional groups, which accepted as carbon precursor to synthesize CDs owing to its natural, nontoxic, inexpensive and biocompatible properties. In this work, we presented a very simple approach to synthesize amino-functionalized CDs by one-step carbonization treatment of chitosan, which was scarcely studied before. In this method, neither a strong acid solvent nor surface passivation reagent was used. Both the formation and the functionalization of CDs were accomplished simultaneously. Meanwhile, this green, cheap and convenient process represented a potential advance for large-scale production. The physical structure, chemical structure and optical properties of the as-prepared CDs were characterized in many ways. The as-prepared CDs possessed desirable amino functional group on their surface and exhibited bright luminescence with absolute quantum yield (QY) of 4.34%, together with the excitation-, pH-dependent and up-conversion fluorescence behaviors. Furthermore, the as-prepared CDs showed good stability, less toxicity, biocompatibility and excellent fluorescence imaging ability, which demonstrated that the as-prepared CDs may have the potential applications in biosensing, cellular imaging and drug delivery in the future.

CELL 15

Synthesis and characterization of hydroxypropyl methylcellulose/xyloglucan blend films for release of gentamicin drug

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Novel blend films of hydroxypropylmethylcellulose (HPMC) and Xyloglucan (XG) were prepared by crosslinking them with citric acid. The HPMC/XG blends were prepared at different weight ratios: 25/75, 50/50, 75/25. The blends and pure polymer films were characterized by FTIR, TGA, SEM and tensile tests. The FTIR spectra showed that the occurrence of the interactions between citric acid with HPMC and XG molecular chains through ester bond formation. The highest tensile strength and Young’s modulus of the blend films were observed for HPMC and XG blend at the ratio of 50/50 as 25 MPa and 689 MPa, respectively. The porous structure of the blend films was demonstrated by SEM. The study on the molecular conformation changes of HPMC and XG upon blending was investigated by means of circular dichroism (CD). The CD spectra showed that HPMC and XG chains in the blends presented disordered conformation (coil), while pure HPMC and pure XG showed ordered (helixes) and coil conformation, respectively. An in vitro drug loading/release experiment was carried out on the crosslinked polymeric films using gentamicin sulphate (GS). The maximum GS loading of 83% was achieved for 50/50 HPMC/XG blends, at pH 5.5. The release kinetics of gentamicin sulphate from all
crosslinked polymeric films were investigated at pH 7.4 and the experimental data were fitted with the Korsmeyer–Peppas model; all formulations presented a non-Fickian release mechanism. The GS loaded HPMC, XG and their blend films showed excellent antibacterial properties against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*), evidencing their potential as a new type of biomaterial for topical biomedical applications.

**CELL 16**

How can a single methyl group drastically modify the microstructure of a biocomposite and affect its mechanical properties?

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According to the global trend in the world, many studies are conducted in order to valorize plant biomass at its best potential, in particular as materials. On one hand, plant fibers are used to reinforce composites and to enhance their thermal and mechanical properties. On the other hand, the lignin fraction produced by wood and paper industries, which is burnt now to produce energy, should be valorized through chemistry for the synthesis of high value-added compound. In this work, ferulic acid and its derivatives, which can be obtained from lignin, were used to influence the aspect ratio of lignocellulosic fibers incorporated in biocomposites materials, one of the key parameters for mechanical thermoplastic's fiber reinforcement. In this work, two ferulic acid derivatives were synthesized by enzymatic chemistry following a green process and subsequently pulverized on hemp fibers. The first ferulic acid derivative was a macrobisphenol while the second one was obtained after the methylation of the phenolic functions of the latter. Then, these pretreated lignocellulosic fibers were incorporated in a polycaprolactone matrix during a single screw extrusion process. Fibers were extracted from the polymer by Soxhlet and analyzed to measure the exact fiber content and the aspect ratio distribution after process. Tensile test specimens were injected and mechanical properties were measured. Chemical analysis were conducted by steric exclusion chromatography to measure the impact of the ferulic acid derivatives on the molar mass of the matrix. Rheological analysis provided information about the plasticizing effect of the ferulic acid derivatives on the materials. Hemp fibers, ferulic acid derivatives and crude polycaprolactone were also analyzed by Raman spectroscopy to define their spectral profile. As a result, the microstructure of the composites after the extrusion process was determined by Confocal Raman Imaging and was correlated with the mechanical properties measured by tensile tests. We evidenced that the very single methylation of the macrobisphenol led to significant differences on the mechanical properties and the structure of the composites. Two hypothesis were investigated to explain such effects: a stronger interaction between hemp fibers and ferulic acid derivative changing the microstructure and/or an increased plasticizing effect of the ferulic acid derivative on the polymeric matrix.

Cellulose Structure & Biosynthesis

N. Carpita, Organizer; D. Cosgrove, Organizer; P. Langan, Organizer; H. M. O'Neill, Organizer; J. Zimmer, Organizer; N. Carpita, Presiding; D. Cosgrove, Presiding Papers 17-24

**CELL 17**

3D Nano-architecture and mechanical properties of *Arabidopsis thaliana* plant cell walls by cryo-electron tomography of vitreous sections

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Plant cell walls provide rigidity and mechanical strength. Primary cell walls consist of hexose- and pentose-based polymers constituting cellulose, hemicellulose and pectin. Mature thick secondary cell walls often display sub-regions dubbed as S1, S2 and S3 and additionally contain the highly cross-linked aromatic polymer lignin, which constitutes 10-25% of the macromolecular dry cell wall mass at maturity, and which is thought to fill the cell wall matrix space. Cellulose forms a tightly-packed ~3.5 nm thick crystalline elementary fiber, whereas hemicellulose and pectin are usually depicted as individual glycopolymeric strands that exhibit various degrees of branching, connecting neighboring cellulose fibers. Partial alignment and close interaction of hemicellulose with cellulose fibers in primary cell walls have been proposed. Pectin is most prominently found in the middle lamella where it is thought to act like a glue, connecting two adjacent cells. The precise 3D organization of the cellulose-rich microfibrils and interconnecting hemicellulose strands has been under debate for at least half a century, with several conflicting models being proposed. In this study, we have determined the 3D architecture of primary and secondary cell walls of Arabidopsis thaliana inflorescence xylem parenchyma cells and xylem tracheary (XTE) elements cells. Using cryo-electron tomography of unstained vitreous sections, extensive quantitative volumetric statistical analysis and computer-assisted design (CAD) modeling, we determined the 3D structure of individual prototypic microfibrils and cross connections, as well as the 3D supramolecular organization. Furthermore, we subjected the density-threshold segmented tomographic density maps as well as idealized models to computational simulations of their mechanical properties, i.e. with respect to radial turgor pressure, axial compression, and shear forces. As a result of our 3D analysis and simulations we conclude that the examined Arabidopsis thaliana XTE cell wall appears to be optimized for ductility and flexibility rather than maximal load bearing.

CELL 18

Visualizing cellulose microfibril movements during stress-induced and endoglucanase-induced extensions of plant primary cell walls

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Growing plant cells synthesize a strong yet extensible cell wall composed of long, thin cellulose microfibrils that are dispersed and laterally bonded to one another in a hydrated matrix of pectins, hemicelluloses, and glycoprotein. Recent advances have led to a rethinking of how these wall components interact with one another (1-4). With AFM we characterize the organization of cellulose microfibrils in never dried cell walls of onion epidermis. The interaction of microfibrils with matrix was visualized in two-color maps based on height and modulus. When the cell walls are stretched to reveal microfibril re-arrangements after plastic or elastic deformation or after endoglucanase-mediated cell wall creep, we find different patterns of microfibril movements. Some of the remaining unsolved problems in primary cell wall structure and cell wall mechanics will be highlighted.
FM images of the surface of onion epidermal cell wall before and after elastic extension. Note the changes in microfibril shape and orientation.

CELL 19

Advances in combining neutron scattering with molecular simulations to understand cell wall structure

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Plant cell walls are hierarchical composites consisting mainly of bundles of crystalline cellulose fibrils embedded in a hydrated matrix of less ordered, covalently coupled, hemicellulose, lignin polymers, and pectins. This complex architecture evolved in plants for strength, resistance to degradation, and to facilitate growth. We have assembled a platform of experimental techniques that allows us to image cell wall morphology over the large range of relevant length scales. These techniques include world-leading neutron scattering and high performance computing user facilities collocated at Oak Ridge National Laboratory. The experimental results are being interpreted using simulation techniques, thereby revealing underlying physical processes that determine plant cell wall morphology, and that drive changes in morphology as cell walls are exposed to different environments or process conditions. We will discuss our most recent advances using this integrated approach.
**CELL 20**

**Microfibril orientation, spacing and bundling in secondary cell walls: Implications for catalytic deconstruction**

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The physicochemical complexity of plant cell walls, evolved to resist deconstruction, remains a challenge for the economic production of fuels and chemicals from lignocellulosic biomass. Using multi-scale microscopy and quantitative image analysis, we have demonstrated how different thermochemical and catalytic treatments alter the micro- and nanostructure of biomass and affect the efficiency of biological and direct chemical catalytic conversion. Efficient catalytic conversion requires high accessibility of the plant cell wall biopolymers to catalysts and is a major hurdle to biomass deconstruction. We have employed an image-based framework using 3D electron tomography data that enables accessibility analysis over a range of catalyst sizes and suggests mechanisms for improving accessibility. In addition to this analysis that focuses on the voids generated within secondary cell walls, we have been analyzing the lamellar organization of the cellulose microfibrils. In our earlier work, we developed methods to discern and model individual cellulose microfibrils within thermochemically pretreated biomass by fitting parametric space curves to tomographic datasets and measuring the nanoscale spacing and curvature of microfibrils. We used the fitted curves to construct atomistic models that reflect the macromolecular geometry of microfibrils in plant cell walls. More recently, we have been applying large-scale shape analysis techniques to study the organization of cellulose microfibrils and their distribution in two-dimensional sheets or lamellae. These methods have enabled the statistical study of cellulose organization within secondary cell walls, including orientation, inter- and intra-lamellar spacing and bundling, and will ultimately lead to a deeper understanding of patterns and mechanisms in cell wall biosynthesis and deconstruction for biomass conversion.

**CELL 21**

**Polymorphic structures and pectin interactions of cellulose in primary plant cell walls from multidimensional solid-state NMR**

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Cellulose constitutes the main scaffold of plant cell walls, but its structure has long been elusive because of the low crystallinity of plant cellulose compared to bacterial and algal cellulose and the significant interactions of cellulose with matrix polysaccharides in plant cell walls. By ¹³C labeling of primary cell walls and employing high-field two-dimensional ¹³C-¹³C correlation NMR, we have obtained highly resolved 2D spectra that reveal the presence of 5 different interior cellulose conformations and at least 2 different types of surface cellulose ¹. These polymorphs have distinct ¹³C chemical shifts, which differ from the chemical shifts of bacterial and algal cellulose. By correlating the chemical shifts between different polymorphs and with the chemical shifts of matrix polysaccharides, and by assessing water accessibility, we have identified the locations of these polymorphs in the microfibril. The resulting model of a conformationally heterogeneous microfibril is in excellent agreement with quantitative ¹³C NMR spectra that indicate at least 24 glucan chains in the primary wall cellulose microfibril ². This cellulose structural polymorphism is found in both dicot and grass primary cell walls, suggesting its chief origin as the interactions of cellulose with matrix polysaccharides in the wall.

Our studies of the primary cell walls of seedlings of model plants showed that cellulose and pectins contact with each other on the molecular scale ². We recently conducted a structural study of the cell
walls of the flowering tissues, or inflorescence, of *Arabidopsis*. Interestingly, the faster growing regions of inflorescence show higher pectin content, higher hydration, and weaker cellulose-pectin interactions, indicating that weakening cellulose-pectin interactions causes cell wall expansion. This finding highlights the importance of cellulose-pectin interactions for the structural integrity and rigidity of the cell wall.

CELL 22

**Mesoscale order of cellulose microfibrils in plant cell walls: Sum Frequency Generation (SFG) vibrational spectroscopy study**

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Crystalline cellulose microfibrils are embedded in wall matrix polymers and assembled into hierarchical structures that are precisely designed for specific biological and mechanical functions of plant cell walls. The cellulose microfibril assemblies inside cell walls are extremely difficult to probe with linear optical spectroscopy such IR and Raman. This quandary can be resolved by the use of sum frequency generation (SFG) vibrational spectroscopy. The SFG process is a non-linear optical process which requires the noncentrosymmetry in space and phase synchronization over the optical coherence length. This principle can be used to distinguish the three-dimensional organization of crystalline cellulose microfibrils interspersed in amorphous polymer matrices such as plant cell walls. The overall SFG intensity, alkyl peak shape, and alkyl/hydroxyl intensity ratio are sensitive to the lateral packing and net directionality of the cellulose microfibrils within the SFG coherence length scale. This talk will address how SFG can be used to reveal the cellulose crystal structure and mesoscale cellulose microfibril packing in secondary cell walls and primary cell walls in their native states.

CELL 23

**Density functional theory modeling of cellulose polymer assembly**

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The assembly of the cellulose microfibril (CMF) from the cellulose synthase complex (CSC) is not yet understood. Recent progress in imaging the CSC and analyzing the size and structure of cellulose makes it possible to envision modeling the CMF assembly process because the initial and final states are fairly well constrained. Previous work has tackled this problem using coarse-grained and classical molecular dynamics simulations. We apply dispersion-corrected density functional theory (DFT) calculations that have proven accurate in reproducing cellulose structure, vibrational frequencies and 13C NMR chemical shifts. In this work, methyl-terminated decamers of cellulose (C62O51H106) interactions were modeled edge-on and in layer configuration with and without explicit H2O to calculate the energy of assembly. Results indicate that the layer-layer interaction is more favorable in water, especially considering entropic effects, consistent with predictions of Cousins and Brown based on classical MD simulations. However, the solvent properties of water within the space where CMF assembly occurs are not necessarily equivalent to bulk water due to slower dynamics. Consequently, we investigated the polymer interaction energies as a function of dielectric constant using polarized continuum models. The results do not change significantly between water (ε = 78.4) and methanol (ε = 32.7), but the favorability of side-on interactions become favorable in a chloroform-like solvent (ε = 4.81). Based on this model prediction, it becomes imperative to better analyze the solvent properties of the CMF formation space.
within the plant cell wall. These results can be used to benchmark force field simulations of the CMF assembly process. Results indicate that the CHARMM force field is reasonably accurate for gas-phase calculations, but improvements in the parameterization are possible.

**CELL 24**

**Impact of alterations in lignin deposition on cellulose organization of the plant cell wall**

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Coordination of assembly of polymeric components of cell walls is essential for plant growth and development. Given the degree of co-mingling among cell wall polymers, cellulose organization must surely be dependent on the organization of other polymers such as lignin. Here we study that codependency by investigating the structural organization of cellulose fibrils in stems from Arabidopsis plants with altered lignin biosynthesis. Scanning X-ray microdiffraction was used to study cellulose architecture in the various tissues of the stem. Several mutations—most notably those exhibiting cell walls deficient in lignin exhibited significant decrease in the proportion of oriented cellulose fibrils. Distinctions between tissues were maintained in all variants and even in plants exhibiting dramatic changes in cellulosic order, the trends between tissues (where apparent) were generally maintained. The resilience of cellulose to degradation was investigated by analysis of samples stored in water for 30 days prior to data collection. This work demonstrates that changes in lignin biosynthesis lead to significant disruption in the orientation and order of cellulose fibrils in the stem. These dramatic phenotypic changes, in mutants with lignin rich in aldehyde or H-units, correlate with the impact the mutations have on the enzymatic degradation of the plant cell wall.

**Nanocellulose Processing & Analysis**

M. Bortner, Organizer; W. Y. Hamad, Organizer; T. Lindström, Organizer; M. Roman, Organizer; M. Bortner, Presiding Papers 25-32

**CELL 25**

**Deep eutectic solvents in nanocellulose production**

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Deep eutectic solvents (DESs) are promising novel chemicals that can function as solvents, reagents, and catalysts in many applications. They are readily available, have low toxicity, are biodegradable, and exhibit negligible vapor pressure. In general, DESs are attained by complexation of the halide salt of quaternary ammonium or phosphonium cation (as the hydrogen bond acceptor, HBA) along with a hydrogen bond donor (HBD), for example, urea, glycerol, or ethylene glycol. A characteristic property of DESs is that they exhibit a lower melting point compared to either HBA or HBD because the strong hydrogen bonding prevents the parent components from crystallizing. Due to the advanced properties, DES has been studied as novel media for pretreatment of cellulose towards the nanocellulose production. DES based choline chloride and urea function as a non-hydrolytic pre-treatment media to promote nanofibrillation of birch cellulose pulp using a microfluidizer to obtain cellulose nanofibers (CNF). On the other hand, DES formed between choline chloride and oxalic acid dihydrate promotes the degradation of natural cellulose fibers and cellulose nanocrystals (CNCs) are successfully obtained after mechanical
disintegration of pretreated fibers. DES can also serve as reaction media for chemical modification of cellulose and for example anionic cellulose was produced using succinic anhydride in DES based on urea and lithium chloride. Anionically stabilized CNFs were then easily obtained after mild mechanical disintegration using microfluidizer. As DESs are only used as pretreatment media before nanofibrillation of cellulose, they are easily separated from cellulose fibers and in best cases even recycled several times.

CELL 26

Ionic liquid-cellulose-in-oil microemulsions: Molecular weight dependence and directed morphology of cellulose nanoparticles

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Cellulose is a non-toxic and biocompatible polymer with potential applications ranging from composites and surface engineering to drug delivery and medicine. Cellulose can be extracted from natural sources using aggressive techniques or more recently shown by using ionic liquids (IL). However, while processing cellulose into fibers, textiles and films using harsh techniques and more recently, ILs, precise control of cellulose nanoparticle morphology has been difficult to demonstrate. For years, microemulsions have been used to fabricate and template the shape and size of both inorganic and organic nanoparticles. Utilization of IL microemulsions can serve as templates to direct the formation and morphology of cellulose and cellulose derivative nanoparticles. However, the solubility mechanism of cellulose in ILs and high solution viscosity are two major challenges that make the formation of IL-cellulose microemulsions difficult. Here we present preliminary work addressing those challenges, elucidating the dependence of surfactant type, as well as cellulose molecular weight on the stability of IL-cellulose microemulsions and the nanoparticles produced from them.

CELL 27

Imidazole: A new tunable reagent for producing nanocellulose

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Imidazolium-based ionic liquid (ILs) have been reported to be efficient reagents to extract cellulose nanocrystals (CNCs) from cellulosic materials. The hydrolysis of cellulose by imidazolium-based ionic liquids has been so far attributed to a H⁺-catalyzed mechanism. However, impurities in imidazolium-based ILs, in particular imidazole, have also shown to give rise to significant side-reactions on cellulose. In this context, this work posed the question of the action of imidazole on wood pulp under similar conditions to those previously shown to effectively produce CNCs with ILs. This study reveals imidazole to be an effective medium (reactant) for the extraction of nanocellulose from wood pulp. Of particular interest is the observation that morphologies and surface properties of the nanocellulose can be tailored with the reaction conditions.
One pot generation of hydrophobic nanocellulose by a multi-functional agent

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This paper presents a novel green approach for combined telomerization and defibrillation of cellulose to generate telomerized cellulose nanofibrils (CNFs). A one-pot process was possible by using multi-functional agent that served as reagent, solvent and acid. Telomerization is already 100% atom efficient, and an elegant way to synthesize stable ethers with minimal environmental impact. This multi-functional reagent further reduced the use of chemicals by serving as reactants to telomerize with cellulose as well as solvent phase to produce ether functional groups on C2, C3 or C6 hydroxyls of anhydroglucose unit. The byproduct of the agent then aid hydrolysis of 1,4-glycosidic bonds and disrupt hydrogen bonding to facilitate the defibrillation of cellulose. The telomerized CNFs generated under optimal conditions were 0.96±0.53 nm (n=80) thick and whose surface chemistry could be characterized by solution phase proton NMR. These telomerized CNFs were hydrophobic than those produced by TEMPO mediated oxidation, suspendable in acetone while remaining dispersible in water. These telomerized CNFs could self-assemble into sub-micron wide (204, n=50) fibers with same thermal stability as the original cellulose, remarkably thermally more stable than other chemically derived nanocellulose reported to date while much thinner than those derived from shear forces.

Cellulose nanostructure obtained by enzymatic hydrolysis: The effects of treatment time

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Nanostructured cellulose is a material which presents low density, high mechanical resistance, biodegradability and huge amount of material available in nature for obtaining. These nanostructures are isolated from lignocellulosic fibers, including industrial residues, reducing the environmental impact of disposal, once the incineration is the most common residue destination. However, the most applied process for cellulose isolation is by acid hydrolysis, which generates toxic residues and may degrade the cellulose structure, reducing their properties. The study of alternative routes has been developed, one of them is enzymatic hydrolysis which is a biological method and non-aggressive to environment. At this study was obtained cellulose nanostructure from wood fiber residues of Pinus by enzymatic hydrolysis combining acid mercerization and alkaline bleaching as pre-treatments. They were produced four samples varying the hydrolysis time by 12, 24, 48 and 72 hours. The enzymes were a combination of commercial endoglucanase and xylanase enzymes at concentration of 6% (m/m) based on pretreat cellulose. The samples were analyzed by Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), scanning electronic microscopic, atomic force microscopy (AFM) and quantification of saccharides resulted from hydrolysis process. It was possible to observe that the pre-treatments acted in the lignin and hemicellulose removal from the fibers, exposing cellulose structures for following enzymatic hydrolysis. The applied methodologies shown, by DLS, that the increase in the enzyme exposition time produced smaller nanostructures up to 48 h, after that the nanostructures presented higher sizes similar to the minor time of hydrolysis. The 48 h sample present particles with hydrodynamic radius of 70 nm. The saccharides quantification shown a similar result with particle sizes, the samples with smaller sizes present a higher concentration of redactor sugars. The obtained nanostructures could be used as good reinforcement materials for nanocomposites production.
Investigation of surface interactions of micro/nano-cellulose with metal ions at micro-nano-molecular scale

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Cellulose particles on micro and nanoscales used as adsorbents for water purification have been an area of great interest in materials science research in recent years. The current report focuses on a deeper fundamental understanding of the adsorption behavior of metal ions on cellulosic material from micro to nano to molecular scale. Atomic force microscopy (AFM) is a powerful tool and has made possible the in situ examination of the morphological and mechanical properties of materials in both dry and wet conditions. We employed two AFM based methods to evaluate the surface interaction and adsorption behavior between cellulosic materials and metal ions; Ag(I), Cu(II) (See TOC Figure). In the first approach, three types of cellulose microsphere (native cellulose and its derivatives with sulfate and phosphate groups) were used to functionalize the AFM probe cantilever. The interactions (adhesion and repulsion forces) between the functionalized probes and substrate was measured and compared in AgNO₃ solution under different pHs. In the second approach, single TEMPO cellulose nanofiber (TOCNF) was anchored on the substrate and PF-QNM mode was applied to measure the topography, adhesion force and stiffness of the fiber at the same position by comparing before and after adsorption in CuSO₄ solution. The AFM, SEM-EDS and XPS results agreed with each other and were further supported by the extensive spectroscopic characterization (FTIR and Raman) and Density functional theory (DFT) simulations. All the results indicate that metal ions were first adsorbed by the functional groups grafted on cellulose chains in aqueous medium and followed by metal nano-layer/ nanocluster formation process during drying in air. This study is of great assistance for understanding the mechanisms associated with water purification and other forms of interfacial interaction domains.
Phosphated cellulose nanocrystals: Isolation and bioengineering applications

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Cellulose nanocrystals (CNCs) are high aspect-ratio, low-cost nanoparticles of renewable nature that account for outstanding mechanical properties, resulting on an interesting component for a large variety of nanomaterials. CNCs have traditionally been isolated via hydrochloric (H-CNCs) or sulfuric acid (S-CNCs) hydrolysis, leading to nanoparticles with an unmodified (H-CNCs) or sulfated (S-CNCs) surface. Due to the large amount of hydroxyl groups present on their surface, H-CNCs tend to aggregate easily being often difficult to disperse. While the introduction of a small amount of sulfate moieties on the surface of the nanoparticles (S-CNCs) results on the generation of ionic repulsive forces that aid on the dispersion of the particles, these ones, suffer of a lower thermal stability that limits their applicability. We introduced a novel protocol for the isolation of CNCs via phosphoric acid hydrolysis (P-CNCs) that leads to nanoparticles with a slightly phosphorylated surface (10.8 ± 2.7 mmol/kg cellulose) that are thermally more stable and readily dispersable in polar solvents. Moreover, we show that these nanoparticles are not only attractive for the fabrication of reinforced materials but are also capable of nucleating the formation of hydroxyapatite in vitro under physiological conditions. Thus, P-CNCs appear as an interesting component for the fabrication of scaffold biomaterials for cartilage and bone tissue engineering applications.

Development of the continuous production process Kyoto process of CNF reinforced plastics

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The Research Institute for Sustainable Humanosphere (RISH) at Kyoto University and Kyoto Municipal Institute are collaborating with Oji Holdings Corp., Nippon Paper Industries Co., Ltd. and Seiko PMC Corp. under the NEDO (New Energy and Industrial Technology Development Organization) project entitled “Development of the technology for the continuous production process of ligno cellulose nanofibers reinforced plastics and their applications for the structural members”. A chemically modified dry-pulp with an improved heat resistance and will be easy to fibrillate but will not be chopped under melt compounding is developed. An integrated production process that simultaneously nanofibrillates the chemically modified dry-pulp and uniformly disperses the CNF in the resins is established. Based on this continuous production process, a test plant with a production capacity of one ton/year of thermoplastic resins with 10wt% CNF starting from wood chips was constructed at RISH. The modified CNF, at 10wt% load as a filler, increases the Young’s modulus and bending strength of PA6, PA12, PLA, POM, PBT, HDPE and PP by 1.5-2.5 times. One of our potential goals is to produce automobile exterior components and home appliance components.
Plant oil-based acrylic monomers for free radical polymerization

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The design of bio-based polymers from renewable resources is a promising step to provide materials with variety of industrial applications and less hazardous waste. The synthesis of bio-based monomers and polymers from plant oils can substitute usage of petrochemical materials as well as promote using vegetable oils as a cheap, widely available and natural renewable feedstock. Plant oil-based monomers (POM's) were synthesized using one step transesterification reaction of crude plant oil (olive, sunflower, soybean and linseed oil). New acrylic monomers are capable to free radical copolymerization with petroleum-based counterparts (St, VAc and BA) as well as to homopolymerization. In terms of polymerizability, plant oils monomers behave as conventional vinyl monomers. The feasibility of plant oil-based monomers undergoing chain addition polymerization was confirmed by studying polymerization kinetics. Degree of unsaturation in plant oil triglyceride was used as a criterion to compare the homopolymerization kinetics of POM’s. Polymerization rate and the number-average molecular weight of homopolymers synthesized at 75 °C decreases with an increasing degree of unsaturation of the plant oil-based monomers. Chain propagation proceeds towards noticeable chain transfer reaction to plant oil-based monomers by the abstraction of allylic hydrogen in fatty acids fragments. The obtained values of $C_M$ (ratio of chain transfer and propagation rate constants) clearly depend on monomer structure as follows: $C_M$(LSM)> $C_M$(SBM)> $C_M$(SFM)> $C_M$(OVM). Glass transition temperature measurements for selected plant oil-based homopolymers[$T_g$ =4.2 °C for poly(SFM), $T_g$ = -6.0 °C for poly(SBM)] indicate that varying bio-based content in copolymers synthesized from new plant oil-based monomers and their vinyl counterparts might considerably change the intermolecular interactions of macromolecules and physico-chemical properties, determined in particular by varying macromolecular flexibility.

Emulsion copolymerization of vinyl acetate with hydrophobic plant oil-based monomers: Effect of plant oil unsaturation of reaction kinetics

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The use of plant oil-based monomers in emulsion copolymerization offers many potential benefits that are simultaneously met with multiple challenges throughout the copolymerization reaction. Plant oil starting materials can be easily derivitized, used as plasticizing agents within contemporary high $T_g$ latexes, which may eliminate the need for coalescing solvents in waterborne systems, and finally, form a crosslinked network through autoxidation of the allylic unsaturation of the plant oil fatty acid chains. However, certain challenges must be overcome at the same time. Due to their extreme hydrophobicity, the incorporation of moderate amounts of plant oil-based monomers in emulsion copolymerization remains a challenge. Similarly, the allylic unsaturation associated with the fatty acid pendant chains of the starting material has been known to greatly affect the rate of copolymerization, as well as act as sites for chain transfer leading to decreased molecular weight and inability to undergo post-polymerization autoxidation to form a complete network. In this work, the mechanism of emulsion copolymerization of vinyl monomers with
plant oil-based starting materials was studied in order to better understand the effects associated with altering the degree of unsaturation in the plant oil comonomer. Latex copolymers based on vinyl acetate were prepared with oils from vegetable resources such as olive, soybean, and linseed. Effects on copolymerization rate, chain transfer constants, molecular weight, and overall emulsion mechanism were investigated. It was found that there was an inverse relationship between reaction rate and the amount of unsaturation in the plant oil monomer.

CELL 35

Random copolymerization of lactones and hydroxyacid bioaromatics using one-pot Ring Opening Polymerization (ROP) polycondensation method

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A generalized and efficient one-pot ring opening polymerization (ROP) polycondensation methodology in the melt between L-lactide or caprolactone and a hydroxyacid bioaromatic as the comonomer was studied. Four bioaromatic candidates were synthesized from syringic acid, vanillic acid, ferulic acid and p-coumaric acid. Eight copolymer series were obtained in good yields and high molecular weight, with number average molecular weight falling into the range of 10,500 to 60,700 Da. The randomness of copolymers were well achieved and confirmed by 1H NMR. The copolymerization strategy improved significantly the thermal stability of the PLA and PCL up to 418 °C and glass transition temperatures up to 107°C. These thermal properties open up the gate for both PLA and PCL to the high temperature applications. The ability of tuning glass transition temperature permitted productions of copolymers with competitive thermal properties to PET and PS. Furthermore, the successful synthesis of random copolymers of caprolactone or lactide with bioaromatics indicates the potential reaction scope to other ROP polycondensation system.

CELL 36

Water pre- and post-hydrolysis of birch wood to produce high-purity cellulose and xylan-based compounds for material and chemical applications

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Cellulose and xylan, the two most abundant polysaccharides in hardwoods, are widely utilized in the manufacture of bio-based materials and chemicals. Prior to their utilization, these polysaccharides need to be isolated from the wood cell walls, preferably following green chemistry principles as well as biorefinery concepts. Within this context, hydrothermal treatment of biomass is a green method to extract the xylan and to produce a high-purity cellullosic pulp, provided an appropriate delignification process is also performed. Hydrothermal treatments are typically conducted on wood prior to Kraft pulping for the production of dissolving pulps, but they may also be conducted on paper-grade pulps for the separation of the xylan and cellulose fractions. In this study, we have investigated the effects of hydrothermal treatments of birch wood before pulping (pre-hydrolysis) and after pulping (post-hydrolysis) on the properties and structure of the pulp as well as on the recovery of xylan-based compounds. The results show that increasing the intensity of pre- and post-hydrolysis increases the purity of the cellullosic pulp. For a similar level of pulp purity, decreasing pre-hydrolysis intensity while increasing post-hydrolysis intensity results in a cellulose fraction with higher yield but lower degree of polymerization. On the other hand, the yield of xylan-based compounds in the aqueous hydrolysates is similar for pure pre-hydrolysis and post-hydrolysis treatments. Pre-hydrolysis in a batch reactor allows the recovery of considerable amounts of xylose, xyl-o-oligosaccharides, and acetic acid, while post-hydrolysis in a flow-through reactor allows the recovery of high-purity polymeric xylan with low degree of substitution. The crystalline structure of cellulose in the pulps and the accessibility of hydroxyl groups is currently being investigated.
utilization of selected cellulosic pulps and xylan-based compounds in high value-added applications is discussed.

CELL 37

Wood-based hemicelluloses as renewable source for functional materials

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Trees are a tremendous source of renewable materials comprising mainly cellulose, hemicellulose and lignin. Hemicelluloses are a complex component of wood cell wall that contribute to the strong network with cellulose fibrils. The structure of the hemicellulose grades depends on the plant species and extraction method. While cellulose is, and has been, of scientific and industrial interest, wood-based hemicelluloses, xylan being the principle type of them, have had very limited use in industrial applications. So far, the main attention of hemicelluloses has been as a raw material for biobased chemicals. In materials technology applications, investigations have been directed in modification of the wood-based hemicelluloses to tune their water-solubility, functionality, film formation, among others. In addition to solid structures such as films, hemicelluloses are suggested as interfacial stabilizers. In this contribution etherified and oxidized hemicellulose grades are suggested for applied materials science purposes. The surface activity and interfacial stabilization capability of hardwood and softwood hemicellulose ethers is contrasted to their structural features. Oxidized xylan grades are presented as a novel material for functional hemicellulose films.

CELL 38

Multifunctional materials based on wood derived biopolymer

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Renewable materials from nature are emerging as attractive solutions to a range of technological challenges. In particular, wood-derived biomaterials are not only biocompatible and earth-abundant but also have nature-provided intrinsic structures for potentially transformative performance. There are still grand challenges in fundamental research and understanding to accelerate wood-derived biomaterials toward commercial reality, which include new materials and structures with tailored properties, novel devices with both excellent functionality and mechanical flexibility, efficient and scalable techniques for nanomanufacturing, and system-level integrations. This talk will include the fundamental structures and chemistries of wood and wood-derived materials, which are essential for a wide range of existing and new enabling technologies. The scope of this talk will cover multiscale materials and assemblies of wood-derived biomaterials, in regard to their major emerging applications. Structure-properties-application relationships will be discussed in detail. Understanding the fundamental properties of biopolymer is crucial for designing and manufacturing products for emerging applications. Today, a more holistic understanding of the interplay between the structure, chemistry, and performance of wood and wood-derived materials is advancing historical applications of these materials. This new level of understanding also enables a myriad of new and exciting applications, which motivate the works covered in this talk.
**CELL 39**

**Novel one step method to prepare carboxycellulose nanofibers from raw biomass and their applications in heavy metal ions remediation**

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A sustainable one-step method has been developed to prepare carboxycellulose nanofibers, directly from raw biomass by using only nitric acid or nitric acid-sodium nitrite. The direct use of raw biomass for the production of carboxycellulose nanofibers, has successfully overcome multi-step processes to convert raw biomass into nanocelluloses. We estimate that the demonstrated method can effectively reduce about 50% toxic chemicals and ~40% electrical energy during the conversion process. In addition, the effluent can be efficaciously neutralized with base to produce nitrogen rich salts that can be used as a plant fertilizer. The versatility of this process has been proven on different sources such as raw jute fiber, spinifex grass and bamboo cellulose. TEM measurement of produced carboxycellulose nanofibers were in the range of 250-400 nm and width 4-5 nm, having PDI ratio of 0.286-0.382. Interestingly, the nanofibers were prominently non-crystalline, indicated by TEM diffraction pattern, WAXD and $^{13}$C CPMAS NMR analysis. The crystallinity index (CI) measured by WAXD, for carboxycellulose nanofibers produced from raw jute was only 38%, which is comparatively low as compared to 62% of jute fiber. The elementary crystallite size measured from $^{13}$C CPMAS-NMR for produced carboxycellulose nanofibers was 4.58 nm, which is consistent with TEM measurement. As the resulting nanofibers are prominent non-crystalline in nature, they behave as a promising medium to remove the toxic heavy metal ions from contaminated water.

**CELL 40**

**Tertiary amine catalysts for oxidizing the unsaturated components in cellulosic pulp**

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During chemical wood pulp production, bleaching process is used for final removal of unsaturated, and often colored, components in the pulp. The process aims principally at removing lignin and xylan-bound hexenuronic acid (HexA), while the pulp’s carbohydrate components, cellulose and hemicelluloses, should remain intact. Modern pulp bleaching is mostly based on the use of chlorine dioxide, oxygen, and hydrogen peroxide as oxidants. Different chemicals are applied at separate bleaching stages with varying conditions and reaction times, thus forming a bleaching sequence. Still even the most advanced
industrial-scale bleaching processes consume significant amounts of bleaching chemicals to remove residual HexA and lignin that account for ca. 2% of pulp weight. The overall delay in the bleaching line is several hours. Indeed, because of the seeming inefficiency of the contemporary bleaching technology, we have been investigating the use of catalysts for enhancing the lignin and HexA removal. Recently we initiated work on the use of tertiary amines (R₃N) as catalysts in Eucalyptus pulp bleaching. Tertiary amines react rapidly with hypochlorous acid (HOCl) forming quaternary chloroammonium cations (R₃N⁺Cl⁻). The chloroammonium cation oxidizes the unsaturated organic compounds in the pulp which takes place very fast. In this work, we studied the kinetics and mechanisms of the catalytic reactions of HexA by utilizing model compounds. The objective in elucidating the reactions is constructing fundamental models for better understanding the complex reactions between different types of tertiary amine catalysts with HexA by HOCl.

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. J. Rojas, Organizer; E. A. Moura, Presiding; M. L. Auad, Presiding Papers 41-48

CELL 41

Development of novelty Fique textile fabrics for clothing applications

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Colombia is a tropical South American country well known for its wide biodiversity. It is rich in renewable natural fibers as Fique and besides, is the only high scale Fique producer around the world. Fique is normally used for ropes and sacks production for agroindustrial product exportation due to its excellent properties as high tensile strength and aspect ratio. However, because of its coarse and rough touch there has not been any development around the fiber for other uses or applications in higher value-added textile products. The main reason is its high content of lignin, pectin and hemicelluloses, which make it unable to spin in yarns for garment fabric production. In this work fique "cottonization" process by a chemical treatment was evaluated to isolate its constituted fibers to obtain cotton-like properties. The cottonized fibers were mixed with cotton and polyester in a traditional spinning process. Then, the yarn was woven and knitted to produce fabrics that were subjected to different laundry processes and sample garments were constructed. In consequence, these results and the technological evolution around the fiber would positively impact the almost 80,000 poor farmer families that get their incomes from Fique and can contribute sustainably to the development of the natural fiber industry.

CELL 42

Novel recycling process for cotton polyester blended waste textiles

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In less than ten years, the global population will exceed 8 billion people. The spread of urban areas and consequences of global warming simultaneously decrease the area of arable land.¹ Cotton industry will consequently compete for acreage with food and biofuels.² The creation of a circular economy therefore
seems indispensable. Currently, the lack of adequate recycling strategies prevents the usage of worn out textiles as a source of raw material for new value added products. Textiles on the market represent almost exclusively multi-component garments with cotton polyester blends being the most prominent mixture, which poses severe challenges onto their recycling due to their inherent heterogeneity. Recently developed recycling strategies propose the dissolution of the cellulosic component in $N$-methylmorpholine $N$-oxide or imidazolium derived ionic liquids. Although these approaches suggest subsequent fiber spinning, they fail to demonstrate the feasibility of the concept. The process presented herein aims to overcome these weaknesses in state-of-the-art methodologies. A superbase-derived ionic liquid dissolves the cotton component selectively without any significant degradation of the residual polyester. After filtration, the cellulose solution is subjected to dry-jet wet spinning to obtain Lyocell-type fibers, while the recovered polyester can be fed back to conventional industrial processes such as melt spinning. The ionic liquid is regained by thin film evaporation.

CELL 43

**Nanocellulose recovery from industrial bagasse of agave tequilana**

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Agave tequilana is an outstanding crop from the western semi-arid region of Mexico and is the base for the internationally renowned drink called tequila. The industrialization of tequila production has led to an extensive farming, being the cause of environmental deterioration and waste production. One of the residues from the industrial activity for tequila production is agave bagasse. This material finds its origin in the core of the plant not in the leaves, as the leaves are left in the ground representing also an unused resource. The importance of lignocellulosic residues in new applications is increasing rapidly, accordingly the methods for processing this materials are being assessed by a wide range of investigators. To produce a liter of tequila agave 8 kg are required, which generate 3.2 kg of agave bagasse as waste. The management of this waste represents a great challenge and so far has been used as compost and for the production of low economic value goods. In this sense, this study has the main goal to obtain nanocellulose from this agroindustrial waste. Cellulose is a polymer that in nanoscale form offers excellent physical properties, this makes it a versatile material for various applications.

CELL 44

**Biocatalytic functionalization of softwood galactoglucomannan through transglycosylation and enzyme engineering**

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Softwood hemicellulose (galactoglucomannan, GGM) is a major renewable resource with a wide variety of potential applications. However, GGM is often removed and discarded in waste streams in wood pulp processing, and is currently greatly underutilized. There is, though, a significant interest in the valorization and functionalization of GGM through its use in biorefinery applications such as the production of second-generation biofuels and novel high-value compounds, e.g. surfactants. Some b-mannanases have the potential to create these compounds by use of their synthetic (transglycosylation) capacity. The transglycosylation capacity of b-mannanases depends greatly on the structural conformation of the aglycone regions of their active sites, where the acceptor molecule binds. By site-directed mutagenesis of b-mannanases from the blue mussel (MeMan5A) and the fungus *Trichoderma reesei* (TrMan5A), we have shown that altering the aglycone region can significantly change both transglycosylation capacity
and acceptor specificity. Thus, enzyme engineering provides an excellent way of optimizing reactions to maximize yields of specific compounds. We have demonstrated the production of several novel conjugates through transglycosylation by b-mannanases. By transferring alcohols onto manno-saccharide donors produced by partial hydrolysis of mannan, using variants of TrMan5A and the Aspergillus nidulans b-mannanase AnMan5C, we have produced alkyl mannosides with potential applications as renewable, biodegradable surfactants. Reaction optimization and protein engineering approaches were used to increase yield and control product formation as analyzed by mass spectrometry (MS) and high-performance liquid chromatography (HPLC) before scale-up and further product characterization with focus on structure and surfactant properties. By taking advantage of the capability of enzymes to transfer acceptors onto mannan substrates in this way, a wide variety of novel high-performance and high-value compounds could potentially be synthesized.

CELL 45

Electrodes with nanostructures used in the electrochemical analysis of pesticides in aquifers means of organic and conventional banana production in Costa Rica

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The nanotube electrodes used for the analysis of preliminary screening of some components such as mancozeb, used in banana production in Costa Rica and is highly damaging to the water and soil, can contribute to sustainable development. "Cyclic voltammetry is a widely used technique, which allows studying a wide range of phenomena in all fields of science. Recent laptops reduce costs and enable focus primarily on the development of new materials and methodologies simple, low cost and high sensitivity. Since the effectiveness of the methodology depends largely on the specificity of the electrode it is important to study the use of different conductive polymers both as nanostructures (nanotubes, or graphene) to improve the specificity and sensitivity of the technique in determining certain components in water. Such a system would facilitate affected communities; take preventive measures such as the concentration of hazardous substances do aquifers.

CELL 46

Modified soy protein as encapsulate excipient in pharmaceutical applications

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Actually, many strategies are studied to propose dosage forms adapted to the hydrophobicity of various Active Pharmaceutical Ingredients (API). An alternative solution to synthetic coating is the use of biopolymers as potential matrices for controlled and sustained delivery. In this way, vegetable proteins offer interesting functional properties as encapsulating materials of hydrophobic API, mainly due to their amphiphilic characteristic. Moreover, their properties could be improved thanks to suitable chemical modification of proteic chains. The objective of this work was to modulate the pH sensitivity of soy protein isolate (SPI) via two chemical modifications: acylation and succinylation, in order to increase protein hydrophobicity and formulate enteric microparticulate forms for oral controlled delivery. In this study, ibuprofen (IBU) was chosen as a model hydrophobic drug. Acylation was performed according to the Schotten-Baumann reaction with dodecanoyl chloride at the molar ratio (C12)2/NH2 (2/1). An acylation rate of 37.3% was obtained. Succinylation was carried out using a succinic anhydride/soy protein molar ratio of 1.5, to obtain a 94% of succinylation rate. Proteins solubility profiles at different pH range showed that both modifications reduced protein solubility in acid medium. Microparticles were prepared at different ratios (%) of SPI or modified soy protein isolate / IBU: 90/10, 80/20 and 60/40, using spray-drying.
process. IBU concentration was measured by HPLC and microparticles characterization included particle size distribution, SEM and TGA analysis. Spray-drying yields higher than 70% and high microencapsulation (ME) efficiencies (all higher than 80%) were obtained for the different proteins. Drug release experiments were performed under conditions recommended by the European Pharmacopoeia. For simulated gastric fluid (pH 1.2 with pepsin), a low release was observed, especially with modified proteins microparticles. Kinetics at simulated intestinal fluid (pH 6.8) presented a quick release (100% in 90 min). In conclusion, both modifications improved interactions between IBU/protein, increasing the affinity for hydrophobic API and higher ME efficiency were obtained, confirming that vegetable proteins can be valorized as encapsulate excipient for hydrophobic API and enteric formulations.

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Incorporating cellulosic passion fruit residues into pectin edible plastics

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Brazil is the largest passion fruit (Passiflora edulis – PF) producer worldwide, nonetheless, merely 30 wt.% of the whole fruit are utilized by national juice industry. Residues engendered in PF juice processing mainly consist of peels and seeds, which frequently end up as an agro-rubbish into the environment. The current work aimed to develop an added value re-use of PF peels (mesocarp/epicarp) by incorporating them at different concentrations (25, 50, 75, 100 wt.%) into pectin edible plastics. These plastics were obtained by continuous casting on a labcoater unit running at a conveyor speed of 12 cm min⁻¹. Edible plastic characterizations were performed by X-ray diffraction (XRD) and uniaxial tensile tests. The former was carried out for identifying possible macromolecules in PF peels that could interact with pectin matrix. The later served to determine tensile properties (Young’s modulus E, true tensile strength σₜ, and true elongation at break εₜ) of edible PF plastics as per ASTM D882-09. XRD revealed the presence of cellulose I-type in PF mesocarp/epicarp due to three diffraction peaks typical of (110), (200) and (040) cellulose crystalline planes. This represents a satisfactory outcome because pectin and cellulose can interact by hydrogen bonding. Moreover, tensile properties demonstrated that PF edible plastics could be elaborated with 25 wt.% (E = 95.86 ± 31.48 MPa; σₜ = 3 ± 1 MPa; εₜ = 2.9 ± 0.7 %) and 50 wt.% (E = 522 ± 203 MPa; σₜ = 9 ± 3 MPa; εₜ = 2.9 ± 1.8%) PF mesocarp/epicarp. In comparison with pure pectin plastic (E = 1881 ± 96; σₜ = 44 ± 12 MPa; εₜ = 2.8 ± 1.0 %), there was a significant decrease in Young’s modulus, an increase in σₜ, while εₜ remained statistically equal with increasing PF mesocarp/epicarp concentration. Therefore, this work represents the feasibility of creating edible passion fruit plastics with a broad range of mechanical properties utilizing agro-residues.

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Residues from agroindustry as reinforcement in foams based on PBAT/PLA blend

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Nowadays, agroindustry residues have attracted great attention in both the academic and industrial worlds. In fact, biodegradable polymers reinforced with residues derived from renewable sources, as avian eggshell waste and ashes from the burning of sugarcane bagasse are economically and ecologically attractive materials to produce a new class of bio-products with eco attributes, which make
them environmentally friendly, completely degradable and sustainable. In Brazil, the food industry generates every year huge amounts of avian eggshell waste, an industrial byproduct containing 95% of calcium carbonate, and its disposal constitutes a serious environmental hazard. Tons of ashes are produced from the burning process of sugarcane bagasse to produce energy in Brazilian sugar and bioethanol industries. These ashes, which are not rich in nutrients for the crop, are usually mixed with organic fertilizers or disposed of in nature without efficient management. However, these ashes containing about 94% of silica. This study aims to the development of bio-foams from PBAT/PLA blend reinforced with bio-calcium carbonate nanoparticles from eggshells and green-silica nanoparticles. Composites were obtained by melting extrusion process, blending PBAT/PLA with 3% of bio-calcium carbonate nanoparticles and 3% of green-silica nanoparticles. The composites were then extruded in a Rheomex 332p single special screw for foaming. Samples were submitted to tensile and compression tests, MFI, DSC, XRD and SEM-FEG analyses.

SUNDAY AFTERNOON

Design & Control in Polysaccharide Chemistry: Anselme Payen Award Symposium in honor of Kevin J. Edgar
P. E. Fardim, Organizer; O. J. Rojas, Organizer; C. M. Buchanan, Organizer; P. E. Fardim, Presiding Papers 49-56

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Tubular biocellulose hydrogels act as temporarily implanted in vivo scaffolds and cause regeneration of bile duct by body own tissue

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Biocellulose (BC), such as that produced by the bacteria Gluconacetobacter xylinus, is an emerging biomaterial with great potential as cell-free medical implants and tissue engineering scaffolds over the past decade. In particular, the biotechnological design of different tubular BC implants is of great importance for the replacement and regeneration of hollow organs of the human body. Our Mobile Matrix Reservoir Technology allows the BC tube formation under control of its dimensions, surface properties, and network architecture directly in the bioreactor. The tube assembly is carried out layer by layer. In this technology, a matrix with integrated templates moves periodically between the aqueous culture medium and the air space of the reactor. The BC formation takes place in the culture medium film, which is generated on the template during dipping. Typical control elements for the tube parameters are the dimension and material of the templates as well as the moving mode of the matrix. Tubular biocellulose implants were investigated as a biliary replacement material in order to allow anatomical reconstructions in case of loss of the extrahepatic bile duct. Such substance defects, whether after cholecystectomy or after liver transplantation, are difficult to repair surgically. In pig studies, a corresponding tube of biocellulose, diameter 5 mm, wall thickness 1 mm, was implanted and a stent was inserted into the anastomosis. After 12 weeks, the bile duct was completely regenerated over the biocellulose implant surface. The BC tube was found repelled in the bile duct lumen and could be removed. Histologically, the typical wall construction of a completely stable and perfect working bile duct with complete epithelial lining could be detected.
Nano-designed polysaccharide-based constructs for tissue engineering applications

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The possibility of regenerating organs and tissues would bring new possibilities of improving current treatments or find solutions for untreatable situations, thus having an enormous impact in the quality of life of patients. Tissue Engineering has been integrating principles of engineering, chemistry, materials science, biology and health sciences in order to develop regenerative-based therapeutic strategies combining stem cells and biomaterials. From the different sources of biomaterials, polysaccharides have been proposed to produce matrices able to interact favourably with cells, being possible to extract them from renewable resources. Due to their hydrophilic nature and richness in chemically active groups, such polymers can be used to produce a variety of structures fabricated using aqueous-based or other environmental-favourable procedures. In particular, the possibility to have charged polysaccharides permits to process such materials using the so-called layer-by-layer technology, where the consecutive layers are well stabilized by electrostatic interactions or other weak forces. Depending the substrates where the multilayers are deposited flat or complex 3D devices may be produced that could be useful in biomedicine, including in tissue engineering and regenerative medicine. For example, by using spherical templates containing bioactive agents or cells it is possible to produce liquefied capsules that can be used in drug delivery applications or that may entrap viable cells. The presence of solid microparticles inside such capsules offers adequate surface area for adherent cell attachment (with controlled mechanical properties) increasing the biological performance of these hierarchical systems, while maintain both permeability and injectability. Examples are shown where the potential of using the layer-by-layer technology to process polysaccharide-based devices and microenvironments is highlighted.

Chemoenzymatic strategy to design alginates for tissue engineering

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In the last decade there has been an increasing interest in the use of alginates in biotechnology biomedicine and the possible use of such systems are numerous. Chemically alginate is a family of linear glycuronans composed of (1-4) linked residues of β-D-mannuronic acid (M) and α-L-guluronic acid (G). The residues are arranged in a block-wise fashion along the polymer chain forming. They are highly soluble in water and form ionotropic gels with multivalent cations such as calcium. Novel understanding of the genes controlling the alginate biosynthesis makes it possible control the production as well as the sequential structure of these polymers. Of special interest is the last step in the biosynthetic pathway where mannuronic acid residues (ManA) are converted into the C-5 epimer, guluronic acid residues on the polymer level. This type of post-polymerisation epimerisation, first discovered our institute, is also exemplified by the C-5 conversion of D-Glucuronic acid into L-iduronic acid in heparin/heparan sulfate. By using these enzymes either in vivo or in vitro it is for the first time feasible to produce alginates with predetermined structures such as compositionally homogeneous alginates (mannuronan, guluronan and polymers with a strict alternating ManA-GulA sequence) or alginates with extreme composition and sequential structure not found in nature. By combing chemical selective modification with enzymes, selective modification on these hetero-polysaccharides can be achieved. The lecture will discuss how we can control the composition and sequential structure as well as the compositional heterogeneity of alginates and thus tailor their properties essential for new applications as gel matrices in pharmaceutical drug delivery, in bioreactors tissue engineering and cell therapeutic systems.
Manufacturing, characterization and use of substrates for regenerative medicine based on the specific properties of polysaccharide derivatives and biodegradable polymers

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Many of the properties governing the function and efficacy of substrates used in regenerative medicine are regulated by molecular interactions at the interface between the biological system and the biomaterial. An in-depth understanding of their surface chemistry is therefore prerequisite for the discovery of new phenomena and their exploitation in the form of new products. Due to their versatility, ease of processing and defined nature, synthetic polymers are one of the most frequently used biomaterials in regenerative medicine. However also polysaccharides and their derivatives possess a significant potential owing to their biological origin and in many cases their similarities to the physicochemical properties of tissues in the wet state. Polysaccharides provide a diverse set of functions depending on the types of monosaccharides that constitute the chain which often contain multiple functional groups (e.g. hydroxyl, amino, carboxyl etc.). A careful chemical derivatization of these groups using esterification and amidation reactions allows for significant changes in the physicochemical properties and the introduction of cell- and biomolecule specific responses. Following derivatization, polysaccharides can be processed into two or three dimensional objects by techniques such as spin-coating, 3D-printing, electrospinning, freeze drying or solvent casting. Understanding and exploiting the solution state and reactivity of polysaccharide derivatives during and after processing allows for the manufacturing of substrates with unprecedented properties suitable to be used in various fields of regenerative medicine.

Glycosaminoglycan nanostructures as mimics of the vascular endothelial glyocalyx

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The inside surfaces of healthy blood vessels are lined with endothelial cells that present a polysaccharide-rich layer forming the interface between the flowing blood and blood vessel wall. This vascular endothelial glyocalyx performs several important dynamic physiological functions that make the inside surfaces of healthy blood vessels the most blood-compatible surface known. In fact, all other synthetic or biological materials that contact blood can induce inflammation, blood clotting, and infection. The structure and composition of this glyocalyx inspires us to investigate how the presentation of similar polysaccharide chemistries on surfaces should be tuned to improve blood-material interactions. The polysaccharides in the vascular endothelial glyocalyx include important glycosaminoglycans – polyanionic macromolecules – presented in a brush-like layer as the side chains on proteoglycans. The formation of dense polyelectrolyte brushes with thicknesses approaching the thickness of this unique biological structure (100s of nm to a few microns) is energetically unfavorable, due to both enthalpic (electrostatic repulsion) and entropic (chain stretching) barriers. Nonetheless, we hypothesize that this thick, brush-like presentation of glycosaminoglycans may enable favorable blood-surface interactions, such as blood protein stabilization, protein-surface interactions, and protein-protein interactions.
We have developed brush-like glycosaminoglycan (polyanion) coatings with dimensions approaching the dimensions of the endothelial glycocalyx. The composition and structure of these coatings can be controlled over a range of parameter space that enables us to determine structure-property relationships. We characterize their surface chemistry by vibrational and X-ray spectroscopy, and confocal fluorescence spectroscopy. We characterize their structure and nanomechanical properties by atomic force microscopy using peak force quantitative nanomechanical property mapping (PF-QNM), in liquid. We are using these to further elucidate structure-property-function relationships by single-particle protein diffusion experiments in these polymer brushes, to discern how key blood proteins interact differently within these polymer brushes than on flat surfaces. This work will provide a new model system upon which to test hypotheses about blood-material interactions, and a strategy for designing blood-contacting materials with improved blood compatibility.

CELL 54

Polysaccharide based micro-nano structures for tissue engineering

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Tissue engineering efforts focus on the use of development of three-dimensional (3-D) tissue-inducing scaffolds that mimic the hierarchical architecture of native tissue extracellular matrix (ECM). The primary purpose of the scaffold is to provide tissue with structural stability to the damaged tissue while proving conducive environment for the cells to aid tissue regeneration. Scaffolds are designed to cater the specific requirements of the regenerating tissue in terms of mechanical strength to support the repair and pores to promote cell infiltration, nutrient supply and metabolic waste removal. Micro-structures in the scaffold design satisfy the mechanical and pore-properties suitable for tissue repair. However, microstructure alone may not be effectively control cellular events during tissue regeneration. Cells identify and interact with scaffold architecture and topography via ECM proteins. A wide range of polymers both natural and synthetic origin have been adopted to create scaffolds for the repair and regeneration of musculoskeletal tissues. Each class of materials offers their unique advantages from the engineering and biologic standpoint. Synthetic polymers can be produced with desirable structure and molecular weight that offer great control over the scaffold mechanical strength and degradation rate. However, the degradation byproducts and associated toxicity might hinder the tissue regeneration. Polymers of natural origin offer several advantages including natural abundance, relative ease of isolation and the availability of chemical modification to meet technological needs. These polymers have biochemical similarity with human extracellular matrix components and hence are readily accepted by the body. In spite of many merits as biomaterials, polysaccharides suffer from various drawbacks including microbial contamination, uncontrolled water uptake, poor mechanical strength, unpredictable degradation pattern and variations in material properties based on the source. These material inconsistencies can be overcome by combining these materials that display useful features of both natural and synthetic polymers. Various cross-linking techniques to restrict polysaccharide chain movement and control water uptake, degradation and mechanical properties have also been developed.

CELL 55

Development and characterization of biomembranes combining chitosan and natural-nanoliposomes for tissue engineering applications

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Tissue engineering and cell therapy comprise a market for regenerative products that is expected to grow worldwide from $6.9 billion in 2009 to almost $32 billion by 2018 [1]. Advances depend increasingly on the availability of specific biomaterials that allow controlling biological systems behaviour [2]. Therefore, many efforts have been devoted in proposing both biologically derived and synthetic materials in contact with biological materials and new tissue engineering strategies that could enhance the regenerative potential of the products. However, outcomes extracted from both experimental and early clinical settings show a number of products limited and often poor therapeutically benefices. In this context, chitosan membranes have been functionalized in volume by incorporating nanoliposomes based on soya (vegetable origin) and salmon head lecithin (animal origin). The properties of chitosan and natural nanoliposomes/chitosan blend membranes were evaluated by numbers of multi scale techniques such as water contact angle (WCA), water uptake ability, Fourier Transform InfraRed spectroscopy (FT-IR) and Torsional Harmonic Atomic Force Microscopy analysis (TH-AFM). The biological performance effect of chitosan before and after functionalization with nanoliposomes were performed using human mesenchymal stem cells (hMSCs). This study provides the information about the potential of chitosan membranes functionalized with natural-nanoliposomes to be used as multifunctional biomaterials for supporting cell activity, facilitating regeneration, and guiding tissue repair. In particular, we will show that concentration 1mg.mL⁻¹ of salmon nanoliposomes in the chitosan has the highest potential in the development of chitosan-based biomaterials, in particular for tissue engineering applications [3].

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Bottom-up fabrication of hybrid polysaccharide/peptide amphiphile supramolecular multilayered biomaterials by combining self-assembly and layer-by-layer assembly approaches

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Nature has demonstrated to be an extraordinary source of endless inspiration for designing and engineering a variety of complex and functional materials and systems to be used in numerous applications. Inspired by several fascinating and stimulating natural systems, which include the example of tobacco mosaic virus, or even the cell membrane, scientists have been boosted towards the development of increasingly complex supramolecular functional biomaterials aiming at addressing key biomedical and biotechnological applications, including tissue engineering, regenerative medicine, or drug delivery. In this work, we took advantage and maximize the use of materials from renewable sources, including polysaccharides, by developing novel hybrid supramolecular nanostructured multilayered biomaterials comprising high-molecular-weight biopolymers and oppositely charged low-molecular-weight self-assembling peptide amphiphile molecules, through combination of self-assembly and electrostatically-driven layer-by-layer (LbL) assembly approaches. Alginate, an anionic biocompatible polysaccharide extracted from brown seaweed, was used to trigger the self-assembling capability of positively charged peptide amphiphile molecule and formation of one-dimensional supramolecular nanofiber networks. Then, the LbL technology was employed to fabricate well-defined supramolecular multilayered biomaterials with tailored composition, thickness, and structure at the nanoscale by repeating the alternate deposition of both molecules. The buildup process was monitored in situ by quartz crystal microbalance with dissipation monitoring, which proved that both materials can be successfully combined to conceive stable supramolecular nanostructured multilayered systems. Their morphological properties were assessed by advanced microscopy techniques, revealing the nanostructured dimensions and one-dimensional nanofibrous network of the assembly formed by the two molecules. The in vitro biological performance of the supramolecular biomaterials was inspected using C2C12 myoblast cells. Enhanced cell adhesion, proliferation, and differentiation was observed on supramolecular systems having peptide amphiphile as the outermost layer. Our results suggest that such supramolecular
biomaterials could be used in the near future as promising biomimetic supramolecular matrices for biomedical applications, including those in muscle tissue regeneration.

**Processing & Properties of Bio-based Composites & Blends**
J. R. Barone, Organizer; P. R. Navard, Organizer; J. R. Barone, Presiding; P. R. Navard, Presiding Papers 57-64

**CELL 57**

**Role of non-cellulosic components on the microstructure and physical properties of natural fibres and their biocomposites**

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Mechanical and chemical processes used in the separation of natural fibers for the production of technical fiber based products for composite applications are likely to modify the surface chemistry and the intra and inter-cellular supramolecular structures of the fibers, especially due to the extraction of non-cellulosic components. One might wonder about the influence of these treatments on the resulting physical properties of the fibers and their biocomposites. In this work, we investigated the effect of selective chemical extraction treatments on the biochemical composition and physical chemical properties of flax fabrics, and the microstructure and mechanical behavior of thermo-compressed flax fabrics reinforced epoxy biocomposites. A unidirectional (UD) flax tow woven fabric with minimal processing was chosen in order to retain as much as possible the original flax cell wall structure. The flax fabrics were treated by various aqueous and organic solvents with increasing solvation capacity, so as to gradually extract inter and intra-cellular non-cellulosic components from the fibers. The treated flax fiber fabrics were characterized in terms of biochemical composition, wettability and dimensional characteristics. The influence of chemical extraction treatments on the microstructural and mechanical properties of UD flax/epoxy biocomposites were investigated and discussed by means of Scanning Electron Microscopy (SEM), image analysis, and transverse tensile tests. Our results demonstrate that the extraction of non-cellulosic cell wall components from flax fibers modifies greatly the dispersion of flax yarns within the epoxy matrix, hence generating a higher specific interface area between the fibers and the matrix. The transverse mechanical behavior related to interfacial adhesion is also significantly influenced by the treatments, attesting for the key role of non-cellulosic components in the stress transfer mechanisms from fiber to fiber and fiber to matrix within biocomposites. These results give evidence for the need to tailor plant biomass production and processing for composite applications.

**CELL 58**

**Influence of biochemical and histological characteristics on the properties of miscanthus-polypropylene composites**

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The biochemical composition and structure of a series of 21 miscanthus genotypes cultivated under controlled conditions and harvested at the end of the growing season (February 2013, 2014 and 2015)
were analyzed. After grinding down to micrometer size selected stem sections, the stem fragments obtained were used as reinforcement of polypropylene. The composites prepared were subsequently characterized in order to determine if their mechanical properties were affected by genotype-related variations in the biochemical structure of the plant. After assessing the absence of relationship between the processing parameters and the mechanical properties of composites, the influence of genotype characteristics onto their reinforcing potential was evaluated. The results obtained showed clear correlations between the mechanical properties of composites with harvest year, clone and with various morphological, biochemical and structural characteristics of miscanthus plants. The determination of the possible reasons behind the observed correlations could help developing a plant breeding process for identifying the best varieties to be used for preparing polymer composites.

**CELL 59**

**Lignin- polyvinyl alcohol photo-cured composite films. Effect of lignin and UV curing agent quantity on the mechanical, optical and chemical properties**

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Lignin is one of the most available material in earth. Actually can be obtained as a byproduct of the paper industry. Lignin obtained from coffee husk and recovered by solubilization and precipitation in water was used for the fabrication of polyvinyl alcohol (PVOH) lignin composite films at different lignin/PVOH ratios. Also, an curing agent “Darocur®” and 24 hours of UV exposition was used. Drying process was made by using air in a chamber at 32° C. Films were characterized by FTIR, UV-Vis, solubility, DSC, SEM and mechanical stress tests according to ASTM D882 and ASTM D547. Resistance to solubility in water is improved with the increase of the lignin and Darocur® content. The resistance of the films show that the lignin reduce the tensile strength of the composites. Besides, the incorporation of the curing agent improves the tensile strenght, which rise with the increasing of curing agent. SEM images show a smooth surface, free of defects besides the impurities, or lignin particles of large size (fig 2). FTIR spectra shows that the incorporation of Darocur® improves the order of the polymeric films and is reflected in to a lesser absorbance of the spectra compared with PVOH films.

![Image of films](image-url)

*Figure 1. Films obtained for the formulations lignin/PVOH – Darocur®%. a. 0/100 – 0%, b. 0/100 – 1%, c. 0/100 – 2%, d. 5/95-0%, e. 5/95 – 1%, f. 5/95 – 2%, g. 15/85 – 0%, h. 15/85 – 1%, i. 15/85 - 2%, j. 35/65 – 0%, k. 35/65 – 1%, l. 35/65 – 2%.*
Challenges of utilizing different lignins and blends for carbon fibers

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Newly implemented lignin recovery methods in kraft pulping and the beginnings of a lignocellulosic biorefinery industry has facilitated opportunity to obtain technical lignin in commercial scale quantity for industrial conversion into new materials. One potential outlet is in carbon fiber composite materials, where lignin has been considered as a precursor of carbon fibers to replace petroleum based precursors and reduce processing cost for carbon fiber production. Although considerable studies have been focused on micro-sized lignin fibers produces by melt spinning or gel spinning to achieve uniform structure of the
carbon fibers, only few studies showed the structure and properties of lignin based carbon nanofibers. Electrospun fiber mats have less defects, high surface area, and highly oriented molecules. In this study, lignins from various sources were turned into fibrous materials by electrospinning process for carbon fibers production. Electrospun organic solvent fractionated softwood kraft lignin, organosolv hardwood lignin and flax shive lignin blended with small portions of polyethyleneoxide were subsequently carbonized at 1000 °C in an inert atmosphere after oxidative stabilization under airflow. Thermal stabilization processes were studied to optimize conditions for each lignin fiber mats before carbonization process. Different electrospun lignin fiber mats were characterized for morphology and average fiber diameter, thermal rheological properties, structure by scanning electron microscopy (SEM) and molecular spectroscopy, and tensile testing. Carbonized fiber mats derived from different lignins showed varying internal carbon structure revealed by Raman spectroscopy. A discussion related to lignin structure-fiber property relationship is presented based on the molecular structure of lignin from different sources.

**CELL 61**

**Molecular dynamics simulation study of moisture effects on chain mobility in hemicellulose-based bio-nanocomposites as observed by $^{13}$C CP/MAS NMR relaxometry**

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Exploring the molecular properties of carbohydrate polymers under moist conditions is of fundamental relevance for improving the moisture stability of novel bio-composites in all their existing and potential applications. As a first step towards cellulose/hemicellulose composites, we start with xyloglucan hemicellulose itself. Here, we present a molecular dynamics (MD) simulation study of the $^{13}$C CP/MAS NMR longitudinal relaxation times ($T_1$) observed in xyloglucan at increasing moisture content. Experimentally, the $^{13}$C $T_1$ values of hemicellulose chains were successfully assigned to the different C-H vectors therein and correlated with nano-structural changes induced by hydration via the observed decrease of $T_1$ upon increasing moisture content. Our MD simulations reproduce well the experimental observations and explain the observed decrease in $T_1$ by the gradual replacement of polymer-polymer hydrogen bonds by polymer-water hydrogen bonds, which indeed accelerates the dynamics of polymer chains as water molecules move faster than polymer chains. Furthermore, the wide experimental distributions of $T_1$ for each carbon site could be successfully decomposed, with the aid of simulations, into separate contributions from backbone, side chains and end groups of the polymer chain, in turn associated with differing levels of motional freedom. Our combined experimental and simulation methodology successfully captures the physical picture of the water-polymer interaction in xyloglucan and opens new possibilities to the molecular understanding of more complex systems, like cellulose/hemicellulose nanocomposites.

**CELL 62**

**What defines fiber quality in wood refining?**

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Wood fiber-based composite materials fill major consumer product categories, principally for functionalization and adornment of home interiors. Manufacturers of these high-volume, low profit-margin materials constantly seek innovations that neutralize economic and legislative pressures, and that provide new market opportunities. Fiber production involves steam digestion and high energy refining operations that cause major chemical change. Relationships between these chemical transformations and fiber
quality are poorly understood. For instance, manufacturers typically judge fiber quality solely on the visual appearance of the fiber. This research is an exploration of chemical changes associated with steam digestion and refining energy. Changes in fiber pH, buffering, lignin chemistry, porosity, and surface area are discussed with respect to processing parameters as we search for novel aspects of fiber quality.

CELL 63

Potential of plasma surface modification for improving natural fiber-matrix adhesion

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Compatibility between natural lignocellulosic fibers and polymeric matrices is a topic of ongoing research, as no single process has definitively solved this issue. Among the many different researched strategies, surface modification of the fibers by plasma treatment is considered a promising and environmental friendly option. By using cold plasma treatment with different gases it is possible to cause different superficial changes to the fibers, according to what is needed to compatibilize a specific fiber with a specific matrix. In this work we discuss our experience with two very different effects of plasma treatment: Surface etching in oxidizing atmosphere; and chemical modification by surface incorporation of fluorine, using and SF$_6$ atmosphere. The effectiveness of each of these approaches is discussed in terms of the chemical and morphological characteristics of the fiber, the polymer with which the composite will be made and the fabrication method. Using oxygen plasma it was possible to remove the amorphous lignin-rich layer on the surface of coir fibers, exposing and internal structure with higher cellulose content, increasing roughness and the O/C ratio on the surface. These modified fibers, after incorporated in thermoplastic starch matrix, resulted in a composite with three times the elastic modulus and twenty times the tensile strength compared to composites with untreated fibers. This increase was attributed to the improved adhesion and compatibility with the matrix. For various fibers treated with SF$_6$ plasma, the surface roughness was mostly unchanged. However, the former hydrophilic surface (water contact angle of ~24°) became highly hydrophobic (water contact angle of ~130°). This happened due to the incorporation of covalently bound fluorine, up to 25 at%, changing the chemical behavior of the surface. When incorporated in polypropylene matrix, the mechanical properties increased by up to 24%, with potential for further increase.

CELL 64

Treatments of cellulosic fibers to reduce the water absorption in composite reinforcement

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Apart from the well-known use of cellulosic fibers to reinforce polymeric materials, during the last few years, there has been a growing interest in the use these fibers for cementitious materials. Cellulosic fibers can provide well-balanced stiffness, strength, and bonding capacity to cement-based matrices, to mainly enhance their mechanical strength and toughness. Moreover, these fibers are nonhazardous, renewable, and biodegradable, allowing the development of more sustainable and ecofriendly materials for the building industry. Despite all the aforementioned advantages, one of the main drawbacks of cellulosic fibers for cement based composite applications is their high hydrophilicity, which at short term is positive -there is a very good fiber-matrix adhesion- but that constitutes a long term problem -the environmental moisture diffuses through the hydrophilic matrix, leading to materials with low durability to aging-. This lack of durability due to changes in the environmental moisture which induce dimensional changes in the cellulosic fibers is further increased by the effect of the calcium hydroxide present on the cement matrix, which causes a degradation of the fibers. To overcome these problems, the research community basically applies two strategies for improving the durability of these composites: the modification of the composition of the matrix or the physical and/or chemical modification of the fibers to
make them less sensitive to the matrix and environmental humidity. The aim of this research is to evaluate and compare the effects of various treatments on the durability to aging of cement based composites. On the one hand, conventional chemical treatments will be compared with more eco-friendly solutions based on plasma treatments—which use less chemicals and energy-. On the other hand, physical treatments of wet/dry cycling and mechanical refinement of the fibers—which have the advantage of being more simple procedures that only require water and/or mechanical energy—will be also analyzed and compared with the chemical ones.

Cellulose Structure & Biosynthesis
N. Carpita, Organizer; D. Cosgrove, Organizer; P. Langan, Organizer; H. M. O'Neill, Organizer; J. Zimmer, Organizer; C. H. Haigler, Presiding; P. Langan, Presiding Papers 65-72

CELL 65

Evolutionary perspectives on functional differentiation of CESA proteins

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The cellulose microfibrils in the cell walls of charophycean green algae, bryophytes (for example mosses), and vascular plants are synthesized by rosette cellulose synthesis complexes (CSCs) composed of at least 18 cellulose synthase proteins (CESAs), which are responsible for polymerization of the constituent β-1,4-glucan chains. The CESAs of vascular plants appear to function in vivo as hetero-oligomers composed of three isoforms in a 1:1:1 stoichiometry. Based on genetic evidence, the isoforms that form a complex are not interchangeable, and each is thought to occupy distinct positions defined by its interfaces with other components of the complex. However, phylogenetic analysis suggests that the common ancestor of bryophytes and vascular plants had rosette CSCs and a single CESA gene. Furthermore, genetic evidence indicates that cellulose required for development of the leafy shoots of the moss Physcomitrella patens may be synthesized by homo-oligomeric rosette CSCs. This implies that modification of the interfaces between CESA proteins occurred subsequent to the evolution of the rosette CSC morphology. Evolutionary mechanisms that can explain functional differentiation of CESA proteins within rosette CSCs will be presented, along with their implications for the nature of CESA-CESA interactions. A collaborative effort to compare divergent CESA proteins, informed by structural modeling of selected CESA isoforms, has revealed structural features that potentially define isoform-specific function. To evaluate hypotheses arising through this approach, a complementation assay was developed in P. patens for testing the effects of engineered mutations on CESA function. The results of these assays are beginning to shed light on which structural features define the functional differences between CESA isoforms, and potentially their interfaces with other components of the CSCs.

CELL 66

Using animal models to study cellulose biosynthesis

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Tunicates are the only animals known to synthesize cellulose. In the past, tunicate cellulose has contributed to our understanding of the physicochemical properties of cellulose, but it has rarely been addressed in a biological context. This biomaterial comprises the body of living organisms, fulfills physiological functions, and faces evolutionary constraints on structure-function relationships in natural environment. Here I review the biology of tunicates in light of their unique capacity to synthesize animal cellulose.
Aminoethyl cellulose in bacteria: Structure, biosynthesis, and implications

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E. coli and other bacteria assemble bacterial communities termed biofilms that consist of cells plus a self-produced extracellular matrix. Most bacteria exist in Nature as biofilm cohabitants, in contrast to bacteria propagated in the lab through growth in shaking flasks. Biofilms pose a challenge to the treatment of infectious diseases because biofilm bacteria exhibit reduced susceptibility to antimicrobials and host defenses. We introduced new approaches, integrating solid-state NMR with electron microscopy and biochemical methods to define the composition of the intact matrix material of different bacterial biofilms. In our NMR analysis of the E. coli extracellular matrix, we made the unanticipated discovery that the polysaccharide portion consisted of a modified form of cellulose—aminoethyl cellulose. We have identified the genetic determinants for the installation of the modification and established that the modification is required for community phenotypes. Thus, solid-state NMR analysis of the intact polysaccharide was able to identify this biologically important modification that is produced naturally in Nature and evaded detection by conventional approaches. This discovery has implications for understanding bacterial biofilms, for the generation of new cellulosic materials, and for potential integration into plants in efforts to improve the conversion of cellulose to glucose for ethanol production.

How many twists in cellulose biosynthesis can we still expect?

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Cellulose is the most abundant macromolecule on earth. Besides plants, bacteria from different branches of the phylogenetic tree produce cellulose. Thereby, at least three classes of cellulose biosynthesis operons have been recognized with the BcsAB cellulose synthase as the central functional unit and various accessory genes of mainly unknown or poorly characterized function. As one of the recognized major function, cellulose production in bacteria aids biofilm formation and is an anti-virulence factor. The gastrointestinal pathogen Salmonella typhimurium harbors a class IIb cellulose biosynthesis operon that is characterized by the divergently transcribed operons bcsRQABZC and bcsEFG. We have recently demonstrated that bcsE encodes a cyclic di-GMP binding protein required for optimal cellulose biosynthesis. The physiological role of the BcsZ cellulase in cellulose biosynthesis has not been defined. We have recently shown that BcsZ contributes to apparent downregulation of cellulose production, but has also a more complex role in biofilm formation and other behavior of S. typhimurium. Of note, BcsZ is required for optimal virulence in vivo in a mouse model of typhoid fever and in ex vivo virulence assays such as proliferation in macrophages. In conclusion, accessory genes of the cellulose biosynthesis operons significantly contribute to modulation of cellulose production and alter the physiology of the bacteria.

Patterns in cellulose fibril formation

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The mechanisms of the formation of cellulose nanofibrils in plant cell walls are unfolding with the discovery of the structure of cellulose synthases and imaging of terminal synthase complexes. We report the results of simulation and modeling of the formation of elementary fibrils from glucan polymers. The conformational analysis shows that the polymers prefer to exclude water by forming sheets that match the hydrophilic faces of cellulose I-beta and I-alpha primarily. Further, the continuation of formation of cellulose I nanofibrils is kinetically limited by the exclusion of water and can possibly result in crystalline defects from trapped water molecules. We also report on the possibilities of inclusion of non-glucose monomers and polymers in the otherwise pure glucan-chain cellulose fibrils. This work is a summation of systematic studies using molecular simulation and advanced sampling techniques to determine some of the likely mechanisms of fibril formation and deposition into cell walls. We include analyses of hydrophobic and hydrophilic interactions, the role of water, and the order of factors contributing to fibril structure, formation, and stability.

CELL 70

Can an 18-chain cellulose microfibril explain the scattering/diffraction data?

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The number of chains in a single microfibril is highly related to the biosynthetic machinery, and has been discussed for long time based on limited experimental data. X-ray or neutron scattering/diffraction experiments are relatively simple and reproducible. The data are directly reflecting the spatial organization inside the specimen but the interpretation can be controversial. Mathematical representation gives the diffraction peak-width inversely proportional to the number of diffracting planes, and this property has been used to estimate the lower bound of the crystallite size considering that the planes corresponds to the plane going through the center of molecule. Lower bound since disorder can also contribute to the broadening. Under this consideration, an 18-chain model would be too thin except if extensive co-crystallization exists. However, we are going to demonstrate that the diffraction and scattering data are compatible with the 18-chain microfibrils that are not touching each other, if we take the matrix component into account. Indeed the amorphous matrix surrounding the microfibrils is also contributing to the diffraction since the periodic electron density fluctuation is the physical origin of the diffraction. The compatibility of small angle X-ray scattering features with the 18-chains microfibril will be also discussed.

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Relations between co-crystallization and multiscale hydration in celluloses isolated from plants

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Celluloses isolated from higher plants are hierarchically nanostructured solids, which in aqueous environments are interpenetrated by water. Interplay between water and the distinct nanostructural levels is important but not yet clearly understood. In this work we generated a variety of celluloses isolated from higher plants, in which the feedstocks as well as the thermochemical isolation processes were varied. The resulting sample panel was characterized by X-ray diffraction, dynamic vapor sorption, calorimetric thermoporometry and compositional analysis. We explore the correlations among the measured attributes and seek phenomenological models able to explain the observations. With this approach, the still mysterious phenomenon of cellulose co-crystallization (increasing crystallite width) is proposed to cause multiscale impacts on cellulose hydration and swelling, affecting from monolayer hydration to water-filled nanoscale pores.
Understanding the mechanical induction of macromolecular defects in cellulose nanofibrils by molecular dynamics simulation and scanning probe microscopy

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Mechanical processing of cellulosic substrates is an important step in many processes such as nanocellulose production and pretreatment of biomass prior to enzymatic saccharification. Developing a deeper understanding of the way in which mechanical energy affects cellulose at the molecular and macromolecular scales will help optimize such processes. Previously, we demonstrated that relationships exist between the macromolecular geometry of cellulose fibrils and their propensity to concentrate stress into the formation of kink-defects that lower the overall free energy of the structure when constrained to curvatures above a certain threshold. In this presentation, I will describe recent developments towards understanding the mechanical induction of crystalline defects by 2 and 3-point bending tests performed both in-silico and with a scanning probe microscope. In addition to modeling and measuring the molecular mechanics of fibril bending, we incorporate quantum mechanical simulations to predict breakage of strained glycosidic bonds during the course of fibril bending. This phenomenon of mechanically-induced bond breakage may contribute to the enhanced enzymatic digestibility of biomass subjected to high-shear processing, such as disc-refining, by introducing new reducing and non-reducing ends for the initiation of processive hydrolysis. Finally, we investigate the reversibility of fibril bending and determine the threshold at which the mechanics of bent fibrils are permanently altered such that they may no longer spontaneously recover their initial configuration when the mechanical stress is released.
CELL 73

Limiting factors for cellulose nanocrystal yield assessed via TEMPO-mediated oxidation of microcrystalline cellulose

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Cellulose nanocrystal (CNC) production suffers from low yields, among other problems. The focus here was to investigate the universal effect of charge density, centrifugation, and mechanical treatment as the limiting causes of yield. Microcrystalline cellulose (MCC) was used as the starting material in order to eliminate the yield losses caused by the hydrolytic conditions. To disintegrate MCC into nanocrystals, high surface charge in the form of carboxylic groups was introduced by TEMPO-mediated oxidation. Thereafter, the material was mechanically treated with different degrees of sonication, and separated into fine and coarse fractions. The fine fraction was collected as supernatant after separation by centrifugation and it had a yield of 17-20 %, independent of the mechanical treatment method or time used. The particle sizes of these fractions did not significantly differ from each other, which raises questions on the efficiency of the mechanical treatment (sonication) as well as centrifugation in CNC production.

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Characterization and patterning of anthraquinone functionalized cellulose nanocrystals

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Cellulose nanocrystals (CNCs) are well-known reinforcing agent for polymeric materials, due primarily to their strong mechanical property, environmentally friendly origin and high sustainability. For specific applications, functionalization of CNCs are frequently required, where the first step is to covalently bond anthraquinone to the base materials to enable further modification. To ensure quality and success of subsequent materials synthesis and modification, anthraquinone (AQ) modified CNCs are prepared and characterized in this work. High-resolution imaging and spectroscopy were utilized to characterize the structure of anthraquinone functionalization in comparison to unmodified CNCs, which have a sulfated surface. The diameter and length of individual CNCs were visualized and measured with nanometer precision, as shown in Figure 1. The diameter and length show minimal changes upon anthraquinone addition, however, CNCs are much more prone to form aggregates due to functionalization (see Figure 2). The presentation will also discuss concentration-dependence of the aggregation, and potential applications such as further processing and patterning.
Figure 1. Topographic image of AQ-CNC on poly-l-lysine mica.
Surface polarity engineering of crystalline nanocellulose using a food-grade surfactant for improved sustainable biocomposites

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Isolated from the most abundant and renewable biopolymer, nanocelluloses have become structural building blocks for many advanced functional materials. Both existing and new enabling applications of nanocelluloses depend critically on their surface characteristics. However, due to their inherent hydrophilicity, their utilization is limited to applications involving hydrophilic or polar media. Many surface modifications have been explored, but most employ chemistries that would not be acceptable from a health and safety or an environmental lifecycle standpoint. In the present study, we demonstrate a green, facile surface functionalization of crystalline nanocellulose (CNC) using lauric arginate, a food-grade cationic surfactant via ionic binding of its positively charged guanidinium groups onto the negatively charged surface of CNC. The amount of surfactant required to coat CNC is optimized, aiming at preventing excessive addition of the surfactant and undermining the properties of the resulting composites. The presence of absorbed surfactant on the modified CNC is confirmed using FTIR spectroscopy and its effects on morphology, polarity and thermal stability of the ensuing CNC are examined. Further, the functionalized CNC is incorporated into a hydrophobic poly(lactic acid) matrix and shows better dispersion than pristine CNC. The crystallinity, mechanical and thermal properties of the composite are greatly improved with the incorporation of the modified CNC. It is expected that this high performance bionanocomposite will expand the practical utilization of CNC and bioplastics in many industries including packaging, automotive, construction and others.
CELL 76

Microfibrillated cellulose produced with a high consistency enzymatic process

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One of the most important developments in cellulose technology in the last decade is the emergence of a class of cellulosic materials; microfibrillated celluloses (MFC). MFC, or its finer scale counterpart, nanofibrillated celluloses (NFC) may be an important raw material for a range of new fiber products. However, many of the processes that are used to produce MFC or NFC are not robust enough, nor cost efficient enough, for industrial application. In the present work, we explore a high consistency enzymatic hydrolysis process that appears to be highly scalable and has a potentially attractive cost structure. In this research, the effect of hydrolysis time at optimal pH and temperature and at 20% pulp solids is examined. A commercial endoglucanase enzyme is used. A previously dried, bleached Kraft Birch was used in all experiments. Thus, we examine how the virgin pulp fibers are broken down from the intact fibers to a fully defibrillated state. The MFC properties are considered in some detail. This includes, crystallinity, swelling, dimensions, DP and rheological parameters. Films were formed from the MFC and various physical properties were examined. The film properties were compared to films produced from the same pulp, but mechanically refined. In some experiments, the swelling of the MFC is modified to improve its bonding characteristics. The high consistency process is an extremely efficient way to break down macroscopic fibers to, small fibrillated fragments. The disintegration continued over the range of the experiment – up to 300 minutes. However, by some metrics the pulp was fully broken down by about 120-180 minutes. The high consistency conditions allowed for an increased enzyme concentration at the fiber internal surfaces, while the mixing at high consistency caused the fibers to flex and facilitated both diffusion of the enzyme throughout the cell wall and the attrition of the fibers. The swelling of the enzymatic MFC was quite low compared to other grades of MFC. This, together with low DP of the cellulose, resulted in low film strength properties. There are several viable options for increasing the swelling and improving the bonding potential of the MFC. The MFC is shear thinning and its viscosity decreases monotonically with hydrolysis time. This allows the enzymatic MFC to be pumped and processed at fairly high solids contents. Likewise, the dewatering properties of the enzymatic MFC are quite good due to its low swelling.

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Determination of hydrophobicity in amphiphilic nanocellulose imparted by Aqueous Counter Collision (ACC)

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Surface properties such as either hydrophilic or hydrophobic of nanocellulose are critical characteristics for the functionalization and/or utilization. Aqueous counter collision (ACC) process proposed by Kondo et al., which is capable to downsize materials into the nano-objects by impinging of dual high speed water jets containing samples, have recently been found to exposed the inherent hydrophobic surfaces engaged in van der Waals forces of cellulose pulp fibers onto the resulting ACC-nanocellulose surfaces. In this article, the authors attempt to quantitatively determine the exposed hydrophobic surfaces in order to elucidate the amphiphilic properties as the entire ACC-nanocellulose. As the indicator, Congo red, which is assumed to preferably adsorb onto hydrophobic faces in anhydroglucose units, was employed. The most striking impact in the results indicated that the degree of hydrophobicity imparted by ACC was dependent upon origins of the initial microfibers. Namely,
hydrophobicity for ACC-nanocellulose from bamboo pulp, which exhibited the similar characteristics for bacterial pellicle, was almost twice greater than that for wood pulp.

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Understanding cell wall longitudinal structure for producing cellulose nanofibrils by disk milling with dilute acid prehydrolysis

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Here we used dilute oxalic acid to pretreat a kraft bleached Eucalyptus pulp (BEP) fibers to facilitate mechanical fibrillation in producing cellulose nanofibrils using disk milling with substantial mechanical energy savings. We successfully applied a reaction kinetics based combined hydrolysis factor ($CHFX$) as a severity factor to quantitatively control xylan dissolution and BEP fibril depolymerization. More importantly, we were able to accurately predict the degree of polymerization (DP) of disk-milled fibrils using $CHFX$ and milling time or milling energy consumption. Experimentally determined ratio of fibril DP and number mean fibril height (diameter $d$), $DP/d$, an aspect ratio measurer, were independent of the processing conditions. Therefore, we hypothesize that cellulose have a longitudinal hierarchical structure as in the lateral direction. Acid hydrolysis and milling did not substantially cut the “natural” chain length of cellulose fibrils. This cellulose longitudinal hierarchical model provides support for using weak acid hydrolysis in the production of cellulose nanofibrils with substantially reduced energy input without negatively affecting fibril mechanical strength.

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Cellulose fibre in situ fibrillation by twin screw extrusion

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Nanofibrillated cellulose (NFC) has gained increased attention during the last decades. Indeed, nanocellulose is an interesting renewable, biodegradable, and biobased material for many applications in such fields as: composites, papermaking, food, or more recently medical/ or pharmaceutical products. However, the production of nanofibrillated cellulose is still challenging due to the high energy consumption of mechanical treatment and high water content of the final product. Those two points are key issues for cost, transport, and formulations. The aim of this work is to find a new energy efficient process to produce NFC at high solid content. Nanofibrillated cellulose with a high solid content (20-25wt%) were produced from pretreated eucalyptus pulp thanks to a twin screw extruder equipped with kneading and feeding screws. Different chemical or biological pretreatments were used in order to facilitate the fibrillation and decrease the energy needed. Nanopaper with a Young’s modulus greater than 10 GPa were produced after one or more passes through the extruder. The ensuing NFC were characterized and compared with NFC produced using an ultrafine friction grinder Supermasscolloider. Finally, the energy used with the twin screw extruder was 50% lower than the one used with the masuko grinder with similar properties obtained from each mechanical treatment. New applications are considered for theses high content NFC.
In the present study cellulose isolated from CH (corn husk) and BR (banana rachis) was nanofibrillated by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-mediated oxidation; followed by a mild homogenizing treatment with a magnetic stirrer. The monosaccharide composition of cellulose obtained from CH and BR was evaluated through UHPLC (ultra-high performance liquid chromatography). To verify the influence of the monosaccharide content of cellulose on the TEMPO-mediated oxidation, different reactions were performed, varying the time between 0 and 10 h. TGA (thermogravimetrical analysis) and ATR-FTIR (attenuated total reflectance-Fourier transformed infrared spectroscopy) indicate the oxidation of the C6 hydroxyl groups of cellulose, obtaining sodium carboxylate groups, associated to a selective oxidation by TEMPO in both specimens. The oxidation degree (OD) and content of sodium carboxylate groups were different between CH and BR. The OD of BR increased with time in the studied interval, while CH reached a plateau at 5 h without an observable modification at higher times. The TGA of the samples indicates a decrease of the thermal stability of oxidized cellulose. Crystalline and compositional changes after TEMPO are being analyzed by X-RD (X-ray diffraction) and UHPLC. The oxidized cellulose will be characterized by AFM (atomic force microscopy) and TEM (transmission electron microscopy) to assess its morphology.

New Horizons in Sustainable Materials
M. G. Laborie, Organizer; S. H. Renneckar, Organizer; N. Robitaille Brown, Organizer; N. Sathitsuksanoh, Organizer; S. H. Renneckar, Presiding Papers 81-88

Adaptable materials are of great interest in a number of fields where real-time mechanical adjustments to environmental stimuli in situ are of crucial importance to a materials long-term endurance. These include materials for bone or dental grafting systems, the reinforcement of wood for sustainable building construction or the conservation of organic objects of cultural importance. The benefits of mechanically adaptable materials in such situations is clear. Being able to design such materials from bio-based polymers, particularly those extracted from biomass (e.g., polysaccharides, such as, chitosan, cellulose, or alginate), is of particular interest due to their specific chemical structures and renewability, as well as their biocompatibility. However, given that these biopolymers are not synthesized from fossil resources through controlled chemical reactions, their structures, their behavior and the behavior of the corresponding materials under complex environmental conditions are not always clearly understood. One reason for this is an incomplete understanding of the role of environment in intermolecular interactions in biopolymers, as well as their behavior over multiple length scales. To achieve the goal of designing complex hierarchical networks based on biopolymers that mimic Nature’s own mechanically adaptable
networks (e.g. collagen, dentine, wood), but which can be controlled and manipulated to suit different application environments, a better understanding of the molecular to macroscale behavior of polysaccharide chains (chitosan, alginate) and nanocrystals (cellulose) is required. Herein, preliminary work on the characterization and functionalization of biopolymers and polysaccharide nanocrystals is presented, with specific focus on the effect of the environment (i.e., variations in salt nature and concentration, pH, temperature and humidity) and/or the functionalization strategy on the organization, interactions and assembly behavior of the network components and how this ultimately relates to macroscale mechanical properties and adaptability.

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Hydrodynamic stability of reacting multilayer flows in a Hele-Shaw cell

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The focus of the present work aims at exploring the hydrodynamic production of bio-based materials from an experimental and numerical point-of-view. The transition of biopolymer or colloidal dispersions to visco-plastics with high yield stress is largely affected by the hydrodynamic stability and diffusivity of a reactive agent. To produce new bio-based products which material properties can compete with those that are made with more conventional materials, such as nylon, kevlar fibre, and synthetic organic polymers, it is crucial that we explore the chemical and hydrodynamic stability during formation. We investigate the transition of biopolymer and colloidal dispersions from a weak to strong visco-plastic fluid with high yield stress in a reacting Hele-Shaw cell, or thin gapped channel. We track the interface of reaction using optical coherency tomography (OCT) and confocal microscopy through particle image velocimetry (PIV) analysis. The results suggest that multilayer reacting flows of biopolymer and nano-cellulose dispersions are hydrodynamically stable, which is largely because surface tension is negligible at the reacting front. Numerical tools are used to assess the effects of reaction rates, and reversibility on the stability of the reacting front. Up to now we have limited the work to hydrogels which form from cross-linking or Van der Waals forces, both of which develop from one way reactions. These findings give rise to a number of opportunities in the production of biomaterials outside of nano-cellulose or biopolymeric threads.

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3D printing of cellulose nanocrystals and nanocomposites

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Cellulose is an abundant biomaterial that can be used as reinforcing elements in a wide range of polymer composites at different length scales, ranging from macro (natural fibers) through micro (micro-fibrillated fibers) down to nano scale (nanocrystals). Because of the high surface-to-volume ratio and the high density of available primary hydroxyl groups on their surfaces, cellulose nanocrystals are highly prone to surface functionalization, which increases their chemical compatibility with different polymer matrices. Developing techniques to control the orientation and spatial distribution of these nanocrystals can allow us to fabricate composites with tunable mechanical properties. In this work, we investigated how direct-ink writing can be explored to assemble complex cellulose-based materials with controlled orientation and spatial distribution of nanocrystals. By varying the concentration of reinforcing nanocrystals, high degree of alignment and improved mechanical properties were obtained, paving the way for the fabrication of
high-performance materials with renewable sources of reinforcing elements using additive manufacturing techniques.

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Cellulose nanofibril-cell adhesive peptide conjugates for 3D bioprinted tissue models

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Most common in vitro cell culture models have been implemented as 2-dimensional so far, where the cells are layered at the bottom of a cell culture dish. However, cells are configured and vascularized three-dimensional (3D) in a tissue for an effective transfer of nutrients and oxygen. 3D bioprinting is a facile method for fabrication of 3D tissue models and body organs with advanced functionality. The technique requires biocompatible hydrogels, so called bioinks, to be used in 3D Bioprinters for rapid manufacturing of 3D tissues and organs in the laboratory conditions. We design cellulose nanofibril (CNF)-based functional bioinks for the preparation of model tissues using 3D Bioprinters. The cellulose nanofibrils were functionalized chemically with cell adhesive peptides, RGD (R: arginine; G: glycine D: aspartic acid), laminin and TGF-B in order to promote human dermal fibroblast adhesion and viability within the 3D Bioprinted CNF network. The degree of peptide/protein substitution, colloidal stability and gelation of the functionalized fibrils were characterized by dynamic light scattering, FT-IR and XPS. The printability tests were performed with a 3D Bioprinter under various printing pressure and speed. The influence of peptide conjugation and bioink composition on fibroblast adhesion, viability and proliferation was analysed. In vitro cell studies performed with 3D Bioprinted tissue models showed that the adhesion and viability of fibroblast cells were promoted significantly in CNF-conjugated bioinks compared with non-modified CNF bioinks.

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Functional lignocellulosic materials: Engineering smart bio-hybrids from a natural anisotropic scaffold
The transition from oil-based to renewable resources is of major importance, and wood has the potential to become one of the key materials of modern sustainable societies: it is an abundant and widely available renewable resource, with exceptional mechanical properties and with an essential role in carbon management (CO₂ storing material). Recently, a renewed interest in the utilization of wood for diverse applications has been observed, as a result of pressing concerns regarding environmental issues that an increased utilization of the resource wood may help to solve, but also associated to the development of novel modification techniques that can be used to improve wood intrinsic properties or to develop advanced lignocellulosic based materials. We will present our approaches to the design of polymer and inorganic bio-hybrid materials with unusual properties. As shown in Fig. 1A, the natural wood anisotropy may be used advantageously, to introduce new material at various locations. Using the wood surface roughness and ATRP-grafted fluorinated polymers, we developed a surface with striking superhydrophobic properties (water CA~170°, Fig. 1B). ATRP was also employed to graft poly(NIPAM) chains inside the wood cell walls, yielding a hybrid material with temperature controlled hygro-responsive behavior (Fig. 1C). New composites were also obtained via a pore-filling technique, where PNIpAM was introduced within the luminal area via a grafting-through method (Raman image, Fig. 1D). Finally, we will also show that the structural and chemical anisotropy of wood might be used to selectively alter its properties, and yield surfaces with patterned hydrophilic/hydrophobic domains after a sol-gel chemistry method is applied (pinned water drop on late wood region, Fig. 1E). We believe that these pioneering approaches to functionalize lignocellulosic materials will be of high importance in the future to promote new utilizations of the resource wood.

Figure 1: Modification of the wood microstructure to afford functional lignocellulosic materials.
Non-proteolytically digestible micro-patterning cell scaffolds by inkjet-printing of chitinous nanocrystals

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Micro-patterning cell scaffolds permit fruitful applications such as controlling of cellular shapes, precise monitoring molecular events in biochemistry, and drug screening. Here, by using inkjet printing of cytocompatible chitinous nanocrystal (NC) inks, we demonstrate microscopic localization of cellular adhesion. The bio-NC materials including cellulosic one have currently attracted attention and their dimensions are actually comparable with those of pigments for practical inkjet printers. We display how to regulate the occupied area and maximum height of the chitinous NC microstructures (dots and lines) using a research inkjet printer. Cellular adhesive capability was much improved for deacetylated chitin NC (dChNC), as already known for chitinous bulk materials. The dChNC remained nanocrystalline shape even after severe deacetylation and exhibited wide-angle X-ray diffraction pattern of chitosan. The obtained cellular adhesive dChNC ink may be digested enzymatically but non-proteolytically, therefore, essentially gives rise to no damage on cells when removing from the substrate. This is a promising approach for tailor-made tissue engineering.

Mouse fibroblast cell growth on the chitinous NC micro-structures inkjet-printed in a linear shape

Chemical modifications for the synthesis of functional materials from sustainable nano/cellulose

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Cellulose, as the most abundant sustainable materials on earth, still needs further exploration for its role in the field of advanced technology. Although cellulose is ubiquitously used in our daily life as commodity products, e.g. paper and textile, it has less been applied for fields with critical requirements, such as for health care products, functional interfaces and surfaces. The chemical design for the preparation of smart
materials by introducing functional groups is a promising way for expanding this area. Thanks to the numerous hydroxyl groups within the repeating units of cellulose, diverse groups can be introduced either in cellulose backbone or on nanocellulose surface. The key point is to keep their properties, during the fabrication of microsized materials using polymeric cellulose derivatives or nanocellulose derivatives. In this presentation, functional and smart materials with diverse properties derived from nano/cellulose will be presented. Among others, the formation of stimuli-responsive nanoparticles (NPs), functional surfaces with polymeric nanoflake structure and tough hydrogels will be described. It is therefore obvious that the precise control of the chemical structure of the cellulose-based polymeric compounds and the functional groups on nanocellulose is of particular importance for the materials properties.

**CELL 88**

**Optimizing both thermal and colloidal stability of cellulose nanocrystal through acid hydrolysis**

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Cellulose nanocrystals (CNCs) are rod shaped nanoparticles extracted from natural cellulose sources through a hydrolysis procedure which most commonly uses sulfuric acid. While other acids have been used for hydrolysis, they have rarely been optimized. CNCs hydrolysed with phosphoric acid have been demonstrated to have increased thermal stability [Camarero Espinosa et al. Biomacromolecules, 2013, 14, 1223]; however, we have found that the nanoparticles produced following this protocol are difficult to handle because they remain “hinged” together and have limited colloidal stability due to very few surface grafted charge groups. A design of experiments statistical analysis was performed to optimize CNCs produced by phosphoric acid hydrolysis, in terms of their thermal and colloidal stability. Specifically, acid concentration, temperature and reaction time were varied and the effects of these parameters on CNC morphology and surface chemistry were studied. It was found that the hydrolysis conditions have a significant effect on several CNC properties and the phosphoric acid hydrolyzed CNCs were compared to CNCs produced with sulfuric acid only, as well as acid blends. All CNCs produced were thermally treated in various environments, including at high pressure, and fully characterized following treatment to elucidate the effect of surface grafted groups (and their chemical stability), degree of crystallinity, and cellulose degree of polymerization on thermal and colloidal properties. This is the first step towards a better mechanistic understanding of CNC thermal stability which ultimately will allow for the production of CNCs suitable for high temperature/pressure applications such as oil & gas drilling and completion fluids.

**Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems**

M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. J. Rojas, Organizer; K. A. Oksman, Presiding; J. Campos-Teran, Presiding Papers 89-96

**CELL 89**

**Biomass conversion into functional bioplastics and gels**

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Macromolecular carbohydrates are valuable precursors for the design of a range of functional and green materials. We produce carbohydrate-rich fractions by chelating, aqueous and/or hydrothermal treatments of forestry, agricultural or marine biomass. Pathways are designed for chemical and/or physical modifications and subsequent conversion of such fractions into materials for bulk and high value applications. This talk will present new and benign strategies for the multicomponent fractionation of
biomass as well as purposely developed routes for the preparation of gels and bioplastic materials with targeted property profiles.

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Effect of the culture medium in the production of bacterial cellulose from kombucha

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Kombucha is a fermented drink with probiotic activity in which Acetobacter xylinum, Gluconacetobacter xylinus and other microorganisms have been identified. During the lactic fermentation of Kombucha, a bacterial cellulose (BC) biofilm is formed at the air-culture medium interphase. In general, BC is comprised of fibers of less than 0.1 µm diameters. It has a high crystallinity (ca. 60%), high resistance, high water absorption, it is lignin free and it is also biocompatible. This work studied both; the effect of the culture medium in the production of BC and the effect of a sanitization method. The best culture media, using glucose as carbon source, were a fertilizer (0.435 g BC / g C) and a yeast nitrogen based (YNB) medium (0.398 g B / g C). Yields were 0.176 g BC L⁻¹ day⁻¹ and 0.193 g BC L⁻¹ day⁻¹ respectively and SEM images showed fibers of around 0.1 μm. While chlorine (10%, 3 min) eliminated the microorganisms on the biofilm, it also bleached the BC. The biocompatibility and physicochemical characteristics of BC make it a good material with potential biotechnological applications ranging from hydrogels, super absorbent materials, scaffolding for the treatment of burns and bone regeneration among others. Therefore, studies to optimize its production, characterization and purification are of great importance in the area.

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Sugar produced from corn cob pretreated with the combination of electron beam irradiation and enzymes

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Corncob is a lignocellulosic material composed of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are polysaccharides constituted of simple sugars (hexoses and pentoses). However, these sugars are difficult to access, due to the presence of lignin, which is a polyphenolic molecule that provides a high recalcitrance to plant tissue. An appropriate biomass pretreatment disrupts the hydrogen bonds in crystalline cellulose, breaks down cross-linked matrix of hemicelluloses and lignin, and raises the porosity and surface area of cellulose for subsequent enzymatic hydrolysis. There are several pretreatment methods including, physical pretreatment (electron beam irradiation, grinding and milling, microwave, and extrusion), chemical pretreatment (alkali, acid, organosolv, ozonolysis, and ionic liquid), physico-chemical pretreatment (steam explosion, liquid hot water, ammonia fiber explosion, wet oxidation, and CO₂ explosion), and biological pretreatment. This study evaluated electron beam irradiation (EB) in combination with enzymatic hydrolysis on corncob at different grain size to produce sugars. Dry biomass samples after characterization were exposed to EB radiation doses of 0, 30, 50, 70, 100, and 200 kGy. The pretreated biomass samples were enzymatically hydrolyzed using the Cellic® CTec2 from Novozymes. The structural changes and degree of crystallinity of the pretreated biomass were studied by FTIR, DRX, DSC, TG and SEM analyses. Corncob in natura showed 6.3 % extractives, 40.3 % cellulose, 31.8 % hemicellulose, 17.3 % lignin, and 0.7 % ash. The EB in combination with enzymatic hydrolysis of corncob is an environmentally sound biomass pretreatment.
Chromatographic purification of sugar cane bagasse alkaline extract

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Sugar cane bagasse is a lignocellulosic by-product from the sugar production process that presents a large interest for biofuel production from cellulose and hemicelluloses. But as a substantial amount of phenolic compounds are co-extracted with hemicelluloses, their valorization requires an extra step of purification. The aim of this study was to define how it was possible to separate monomeric from oligomeric compounds and phenolic molecules from hemicelluloses. Two main schemes were studied; direct separation by pulse chromatographic process or combination of nanofiltration (partial purification of the extract and pre-concentration) and chromatographic purification. Sugar cane bagasse was treated in a batch reactor under alkaline conditions. Extraction conditions were set according to a bibliographic study on lignocellulosic biorefinery pretreatments; two different temperatures were compared. Solid/liquid separation was performed by filtration. The extract (liquid) and the raffinate (solid residue) were characterized following NREL methodology and relevant phenolic monomers were analyzed by HPLC. Mass balances were equilibrated with almost all the followed compounds. A small degradation of hemicelluloses and cellulose was detected with a rate of about 8%. Analytical characterizations indicate that the extracts were mainly composed of salts, lignin under oligomeric form, phenolic monomers and hemicelluloses under oligomeric form. After concentration of the extracts by evaporation, several chromatographic resins were used to separate these different fractions. Strong acid cationic (SAC) gel type resin (XA2004-30 Na+ from Novasep), SAC macroporous type resin (XA2054 Na+ from Novasep) as well as adsorption resin (XAD 4 and XAD 16), Strong Basic Anion (SBA) resin and Weak Basic Anion (WBA) resin were compared for their separation efficiency. Trials were performed with a 1 m x 26 mm ID column by injection of 5 mL of extract and elution with demineralized water. Elution fractions of 15 mL were collected and analyzed to follow the retention evolution of the different species. Results show that chromatography separates salt and non-carboxylic phenolic monomers on one side and hemicelluloses, lignin oligomers and carboxylic phenolic monomers on another side with water elution. Synthetic p-coumaric acid solution at alkaline pH confirmed the separation mechanisms between the p-coumaric acid and salts on XA2004-30 Na+.

Energy efficient separation process of nanofibrils from bioresidues and their use in biocomposites

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We have evaluated the production potential of bionanofibrils from different industrial bio-residues: wastes from the juice industry (carrot) and beer production (brewery-spent-grain). The mechanical separation of the nanofibrils was made using ultrafine grinding. The carrot residue was more easily bleached and less energy was needed during the grinding, using only 0.9 kWh/kg compared to 21 kWh/kg for the BSG, moreover, the dried nanofiber networks showed high mechanical properties, with an average modulus and strength of 12.9 GPa and 210 MPa, respectively, thus indicating a homogeneous nanosize distribution. We have also used these fibers for preparation of composite materials. The study showed that carrot residue has great potential for the industrial production of cellulose nanofibers due to its high quality, processing efficiency, and low raw material cost.
Torrefaction analysis of woody biomasses from fast-growing plantations of Costa Rica

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Woody biomasses can be obtained from different sources, including energy plantations, harvest residues and wood processing residues. They represent interesting raw materials to be used in energy processes. Even when their principal use for energy purposes is in direct combustion, there are other types of thermochemical processing that have gained considerable attention in recent years (e.g. gasification and pyrolysis). However, they are limited by several characteristics of the raw materials such as high moisture content and hygroscopic nature, low energy density, low bulk density and difficulties for transportation and storage. To address these problems, different pretreatment and/or densification techniques have been used. Among them, torrefaction is a thermal pretreatment commonly applied to biomasses developed at 200-300 °C in the absence of oxygen that allows to obtain improved properties of the biomasses such as higher heating value, lower atomic O/C and H/C, higher hydrophobicity and lower moisture, improved grindability and more uniform properties. In the present work, a study of five fast-growing species (Cupressus lusitanica, Dipterix panamensis, Gmelina arborea, Tectona grandis and Vochysia ferruginea) was performed using simultaneous thermogravimetric and calorimetric analyses under pyrolysis and different torrefaction conditions (i.e. light, mild and severe). Parameters obtained from such class of analyses (e.g. mass losses, decomposition temperatures and devolatilisation rates) were correlated with characteristics of the biomasses such as composition (i.e. cellulose, lignin, ash components and extractives in different solvents) and energy parameters (i.e. volatile content, net calorific value and C/N ratio). This allowed the determination of the influence of characteristics of the biomasses in the thermal processes developed, as well as the selection of the best torrefaction conditions between the evaluated, representing a good decision tool that can be used for large-scale torrefaction processes.

Scaled-up production of biodegradable pectin plastics using continuous casting

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Pectin is a versatile polysaccharide with important applications in nutrition and foods. Pectin is also an abundant renewable resource, especially in Brazil where it occurs as an agro-waste of the fruit juice and sugarcane production. The current work describes the use of pectin as a feedstock for obtaining biodegradable plastics by continuous casting. This is an emerging and eco-friendly method for producing thin polymer films at large scale. Different pectin solutions containing the plasticizer glycerol at contents of 15 and 30 wt.% were prepared and converted into plastics on a labcoater machine previously set at conveyor speed of 0.10 – 0.20 m min⁻¹, wet layer thickness of 1.5 mm and temperature of 80 - 120 °C. Pectin plastics were characterized by thickness measurements and uniaxial tensile tests at relative humidity (RH) of 50 and 75%. It was observed that pectin plastics exhibited uniform thickness both at longitudinal and transverse casting direction, regardless the glycerol content. Pure pectin plastic exhibited tensile strength of 44 MPa and Young’s modulus of 2.7 GPa. Both mechanical properties changed gradually to 17.9 MPa and 0.6 GPa at 50% RH and to 16.7 MPa and 0.3 GPa at 75% RH with increasing glycerol content up to 30 wt.%. Moreover, a substantial increment in elongation was observed in plasticised pectin plastics, from 2.7% at 0 wt.% glycerol to 21% at 30 wt.% glycerol, suggesting
biodegradable plastics with notable flexibility. Such tendencies in elongation were verified for both RH levels. These outcomes highlight the continuous casting potential towards the production of biodegradable pectin plastics at a rate as fast as 20 cm min⁻¹. This leads to environmentally friendly plastics with broad range of mechanical properties for various applications, including food packaging.

**CELL 96**

**α-Eleostearic acid extraction by saponification of tung oil and its subsequent polymerization**

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The goal behind environmentally alternative research is to replace current fossil fuel-based products with more sustainable and renewable products, such as vegetable oil-based polymers. These bio-based polymers have received a lot of attention in the recent past due to their versatility and tunable properties, which can be easily achieved by adjusting the resin composition. The carbon-carbon double bonds in unsaturated oils make them ideal reactive sites for the chemical industry. Most vegetable oils must be modified before polymerization due to the low reactivity of their non-conjugated fatty acid chains. Tung oil (TO) contains ~83% of a triply conjugated fatty acid (*α*-eleostearic acid), making it an attractive starting material. Without the reinforcing role of fibers, such as cellulose, vegetable oil-based polymers do not have the thermo-mechanical properties to replace petroleum-based polymers.Compatibilizers, such as asolectin and maleic anhydride, have been utilized to increase the adhesion between resin and reinforcement, therefore enhancing the composites' thermo-mechanical properties. In this project, the need for a compatilizer is eliminated through the preparation of a polar polymer matrix from the crosslinking of tung oil fatty acids with divinylbenzene and *n*-butyl methacrylate. It is shown that the polar regions of the fatty acid can interact directly with a polar filler, *α*-cellulose, through hydrogen bonding. The successful isolation of fatty acids from tung oil was checked by GC-MS, ¹H NMR, Raman, and FT-IR spectroscopies. The polymerization of the resins was monitored by dielectric analysis (DEA) to obtain the optimal cure schedule. The final materials' properties were analyzed by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). Similar composites prepared from tung oil methyl esters exhibit a lower binding affinity with cellulose when compared to the fatty acid composites, containing therefore more cracks and inferior thermo-mechanical properties.

**SUNDAY EVENING**

**General Posters**

M. Roman, Organizer; Papers 97-168

**CELL 97**

**Aminoethyl cellulose: *E. coli* ’s building material for a biofilm matrix**

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*E. coli* integrates amyloid fibers termed curli and a modified form of cellulose to assemble a mechanically robust extracellular matrix (ECM). The discovery that *E. coli* produces a modified form of cellulose was made possible by solid-state NMR analysis of the intact matrix material produced by uropathogenic *E. coli*. This modified form of cellulose contains a hydroxyl-substituted O-linked aminoethyl (−OCH₂CH₂NH₃⁺) functionality on the C2 carbon. We determined that the aminoethyl functionality is derived from serine and that three relatively uncharacterized genes in the bacterial cellulose synthesis operon are involved in the
installation of the modification on cellulose. An *E. coli* mutant incapable of modifying cellulose cannot form well-integrated biofilms on agar or at the air liquid interface. Thus, approaches to inhibit the modification of cellulose in *E. coli* may enable the development of new anti-infectives to prevent biofilm formation by uropathogenic *E. coli*, the most common causative agent of urinary tract infections. In addition, the identification of the biosynthetic production of a modified cellulose holds potential value in the generation of cellulosic materials and in efforts to improve the conversion of cellulose to glucose for ethanol production.

**CELL 98**

**From cellulose tissue papers to nanoporous membrane actuators**

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In this poster, we designed a hybrid porous membrane actuator based on a cationic PIL poly[3-cyanomethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide], poly(acrylic acid) and cellulose tissue paper (termed PIL-PAA/tissue paper). This membrane was fabricated by coating a solution of PIL and PAA in DMF onto tissue paper, followed by drying and then treated with aqueous ammonia solution to produce a gradient crosslinking degree and porous membrane. The presence of the pores and the structural gradient enabled membranes to serve as fast and sensitive actuators. Compared to the native PIL-PAA membrane which is too fragile to be processed upon drying, the hybrid porous membrane based on PIL-PAA/tissue paper exhibits superior mechanical properties that can be easily folded into artificial flowers in drying state (Figure 1a). Besides, the hybrid membrane shows reversible actuation in acetone vapor and air. In acetone vapor, a fresh prepared membrane readily bent to a loop with a bending angle of 180° within 6 s. Upon pulling back to air, it recovered to flat state and further bent to opposite direction with -180°. Afterwards, the curving membrane again was put back into acetone vapor with a bending angle recovery from -180° to 180°, then turned to -180° upon back to air (Figure 1b). This is ascribed to the diffusion of acetone vapor into the gradient pores along the membrane cross-section, which creates asymmetric stress in the membrane and thus triggers the movement. Moreover, the composite
membranes show high stability without obvious decrease of bending angle after 5 cycles within 70 s. These membranes can also be designed as contractive deformation and responsive textile (Figure 1c).

Figure 1. (a) Photograph of a paper flower folded from the hybrid membrane, scale bar: 2 cm. (b) plot of bending angle (°) of the membrane actuator against time in acetone vapor and air. (c) The design of the membranes as S-shape deformation and responsive textile.

CELL 99

Understanding protein adsorption to TEMPO-oxidized cellulose microfibrils

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Cellulose has gained attention as a remarkably versatile biomaterial, owing to its desirable physical properties and biocompatibility, for various biomedical applications. TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) radicals oxidized cellulose and nanocellulose microfibrils, in particular, have been recently explored as tissue scaffold materials for wound care and tissue regeneration. However, we currently have a poor understanding of the structure-function relationships guiding protein adsorption to cellulose fibrils and its derivatives that can impact the design and performance of such biomedical devices/implants. In the current study, we have used a carbohydrate binding module or CBM from family 3a (CBM-3a), tagged to a green fluorescent protein (GFP), to characterize protein adsorption to TEMPO-oxidized cellulose microfibrils. CBMs are auxiliary protein domains with autonomous folding that target recognition and binding of glycans (like cellulose) through hydrogen bonding with polar residues, van der Waals (CH-pi bonds) interactions with aromatic amino acids, and/or electrostatic interactions with charged/polar residues. We next created a library of oxidized cellulose with varying degrees of carboxylate surface charge densities using TEMPO chemistry to mimic cellulose fibrils surface modifications relevant for biomedical applications. We then used GFP-fluorescence based subtractive mass balance assays to study the impact of pH, oxidized cellulose surface charge, protein concentration, and buffer ionic strength on protein adsorption to TEMPO-oxidized cellulose. It was determined that both pH and cellulose surface charge are strongly correlated to the amount of bound protein. This can be primarily explained in terms of interfacial electrostatic repulsions between the protein and surface of oxidized cellulose. We also hypothesize that the effect of salt concentration on protein adsorption to oxidized cellulose, can be explained by means of electrostatic screening effects. In summary, our results
provide insights into protein and cellulose surface properties that can directly impact the performance of various cellulose-derived biomedical devices or implants.

**CELL 100**

**Combined steam and dry reforming of methane over nickel-based catalysts for upgrading biomass gasification-derived syngas**

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Increasing energy demand, volatility in oil prices and a changing climate have necessitated the study of both sustainable fossil and bio-based means of energy and chemical production. Among fossil fuels, natural gas is seen as a cleaner alternative to coal or petroleum and has recently become more available; however, processes that rely solely on natural gas, especially for production of energy and fuels, can still contribute significantly to increasing levels of atmospheric CO₂. In order to improve overall carbon neutrality, renewable bio-based resources can be co-utilized with natural gas/methane. The goal of this study is to investigate the effectiveness of syngas production by combining methane reformation with biomass gasification. This was achieved through catalyst characterization and experimental lab-scale reactor testing. Catalysts examined for combined methane reformation and biomass gasification are lab-prepared Ni/Al₂O₃, Ni-Co/Al₂O₃ and commercially available Ni-based HiFuel R110 (Alfa Aesar). Catalysts were characterized using successive temperature-programmed oxidation/reduction, EDS and SEM imaging. Fixed-bed catalytic reactor testing was carried out to study reactions between biomass gasification-derived syngas, methane and steam. Experimentally, syngas was shown to increase after reaction (950 C, ~1 atm) to a H₂:CO ratio of 1.5 from an initial value of 1.0 with a 71% increase in calorific value. The resulting syngas was virtually free of CO₂ and the reactor showed a steady state CH₄ conversion greater than 80% during 8 hours time on stream under optimal conditions. Limiting inlet steam to sub-stoichiometric amounts for bi-reformation (3CH₄ + 2H₂O + CO₂ = 8H₂ + 4CO) indicated a direct correlation between the final H₂ concentration and initial steam concentration. Exit-gas H₂ and CO concentrations increased to maximum values of approximately 36% and 25%, respectively, from initial values of 18% each. Carbon deposition on the catalyst surface, based on post-reaction SEM and EDS, appeared to occur as non-deactivating filamentous growth from active sites. These results suggest that methane reformation coupled with biomass gasification is an effective and sustainable tool for both increasing the energy content and controlling the H₂:CO ratio of syngas for utilization in downstream applications. Future research should focus on the investigation of mass transfer limitations and reactor conditions to further optimize desired syngas characteristics.

**CELL 101**

**Acetic acid as a precatalyst to promote cellulose dissolution**

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Nowadays, numerous solvents and strategies have been developed to dissolve cellulose. Efforts have been focused on developing greener, cheaper solvents and facile approaches for cellulose dissolution. In this study, we report on the use of acetic acid at low concentration as a precatalyst to activate hydrogen bonds of cellulose and subsequently promote cellulose dissolution. Unlike derivatizing solvents (e.g. cellulose acetate as an unstable intermediate), no cellulose acetylation occurs during the dissolution and acetic acid can be easily removed by regeneration in DI water. The enhancement in the dissolution of acetic-acid activated cotton cellulose fibers in either LiCl/DMAC or ionic liquid (BmimCl) is linked to the significant reduction in viscosity of cellulose/solvents solution. In addition, the impact of acetic-acid precatalysis on the cellulose was presumably universal for various solvent systems as long as the solvent
contains dissociated cations and anions because it is related to the combined dissociation capability (pKa) of ions present in acetic acid and solvent molecules. Therefore, the investigation of underlying mechanism of acetic acid as a precatalyst may open a new opportunities for developing new solvents and approaches to dissolve cellulose.

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Molecular dynamics study of chitin crystal models in ionic liquids

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Cellulose and chitin are known to be poor in processability and solubility due to a highly crystalline feature, while they are the most abundance in nature. Ionic liquids, which form liquid state at temperatures below the boiling point of water, have been attracting attention as solvents to dissolve cellulose since it was reported that an ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl), dissolved cellulose. On the other hand, there are only a few ionic liquids to dissolve chitin as the example that another ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), was found to dissolve chitin. The present paper reports the molecular dynamics (MD) simulation study on the crystal models of α-chitin in imidazolium-based ionic liquids to evaluate their dissolution behaviors. It was observed by the MD simulation result that the chitin chains were peeled from the crystal surface, accompanied with breakup of intermolecular hydrogen bonds and structuring ionic liquid molecules on the crystal surface (Fig.1). As the experimental phenomenon is remarkable in the dissolution process of chitin by AMIMBr, this result indicates that Br⁻ contributes to breaking of intermolecular hydrogen bonding, whereas AMIM⁺ prevents to return to the crystalline phase after the peeling. In addition, the MD simulation for chitin crystal model in various ionic liquids with different counter anions, which cannot dissolve chitin, showed elimination of hydrophobic sheets bundled with chitin chains, whereas no peeling the molecule chains was observed. It is concluded that dispersion behaviors of the molecular chains contribute dissolution of chitin. Furthermore, in order to assess the factors of dissolution, it was simulated with varying states of the system. As a result, there was no influence of water coexistence, while slightly deacetylation led to improving solubility.

Fig.1 Structure of a α-chitin bundle in AMIMBr showing Br⁻ (red) and AMIM⁺ (blue) near the chitin chains after 100ns at 500K.
Chitin and amylose are abundant polysaccharides in nature. Although the construction of nanostructures in water is an efficient method for chitin materialization, they generally tend to aggregate by drying. We reported that re-dispersible amidinium chitin nanofibers were provided from an amidinated chitin by CO₂ gas bubbling-ultrasonic treatments in water. On the other hand, amylose is synthesized by phosphorylase-catalyzed enzymatic polymerization, which spontaneously forms double-helix. In this study, we performed the phosphorylase-catalyzed enzymatic polymerization from the surfaces of amidinium chitin nanofibers to prepare amylose-grafted chitin nanofibers (Scheme 1). Maltoheptaose (G₇) as a primer for the polymerization was first introduced on the surfaces of amidinium chitin nanofibers by reductive amination. The enzymatic polymerization was then performed from G₇ on the nanofibers with various monomer feed ratios (250, 500 and 750 equiv.) at 45 °C for 6 h. Monomer conversions and molecular weights of the grafted amylose chains increased with increasing the monomer feed ratios. The reaction mixtures turned into hydrogels after cooling at 6 °C overnight. The SEM images of the products prepared by lyophilization of the hydrogels showed that the morphologies were changed from fibrous to porous with increasing the monomer feed ratios. The XRD pattern of the lyophilized sample suggested that amylose chains partially formed double-helix, whereas mostly were amorphous. The TEM image of the same sample showed network morphology of the nanofibers. These results suggested that hydrogels were obtained by formation of network structure by the partial double helix formation from amylose chains among the nanofibers.
Chemoenzymatic synthesis and gelation behavior of amylose-grafted poly(γ-glutamic acid)

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Because branched or grafted biological polymers are often appeared in nature and such complicated structures contribute to exhibiting important in vivo functions, synthetic method for combining several biological polymers into branching or grafting is expected to produce new functional polymers. On the basis of the viewpoint, we have report the synthesis of amylose-grafted heteropolysaccharides by chemoenzymatic approach, which is a combined method of phosphorylase-catalyzed enzymatic polymerization of α-D-glucose 1-phosphate (G-1-P) monomer for the amylose production with appropriate chemical reactions. In this study, we synthesized amylose-grafted poly(γ-glutamic acid) (PGA) as a new graft copolymer by chemoenzymatic approach (Scheme 1). Maltooligosaccharide as a primer of the enzymatic polymerization was first introduced on PGA by condensation reaction using condensing agent in NaOH aq. Phosphorylase-catalyzed enzymatic polymerization of α-D-glucose 1-phosphate as a monomer was then performed from the chain ends of primers on the product to obtain amylose-grafted PGA, which formed hydrogels in reaction media depending on G-1-P/ primer feed ratios. The hydrogels showed high water retention ability as more than 90% of the water contents. The XRD pattern of a cryogels, prepared by lyophilization of the hydrogels, suggested that amylose formed double-helix, which probably acted as crosslinking point for hydrogelation. The SEM images of the cryogels showed porous morphology. Moreover, the pore sizes of hydrogels increased as increasing the G-1-P/ primer feed ratios. Longer amylose chains are produced with increasing the feed ratios, resulting in the formation of looser networks.

Scheme 1. Synthesis of amylose-grafted PGA.
Topical wound care applications of nanocellulose hydrogels

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Nanocellulose (NFC) is an emerging biodegradable, recyclable and renewable biopolymer of enormous industrial importance. In recent years, NFC has been identified as a promising candidate for biomedical applications. NFC based materials are generally regarded as biocompatible, however the interactions with biological systems can be affected by the physicochemical properties and the nano-structure of the studied material. It is therefore of great importance to evaluate the biocompatibility of novel NFC based materials as a complement to the physiochemical characterization. In the present work, ion cross-linked hydrogels of NFC were prepared to be further evaluated for topical wound care applications. Anionic wood-based NFC prepared through TEMPO-mediated oxidation, was combined with bioactive compounds to obtain polymeric dispersions with application tailored properties. Through subsequent ionic crosslinking with polyctaticonic calcium, self-standing hydrogels were obtained. Rheological measurements confirmed the successful ionic crosslinking of the gels while water retention tests brought clarity to the distinct water conservation abilities of the products. Biocompatibility tests using the monocyte-like THP-1 cell line, human dermal fibroblasts and blood-isolated mononuclear cells were performed, revealing that no toxicity was introduced during the preparation of the materials, and that the cells maintain their viability and an inert inflammatory response upon direct contact with the materials. Further application close tests were also performed to assess the feasibility of using the hydrogels as a novel topical wound care application.

Polyamide-polysiloxane-copolymers as examples for partially biobased thermoplastic elastomers

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The research of thermoplastic elastomers (TPE) is a very prospective part of polymer chemistry. They combine elastic rubber-like properties with the possibility for standard thermal processing techniques. TPEs are already used e.g. in medical applications (catheters; nylon based TPE) or in the automotive industry (e.g. for glass run and dynamic weatherstripping car profiles; siloxane based TPE). One specific type of TPE are block copolymers consisting of hard segments that can bond across chains and inert soft chains. A very promising combination for this purpose is nonpolar polydimethylsiloxane (PDMS) as the soft segment alternating with polyamides (PA, building hydrogen bonds between the chains). In consideration of sustainability and ecology, we created partially biobased TPEs by using amino acids for the polyamide segments, enabling a large proportion of biobased sections. The amino acids and additionally biobased diamines or dicarboxylic acids were used as precursors to build up alternating polyamide-polysiloxane-block copolymers. Through peptide synthesis and click-chemistry techniques, we derived interesting systems for the development of new biobased TPE materials. The advantage of designing a process for TPEs using amino acids is the facile subsequent screening of the impact of different side groups in the hard segments on the thermal and mechanical properties of the materials. Additional investigations on the effects of different lengths of the PDMS and the PA blocks on the performance of the polymer will enable designing materials adjusted to particular applications, such as 3D-printing or injection molding of parts for the automotive industry, while using already established manufacturing processes.
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Antibacterial chitosan films containing quaternary ammonium salts modified nanocrystalline cellulose

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Etherification of nanocrystalline cellulose (NCC) with three kinds of quaternary ammonium salts was successfully carried out via a nucleophilic addition reaction. The synthesized quats were characterized by NMR. The modified NCC particles were characterized by EDS. Nanocomposite films based on chitosan (CS) containing the quaternary ammonium salts modified NCC were prepared with nanoparticle loadings of 5.0%, 7.5% and 10.0%. The effect of nanoparticle content on the tensile strength of composite films was studied. The results indicated that the films with 5.0% nanoparticle loading exhibited the biggest increase in tensile strength. Surface morphology, smoothness, and antibacterial properties of composite films containing 5% modified NCC were also studied. The composite films presented excellent biocidal abilities against both Gram-positive *S. aureus* (ATCC 6538) and Gram-negative *E. coli* O157:H7 (ATCC 43895). The bio-based nanocomposite films with increased mechanical strength and excellent antibacterial properties show great application potential as food packaging materials.

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Facile synthesis of high strength and oxygen-barrier performance of hot-water wood extract films

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Biobased nanocomposite films with high mechanical and low oxygen-barrier performance were designed based on the hot-water wood extract that could not only provide added value to wood converting industrial processes but also have potential applications in agriculture, food packaging application. In this work, a facile approach to efficiently produce hot-water wood extract (HWE)/montmorillonite (MMT) based nanocomposite films with excellent physical properties are presented. The focuses of this study were to investigate the effects of MMT content on the structure and mechanical properties of nanocomposites, and the effects of CMC on the physical properties of HWE-MMT based films. The results suggested that the intercalation of different ratios of hot-water wood extract and CMC in montmorillonite could provide compact and robust nanocomposite films with nacre-like structure and multifunctional characteristics. This study revealed that the mechanical properties of the nanocomposite film F_{CMC0.05} (91.5 MPa) was dramatically enhanced and higher approximately 21.4% than the nanocomposite film F_{1-1.5} (75.4 MPa). In addition, the nanocomposite films HWE-MMT-CMC with an low oxygen permeability, also exhibited good thermal stability due to the small amount of CMC. These results offer comprehensive understanding for developing high-performance nanocomposites which are based on natural polymers (HWE) and assembling layered clays (MMT). These nanocomposite films have great potential in the field of renewable packaging applications.
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Kinetics of chain scission and of total oxidative damage in the Fenton-induced degradation of cereal β-glucan

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Mixed-linkage $(1\rightarrow3,1\rightarrow4)$-β-D-glucan (BG) from oat and barley grains is similarly to cellulose a linear homopolysaccharide of β-D-glucopyranose. In contrast to cellulose, cereal BG is water-soluble due to β-(1→3)-linkages that interrupt the β-(1→4)-cellulosic domains every 3 or 4 repeating units, resulting in flexible chains. Regular intake of BG has several well-established health benefits such as attenuation of blood cholesterol and glucose levels, and is linked to BG's ability to form viscous solutions. However, the molecular integrity of BG can be affected by the Fenton reaction (e.g. during food processing), where reactive hydroxyl radicals (HO$^\cdot$) are generated that randomly abstract H-atoms on any of the carbohydrate backbone carbons, initiating lytic and non-lytic BG oxidation in unknown proportions. Although numerous studies on the Fenton-degradation of cereal BG have been published, their chain scission and total oxidative damage kinetics have not been reported so far. In this study, commercial and purified oat and barley BG with varying molecular weights ($M_w$) were degraded under Fenton-conditions ($Fe^{2+}/H_2O_2$) in order to determine the rate constants of chain scission ($k_{cs}$) through the $M_w$ by size exclusion chromatography. The total oxidative damage rate constants ($k_{tod}$) were deduced mathematically from a) competition kinetics data using $N,N$-dimethyl-4-nitrosoaniline (PNDA) as photometric HO$^\cdot$-probe and b) from the determined rate constant of HO$^\cdot$-attack on BG ($k_{HO} = 3.23\times10^8$ M$^{-1}$s$^{-1}$). For the first time, the fraction of HO$^\cdot$-attack on BG that leads to chain scission was estimated by the ratio $k_{cs}/k_{tod}$ and reported to be ~35%. Lastly, differences in degradation kinetics between oat and barley BG were revealed, correlating with the material’s iron complexation capacity. Samples with higher iron complexation affinity degraded more slowly, as less iron could enter the Fenton-cycle to produce HO$^\cdot$. The relationship found between iron-binding and oxidative damage on BG has implications regarding both the stability of BG in foods, as well as the bioavailability of iron, and was found to be caused by residual phytic acid in the commercial oat and barley BG materials and not by the polysaccharide itself.
Drug delivery mechanism of sulfathiazole in films

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Urinary catheters, made of polyurethane, are used in patients for extended periods of time. As a result of a catheter’s location and prolonged use, the catheter is vulnerable to contaminants that lead to infections such as Escherichia coli and Candida spp. A polymer that can prevent the development of these microbes, without compromising the functionality of the catheter, would be an ideal solution to this problem. The purpose of this experiment is to develop a polymer that contains an antimicrobial commonly used to treat the various causes of catheter-induced urinary catheter infections. Polyurethane is the preferred material for catheter production due to its biocompatibility with patients, and, thus, became the material of choice for trials. Sulfathiazole, similarly, has a history of being prescribed to various infections, including UTIs. Sulfathiazole also has the added benefit of being soluble in water, an important factor for testing the concentration of drug releasing from the polyurethane during testing. Samples are created by dissolving sulfathiazole and polyurethane in a solution of dimethylformamide and tetrahydrofuran, then allowing the mixture to mix for 24 hours. The resultant solution is poured into molds, placed in an oven at 37°C for 24 hours, and the films are stored in a dessicator. In order to confirm that sulfathiazole can diffuse out of the polyurethane, a portion of the drug-loaded polymer is suspended in an Erlenmeyer flask containing distilled water in a water bath kept at a constant 37°C for 24 hours. Every hour, 5 mL of the water in the flask is removed and placed in vials for testing. All the water samples are tested with a Shimazdu UV-2450 spectrometer at 270 nm, the wavelength explicitly cited in a publication on sulfathiazole. Spectrometer readings are compared to the calibration curve made with different concentrations, ranging from 1.25 µg to 100 µg, of sulfathiazole dissolved in distilled water. Two sulfathiazole concentrations, 0.3 wt/wt% and 1.5 wt/wt%, suspended in the polymer were sampled. Both concentrations show similar release mechanisms which follow the Korsemeyer-Peppas kinetic model of diffusion. From the similarity in release rates and kinetic modeling, it seems that the diffusion behavior of sulfathiazole is independent of its concentration. The most important result is that the sulfathiazole is capable of diffusing out of polyurethane at a dependable rate.

3D Porous structures based on lignin

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During the project we developed a simple and green approach to produce conductive 3D porous structures with high surface area and excellent bulk conductivity. Lignin is the third most abundant natural polymer, next to cellulose and chitin, and ranks as one of the most abundant phenolic natural polymers. Lignin is usually obtained as a byproduct of the chemical pulping and biofuel production. With only a small fraction being burned as low-valued fuel, lignin represents a significantly under-utilized biomass. 3D porous carbon structures based of nanocellulose and lignin were manufactured during the project using wet spinning and electrospinning techniques. Different carbonization and activation (KOH and NaOH) procedures were explored in order to maximize the electrochemical properties. Finally, we characterized the chemical and mechanical structure of the carbon fibers, in addition to the electrical conductivity, wettability and microstructure.
What are the ranges and basis of auxeticity in the phases of cellulose microfibrils?

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The 1D bundles of cellulose microfibrils (lignified flax fibre) and 2D networks of cellulose microfibrils from tunicate, bacterial and microfibrillated cellulosic were strained in tension, and their molecular deformation followed by Raman spectroscopy in order to fully understand the ranges and basis of in-plane auxeticity for informing innovation in material processing and application. Cellulose is found to exhibit four distinct yielding points. Both crystalline and amorphous cellulose are found to be auxetic so long as interchain hydrogen bonding remains intact. Auxeticity of crystalline cellulose is found to be around unity (-1) while that of cellulose amorphous is found to be around twice (-2) that of crystalline cellulose with the possibility of auxeticity higher than -7 in 1D bundles of cellulose microfibrils in the absence of lignin. Though the network structure enhances strain to failure, they also significantly limit auxeticity in single 1D cellulose microfibrils in networks. Amorphous must exhibit higher auxeticity than crystals be- cause amorphous has less interchain hydrogen bonding than crystals linking the chiral cellulose molecules together. The chirality of cellulose molecules must be responsible for auxeticity of cellulose microfibrils. Auxeticity must be directly correlated with the number of interchain hydrogen bonding. The similarity of the pattern of in- plane auxeticity of cellulose microfibrils to the off-axis auxeticity of zeolites (especially thomsonite zeolites) indicates the possibility of combining both phase change, semi-crystalline materials in nanosized composites with photo- electromechanical properties.

Laccase-polymerization of ultrasound extracted bamboo substrates

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Bamboo powders were subjected to ultrasonic treating using distilled water as the medium. The ultrasonic reaction system was calibrated according to calorimetric and dosimetric characterization, in which the power intensity and probe insert-depth were the main parameters concerned. The results indicated that the proper condition for launching the ultrasonic performance was at the power intensity of 200w with the probe insert-depth of 15mm, considering the highest levels of hydroxyl radical production and the lowest energy input. UV test of the reaction liquid showed an obvious peak generated around wavelength of 280nm, indicating the existence of phenolic compounds extracted from bamboo by ultrasound. Chemical components analysis indicated the presence of Gallic Acid, 5-Hydroximethyl-furfural 99%, 3,4- Dihydroxybenzaldehyde 99%, 2-furaldehyde 99%, Vanillic Acid 97%, Vanillin 99%, Syringic Acid 98% and Guajacol 98% in the reaction liquid. Based on the compound analysis, it shows the possibility for laccase-polymerization of ultrasound extracted bamboo substrates.

Toward development of new generation of peat granular products for waste water remediation: Reaction mechanism of peat surface with cations of heavy metals

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Peat is a slowly renewable resource; therefore, it is essential to add value to products that are produced from peat. Our laboratory developed two peat products for removal of heavy metals, namely APTsorb II*Na™ and APTsorb III™. In order to increase efficiency of the next generation of peat products, it is important to understand the distribution of cation exchange sites in comparison to the total sorption sites in different types of peats and their fractions. Seven peat samples were obtained from different geographical areas in Minnesota and represented two types of peats: reed-sedge and sphagnum moss. Each sample was subjected to a series of treatments: i-PrOH, 4% HCl, 0.25N NaOH, and 72% H2SO4. Consequently, six different fractions were obtained: raw peat, extracted peat, hemicellulose, humic acids, cellulose, and peat Klason lignin. Each fraction was measured for cation exchange capacity (CEC) using a Ba(AcO)2 test and copper sorption capacity (CSC) using a solution of Cu2+ at pH = 4.4. Ba(AcO)2 test is designed to measure a number carboxylic acid groups that is reported as CEC, whereas Cu2+ test is measuring the total amount of Cu2+ that was sorbed by peat material and reported as CSC. The difference between CSC and CEC numbers indicates the number of complexation and chelation sites available for heavy metal sorption. All the fractions exhibited both CEC and CSC, including the peat lignin fraction. The highest CEC (161 mEq/100 g) and CSC (197 mEq/100 g) was found for woody reed-sedge peat collected near the City of Boy River, MN. Data also suggested that extractives are blocking the complexation and chelation sites and do not interfering with cation exchange sites. Moreover, the CSC of the lignin fraction of Sphagnum moss peat was twice the CEC of the same fraction, with a value of 209 mEq/100 g CSC compared to 110 mEq/100 g CEC.

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Preparation and characterization of antibacterial films by pretreatment of dioxane from Phyllostachys pubescens

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The ball milled bamboo was firstly pretreated by dioxane, and then dissolved in 1-butyl-3-methylimidazolium chloride. The obtained solution was also blended with chitosan, TiO2, and ZnO, respectively. At last, the blend films were prepared by regenerated with distilled water. To investigate the structures and properties of the blended films were characterized by XRD, FT-IR, TGA, mechanical strength, and antibacterial ability. The results of FT-IR and XRD indicated that the main structure of blend films were unchanged comparing to lignocellulose film. The results of DTG presented that the residual mass of bamboo/chitosan, bamboo/TiO2, bamboo/ZnO films were 23.43%, 19.27%, 27.68% at 700 oC, respectively. The mechanical properties of the blend films were reduced comparing to lignocellulose film during the dissolution and the regeneration processes. The blend films exhibited remarkable bacteriostatic ability against S. aureus and E. coli. The potential antimicrobial applications in the orthopedic field and perspectives regarding future studies in this field are also considered.
High strength of biocomposite film prepared from hemicelluloses and cellulose

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This study described an effective and convenient approach to produce composite films with enhanced mechanical properties and thermodynamic properties by incorporation of carboxymethyl cellulose (CMC) into quaternized hemicelluloses (QH). The structure and morphologies of films were analyzed by SEM, AFM, FT-IR, XRD. From the SEM and AFM pictures, tight and smooth surface topography of films were obtained. In addition, the transparency, oxygen barrier properties, and water vapor permeability of the composite films were improved. The results of mechanical properties indicated that the tensile strength of film1 (QH:CMC=1:1 wt/wt) was 25.6 MPa, which suggested that the addition of CMC was supposed to contribute to mechanical properties by the strong electrostatic interactions and the enhanced hydrogen bondings with OH. These results provide insights into the understanding of the structural relationships of hemicelluloses-based composite films in coating and packaging application in the future.

Grafting of polyoxazoline on chitin nanofiber film to form organo- and hydrogels

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Chitin is widely distributed in nature and an important renewable resource. However, it has been difficult to provide material applications from chitin, due to poor solubility and processability. We already found that an ionic liquid of 1-allyl-3-methylimidazolium bromide (AMIMBr) swelled chitin. Furthermore, we also reported that self-assembled chitin nanofiber film was obtained by regeneration from the chitin ion gel with AMIMBr using methanol, followed by filtration. In this study, we attempted grafting of a living propagating end of poly(2-methyl-2-oxazoline) to the surface of the chitin nanofibers to obtain poly(2-oxazoline)-grafted chitin nanofibers (Scheme 1). The product formed a gel with DMSO, which was further converted into a hydrogel. For grafting by the reaction of a living propagating end with reactive groups on the nanofibers, amino groups were first introduced by deacetylation in NaOH aq. Ring-opening polymerization of 2-methyl-2-oxazoline with methyl p-toluenesulfonate as an initiator was performed in DMSO to generate a living propagating end, which was then reacted with the produced amino groups on the nanofibers. With progress of the reaction, the mixture turned into gel form. The IR measurement of the isolated product indicated the progress of grafting of poly(2-methyl-2-oxazoline) on the nanofibers. The SEM images of the products in accordance with reaction times indicated that the chitin nanofibers were gradually disentangled with prolonged reaction times. The hydrogel was obtained by immersing the product in water.
Today, large amount of hemicelluloses are ended up in waste-streams from industrial and agricultural processes and are burnt to give energy back to the processes. Hemicelluloses have a rather low heating value and would be more valuable to use in new materials or products. After end-use the hemicelluloses can be burnt for energy contribution. The hemicellulose, arabinoxylan, can be isolated from agricultural crop residues through e.g. an alkaline extraction process. Arabinoxylan itself has a high glass transition temperature ($T_g$), close to its decomposition temperature, why its suitability for use in commonly available process techniques such as extrusion is low. By lowering the $T_g$ of arabinoxylan, it can find use as a thermoplastic in a variety of products e.g. films, barriers or biocomposite materials. We have in our study looked into different ways of affecting the $T_g$ for arabinoxylan isolated from wheat bran. $T_g$ are known to be affected by the polymer flexibility. Two routes were tried to achieve increased flexibility, 1) oxidation of arabinoxylan and, 2) grafting of arabinoxylan with flexible substituents. Here we present the effect of the oxidation route. Variation in backbone flexibility was achieved by periodative oxidation, which opens up some of the ring-structures of the arabinoxylan. We have studying different degrees of oxidation and how

Scheme 1. Preparation of poly(2-methyl-2-oxazoline)-grafted chitin nanofibers

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Novel approach to achieve thermoplastic arabinoxylan

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Today, large amount of hemicelluloses are ended up in waste-streams from industrial and agricultural processes and are burnt to give energy back to the processes. Hemicelluloses have a rather low heating value and would be more valuable to use in new materials or products. After end-use the hemicelluloses can be burnt for energy contribution. The hemicellulose, arabinoxylan, can be isolated from agricultural crop residues through e.g. an alkaline extraction process. Arabinoxylan itself has a high glass transition temperature ($T_g$) close to its decomposition temperature, why its suitability for use in commonly available process techniques such as extrusion is low. By lowering the $T_g$ of arabinoxylan, it can find use as a thermoplastic in a variety of products e.g. films, barriers or biocomposite materials. We have in our study looked into different ways of affecting the $T_g$ for arabinoxylan isolated from wheat bran. $T_g$ are known to be affected by the polymer flexibility. Two routes were tried to achieve increased flexibility, 1) oxidation of arabinoxylan and, 2) grafting of arabinoxylan with flexible substituents. Here we present the effect of the oxidation route. Variation in backbone flexibility was achieved by periodative oxidation, which opens up some of the ring-structures of the arabinoxylan. We have studying different degrees of oxidation and how
it affect the $T_g$ of arabinoxylan films. Lowering of $T_g$, improve its thermo-processability and by that the possibility of using hemicelluloses as new materials in commercial products.

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Development and investigation of a cellulose-based low adhesion coating for adhesive tapes

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Low adhesion paper coatings are produced in industrial scale and they are mainly composed of silicone. These coated papers are used as "release liner" for adhesive tapes. The silicone layer of the "release liner" protects the adhesive against dirt and enables an easy and undamaged release of the adhesive tape without loss of adhesion. The substrate, used for siliconization, should have a non-porous surface in order to avoid penetration of the silicone into the substrate. Hence, most papers are coated with clay (aluminosilicates) to close the porous paper surface. The highly viscous silicone is coated onto the paper surface and thermally cured by hydrosilylation reaction. An expensive platinum catalyst is necessary for this crosslinking reaction. Furthermore, it is difficult to recycle the siliconized papers which is another drawback. In this project, we develop a silicone-free release coating based on modified cellulose. This bio-based coating is applied to the paper surface by roller or blade coater and it is thermally dried. By the addition of a thermal crosslinking agent to the modified cellulose, layer stability is increased and the anchorage to the paper surface is improved. This coating represents a new bio-based alternative to the common used silicone coatings for low adhesion without using an expensive catalyst.

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Influence of nanofibrillation degree on nanocellulosic aerogel properties

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Attempts to reduce petrol consumption highlight the renewable, biodegradable and non-toxic properties of cellulosic materials. At nanoscale, the cellulose nanofibrils combine these advantages with high surface specific, high aspect ratio, large number of OH-bonding, leading to impressive mechanical properties and wide possibility of functionalization. Nano-cellulosic aerogels are highly porous materials characterized by an extremely low solids content and considerably lightweight nature. The highly open microstructure with lots of connected pores lead to ultra-low density, high strength, and have good dimensional stability. These extremely open materials (~97 + % air) are promising materials for various applications such as bio based materials for thermal insulators, insulation materials for the aerospace and aviation industry, storing media for gases in fuel cells, filter materials for extremely fine particles, or drug delivery systems. The two most attractive properties of these nano-cellulosic aerogels are their insulation properties and their high mechanical properties. To ensure the lower pore-size repartition on the aerogel, and hence the better thermal properties, cellulose nanofibrils have been sprayed, cooled at -80°C and freeze-dried. Different quality of cellulose nanofibrils obtained with different mechanical disintegration energies have been prepared using mazuko grinder. Morphological and structural characterizations, Thermal conductivities and mechanical properties of aerogel have been studied. To understand and find solution for limiting the sensibility at humidity, the mechanical tests have been carried out at various humidity levels. A clear link between the aerogel properties with the nanocellulose defibrillation degree has been observed.
Direct comparison of protein and lignocellulose fibers as reinforcements in polymer matrix composites

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Natural fibers are a sustainable and high performance reinforcement for polymer composites. Here, flax fibers, made of lignocellulose, and human hair fibers, made of keratin protein, are used to reinforce polypropylene (PP) matrix composites. The fibers are ground and sieved to the same lengths and used in equal mass fraction in the composites. Both types of fibers are effective at increasing elastic modulus, which is measured in the low strain linear region, although protein fibers result in a larger increase in elastic modulus. Lignocellulosic fiber composites require maleic anhydride modified PP (MAPP) coupling agent to reach the same modulus as protein fiber composites. MAPP is not as effective at increasing the stress at break in protein fiber reinforced composites as it is in lignocellulose fiber reinforced composites. Strain at break decreases in all fiber reinforced composites but MAPP use produces less of a decrease. The differences in the reinforcing effect are rationalized in terms of the more hydrophobic nature of the protein fibers as measured with Fourier transform infrared (FTIR) spectroscopy and transcrystallinity differences measured using differential scanning calorimetry (DSC).

Technical lignins modified by hydroxymethylation for the production of high pressure laminates: Synthesis, characterization and mathematical modelling

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Technical lignins are natural and renewable poly-phenolic polymers obtained mainly as a byproduct from the pulp industry. They present a complex structure that depends on the wood type and the pulping process adopted to separate cellulose. Nowadays, lignins are used as partial replacement of phenol (P) – a non renewable resource, expensive and toxic- in the formulation of phenolic resins (PF). However, lignins must be chemically modified to increase their reactivity toward formaldehyde (F).

In the literature there is a lot of information about the use of PF resins modified with lignins (LPF) as adhesives for the production of wood-based composites. However, the use of LPF resols for paper impregnation to obtain high pressure laminates (HPL) has been scarcely studied. A HPL comprises a decorative paper-based surface and a substrate of Kraft-type papers impregnated with PF resins. In this work, commercial hardwood (sodium lignosulfonate and Kraft-type) lignins were modified by hydroxymethylation and used to replace P in PF resins. The LPF resins were employed to produce HPL. The work involved: i) the modification of lignins by hydroxymethylation at different temperatures (40, 50 and 70 °C) and pHs (9 and 12), ii) the characterization of lignins and hydroxyethylated lignins by volumetric, gravimetric, spectroscopic and chromatographic techniques; iii) the development of a mathematical model of the hydroxymethylation of sodium lignosulfonate and the estimation of the associated kinetic constants; iv) the synthesis of industrial (conventional and modified) PF resins by replacement of 10, 20 and 30%w/w of P, v) the production and characterization of (laboratory and industrial) HPL including dynamic mechanical analysis to compare conditions of curing and the measurement of tensile modulus, bending strength, biaxial flexural impact strength and Mode-I interlaminar fracture toughness in both processing directions to evaluate the mechanical performance. The optimal conditions of hydroxymethylation were 50 °C and pH=9. Simulations were in accordance with
experimental measurements. All resins (conventional and modified) had similar final properties. The best curing conditions were 70 kg/cm² and 150 °C. Also, it was shown that the higher the lignin content, the less crosslinking of the resins. Finally, modified laminates exhibited mechanical properties comparable with those of conventional laminates, indicating a negligible depreciation of them.

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Dimensional stability analysis of flax fiber reinforced polypropylene composites

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Flax fibers are a sustainable and high performance reinforcement for polymer composites. Molding polymers and polymer composites nearly always results in warpage or compromised “dimensional stability” of the part. However, there are very few reports on the quantitative analysis of dimensional stability, especially for natural fiber reinforced polymer composites. A systematic study of the dimensional stability of flax fiber reinforced polypropylene (PP) composites is undertaken by measuring the shrinkage of the composites after molding. Shrinkage is directly related to dimensional stability. Using flax fibers decreases part shrinkage or increases dimensional stability. Shrinkage in the molding direction is less than shrinkage perpendicular to it. Using maleic anhydride modified polypropylene (MAPP) as a coupling agent further decreases the shrinkage. It is found that less shrinkage occurs in composites of higher modulus. The role of fiber-polymer chemical interactions and polymer crystallinity and transcrystallinity is used to discern the differences amongst the samples.

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Evaluating seafood industry waste products as valuable sources of chitin and chitosan

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The demand for chitin has increased recently due to emerging applications in water filtration, novel organic electronics, industrial chitosan production, and most significantly, in carbon dioxide capture. However, little comprehensive work has been conducted to determine the concentration of chitin in the large number of marine organisms which synthesize the material. We applied a standard multi-step chitin extraction procedure to the shells of a variety of crustaceans and mollusks common to the seafood industry of the U.S. East Coast in order to quantify the bioconcentration of chitin in different species. Isolated chitin was characterized by ATR-FTIR and NMR studies. It was determined that crustaceans generally possessed a significantly higher concentration of chitin than did mollusks and that the chitin isolated from crustacean body structures was of greater purity than that separated from mollusk shells. This work helps shed light on the relative merits of different shell types for use as renewable sources of chitin in emerging technologies.

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Mussel-inspired polysaccharide derivatives as examples of novel strong bioadhesives

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One of the most limiting challenges for biological and synthetic adhesives are wet conditions, which restrict their versatility for numerous applications. Especially in surgery and medical wound management, tissue adhesives are required to show enhanced biocompatibility and adhesion strength for in vivo use (e.g. for mucosal membranes). In recent years, marine mussels have drawn significant interest both in basic research and as replacements for current bioadhesives based on their outstanding adherence to a large variety of natural and synthetic surfaces including adhesion-resistant materials such as polytetrafluoroethylene (PTFE) and their magnificent adhesion strength in wet environments. The presence of up to 30 mol% of the amino acid 3,4-dihydroxyphenylalanine (DOPA) in mollusc foot proteins is the fundamental chemical reason for their versatile adhesion behavior. We present a novel approach to combine mussel-inspired components with cellulose derivatives to develop a new group of functional polysaccharide-based compounds and materials combining beneficial properties of different sustainable functional biopolymers. One aim is to optimise the yield of catechol-functionalisations and to examine a wide range of catechol- and phenol-containing compounds such as caffeic acid, protocatechaldehyde and L-tyrosine. Furthermore, the resulting mechanical and chemical properties such as tensile strength, adhesion capability on dry and wet surfaces and the effect of different spacer-molecules of the cellulose derivatives are characterised and discussed. The applied synthetic methods are based on "click-chemistry" in order to bind catechol-containing compounds to cellulose and other polysaccharides under mild reaction conditions and with high yields. The proposed "mussle-inspired polysaccharides" approach is multidisciplinary and includes biology (bioadhesion, biocompatibility) and chemistry (organic synthesis, polymer science) in addition to materials science and engineering (structural and polymeric functional materials).

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Disruption of cellulose fibers structure by Lytic Polysaccharide Monooxygenase (LPMO) enzymes

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Lytic polysaccharide monoxygenase (LPMO) enzymes are recently discovered fungal enzymes possessing a type II copper active center coordinated by a histidine brace. Their interest arises from their observed "boosting effect" on the enzymatic polysaccharide degradation. LPMOs are classified into the auxiliary activity (AA) family from the CAZy database; and they have demonstrated to disrupt cellulose by an oxidative cleavage, which could be an entry point for further degradation or hydrolysis. In this work, we studied the action of a LPMO enzyme from the coprophilic ascomycete Podospora anserina (PaLPMO9H) that was produced heterologously. The enzyme PaLPMO9H is known to introduce an oxidized group on C4 and eventually on C1. In an attempt to get more insight into the mechanism of action of LPMOs, kraft pulp fibers were treated with both PaLPMO9H. Ascorbate was used as electron donor, and different reaction times and enzyme/substrate ratios (1:50-1000) were tested. After the enzymatic step, a soft mechanical treatment was applied to the fibers to facilitate their fractionation. After 48 h of enzymatic treatment and mechanical dispersion, LPMO-treated fibers showed intense defibrillation whereas control samples remained intact. Optical microscopy showed cellulose defibrillation occurred even at low enzyme/substrate ratios (1:500) for PaLPMO9H. Cellulose structure modifications were investigated by several techniques including FTIR, SEC, ¹³C CP-MASS solid state NMR and analysis of solubilized fractions. AFM and TEM were also used to characterize fibers and high degree of defibrillation was observed. Therefore, LPMOs can be viewed as promising candidates for enzymatic modification or degradation of cellulose fibers including the preparation of nanocelluloses.
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Easy process to cellulose-silica hybrid aerogels

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Cellulose is a highly promising resource in sustainable aerogel developments, but is less suited for insulation applications. Silica aerogels on the other hand are outstanding thermal insulators but often show insufficient mechanical properties like low stiffness and high brittleness. Aiming for improvement of both, the thermal properties of cellulose aerogels and the mechanical properties of silica aerogels, hybrid aerogel composites are of a special interest. For developing cellulose-silica aerogel composites using a "one-pot" approach, cellulose was dissolved using a salt hydrate melt based on cheap zinc chloride tetrahydrate and mixed with a silica sol based on tetraethylsilicate. The gelled cellulose-silica samples were regenerated in ethanol, dried with supercritical CO₂ and characterized with respect to shrinkage, density, surface area, mechanical and thermal properties as well as micro-structure via SEM. The resulting cellulose-silica composites are white in colour and apparently homogeneous. Varying the ratios of both components yields a wide field of properties. The silica phase was shown to have a reinforcing effect on the cellulose aerogel by effectively increasing its Young's modulus. Furthermore, the resulting composites yield densities in the range of 0.10–0.20 g cm⁻³ and specific surface areas in between 600 and 1000 m² g⁻¹ outlining an excellent combination of both gel components.

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Algae-based biorefinery of Chlorella vulgaris

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The industrial deployment of microalgae crops as a source of biodiesel is limited by a dramatic fall in the productivity of oils in the pre-industrial scale phase, which is exerting a negative effect on the whole process. The CYCLALG project is providing new approaches to the problem by introducing the heterotrophic cultivation of species of oleaginous microalgae as an alternative mean for improving the productive efficiency of the process. In terms of productivity, the heterotrophic cultivation of microalgae
offers clear advantages over conventional phototrophic crops for obtaining biodiesel, even though they require organic sources of carbon and nitrogen that are so far more expensive than traditional inorganic fertilizers. This European project aims to improve efficiency in resource management by involving a setup based on the circular economy. It proposes to use the residual biomass coming from *Chlorella vulgaris* oil extraction and by-products of the food industry (rich in sugars and proteins) on the preparation of nutritive media that will feed the microalgae again. Among the technological objectives of the project we have to develop and validate technologies involving the hydrolysis, extraction and fractionation of waste into nutritional extracts. Furthermore, CYCLALG project includes the development of other technologies that allow the upgrading of waste and co-products into value-added products: as a raw material in the synthesis of biopolymers and other biomolecules, as a bio-fertilizer, as an animal feed, or an input for the production of biomethane, to improve the economic framework of the whole process. A consortium of six R&D centers in France and Spain - NEIKER-Tecnalia, National Centre of Renewable Energies (CENER), Tecnalia Research & Innovation, Association of Industry of Navarre (AIN), Association for the Environment and Safety in Aquitaine (APESA) and the Centre for the Application and Transformation of Agro-resources (CATAR) - are participating in this European project for 36 months with a budget of 1.4 million euros, of which 65% is being provided by ERDF funds through Interreg POCTEFA.

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**Fabrication of CNC/glycerol thin films as substrate for electronic applications**

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Organic solar cells are an attractive technology for his low-cost fabrication, lightweight, and good mechanical flexibility. Cellulose substrate materials are been used a lot lately because they can be synthesized from natural sources, such as wood, at a low cost. This gives way for the creation of sustainable solar cell technology. Cellulose nanomaterials (CN) are cellulose-based nanoparticles that have good mechanical properties like: low density, high aspect ratio, low thermal expansion, low toxicity, comes from renewable source, and have the potential to be produced in industrial-size quantities. The purpose of this investigation was to create a flexible, transparent and conductive Cellulose Nano Crystals (CNC) films as substrates for electronic applications. To achieve this, several solutions of aqueous CNC (1.65% wt) and glycerol (1% wt) at different ratios were prepared. All films were characterized using UV-visible spectrophotometer and the percent of transmission was obtain at the wavelength 550nm. The film with ratio 5:1 exhibited the best transmittance and good flexibility. A metal thin film of Ag was deposited on the CNC/Glycerol film, with 6:1 ratio, using the sputtering technique, at different time intervals to produce conductive transparent films with different thickness, as shown in figure 1.
Transmittance vs wavelength of the films with Ag deposited by sputtering. The deposition with 3 seconds (black) shows more transmittance as expected. Moreover the film with deposition time of 9 seconds (blue), exhibit more transmittance than the film exposed to 6 seconds (red) of Ag deposition.

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Optimization of phenolics extraction from walnut shells through ultrasound treatment

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Walnuts, along with other nuts, constitute a significant part of the food industry. Walnut kernels are covered by a brown seed coat that protects and preserves the oil-rich seed from atmospheric oxygen.
After extracting the seed kernels, the brown seed coat is discarded as waste. However, it could be a valuable by-product as seed coat is rich in phenolics; and thus holds potential in adding nutritional value to foods and food supplements. This study aims to utilize ultrasonic protocols for the extraction of phenolic compounds from the walnut shell biomass. The dried walnut shells were pulverized and subsequently subjected to sonication in the presence of three solvents (ethanol: 50, 100%; methanol: 50, 100%; and water: 100%) at two reaction temperatures (-2 and 30°C) for six treatment times (1, 2, 5, 10, 15 and 20 min) with four ultrasonic drive signal amplitudes (200, 400, 600 and 900 mVpp) so as to optimize extraction conditions and to maximize overall phenolics yield. The data was analyzed through the surface response methodology. A highest yield of 34.8 mg GAE/g DW (mg gallic acid equivalents/g dry weight) could be obtained in 50% ethanol for 20 min at 30 °C with 600 mVpp drive signal. This study certainly outlines the potential application of ultrasonic treatment on agricultural by-products such as walnut shell biomass for extracting bioactive compounds (e.g. phenolics) in developing novel nutritional food products.

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Cellulose nanofiber surface functionalization for functional medical membrane applications

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Microfibrillated cellulose (MFC) appears like the next generation of biorefinery high value added product. During the last decade, the interest towards these new bio-based materials exponentially increased due to their outstanding properties and the announced industrialization in 2011. In this project, we intend to use this MFC to develop a novel class of biomaterial substrate device with controlled release of active molecules for improving soft tissue repair. It will offer clear and expected solutions for addressing remaining clinical needs, such as infection, pain and recurrence. The main idea of this project is to start from biomass to biomedical applications with using functionalizing and characterizing the MFC based substrate. Both antiseptics or drugs with different modes of action will be chosen and grafted thanks to the microfibrillated cellulose treated medical device. First, high-quality grade of MFC will be grafted with several components like cyclodextrine or thiol molecule. In the meantime, active bioconjugates will be synthesized with innovative chemical ligation with active molecules. Subsequently, medical devices will be prepared following different possibilities. Chemical grafting have been studied with FTIR, EA, NMR. The efficiency of the final materials and drug release studies will help confirming the promising effect.

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Effects of catalytic fast pyrolysis derivatives on mechanical, thermal and surface properties of nanocellulose films

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In recent years, much attention has been focused on research to replace petroleum-based commodity plastics, especially with biodegradable materials offering competitive mechanical properties. Nanocellulose (NC), which are renewable biomaterials produced chemically or enzymatically from cellulosic feedstocks (biomass), stands out in comparison with other candidates. However, the fragility and brittleness exhibited of pure NC-based films and assemblies generally present poor mechanical properties regarding processability and performance that limit their utility for end-use applications. In order to overcome these problems, we are investigating the use of renewable additives produced by catalytic fast pyrolysis (CFP) to integrate with NC to modify the properties of the resultant assemblies.
Furthermore, aqueous-phase compounds that are miscible with most NC suspensions are underutilized or treated as a waste product of CFP due to their high oxygen content. Therefore, using these compounds as matrixing materials for NC composites enhances the economic feasibility of the CFP process in general by valorizing waste products, and provides polymer composites of completely renewable components. We will describe how modification of NC with different functionalities can achieve desirable properties when physically mixed or covalently linked with CFP derivatives. The resultant solvent-cast films are flexible and semi-transparent depending on the surface modification and NC/CFP product ratio. Mechanical, thermal and surface properties of those NC composites were characterized by means of tensile-test, dynamic mechanical analysis (DMA), dynamic scanning calorimetry (DSC), thermal gravimetric analysis (TGA), atomic force microscopy (AFM), scanning electron microscope (SEM), transmission electron microscope (TEM) and ultraviolet-visible spectroscopy (UV-Vis).

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Impact of vanillin on the rheological and phase behavior of Cellulose Nanocrystals (CNCs)

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Liquid crystalline behavior of aqueous suspensions of sulfonated cellulose nanocrystals (CNCs) has been largely investigated. Characteristics of CNCs including particle morphologies, surface properties, suspension’s ionic strength and temperature are important factors affecting CNC phase behavior. Moreover, blending CNCs with other molecules such as glucose, 2-hydroxyethyl methacrylate, etc has been shown to affect their phase behavior. In this work, we aim to get some insight on the impact of lignin on the liquid crystalline behavior of CNCs, with the ultimate goal to design and process template lignin/CNCs nanocomposites. We therefore first study the impact of vanillin, as a model compound of lignin, on the liquid crystalline behavior of CNCs. In particular the rheological and phase behavior of vanillin/CNCs in aqueous solutions is reported.

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Enhancement of PVA/MMT composite film by chitin nanowhiskers

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Chitin is an abundant biomacromolecule, and widely found in the exoskeletons of arthropods, the shell of crustaceans, and the cuticles of insects. The chitin nanowhiskers were prepared by the acid hydrolysis, and the average length and width were 200 nm and 40 nm, respectively. Composite films were prepared with chitin nanowhiskers, polyvinyl alcohol, and montmorillonite. The morphology and structure of composite films were characterized by spectroscopy (FT-IR), X-ray (XRD), scanning electron microscopy (SEM), and transparency property. The results show that PVA/MMT/NCH composite films have a highly ordered lamellar structure and the smooth surface. The composite films have a high tensile strength and high thermal stability. According to the properties of films, they could be widely used in the fileds of packages.

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Applications of cellulose nanofibers for 3D printing of a low viscosity of polypeptide solutions

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Cellulose nanofiber (CNF) suspensions were produced from craft pulp. Prior to grinding, the pulp fibers were beaten using a laboratory valley beater for 30 min. The beaten pulp suspension was passed through a grinder to produce the CNF suspension. The consistency of the pulp suspension during grinding was 2% w/v. The operation speed and gap distance between the grinder stones were 1500 rpm and 100 µm, respectively. The number of passes through the grinder was fixed at 30. To prepare the bioink precursor solution, the concentrated CNFs were mixed intensely and steam sterilized in an autoclave. Five different concentrations of CNF solution were prepared in DI water and 5% w/v MA-modified polypeptides were dissolved in the solutions. Ammonium persulfate (APS), used for a radical initiator, was purified via distillation under reduced pressure and recrystallizations and added to the CNF solutions at the different concentrations to crosslink the polypeptides after 3D printing. The activation of radicals was performed by adding the same concentration of tetramethylethylenediamine as APS. 3D structures were fabricated by printing 3D patterns using a custom-built 3D printer.

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Aqueous dispersions of TEMPO-oxidized cellulose nanofibrils with various metal counterions, and their super deodorant performances

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Fibrous TEMPO-oxidized cellulosics (TOCs) with carboxylate contents > ~1 mmol/g can be completely nanodispersed in water by gentle mechanical disintegration, providing TEMPO-oxidized cellulose nanofibrils with sodium carboxylate groups (TOCN-Na) with homogeneous ~3 nm in width. The sodium ions of TOCN-Na were then exchanged with other monovalent, divalent, and trivalent metal (M) ions. When an aqueous metal acetate or AlCl3 solution was added to a 0.1% TOCN-Na/water dispersion or TOCN-COOH gel/water mixture under suitable conditions followed by sonication in water, individually nanodispersed TOCNs-M with divalent and trivalent metal counterions were obtained in yields of 24–87%. The amount of metal introduced into TOCN-M was approximately 20–50% of the TOCN carboxylate content when divalent and trivalent metal ions were used. These results indicate that intrafibrillar ionic linkages are selectively formed and these TOCN-M species nanodisperse at the individual nanofiber level without agglomeration in water. When the TOCN concentrations in the metal counterion exchange treatment were higher, interfibrillar ionic linkages were preferentially formed, resulting that nanofibrillation could no longer be achieved and remained as agglomerated gels. The obtained TOCN-Cu/water and TOCN-Ag/water dispersions were adsorbed on filter papers. These filter papers containing TOCN-Cu TOCN-Ag were found to efficiently decompose or adsorbed H2S and CH3SH gases. In contrast, filter papers containing fibrous TOCs with Ag+ or Cu2+ counterions had much lower gas-decomposition efficiencies. Thus, super deodorant performances were observed for filter papers containing TOCN-Cu and TOCN-Ag. The high surface areas of Cu and Ag ions in the filter paper may have caused such excellent deodorant behavior.
Microwave-hydrothermal rapid synthesis of cellulose/Ag nanocomposites and their antibacterial activity

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Silver-based antimicrobial nanomaterials are considered as the most promising antibacterial agents due to their outstanding antimicrobial efficacy and their relatively low toxicity to human beings. In this work, we report a facile and green microwave-hydrothermal method to prepare cellulose/Ag nanocomposites using hemicellulose as reductant. The cellulose/Ag nanocomposites were characterized by XRD, FT-IR, FE-SEM, EDX, TG and DSC analysis. The influences of the microwave-hydrothermal heating time and temperature, and hemicellulose concentration on the formation of cellulose nanocomposites were investigated in detail. Experimental results indicate that the hemicellulose was an effective reductant for silver ions, the higher temperature and longer heating time favored the formation of silver with higher crystallinity and mass content in the nanocomposites. Moreover, the antimicrobial properties of the as-prepared cellulose/Ag nanocomposites are explored using Gram-positive S. aureus ATCC 6538 and Gram-negative E. coli HB 101 by disc diffusion method. The inhibition zones for S. aureus and E. coli were 15.0-15.2 mm and 3.0-4.0 mm, respectively, which revealed high antibacterial activity. The minimum inhibitory concentrations (MICs) of the as-prepared nanocomposites were also carried out by agar dilution method against S. aureus ATCC 6538, and the MICs were found to be 1.0-2.0 mg mL⁻¹. These results demonstrated that the as-prepared cellulose/Ag nanocomposites, as a kind of antibacterial material, are promising for applications in a wide range of biomedical fields.

Rice husks pretreatment with ionic liquid

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Rice husk biomass is a challenging feedstock because of its high ash and lignin contents, which make separation to different components difficult and result low reducing sugar yields in enzymatic hydrolysis. Due to complex structure, it requires an additional step before carrying out enzymatic processes. The option is to extract lignin by dissolving in ionic liquid to obtain silica-enriched cellulose pulp. This pulp can be feedstock for production of fuel ethanol or produce other value-added products. Herein, a new approach for utilisation of rice husk will be developed where both silica-enriched cellulose pulp ang lignin fractions are obtained to produce new materials. The optimal conditions for producing fractions with ionic liquids have been investigated. The lignin component will be used as a precursor to aerogel and the pulp fraction will be used to produce silica-modified cellulose fibers. Fiber structure changes, chemical, topological and morphological properties are studied with various methods (IR spectroscopy, SEM, XRD) and compared with pure cellulose fiber properties.

Sustainable polymer synthesized from Gemini monomers

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A family of gemini monomers were synthesized from the biomass-based chemicals furfural, malonic acid and aliphatic diols. The reactive centers of the monomers were prepared from furfural and malonic acid through a condensation reaction. The monomers were obtained by connecting the reactive centers with
diols through a nucleophilic substitution reaction or an esterification reaction. Single crystal X-ray diffraction was used to analyze the crystalline states of the six monomers. Seven crystal structures were collected. Polymorphism was observed in one of the monomers and a crystal of two conformational isomers was observed in another monomer. Two sustainable polymers was successfully synthesized from these monomers. TEM and SEM showed the nanofibers. The polymers were characterized by Maldi, P-XRD, TGA, and DSC.

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Analysis of Liquid Fuels from Thermal Depolymerization of Polypropylene in a Bench-Scale Reactor

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Clean Oceans International, a non-profit whose vision includes converting plastic waste to liquid transportation fuels in remote locations on land and at sea, via mobile PTF (Plastic to Fuel) depolymerization reactors, is actively involved with the colleges near their Santa Cruz, California headquarters. They have provided opportunities for students at Cabrillo College (part of the California Community College system) to conduct research in support of their program. This presentation summarizes a portion of these results. Polypropylene (PP, recyclable plastic #5) is a versatile thermoplastic, whose heat- and fatigue-resistant properties lend it to many consumer applications, including rope. It is also one of the more abundant plastics found in the oceanic gyres of floating plastic, including that in the Pacific Ocean, as well as countless other marine and terrestrial environments. Studying its suitability as feedstock for PTF reactors provides key data for designing the small-to-medium-scale reactors for remote use. Polypropylene in the form of high density homopolymer, as well as consumer grade polypropylene rope, was vaporized in a Be-h desktop plastic to oil thermolysis machine, producing a form of crude oil. The crude products were then distilled using fractional vacuum distillation, producing separate fractions based on literature temperatures for commercial gasoline, diesel #1, and diesel #2 fraction temperature ranges. These fractions were analyzed through gas chromatography (GC) and compared to the GC graphs of kerosene, gasoline, pentane, hexane, methylcyclohexane, heptane, octane, nonane, decane, undecane, and dodecane standards. GC analysis showed clearly different elution graphs for each of the three fuel fractions. While features of each of these graphs were consistent with the presence of the one or more of the standards in that fraction, further work to characterize the chemical constituents in each fraction is in progress.

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Conductive films prepared from cellulose, graphite and polyaniline nanoparticles with highly thermal stability and antibacterial activity

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Cellulose/graphite(GP)/polyaniline(PANI) composite films were successfully prepared by the combination of physical and chemical processes. The GP was dispersed in N-methylmorpholine-N-oxide monohydrate (NMMO) before the dissolution of cellulose, and the cellulose/GP/PANI film was prepared by in-situ chemical polymerization of PANI nanoparticles on the film surface. The structure of the composite films was investigated by XRD, FT-IR, SEM and SEM-EDX. The properties of the composite films, such as mechanical strength, thermal stability, conductivity and antibacterial activity, were studied in detail. Results showed that the composite films had a multilayer structure with GP flacks embedded in the cellulose
matrix and PANI nanoparticles tightly wrapped on the films’ surface. The flexibility and mechanical properties of the films were guaranteed by the cellulose matrix, and the films’ thermal stability was significantly improved by GP fillers. The PANI coating acted as a protective layer during burning and provided good electrical conductivity and antibacterial activity against *Escherichia coli*. The PANI/cellulose/GP composite film could be considered as a potential candidate for electronics, antistatic packing, and other applications.

Diagrammatic structure and burning process of the films
area scan analysis of the films' cross section

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Recycling of non-metallic fraction of printed circuit boards as reinforcement in poly(methyl methacrylate) composites

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The printed circuit boards (PCBs) are a fundamental part for mounting the micro-electronic components of electronic equipment. In addition, the non-metallic fraction (NMF) of PCBs waste is disposed in landfills due to their low economic importance, which cause a high environmental impact. Thus, the aim of this study is to recycle the NMF of the PCBs incorporating them as a reinforcement of Poly(methyl methacrylate) composites. First, the non-metallic fraction of PCBs was extracted and its content was determined. Second, the mechanical properties (tensile and flexural) of composites were evaluated. Six composites were made, with three concentrations (10, 15 and 20%) and two particle sizes (0.15 and 0.075 mm). Finally, the composite which exhibited the highest mechanical properties was analyzed by Scanning Electron Microscope (SEM). The results of the study were: the non-metallic fraction of PCBs is composed mostly of glass fiber (between 67.22% and 78.78%), and the smaller particle size (0.075 mm) had the highest glass fiber concentration. Composites with smaller particle size showed the best mechanical properties. About tensile properties, the composite that contains 20% and 0.075 mm particle size of waste showed an increase of 19.5% and 43.1% in the stress at peak and Young's modulus respectively, compared with pure material (PMMA). Also, in terms of flexural properties, this material showed an increase of 27.1% and 42.0% in stress at pick and flexural modulus respectively. SEM showed that the fiberglass of the waste had a good adhesion with Poly(methyl methacrylate), then the growth in the mechanical properties of Poly(methyl methacrylate) composites.
Applications of cellulosic waste. Development of insulation panels

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In the study of sustainable construction, the concept of energy efficiency of buildings is considered fundamental. This efficiency can be obtained, among other forms, with the use of materials with great capacities of thermal insulation. Also significant is the contribution for sustainable construction, the use of recycled materials that would otherwise be deposited in landfills. In the production cycle of beer, the packaging is made in returnable glass bottles. In the cleaning step of returnable bottles, all the material adhered is removed with an aqueous solution of caustic soda leaving the entire waste ready to be discarded. This research proposes to assess the feasibility of recycling industrial waste from a beer company for generation of panels used in construction. According to the information provided by the company, the waste consists mainly of cellulosic material (paper), caustic soda, contaminating inks and additives incorporated to obtain the characteristics of the label. The production volumes of the waste are variable according to the season of the year. From the perspective of recycling, it is proposed to investigate the use of this residue in the generation of insulation panels of interior lining, whose composition material is a mixture based on cellulose and cement. Based on the results obtained, it is expected that the materials generated will form part of the country's sustainable architecture, introducing not only the reuse of waste material but also promoting the responsible use of energy for the conditioning of houses.

Controlling latex morphology with cellulose nanocrystals and methyl cellulose

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Cellulose nanocrystals (CNCs) are a sustainable nanomaterial that possess desirable properties such as their ability to form colloidal suspensions in water, their surface hydroxyl groups that allow for surface modification, and their industrial production. The orientation of cellulose chains within a single nanocrystal result in the formation of an amphiphilic nanoparticle with a hydrophobic edge, leading to the potential for CNCs to be used as stabilizing agents in foams and emulsions. In this work, we have modified CNCs by adsorbing the surface active polymer methyl cellulose (MC), resulting in polymer-coated CNCs that readily partition at the oil-water interface. The modified CNCs were used to stabilize micro suspension polymerizations of methyl methacrylate which yielded PMMA particles with a double morphology. At a given CNC:MC ratio, both micro- and nanoparticles were formed. When a higher concentration of MC was used, more nanoparticles were present, whereas when a higher CNC concentration was used, mostly microparticles were present. This suggests that the nanoparticles were stabilized solely by MC, while the microparticles were stabilized by CNC coated with MC. Based on this, we show the ability to tune the particle size and morphology based on the ratio of CNC:MC added. This work will extend the potential applications for CNCs to emulsions and latex-based products such as adhesives, toner, and coatings.
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Synthesis of encapsulated bio-pesticides/fertilizers based on superabsorbent crosslinked alginate microbeads

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Encapsulated fertilizers and pesticides are a key approach to slow the release of nutrients for long-term feeding and protection of plants, while simultaneously reducing losses and minimizing the associated economic costs and environmental problems. The use of hybrid systems (fertilizers and pesticides) for drug encapsulation in organic based agriculture has been a growing field of interest. Long term goal of this research is to develop value added slow release encapsulated bio-pesticide and fertilizer based on crosslinked alginate microbeads for soil remediation. The work focuses on the processing and characterization of microbeads based on alginate containing nitrogen rich compound (soil nutrient) and bio-pesticide bacterium Bacillus thuringiensis (B.t). Microbeads were formed using wet extrusion technique using different formulations of soil nutrient (N, P, K) and pesticides. The samples were characterized in terms of size, morphology, degree of swelling and encapsulation efficiency. The results showed that microbeads have narrow size distribution ranging from 1.4-1.5 mm.

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Characterization of cellulose membrane filters deposited by electrospinning

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Cellulose constitutes the most abundant renewable polymer resource available today and has been used for centuries in the form of fibers or derivatives for a wide range of products. In the form of fiber mats, cellulose has been modified with ligands to be used as an affinity membrane for the separation of biological active proteins. The binding capacity of the membrane is expected to depend on the surface ligand density, length of the ligand spacer arm, available surface area and the size of the membrane pores. In this work, the size of the pores, formed by the spaces between fibers, will be controlled with the alignment of the fibers produced by electrospinning, a novel process used for the forming of polymer fibers with micro/nano diameters, in which the viscosity of the solution is the main factor that control the fiber diameter. This method is based on the action generated from the electrostatic forces under a polymeric solution jet (in this case, cellulose acetate) generating its deformation until submicron scale diameters and solidification over the metallic collector. In this work, the amount of cellulose acetate fibers deposited on top of a substrate filter with different pore sizes is varied in order to increase the available surface area of attachment of ligands of bioactive proteins.

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Sequential fractionation of lignin macromolecules with organic solvents and investigation of their potentials for utilization as lignin-PLA copolymers

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Milled wood lignin (MWL), organosolv lignin (OL) and soda lignin (SL) were sequentially fractionated with in order of ethyl acetate (F1), 2-butanone (F2), methanol (F3), acetone (F4), and dioxane/water (F5). Yields of the five MWL fractions F1 to F5 were 11.7%, 11.7%, 15.3%, 11.8%, and 49.6%, and yields of the OL fractions were 26.2%, 26.1%, 18.7%, 3.7%, and 25.4%. In case of the SL, yields of the fractions
were 30.1%, 25.5%, 24.7%, 2.0%, 11.2%, and 6.5% of the insoluble fraction (INS). In all lignin, F1s showed the lowest molecular weights which ranged from 1000 to 2400 Da, while F5 had the highest molecular weight above 10000 Da. In addition, polydispersity index (PDI) values of all fractions were low compared with that of original lignins. This indicates that similar size of lignin fragments were rearranged during sequential solvent fractionation of lignin. According to functional group analysis, the contents of phenolic hydroxyl groups and methoxyl groups decreased gradually with increasing molecular weight. DFRC analysis, a parameter for frequency of β-O-4 linkages, revealed that the higher molecular weight fractions yielded larger amounts of DFRC monomers, indicating that those fractions more frequently contain aryl ether linkages. TG/DTG analysis suggested that the low molecular weight fractions generally have lower thermal stability due to their high content of functional groups. The T_g of the fractions ranged from 126 °C to 156 °C, increasing as the molecular weight of the lignin fraction increased. Among lignin fractions, SL fractions were used to investigate the possibility to utilize them as lignin-PLA copolymers. Each fraction was grafted with L-lactide to form lignin-grafted-poly(L-lactide) (lignin-g-P(LLA) via ring opening polymerization (ROP) catalyzed by triazabicyclodecene (TBD). Conversion ratios of L-lactide to lignin-g-P(LLA) were analyzed by 1H NMR and showed that F1 had the highest conversion ratio while F5 had the lowest. Hydroxyl groups of lignin play a role as initiation site of L-lactide polymerization, thus F1 which contains relatively high amount of hydroxyl groups gave L-lactide more chances to be polymerized. Further investigation of mechanical and thermal properties of lignin-PLA copolymer will be performed.

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Development of reinforced rigid polyurethane foam composite based on cabuya fiber

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Natural fibers have attracted the interest of researchers and industries due to their specific advantages compared to synthetic fibers. The growing global concern about the environment is encouraging the use of renewable source materials that do not harm nature and come from an alternate source of good economic potential. Thus, the aim of this study is to develop a composite made from rigid polyurethane matrix reinforced with cabuya fiber. The fiber used in this study was recollected from the Ecuadorian Andes. First, the fibers were cleaned, ground, sieved and dried. To improve the boundary matrix-fiber, fibers were subjected to a process of acetylation. Composites were prepared with concentrations by weight of loading fiber: 5%, 10% and 15% and a particle size of 0.025 mm. Second, tensile and flexural tests were performed in order to evaluate the mechanical properties of the materials. In terms of flexural properties, the material formulated with 10 wt% by weight of fiber showed the best results, with an increase of 37.63% and 50.62% in stress at pick and flexural modulus respectively, compared with pure material. While for tensile properties, the composite formulated with 5 wt% presented the best results, with an increase of 18.19% and 35.32% in the stress at peak and Young's modulus respectively. The material with 15% by weight of fiber shows equal or superior mechanical properties to the material made from pure polyurethane. In both mechanical tests, the material formulated with acetylated fiber presented slightly better results compared to the material made from fiber without chemical treatment.

CELL 149

Biopolymer synthesis: Esterification of wood cellulose from different guatemalan tree species with phthalic anhydride and their use as triclosan adsorbents in aqueous solutions

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Biopolymers were prepared through esterification reaction between three different free-lignin woods (the lignin were removed by treating wood with 1M HCl for 72h at 333K in oil bath), pine (Pinus maximinoi), cypress (Cupressus lusitanica) and matilisguate (Tabebuia rosea) with phthalic anhydride using
trietanolamine as catalyst in dimethylformamide. The synthesized materials were characterized by FTIR spectrometry where a contracted region corresponding to O-H bond in hydroxyl groups was observed at ~3350 cm\(^{-1}\) due to a lower presence of free OH groups after the reaction, additionally the biopolymers showed new absorption bands at 1714 cm\(^{-1}\) (carbonyl group in ester) and 1600 cm\(^{-1}\) (aromatic ring) relative to the FTIR spectrum of the unmodified cellulose. The adsorption capacity of triclosan (TCS) for the biopolymers in aqueous solutions were measured by an UV-Vis spectroscopy method at 290 nm, since TCS is an emergent contaminant with high environment persistence and represents risk to human health as endocrine disruptor. Adsorption capacities between 25 and 30 mg of TCS per gram of adsorbent were obtained, representing an increase between 32 and 47% compared to the adsorption capacity of TCS of unmodified wood cellulose with the additional advantage of not introducing additional contaminants to solutions.

Figure 1. FTIR spectrum of unmodified wood

Figure 2. FTIR spectrum of modified wood by esterification with phthalic anhydride
**CELL 150**

Cleavage of β-O-4 ether bonds in acidic lithium bromide trihydrate for lignin depolymerization

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Depolymerization of lignin is essential in many pulping and biorefining processes. It was observed that lignin was extensively depolymerized when cellulose and hemicelluloses were hydrolyzed in acidic lithium bromide trihydrate media. In this study, the mechanism of lignin depolymerization in acidic lithium bromide trihydrate was investigated. First, it was demonstrated that the native lignin in lignocellulosic biomass was easily depolymerized under mild conditions (e.g. in 60 % LiBr with 40 mM HCl at 110 °C). Six types of biomass, including hardwood, softwood, and herbaceous biomass, were treated in acidic lithium bromide trihydrate, and the isolated lignin fractions were characterized with GPC and NMR. The result indicated that the β-O-4 ether linkages of the native lignin were selectively cleaved, leading to lignin depolymerization (M<sub>w</sub>: 2000-4000). Second, lignin model compound (guaiacylglycerol-β-guaiacyl ether) was used to elucidate the mechanism of the cleavage of the β-O-4 ether bonds. It was verified that both the LiBr trihydrate media and HCl were crucial to the cleavage of the ether bonds via the enol ether pathway initiated by the a-C cationization. In addition, new C-C bonds were formed, resulting from nucleophilic attack of the benzyl carbocations by the electron-rich lignin aromatic rings. Third, this lignin depolymerization strategy was applied to technical lignins isolated from pulping and biorefining processes. It was found that the β-O-4 ether linkages of the lignin were selectively cleaved as well.

**CELL 151**

Conductive hydrogels for use in tissue engineering and biocompatible electronics

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Hydrogels are crosslinked polymers that can reversibly absorb and release large amounts of water. They fall into the category of superabsorbent polymers (SAPs) and are used in industry for coal dewatering, diapers, and food additives among other things. Current hydrogel research is largely focused on developing this technology for medical applications such as 3D printing artificial human tissue and controlled drug release. Going one step further, we will be engineering a hydrogel that is biocompatible, mechanically strong, and electrically conductive as well as porous and superabsorbent. This material could then be used for biocompatible electronics or electrically conductive implants, which could replicate nerve activity. To the best of our knowledge, this has not been accomplished to date with an interpenetrated network. The mechanical strength of biocompatible hydrogels is often a limiting factor in their design. To create a mechanically strong biocompatible hydrogel, a cellulose/alginate network was interpenetrated with an acrylate network. This effectively increased the crosslink density of the resulting interpenetrated network (IPN) without decreasing the elasticity. This IPN also showed significant mechanical strength improvements while still maintaining a high swelling ratio. Also, more uniform porosity was shown to be obtained through sequential network synthesis. This uniform porosity came at the expense of higher mechanical strength, which simultaneous synthesis obtained. The interpenetrate network polymer from above will next be made conductive. This is to be done through dispersing carbon nanotubes in the IPN, creating a conductive composite. By using carbon nanotubes, the volume fraction at percolation is quite minimal. This will create a conductive composite without losing the elasticity or high swelling ratio of the resulting polymer. This conductive composite will then be shown to 3D print conductive, strong, and biocompatible cell scaffolds for human tissue or biocompatible electronics.
Preparation of electrospun mats of functionalized Nano-Crystalline Cellulose (NCC)

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The use of NCC to electrospin a nanofiber mat could produce a nonwoven material superior in strength when compared to other materials. A NCC nanofiber mat would have many potential applications, ranging from filtration to medical devices. The goal of this project is to obtain NCC nanofiber mats and study their morphology and physical properties. Polyvinyl alcohol (PVA) will be used as carrier polymer to the NCC particles. NCC will be used in its original form and after been functionalized. Functionalization is expected to make the NCC particles to attached better to each other and to the carrier polymer. The factors considered in the fiber formation process are the needle gauge, working distance, volumetric flow rate, voltage, and collection speed, as well as concentration of the carrier polymer and NCC in the solution, all of which will be evaluated in the study. After the cellulose mats have been formed, the fibers will be observed under a scanning electron microscope for dimensions and configuration of the fibers, in addition to being tested for the physical properties of the material. We predict the solution concentration and the electric voltage will determine the morphology and physical properties of the final product.

Cellulose nanocrystal thin film swelling to probe particle-particle interactions in solvents and aqueous media

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Cellulose nanocrystals (CNCs) are sustainable and biocompatible nanoparticles, which have exciting mechanical, rheological and optical properties. Their interaction with water and solvents remains poorly understood but is of fundamental importance for the commercial development of CNCs and other cellulose-based materials. This work uses “CNC only” model films to investigate particle–particle interactions by thin film swelling in aqueous solutions (with sodium chloride) and organic solvents (ethanol, methanol, isopropanol, acetone and acetonitrile). CNC film thickness and solvent uptake were continuously monitored via surface plasmon resonance spectroscopy and the kinetics of liquid uptake were quantified. In aqueous media, CNC films with different surface chemistries and charge densities were evaluated to better understand the contribution of double layer forces to film swelling. All swelling followed Fickian diffusion behaviour and diffusion constants, determined from early time solutions, decreased with the gradient of ionic strength. Overall, film thickness after swelling was observed to be independent of ionic strength, suggesting that for CNCS in the aggregated state (i.e., in a film) van der Waals forces dominate over electrostatic repulsion prohibiting CNC redispersion. Similarly, in organic solvents, attractive van der Waals forces maintained film stability however, solvents with hydrogen bonding and polar components more effectively interrupted particle-particle interactions allowing for more film swelling. This work highlights that CNC particle–particle interactions are highly dependent on the state of aggregation and these differences must be accounted for when developing cellulose-based materials.

Characterization of edible film based on zein and chitosan

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The aim of this work was to develop zein/chitosan blends and study the heat effect on chitosan in the film-making process. The zein and chitosan solutions were prepared separately; two different chitosan solutions were produced, one heated at 80°C for 1 h, and another just stirred for 1 h and unheated. Thickness, color, water solubility, contact angle and mechanical properties of the blend films were investigated. The data indicated that heating the chitosan solution did not improve the physical characteristics of the film. Instead, the zein-chitosan films prepared with unheated chitosan showed better results for water solubility, contact angle and mechanical properties.

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Pre-treatments to create porous cellulose fibres for nanocellulose production

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Cellulose accessibility is a key factor in conversion and production process in materials more valuable to industry. The cellulose accessibility is mainly made by the pores in the fibers, allowing the interaction of water and chemicals solvents to cellulose chains. This study intends to increase the porosity of fibres with pre-treatments to ease degradation of the cellulose fibers. This target was achieved using either enzymatic treatment or chemical swelling. The enzymatic treatment conditions 1, 5, 8 and 15% enzyme load and reaction time 10, 30, 60, 120 and 180 minutes. The pulps porosity was measured by WRV and the nanometric porosity by thermoporometry. Cellulose nanocrystals (CNC) were produced with sulfuric acid 65% wt. and reaction times 10, 20 and 30 minutes reaction times. The CNC production were characterized by measuring the yield, the sugar content un-hydrolysate solid. The CNC properties were measure by dynamic light scattering (DLS), atomic force microscopy (AFM). The second pretreatment was based on solvent exchange and Cellulose nanofibers (CNF) were produced using mazuko with classic characterizations by measuring the energy consumption.

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Succinylation of glucomannans from spruce for hydrogel formation

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Glucomannans represent the major fraction of hemicelluloses in conifers, amounting up to 15 wt. %. Their abundance, polymeric, and natural characteristics, coupled to the urgent demand for sustainable raw materials and end products, make glucomannans excellent biopolymers useful in diverse commodities such as packaging, coatings, stabilizers, solubilizers, adhesives, and especially compounds like drug-delivery carriers, health-care agents, etc. Glucomannans contain labile hydroxyl groups that can be modified with carboxyl moieties, resulting in more versatile materials. In this work glucomannans were isolated from Norway spruce holocellulose and purified via dialysis (MWCO 1000 Da). Chemical characterizations with ATR-FTIR and sugar analysis were carried out. The ratio Glc:Man was 46:54 w:w. Typical infrared bands for glucomannans were found at 3300 cm⁻¹ corresponding to hydroxyl groups and the orthogonal directed hydrogens in mannose ring at 870 cm⁻¹ and 814 cm⁻¹. Succinylation was realized in DMF with succinic anhydride, at various reaction times in order to achieve different degrees of substitution. Conjugation with tyramine was carried out with EDAC/NHS. HRP was used to initiate crosslinking. Gels were formed in less than a minute.
Biomass potential for the development of advanced materials and bio-based products

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The concept of circular economy is increasingly becoming an important driving force for innovations. Effective use of materials enables the creation of more value, both by cost savings and by developing new markets or growing existing ones. In the frame of the Slovenian national smart specialization program CELLCYCLE, under priority area Natural and traditional resources for the future – Networks for the transition to circular economy, we are focusing on the use of discarded local biomass for the development of advanced functional materials, i.e. bio-composites for electronics, construction and textile the industry. Isolated natural species, i.e. cellulose fibres (from micro to nano-size dimensions) are used and modified, creating desired functional properties. The main focus is given on designing and constructing a variety of 3D fiber-based materials following multiple paths (i) construction of aerogels from micro- and nano-fibrillated cellulose, with special attention given to the elaboration of cost effective preparation procedures; resultant aerogels will possess suitable mechanical stability with required porosity and pore size, (ii) formation of 3D nonwovens, focusing on pore size reduction and enhancement of the active surface.

Gelation of 3D printed nanocellulose induced by crosslinked hemicellulose

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The cells, during secondary cell wall synthesis, extrude cellulose chains in well-established patterns, decorate them with hemicelluloses and then, when apoptosis occurs, triggers lignification and crosslinking of the cell wall. Bottom up biofabrication of wood based materials can be carried out by using 3D printing. Nanofibrillated or ionic liquid dissolved celluloses have been previously evaluated as bioinks in layer-by-layer fabrication. Consolidation of 3D shapes was achieved by ionic crosslinking with alginate or by coagulation in a non-solvent. In this work we focus on exploiting the gelling properties of crosslinkable hemicelluloses, as “inks” components for 3D printing. We have functionalized spruce arabinoglucuronoxylan (AGX) with acryloyl chloride-HEMA-AIBN and HEMA-Im, and studied HEMA polymerization/crosslinking with UV radiation. Xylan gels were characterized by rheology and tested under printing conditions. Mixtures with nanofibrilated cellulose gels, xylan bearing vinyl groups and HEMA were tested as “inks” components in 3D printing.

Effect of the change of the crystalline structure on the infrared spectra by ATR of cellulose from banana rachis, corn husk and bacterial cellulose

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The present study evaluates the crystallinity of cellulose isolated from banana rachis (BR) and corn husk (CH); as well as from bacterial cellulose (BC) before and after cryogenic milling. Samples from CH and BR were chemically treated according to Zuluaga et al. (2005) to remove the non-cellulosic components, while BC was purified by an alkaline process. The samples were subsequently homogenized using a grinding equipment (Masuko Sangyo, Supermascoloinder MKCA6-2) and freeze dried. The product was processed by a cryogenic mill (Retsch, Cryomill) at four different times (10, 20, 30 and 40 min). The milling effectively decreased the crystallinity of the cellulosic samples, with an almost complete conversion to amorphous cellulose at the higher times. The infrared spectra obtained of the specimens using an attenuated total reflectance accessory indicate changes in the 800-1200 and 3000-3600 cm\(^{-1}\) regions, related to cellulose crystallinity. These observations were confirmed by X-ray diffraction and thermogravimetric analysis.

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**Bacterial nanocellulose based bioink for 3D bioprinting**

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Bacterial nanocelluloses, BNC possesses significant advantages compared with plant derived nanofibrillated cellulose, such as being free of lignin and hemicelluloses, as well as being already FDA approved as a biomaterial in several applications. These features make BNC an attractive nanofiber to use as bioink in additive manufacturing in tissue engineering. However, the strong entanglements created during bacterial cellulose biosynthesis make difficult to use BNC as a bioink for 3D bioprinting applications. Such entanglements resist mechanical defibrillation and require use of strong acid hydrolysis in order to liberate the nanocellulose and make it flow through the 3D bioprinting nozzles. This research examines different conditions for hydrolysis of BNC and its use in 3D bioprinting. Also another technique for defibrillation of cellulose was evaluated, i.e. aqueous counter collision, which renders excellent BNC for use as bioink. Cultivation of fibroblasts was used to evaluate the BNC as potential scaffold for tissue engineering.

**CELL 161**

**Characterization of wood and cellulose from different eucalyptus species**

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Wood from Eucalyptus genus is an important raw material for pulp and cellulose derivatives production. With the aim to understand the differences and the further use for production of cellulose derivatives, eight six-year-old Eucalyptus species were sampled and analyzed for anatomical, chemical and infrared spectroscopic and TGA characterization. The species studied corresponded to *E. badjensis*, *E. benthamii*, *E. dunnii*, *E. globulus*, *E. nitens*, *E. smithii* and two hybrids of *E. nitens* x *E. globulus* (coded x64 and x65). Wood density values ranged from 419.9 – 484.0 kg/m\(^3\), with *E. globulus* and *E. smithii* with the higher wood density trees, and *E. badjensis* with the lower one. Fiber length ranged from 0.60 – 0.70 mm, being *E. globulus*, *E. smithii* and EnxEg (x65) the higher values, while *E. badjensis* showed the lower fiber length. Chemical characteristics of the different Eucalyptus species are shown in table 2. The higher
extractives content was obtained for E. benthamii (6.7%) and the lower for E. globulus (1.5%). E. globulus also showed the lower lignin content (23.2%) and the higher holocellulose content (73.5%). While the higher lignin content was obtained for E. benthamii (27.7%) and the lower holocellulose content for E. benthamii and E. dunnii. About alpha-cellulose isolation, the higher content obtained was a 55.5% in E. dunnii, while the lower content was observed in E. badjensis (48.5%). FTIR spectra were obtained for wood, holocellulose and alpha-cellulose samples from the eight Eucalyptus species studied. The ratio between the bands at 1372 cm⁻¹ and 2900 cm⁻¹ was considered as total crystalline index (TCI), and the ratio between the bands at 1429 cm⁻¹ and 897 cm⁻¹ was used as a lateral order index (LOI), which is defined as an empirical crystallinity index. The TCI is proportional to the crystallinity degree of cellulose and LOI is correlated to the overall degree of order in cellulose. For wood samples, the higher TCI ratio was obtained for E. dunnii (0.394), while the lower value was for E. nitens (0.292). The higher LOI was obtained for E. badjensis (2.698) and the lower for E. nitens (1.013). TGA data are under analysis. The Eucalyptus species showed different variation patterns for the structural features of cellulose, which could be attributed to chemical and structural properties of the inherent properties of wood components from each species.

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Biomaterial polymer blends for material extrusion 3D printing

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There is a renewed interest in replacing fossil-derived synthetic plastics with renewable polymeric materials due to increased environmental concerns and end-of-life disposal challenges. This can be achieved through the control of the feedstock, chemical, and physical structures of polymer materials during extrusion process. We investigated the effect of nanocellulose blending with acrylonitrile-butadiene-styrene (ABS) to develop nanocomposites with enhanced properties. We produced composites of ABS and nanocrystalline cellulose (NCC) through a melt blending process via twin-screw extruder. A set of experiments were performed and the produced polymer composites were analyzed using multiple techniques. TGA analysis shows that ABS-NCC composites weight loss starts at 260-280°C, which is approximately 80°C lower than that of ABS alone. Mechanical testing shows an increase in ductility with the addition of NCC to ABS. This indicates that NCC acts as a plasticizing agent in ABS composites. SEM images of the polymers in both surface and cross-section views showed enhancement in polymer morphology. This approach can be very beneficial since extrusion process is considered an economical method for making filaments on a large scale especially for 3D printing, yet the presence of nanocellulose makes it more sustainable.

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Solution/aggregation behavior of spruce xylan as function of isolation/purification conditions

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Hemicelluloses pose a great opportunity to develop sustainable polymeric products because of their abundance, renewability, and physicochemical characteristics. Particularly, xylans from Norway spruce (arabinoglucomuronoxylan, AGX) have shown to have excellent film forming ability and outstanding oxygen barrier properties. A fundamental understanding of factors affecting the solubility of this polymer and its
physicochemical characteristics will undoubtedly provide the tools for a better design of end products. In this work we have carefully isolated AGX and subjected it to different purification treatments in order to correlate them with the solution/aggregation behavior of AGX. A battery of analytical tools in solution/dispersion, such as dynamic and static light scattering, molecular mass distribution through size exclusion chromatography (SEC), and their morphology in dry state by scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been used in order to characterize these samples.

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Extraction and characterization of nanocellulose from different biomass sources

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Previous investigations published within our group revealed that the acid strength and biomass source strongly influenced the resulting thermal and structural properties of the extracted cellulose crystals. Thus, in this work, a systematic investigation on the feasibility of extracting nanocellulose from different biomass (i.e., cotton, wheat straw, and Hibiscus sabdariffa), by means of two different procedures, was carried out. Under both methods, chemical procedures such as acid hydrolysis, alkaline extraction, and bleaching were included in the extraction process. Morphological characterizations of the final product were performed using Transmission Electron Microscopy, Atomic Force Microscopy, and Fourier Transform Infrared Spectroscopy to monitor the removal of non-cellulosic constituents. The thermal stability of the extracted cellulose was explored using Thermal Gravimetric Analysis. Finally, XRD and FTIR were used to monitor the crystallinity and composition, respectively, of the cellulose upon treatment via both extraction methods.

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Synthesis and fabrication of CNF-based plastic nanocomposites

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Currently, most BioPlastics are produced using renewable biomass resources, such as vegetable fats, oils, and sweet potatoes, which readily decomposes (or biodegrade) once they are buried in the ground. These materials lack the necessary strength and flexibility required to extend their use to the packaging or electronic industry, and thus have limited its use worldwide. To address this issue, we have explored the use of cellulose nanofibrils, CNFs, due to their high mechanical strength as an avenue of enhancing the overall performance of plastic composites. Thus, we report have investigated the use of cellulose nanofibrils, CNFs, in the development of environmentally friendly cellulose-based plastics using both biodegradable and nonbiodegradable polymer matrices. Unlike earlier bio-based plastics, Thermal Gravimetric Analysis, TGA, and DMA reveal that the CNF-based plastics show significant improvements in their mechanical and thermal stability properties demonstrating their potential use in a wider range of applications for the cellulose-based plastics. Finally, preliminary data collected through a biogas study indicates that the CNF-based composites are biodegradable.
Molecular blending and reinforcing effect of lignin in ductile epoxy resins

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Lignin is an undervalued but abundant natural resource available as a byproduct in the pulping industry. In this work, the potential of Kraft lignin as reinforcement for commercially available soft epoxy matrices was evaluated. Composites with lignin content up to 40 wt% were prepared using a solvent-free mixing process. The composites were characterized using dynamic mechanical and uniaxial tensile tests, and their morphology observed with electron microscopy. The preparation of the composites relied on molecular blending of the components, rather than complex chemical modifications on the lignin, to achieve remarkable improvements in mechanical and thermal properties. The reinforcement mechanisms were evaluated with respect to chemical and morphological characteristics of the composites.

TEMPO-oxidized Nanofibrillated Cellulose Film (NFC) incorporating Graphene oxide (GO) nanofillers

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Novel TEMPO-oxidized cellulose fibrils (TOCNs) composite films were fabricated with never-dried wood nanofibrillated cellulose (NFC) and graphene oxide (GO) as functions of degree of oxidation (0.5X, 1X, and 2X) and GO percent loadings: 0.4, 1.2, and 2.0 wt %. Despite the presence of carboxylate groups and graphene oxide (GO), the crystallinity of the bio-nanocomposite was not altered according to the results obtained from X-ray diffraction (XRD). Energy Dispersive Spectroscopy (EDS) analysis on the scanning electron microscope (SEM) was used to characterize their morphologies and it shows that GO in the matrix of TOCN was well distributed. The thermal degradation of TOCN/GO composite films, measured by Thermal Gravimetric Analyzer (TGA), shifted to a lower temperature upon the degree of tempo oxidation due to their high disintegration and oxidation. Dynamic mechanical analysis (DMA) signified strong intermolecular interactions with the improvement in Young's storage modulus, and tensile strength. Based on Fourier transform infrared spectroscopy (FTIR) evaluation, the intensity of carbonyl group stretching (at 1726 to 1730 cm⁻¹) increased as a function of degree of tempo oxidation while GO didn't show any effect on FTIR. Gas barrier properties, such as water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were analyzed. The values in OTR of TOCN GO composite decreased, indicating improvement in oxygen barrier property due to GO filler, whereas WVTR was not significantly affected by the reinforcement with GO and oxidation. Based on our observation, the newly fabricated TOCN/GO composite film can be utilized in a wide range of life science applications, such as food and medical industries.

Enhanced solar driven water evaporation rates through graphitic surface film suspensions

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From a Central American perspective, the recent emergence and proliferation of new materials with nanometer dimensions and hence unprecedented bulk and surface properties are potentially very
promising, if focused on the basic needs of the majority of the people living in the region (food, water, health, energy, education) and, importantly, provided the case that the ecological footprint of such new materials is low, when compared to fossil fuels, heavy metals, and persistent organic substances, including plastics. In this study we focus on the improvement of light powered water distillation, a technique described as early as ~2500 years ago. One major drawback of traditional light powered distillation is its relative poor energy efficiency. Actually only a very small fraction of the sunlight is being used to induce actual evaporation of the water located in the top surface layers exposed to the sunlight. A substantial amount of the solar energy will be used but to heat the bulk water layers, rising their temperature in time – but contributing only indirectly to the evaporation process at the water/air phase boundary. New nanotechnological approaches dedicated to gain more energy efficiency in light-driven water evaporation have shown stunning results, showing marked water evaporation rates increases. In our contribution, we present and discuss the results of light-driven water evaporation experiments performed with water surfaces covered with different graphite powders from sources which are commonly available in Central America (pencil cores, battery electrodes, graphite lubricants, etc). The experiments are conducted under controlled temperature, humidity and airflow conditions, within customized, 3D printed reaction vessels. First findings show that aforementioned “common source graphite films” enhance water evaporation close to the level obtained with “high end” nanomaterials.

MONDAY MORNING

Design & Control in Polysaccharide Chemistry: Anselme Payen Award Symposium in honor of Kevin J. Edgar
P. E. Fardim, Organizer; O. J. Rojas, Organizer; C. M. Buchanan, Organizer; O. J. Rojas, Presiding Papers 169-176

CELL 169

Repeating unit of cellulose is glucose, and why that matters

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Statements and drawings in the cellulose literature frequently describe cellulose as a chain of repeated cellobiose residues. Alternatively, Wertz, Bédéué and Mercier state that “Current evidence suggests that glucose and not cellobiose is the fundamental unit.” In this writer’s opinion, cellobiose is not the repeating unit, nor is the issue subject to arguments based on technical evidence, but instead on semantics. IUPAC clearly defines the repeating unit of a polysaccharide, namely “The monomeric unit is the monosaccharide.” The lecture will cover the intended implications of the descriptions of cellobiose as the repeating unit as well as the unfortunate limitations of that thinking.

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Findings on the way of cellulose ether analysis

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The analysis of the substituent distribution over the chains of cellulose ethers is based on the determination of DS/DP profiles and the comparison of such profiles with the calculated random pattern. This analytical method requires that the polymer is degraded randomly and that the mass spectra of the oligosaccharide mixtures can be evaluated quantitatively. While this approach is well established for methyl cellulose (MC), the application to other types of cellulose ethers is much more challenging. To find
out whether depolymerization occurs in a random manner, kinetics of hydrolysis was studied for various cellulose ethers. Relative response of Electrospray Ionization (ESI) was also studied in dependence on chemistry and concentration of analytes. Results are presented and discussed.

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**Lytic polysaccharide monooxygenase – from the NMR point of view**

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Lytic polysaccharide monooxygenases (LPMOs) are key components of enzymatic biomass (e.g. chitin and cellulose) degradation processes. LPMOs catalyze a reaction cycle that requires copper, molecular oxygen and an electron donor, such as cellulose dehydrogenase (CDH). We have used mainly NMR spectroscopy to study LPMO structure, interaction with metal ions, dynamic features, interaction with solid and soluble substrates, electron transfer ‘pathway’, and the products formed by the LPMO reaction. Here we provide a comprehensive overview of our findings, from an NMR perspective.

![Illustration of the different aspects where NMR spectroscopy has been used to study LPMO](image)

CELL 172

**Rheo-optical and optical studies of cellulose derivatives**

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Polysaccharide solutions and melts are behaving like classical polymers, showing flow-induced changes due to their chain entropic behavior. In addition, when solutions or melts are either self-structured like in liquid crystals or mixed with other compounds like in blends or suspensions, the structure of the flow and thus its measured rheological traces are becoming complex. One method to characterize and control these flow-induced structures is to perform physical observations during flow in addition to mechanical measurements. We will illustrate the benefits to use rheo-optical tools for studying cellulose derivative solutions in several cases including structures in liquid crystalline phases, dispersion of agglomerated particles and dissolution. Another example will be how to use isotropic-anisotropic phase transition to study swelling of a gel.
Insights in the control of glycosaminoglycan structure

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Glycosaminoglycans are complex polyanionic, polydisperse polysaccharide that are ubiquitously found in animal tissues. These polysaccharides include heparin/heparan sulfate, chondroitin sulfates, keratan sulfates and hyaluronan and are critical biological molecules in cellular communication. This presentation focuses on sulfated glycosaminoglycans that are synthesized in the Golgi and assembled on a core protein as proteoglycans. The biosynthetic pathway for these biopolymers provides some critical information on their structure. Recently it has been possible to perform top-down sequencing of the simplest glycosaminoglycan structures using fractionation methods coupled with tandem mass spectrometry. Insight is provided on how these complex carbohydrate structures contain information that can be read by glycosaminoglycan-binding proteins and then can influence complex biological processes such as cell proliferation, migration and differentiation.

Precision biomaterials based on synthetic heparan sulfate oligosaccharides

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Glycosaminoglycans (GAGs), such as heparin and heparan sulfate, are naturally occurring polydisperse linear polysaccharides that are heavily O- and N-sulfated. The interaction between GAGs and proteins can have profound physiological effects on hemostasis, lipid transport and adsorption, cell growth and migration and development. We have developed an integrated approach for the identification of ligands for HS-binding proteins employing affinity purification, sequencing of HS oligosaccharides by novel mass spectrometric approaches and the chemical synthesis of libraries of HS oligosaccharides for structure activity relationships. Synthetic HS-oligosaccharides of interest have been used for the preparation of well-defined hydrogels, which could support stem cell growth and differentiation.

New views of plant cell wall non-cellulosic polysaccharide and proteoglycan structure from studies of pectin biosynthetic enzymes and plants modified in their expression

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Most plant cell wall models depict a matrix of three types of polysaccharides and, in most cells with secondary walls, the polyphenolic lignin. The polysaccharides are cellulose, and the two families of matrix polysaccharides, hemicellulose and pectin. However, with the identification of the cell wall proteoglycan, arabinoxylan-pectin-arabinogalactan protein 1 (APAP1), that contains both hemicellulosic and pectic glycans, such wall models have come into question. Furthermore, the phenotypes of biomass feedstock modified in the synthesis of relatively minor wall components, such as pectin in grasses and in woody tissues, indicate that current wall models are insufficient to account for the effects that such changes have on plant cell wall structure and wall properties. Pectin is the most structurally complex family of the cell wall polysaccharides. It is comprised of the three pectic glycans homogalacturon (HG),
rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II). The most abundant pectic glycan is HG, accounts for roughly 65% of pectin. HG is a partially methyl-esterified and acetylated homopolymer of alpha-1,4-linked galacturonic acid. It is synthesized by the GAUT gene family of proven and putative HG alpha-1,4-galacturonosyltransferases (HG:GalATs), with 15 members in Arabidopsis. During efforts to generate biomass feedstock with reduced recalcitrance for biofuel production, we discovered that modification of GAUT gene expression in woody and grass feedstock leads to reduced biomass recalcitrance and enhanced biofuel production by microbes, as well as improving plant agronomic performance. The result of efforts to identify the specific matrix polysaccharide polymer(s) effected and the mechanism(s) for the improved wall properties has led us to hypothesize that specific GAUTs synthesize specific HG glycans that function in unique polysaccharides and proteoglycans with unique roles in the wall. We propose that the wall is not merely a matrix of three classes of polysaccharides, but rather a matrix of polysaccharides and matrix-glycan containing wall proteoglycans that contribute to cell wall physical, biochemical and agronomic properties. We put forward that an in depth understanding of (1) the specific polymeric structures, (2) their mechanism of synthesis, and (3) their chemical, biophysical and biological properties are critical to enable the most effective use of biomass as a source of energy and bioproducts in a sustainable bioeconomy.

CELL 176

Conversion of agricultural by-products to methyl cellulose

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Alkyl cellulosates are industrial polymers used as adhesives, protective coatings, personal care, and in agriculture. We will discuss an alternative, simplified synthesis of alkyl cellulose, using microwave irradiation and aqueous alkaline medium. No alcohol is needed during the reaction. Reaction time is less than 30 min. Conversion varies from 54 to 87%. The degree of substitution varied from 0.2 to 1.0. It was also shown that agricultural residues such as wheat straw, barley straw, and rice hull can be converted to methyl cellulose. Weight yields range from 30 to 70%. The degree of substitution (DS) varies from 0.8 to 2.8. In addition, the methyl cellulose was further converted to acetylated methyl cellulose. The production of methyl cellulose and ethyl cellulose was confirmed by 13C NMR and FTIR analysis.

Processing & Properties of Biobased Composites & Blends

J. R. Barone, Organizer; P. R. Navard, Organizer; J. R. Barone, Presiding Papers 177-184

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Mechanical properties improvement of natural rubber/pineapple leaf fiber composites: Effects of silane treatment of fiber and incorporation of carbon black

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Recently, the development of green composites has been gaining more interest and attention due to the depleting petroleum reserves and environmental awareness. Natural fiber is the one of green fillers with high strength that can be used to reinforce polymer materials. Short and fine pineapple leaf fiber (PALF) has been successfully developed by our research group at Mahidol University, and has been used to
reinforce polypropylene (PP), nylon, Santoprene and also nitrile rubber effectively. Natural rubber (NR), one of Thailand’s top exports, was chosen as the matrix for fiber reinforcement in this study. The major component of NR is high molecular weight cis-1,4-polyisoprene polymeric movable chains. Due to the difference in polarities between NR and PALF, the adhesion and hence stress transfer between them is low. In this study, the stress transfer between NR and PALF was enhanced by silane treatment of the fiber. Since PALF would improve the mechanical properties only at low deformation, carbon black was also incorporated into NR/surface-treated PALF composite to improve mechanical properties at high deformation.

The fiber was first treated with sodium hydroxide solution to clean out non-cellulosic substances on the fiber surface. After that, the treated fiber was treated with silane-69, which is a silane containing sulfur atoms. Silane-69 allows chemical bonding between the fiber and the rubber matrix to form during the vulcanization process. This would thus improve the stress transfer between the NR matrix and PALF. The results on XPS for successful fiber surface modification and stress-strain curves for mechanical properties improvement will be reported and discussed.
obtained phenolic resins from substituted vanillin, thus without the use of any aldehyde compound classified as CMR. The analytical tests confirmed that those bio-based resins exhibit very high levels of performance with high thermal stability and high rigidity properties.

CELL 179

Manufacturing strong regenerated cellulose fibers reinforced with cellulose nanocrystals

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In this study we report manufacturing of strong cellulose fibers using ionic liquids solvents, and cellulose Nano crystals (CNCs). Cellulose fibers were manufactured with different weight percentages of CNCs using dry jet wet fiber spinning method and water as a coagulation solvent. The CNC reinforced cellulose fibers spun at high winding speeds showed excellent mechanical properties (modulus above 35GPa). The X-ray diffraction study shows very high alignment of cellulose chain along the fiber axis direction. By controlling the weight fraction of CNCs and the winding speed we can control the mechanical properties of the regenerated cellulose nanocomposites fibers. These fibers can be used to replace heavy glass fibers in traditional composite materials to produce more lightweight and renewable composites for potential use in composites for automotive and sports applications.
Figure 1: SEM images representing the cross-section fractured surface of Cellulose fibers.

Figure 2: Wide angle X-Ray diffraction images showing the fibres alignment.
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Micro and nano composites using cotton materials loaded in polylactic acid and applications in 3D printing

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There is strong interest in developing nano and micro composites for 3D printing that include cellulose. The cellulosic material can provide mechanical properties, moisture interaction properties, optical and textural properties that are unique. This research examines the use of PLA as a matrix material and nano and micro particles derived from recycled cotton fabrics at different loadings. The materials are evaluated in 3D printed applications. A twin screw extruder was used to compound the PLA and cotton particles. The resulting materials were then formed into filaments (or films), characterized, and then printed with a 3D printer. Loadings of 31% cotton were able to be compounded. Filaments of up to 20% cotton loading were successfully used in a 3D printer and parts produced. The structure of the nano and micro composite materials and the mechanical properties of the film and 3D printed parts are reported herein.

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Design, fabrication and test of degradable starch based tube for a biomedical application

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Starch-based materials have attracted significant interest for the development of innovative materials for biomedical applications due to its biocompatibility and bioresorbability. Moreover, biopolymers based devices are very well accepted by patients. Thanks to starch thermoplastic behaviour, 3D objects can be easily fabricated by use of process such as extrusion, thermomoulding or injection. In this study, starch-based materials were designed using a special extrusion die in order to conceive a tube-shaped device for an application in the endoscopic field of saliendoscopy devoted to the treatment of salivary ducts disease. For the site of application considered, starch is naturally degraded by the a-amylase enzyme present in saliva, guaranteeing the device disappearance and making it a potential interest in short-term sialendoscopic uses. In this work, the ageing of the starch material plasticized by glycerol has been assessed by the study of its structure, swelling and mechanical properties immersed in physiological medium. They present a high initial rigidity which facilitates the device insertion, with a Young’s modulus of 2 GPa and decreases to about 2 MPa during immersion. In order to predict the mechanical behaviour of the tube once implanted, a finite element study was performed using intrinsic mechanical properties determined for the immersed material. It simulates an external axial pressure, showing a symmetrical distribution of strain in the inner diameter as well as a longitudinal tube extension. It allows the determination of a maximum axial allowable pressure of 0.2 MPa before irreversible damage. The hydrolysis of the starch tube exposed under flow of a simulated salivary solution was studied as well as its glycerol kinetics release. After 2 days, about 55% hydrolysis of the initial material is achieved. Following physical characterization, an animal short-term implantation model for salivary ducts was proposed. Results showed that the tube-shaped devices is adapted to sialendoscopic guidewires and were able to be implanted in salivary ducts from pigs.
Blend configuration in polymeric materials with very high lignin-derivative contents

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Lignins embody 20–30% of terrestrial organic carbon. Yet, it has been surprisingly difficult to create functional polymeric materials with lignin-derivative contents approaching 100 wt%. This problem has delayed the dawn of profitability in converting lignocellulosic plant materials to commodity organic chemicals or liquid fuels. However, it has recently become evident that, on their own, methylated native softwood lignins can form polymeric materials with tensile properties surpassing those of polystyrene. Small quantities (just 5 wt%) of non-biobased blend components as common as poly(ethylene glycol) are capable of increasing tensile strength by 40%. Even without methylation, miscible blends containing 95 wt% native softwood lignin can exceed the tensile strength of polystyrene by a substantial margin. These striking results have been achieved with softwood lignin preparations exhibiting weight-average molecular weights around 2300. In contrast, the polystyrene typically used as an industrial material has a molecular weight that is two orders of magnitude higher. The macromolecular species in materials containing 85–100 wt% levels of simple softwood lignin derivatives are associated complexes composed of two distinct domains. Their integrity is maintained by strong non-covalent interactions between cofacially offset aromatic rings in the interior. On the other hand, the peripheral domains, through which continuity between neighboring complexes is established, embody a high proportion of edge-on arrangements of interacting aromatic rings. Non-lignin blend components interact as plasticizers preferentially with the peripheral domains of the complexes. Their efficacy is reflected in the propensity of the peripheral domains to expand in response to the non-biobased components in the blend.

Lignin acidolysis predicts formaldehyde generation in pine wood

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Pinus virginiana wood was heated (200°C, 10 or 60 min) while dry or after aqueous/acid/base pretreatment in order to reveal mechanisms of formaldehyde (CH2O) generation. Among wood structural polymers, lignin was the overwhelming source of biogenic CH2O, consistent with prior reports. The selection of acid catalyst strongly affected CH2O generation as predicted in the acidolysis literature of lignin model compounds and isolated lignins. Furthermore, pine wood extractives may play a catalytic role during in situ lignin reactions. Lignin methoxyl cleavage was also observed, but was considered an unlikely source of thermochemical CH2O. Alkaline pretreatments suppressed CH2O generation. Regarding wood-based composite manufacture, the implications are that lignin reactions can be manipulated during hot-pressing. Potential benefits include reduced product emissions, and/or novel crosslinking strategies using biogenic CH2O. Perhaps even lignin repolymerization could be promoted for benefit, in direct opposition to biorefinery strategies for lignin removal.

Amyloid reinforced polyvinyl alcohol nanocomposites

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Amyloids are self-assembled protein nanomaterials containing beta-sheets. Amyloid fibrils have moduli of several to tens of gigapascals making them a high performance material. Proteins can be self-assembled into anisotropic amyloid nanostructures in polyvinyl alcohol (PVA) solutions. The PVA solution conditions influence the final amyloid morphology. Amyloids increase the PVA modulus by 350%. Thermal processing the composites increases the PVA crystallinity. It also thickens, lengthens, and entangles the anisotropic amyloid morphology for further control over the nanocomposite properties. However, too severe thermal processing will result in protein and PVA degradation. Fourier transform infrared (FTIR) spectroscopy shows strong beta-sheet formation in the protein phase and strong protein-PVA hydrogen bonding. Differential scanning calorimetry (DSC) shows an increase in the PVA glass transition temperature in protein-PVA nanocomposites indicative of increased hydrogen bonding interactions. X-ray diffraction (XRD) shows that the beta-sheet inter-sheet distance decreases after self-assembly and thermal processing of the nanocomposites indicating a different structure than that formed in water.

Cellulose Structure & Biosynthesis
N. Carpita, Organizer; D. Cosgrove, Organizer; P. Langan, Organizer; H. M. ONeill, Organizer; J. Zimmer, Organizer; A. W. Roberts, Presiding; J. Zimmer, Presiding Papers 185-192

CELL 185

Structure and function of cellulose synthase

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Cellulose synthase is a membrane integrated processive glycosyltransferase that synthesizes and secretes cellulose in a coupled reaction. Structural and functional analyses of bacterial cellulose synthase reveal the mechanism by which the enzyme elongates the nascent cellulose chain and translocates it after each round of elongation. Crystallographic snapshots of a complete cellulose synthesis and translocation cycle reveal that cellulose synthase uses a short alpha-helix to interact with and push the extended polymer into a transmembrane channel formed by its own membrane-spanning region. The movement of this ‘Finger Helix’ is driven by substrate binding to the active site.

While bacterial and plant cellulose synthases likely share a common reaction mechanism, the plant enzymes (CesAs) bundle the individual glucan chains into cable-like structures termed cellulose micro- and macrofibrils. Functional reconstitution of recombinantly expressed poplar CesA8 reveals that individual CesA isoforms are catalytically active on their own and suffice to form cellulose microfibrils in vitro.

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Cellulose microfibril formation in vitro by a single heterologously expressed plant cellulose synthase isoform

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Plant cell walls are a composite material of polysaccharides, proteins, and other noncarbohydrate polymers. In the majority of plant tissues, the most abundant polysaccharide is cellulose, a linear polymer of glucose molecules. As the load-bearing component of the cell wall, individual cellulose chains are frequently bundled into micro and macrofibrils and are wrapped around the cell. Cellulose is synthesized by membrane-integrated and processive glycosyltransferases that polymerize UDP-activated glucose and secrete the nascent polymer through a channel formed by their own transmembrane regions. Plants express several different cellulose synthase isoforms during primary and secondary cell wall formation; however, so far, none has been functionally reconstituted in vitro for detailed biochemical analyses. Here we report the heterologous expression, purification, and functional reconstitution of *Populus tremula x tremuloides* CesA8 (PttCesA8), implicated in secondary cell wall formation. The recombinant enzyme polymerizes UDP-activated glucose to cellulose, as determined by enzyme degradation, permethylation glycosyl linkage analysis, electron microscopy, and mutagenesis studies. Catalytic activity is dependent on the presence of a lipid bilayer environment and divalent manganese cations. Further, electron microscopy analyses reveal that PttCesA8 produces cellulose fibers several micrometers long that occasionally are capped by globular particles, likely representing PttCesA8 complexes. Deletion of the enzyme’s N-terminal RING-finger domain almost completely abolishes fiber formation but not cellulose biosynthetic activity. Our results demonstrate that reconstituted PttCesA8 is not only sufficient for cellulose biosynthesis in vitro but also suffices to bundle individual glucan chains into cellulose microfibrils.

**CELL 187**

**All-atom structural models of plant cellulose synthase and cellulose synthase complex**

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Cellulose synthase (CESA) is an enzyme that polymerizes glucose into cellulose which is a principal component of plant cell walls and lignocellulosic biomass. Despite the importance of plant cellulose to nature and industry, we have little understanding of the 3D structure of proteins required for plant cellulose biosynthesis. However, manipulating the physical properties of cellulose through biochemical engineering of CESA structure offers many prospects for improved biomaterials and biofuels. To date the crystal structure of synthase protein is not known and the mechanism of how CESA produces cellulose is not completely understood. In this talk, we will show how computational models can facilitate better understanding of the CESA function and the assembly of CESAs into cellulose synthesis complex (CSC). We used a combination of de-novo and homology protein structure modeling and molecular dynamics simulations to generate all-atom 3D model of cotton CESAs protein structure. Using our 3D model we observed an agreement in the catalytic mechanisms between bacteria and plants and the specific roles of other conserved regions of CESA. To further understand the biochemical roles of various structural motifs, such as regions unique to plant CESA and Zn-finger, in regulating cellulose production, we predicted how CESAs can assemble into CSC complex and show possible formation of oligomeric assemblies from dimers to hexamers. Our 3D model of cellulose synthase complex suggests that each rosette lobe preferably contains a trimer of CESA producing 18 cellulose chains per CSC and allows for exploration and testing of the structure-to-function relationship of CESAs.

**CELL 188**

**Organization of domains in CESA proteins of the plant cellulose synthesis complex**

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Cellulose synthesis in plants is carried out by the synergistic action of a large number of membrane-bound cellulose synthase (CESA) proteins that form the cellulose synthesis complex (CSC). Knowledge of the structure of individual CESA proteins that form the CSC would provide critical information about the molecular mechanism of cellulose synthesis. Plant CESA proteins are single polypeptide chains of approximately 1000 amino acids. They have three major domains; an N-terminal domain that contains a Zn ring motif, a cytosolic catalytic domain, and a transmembrane domain. Here, we report on our progress in investigating the structures of individual domains of CESA proteins using small-angle scattering (SAS) and transmission electron microscopy (TEM) techniques complemented by computational methods, to gain insight into their role in the assembly and stabilization of the CSC. 

Ab initio models for the catalytic domain of Arabidopsis CESA1 (CESAcatD) derived from the small-angle neutron and X-ray scattering provide the first experimental evidence to support the self-assembly of CESAcatD monomers into stable homotrimer complexes [1]. Possible configurations for the arrangement of CESAcatD monomers in the homotrimer were obtained using computational modeling in which the class specific region is found at the periphery of the complex and the plant-conserved region forms the base of the trimer. The results of this study and TEM analysis of Physcomitrella patens CSC supported by computation, provide strong evidence that there are 18 CESA proteins in the plant CSC [1,2]. SAS, TEM, and computational analysis of the N-terminal domains of Arabidopsis and cotton CESA show that the proteins form stable dimers and provide new insights into the dimerization interface. The experimental and computational results will be discussed in the context of previously published work that proposed a redox dependent N-terminal domain dimerization mechanism and more recent work on in vitro synthesis of cellulose by heterologously expressed CESA proteins [3,4].

CELL 189

Progress toward structural understanding of cellulose synthesis by plants

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While it is clear that a six-lobed membrane spanning cellulose synthesis complex (CSC) contains multiple cellulose synthase (CESA) glycosyltransferases for cellulose microfibril formation, the number of CESAs in the CSC remains unknown. CLSF members applied a combination of methods including improved FF-TEM, 2D image classification and averaging, analysis of small angle X-ray scattering data, negative stain TEM, and computational modeling to study the low resolution structure of rosettes from the nonvascular plant Physcomitrella patens and of the cytosolic or catalytic domain of CESA1 from Arabidopsis thaliana. The inner membrane portion of CESA in rosette lobes were frequently triangular, and their areas fit well with trimers of CESA. Trimeric oligomers of two alternative CESA computational models corresponded well with individual lobe geometry. A six-fold assembly of the trimeric computational oligomer had the lowest potential energy per monomer and was consistent with rosette CSC morphology. Negative stain TEM showed that the cytosolic domain of AtCESA1 is triangular and of a size that fits well to modeling of recent SAXS data. Six trimeric SAXS models nearly filled the space below an average FF-TEM image of the rosette CSC, supporting a rosette CSC with 18 CESAs that mediates the synthesis of a fundamental microfibril composed of 18 or fewer glucan chains. Here we report progress on 3D reconstruction of the AtCESA1 catalytic domain from negative stain and cryoEM images of single particles, structural evidence
for non-redox mediated dimerization of NT-domains of AtCESAs 1 and 3, and GhCESA1, and TEM results showing that a single, heterologously expressed plant cellulose synthase isoform is sufficient for cellulose microfibril formation in vitro.

CELL 190

Cellulose structure and biosynthesis in oomycetes: Similitudes and differences with higher plants

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Cellulose biosynthesis is one of the most important biochemical processes in plant biology. It is also a vital process for other eukaryotic organisms, such as oomycetes, which comprise pathogenic species responsible for severe environmental damage and economic loss. As for the plant enzymes, the proteins associated to the oomycete carbohydrate synthase complexes and their mechanisms are not well characterized. The structure of cellulose in plant primary cell walls and oomycetes will be presented in this lecture. A comparative analysis of the specific structural features of the plant and oomycete cellulose synthases will follow and our latest results on the biochemical properties of cellulose synthases from poplar and the pathogenic oomycete Phytophthora capsici expressed in yeast will be summarized. The capacity of different recombinant plant and oomycete cellulose synthases to form microfibrils in vitro will also be discussed.

CELL 191

Protein structural controls of plant cellulose synthesis

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Cellulose microfibril formation by the plant cellulose synthesis complex (CSC) is a remarkable cellular manufacturing process with critical implications for the properties of many biomaterials and lignocellulosic biomass. Ultimately we would like to control this process within novel engineered plants to generate renewable products with improved properties targeted to particular uses. Achieving this goal requires a complete understanding of the structure/function relationships within cellulose synthase (CESA) and the multi-protein CSC. This presentation will discuss the work of a multi-disciplinary group of collaborators to elucidate: (a) the number of transmembrane helices in CESA, which affects the cellular locations of key functional domains; (b) the function of particular CESA transmembrane helices, with emphasis on glucan chain export; (c) the structure of the plasma membrane component of the CSC, which informs predictions of the number of glucan chains within a fundamental cellulose microfibril; and (d) similarities and differences in effects of analogous amino acid mutations on different CESA isoforms, with implications for designing strategies to modulate plant cellulose synthesis. These results reflect synergy between computational simulations and biochemical, genetic, and cell biological experiments with the model vascular plant, Arabidopsis thaliana, and the model moss, Physcomitrella patens. Both consistent and variable aspects of cellulose synthesis have been revealed through probing structure/function relationships within different CESA isoforms and the rosette-type CSC over a long evolutionary time scale. Some little-understood aspects of cellulose synthesis will be highlighted, e.g. the varying diameter of the CSC that is observed but not functionally understood.
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Structure of the catalytic domain of a plant CesA

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The catalytic domains of plant cellulose synthases (CesAs) are distinguished from their bacterial homologs by the insertion of a Plant-Conserved Region (P-CR) and the Class Specific Region (CSR). Recombinant catalytic domains of rice (Oryza sativa) CesA8 cellulose synthase form dimers reversibly as the fundamental scaffold units of architecture in the synthase complex. Solution X-ray scattering studies demonstrate that the monomer is a two-domain, elongated structure, with the smaller domain coupling two monomers into a dimer. The catalytic core of the monomer is accommodated only near its center, with the plant-specific sequences occupying the small domain and an extension distal to the catalytic domain. The crystallographic structure of a P-CR of rice cellulose synthase, OsCesA8, was solved to 2.4Å resolution. Two anti-parallel α-helices form a coiled-coil domain linked by a large connector loop containing a conserved trio of aromatic residues. The P-CR structure was fit into a solution envelope for the P-CR domain derived from small-angle X-ray scattering data, molecular docking experiments were used to build a detailed topological model of the CesA catalytic domain. The predicted position for the P-CR domain from the molecular docking models places the P-CR connecting loop into a hydrophobic pocket of the catalytic core, with the coiled coil aligned near the entrance of UDP-Glc into the active site. This models supports the prediction that the CSR participates in the dimerization observed in vitro. In this structural alignment the P-CR coiled coil is unlikely to exhibit dynamic conformational changes related to regulation of substrate access to the active site, but it could interact with other CesA catalytic domains or accessory proteins that function in substrate delivery. The arrangement of the catalytic domain within the CesA monomer and dimer provides a foundation for constructing structural models of the synthase complex and defining the relationship between the rosette structure and the cellulose microfibrils they synthesize.

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Solid-State and structural characterization of cellulose nanocrystals

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NMR and X-ray diffraction analyses suggest that cellulose nanocrystals consist of a broad distribution of environments having varying crystalline perfection and dynamics. The vast majority of any particular CNC particle is well structured to diffract X-rays, but because well-ordered material should exhibit the crystalline chemical shifts and be protected from ¹H/²H exchange, at most about 40 % of any acid-hydrolyzed CNCs can be thought of as highly or well-crystallized. The remainder shows varying degrees of disorder. Moreover, acid-hydrolyzed CNC consists not of sharply defined exchanged and unexchanged...
regions as might be expected for highly crystalline, high-surface area particles, rather they are more uniformly partially exchanged. Within the exchanged regions however, the three exchangeable sites appear to be unevenly exchanged, with $H_6$ exchanging more readily than $H_2$ or $H_3$. While the $C_4$ is assigned to less well-structured cellulose chains—expected in amorphous and surface regions, the fact that the $C_4$ peak is also significantly dephased in the REDOR experiments suggests significant exchange into more crystalline material as well. These results indicate that rather than well-defined crystalline and non-crystalline regions, CNC contains a more finely varied distribution of environments. In particular, the incomplete exchange at the amorphous $C_4$ site strongly suggests that acid-hydrolyzed CNC particles contain abundant disordered domains in their interiors, protected from exchange by enveloping crystalline regions. Recently, experimental evidence indicates the ability to effectively use Raman spectroscopy, along with optical techniques, to monitor defects in CNCs structure. This paper will aim to provide an in-depth, up-to-date expose of the scientific developments in characterizing the structure and solid-state properties of cellulose nanocrystals (CNCs), and propose mechanisms of interactions to help advance a more nuanced approach to surface functionalization of these nanoparticles.

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Comparing crystallinities of CNCs by Raman, NMR, and XRD

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Generally speaking, each cellulose crystallinity (CrI) estimation method has its advantages and limitations which in part depends upon sample characteristics (e.g., composition). In the present investigation, CrIs of $H_2SO_4$-hydrolysis produced CNCs from wood (W), bleached kraft-pulp (BKP), cotton microcrystalline cellulose (MCC), bacterial cellulose (BC), tunicate (T), and cladophora cellulose (CC) were investigated using 380-Raman, solid state NMR, and XRD methods. In the case of CNCs, because the samples consisted of mostly cellulose, the analysis from any of these methods was thought to be equally reliable. However, the CrI ranking orders generated by these methods were not equivalent. High to low CrI order by 380-Raman method was, BC = MCC > CC > T > W > BKP. In contrast, similar rankings of CrIs by NMR and XRD were, respectively, CC > T > BC > MCC > W > BKP and BC ≥ MCC ≥ T > CC ≥ W > BKP. This suggested that, at least for the high CrI CNCs, the crystallinity order depended on the method used to estimate the CrIs. Currently, the reasons for this are not clear. Nevertheless, irrespective of the method used, the lowest-but-one and lowest CrIs were obtained for W and BKP CNCs, respectively. To further investigate if presence of water in the CNCs had any impact, CrIs of wet CNCs were analyzed by Raman and NMR. In the wet state, the rankings were CC > BC ≥ T > MCC > W > BKP and CC > T > BC > MCC > W > BKP by 380-Raman and NMR, respectively. This indicated that while in the wet state NMR retained the dry-order, this was not the case in 380-Raman. Moreover, in both the methods, the absolute CrI values in wet and dry states differed. In addition to the CrI information on the CNCs, such information on the feedstocks from which the CNCs were produced will be discussed.

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Analysis of modified cellulose nanocrystals

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Cellulose nanocrystals are widely being investigated for use in a variety of materials and applications. In many of these applications is the surface chemistry and crystallinity of the nanocellulose core important for material properties. Accurate determination of crystallinity and surface chemistry is thus important for reproducible results. Over the past several years, we have fine-tuned several characterization techniques such as X-ray diffraction coupled with Rietveld refinement, elemental analysis and X-ray photoelectron spectroscopy to improve their precision, and to be able to crosscheck results from different techniques. The latter is especially important to get more confidence in the correctness of the obtained results.
In this presentation I will describe the methodology we employ and exemplify this methodology with several examples.

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Characterization of nanocelluloses using small-angle neutron, x-ray and dynamic light scattering techniques

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Nanocelluloses extracted from wood pulps using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation and sulfuric-acid hydrolysis methods were characterized by small-angle neutron scattering (SANS), small-angle X-ray scattering (SANS), and dynamic light scattering (DLS) methods. The dimensions of these nanocelluloses (TEMPO-oxidized cellulose nanofiber (TOCN) and sulfuric acid hydrolyzed cellulose nanocrystal (SACN)) revealed by the three scattering techniques were compared with those characterized with transmission electron microscopy (TEM). The SANS and SAXS profiles could be analyzed by a long ribbon model having rectangular cross-section. The width and thickness of the nanocellulose cross-section were $\sim 8$ nm and $\sim 2$ nm for TOCN, and $\sim 20$ nm and $\sim 3$ nm for SACN, respectively. The fitting results from SANS and SAXS profiles were consistent with each other. DLS was carried out under both regular mode having polarizer and analyzer parallel to each other (VV mode) and depolarized mode having them perpendicular to each other (HV mode). Using rotational and translational diffusion coefficients obtained under the HV mode yielded nanocellulose length qualitatively consistent with that observed by TEM, whereas the length derived by translational diffusion coefficient under the VV mode appeared to be overestimated. This discrepancy could be attributed to factors including polydispersity in size, concentration effect, and existence of aggregates. The lengths of TOCN were generally longer than those of SACN.

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Occupational health and safety characterization and assessment of CNC’s from North American producers

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Seven cellulose nanocrystalline (CNC) powder samples from North American facilities were fully characterized and tested for dustiness and the potential to release nanoparticles upon mixing. In water all of the CNC samples were readily re-dispersible and had similar nanoscale lengths and widths. With respect to the standard dustiness test, some of the CNC powders were highly dusty whereas others exhibited very low potential for dust formation. While the CNC powders were all composed of micron sized particles, closer examination did reveal the presence of nanoparticles in the size range of 500 nm, which appeared to be adsorbed or attached onto the larger particles. Free nanoparticles were not observed in any of the powder samples. Analysis of the air in an exposure chamber using an SMPS sampler, during controlled mixing of the powdered CNC, demonstrated the presence of numerous nanoparticles in two distinct fractions representing nanoparticles from 50-200 nm and 400-800 nm. Samples of the nanoparticles in the chamber were sampled onto grids using a thermophoretic sampler (TPS) and characterized by electron microscopy. For each powder, regardless of the drying technology employed, the nanoparticles captured all appeared similar and were greater than 500 nm in length. In contrast to the SMPS readings, no nanoparticles in the range of 50-200 nm were observed on these sampling grids. It is possible that these nanoparticle size fractions are short lived in the exposure.
chamber and quickly agglomerate onto the larger nanoparticles that are present. It is thought that the particles in the range of 400-800 nm were either being released from the larger particles, due to the energy imparted, or generated from the powders as a result of the increased mixing energy. Overall, the data indicates that during the manipulation of CNC powders, workers could be exposed to nanoparticles that are markedly larger and different from the form of CNC nanocrystals in aqueous solutions.

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European perspective on Environmental, Health and Safety (EHS) aspects on Cellulose Nanofibrils (CNF)

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Cellulose nanofibrils (CNF) are promising biomaterials originating from renewable resources and benefiting from sustainable processing technologies. Due to their unique nano-specific properties, CNF have numerous potential applications, e.g. as replacement of fossil-based materials in packaging and in creating totally new functionalities for diagnostics. However, the same properties may potentially make them hazardous towards humans and the environment. As CNF consist of long, biopersistent fibres of high aspect ratio, inhaled NFC may have similar properties as nano- and microscale mineral fibres which have known occupational hazards. Due to the rapid technology and product development, the environmental health and safety risk assessment of CNF and related legislation is lacking behind, and knowledge on the toxicity of nanoscale celluloses is still scarce. Results published to-date suggest that even though no acute threats with the manufacturing and use of CNF have been revealed, there is evidence of dose-dependent toxicity, genotoxic effects and inflammatory effects. A key question in the risk assessment of CNF is whether the inflammatory and genotoxic effects observed were transient or could persist for a longer time, contributing to cancer risk. The existing evidence on the biopersistence and low clearance of CNF rise concerns on their toxic hazards which need to be further assessed by longer-term studies. It is recommended that testing is performed case-by-case, because e.g. chemical modification and raw material have been shown to influence the toxicity of CNF. Currently, the existing chemicals legislation and regulations based on the intended use of the material seldom consider nanomaterials separately from the corresponding bulk materials. However, there are several European, national and international initiatives for developing and implementing nanomaterial-specific regulations to ensure their safe manufacturing and use.

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TEMPO-Oxidized Cellulose Nanofiber (TOCN) materials show good biomedical applications

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Cellulose is the most abundant renewable biomass in nature and has wide applications in biological fields. The bacterial cellulose (BC)-based materials have great success in tissue engineering because BC has network structures consisting of ribbon-like fibrils. However, mass-production of BC is facing many problems. Meanwhile, the nanofibrillation of plant cellulose makes employing them in tissue engineering possible. As chemical pretreatments of plant cellulose for disintegrating into nanofibers, the TEMPO-mediated oxidation has some particular advantages. After TEMPO-mediated oxidation and mild disintegration in water, plenty and uniformly distributed C6 carboxylates exposed on the microfibril surfaces and completely individualized cellulose nanofibers (TOCN) with 3-4 nm in width and few microns in length can be obtained. TOCN materials have high hydrophilicity, transparency, surface modifiability, and good mechanical properties, which makes them have huge potential in biological applications.
However, we can hardly find any report of the applicability of TOCN materials to this field. In our experiment, biocompatibility of TOCN water dispersions and hydrogels were evaluated from the perspective of cytotoxicity using cell counting kit-8. Cell viability during the adhesion step and proliferation step of one normal cell line (HUVEC) and two tumor cell lines (HepG2, HOS) incubated on TOCN hydrogel surfaces or in culture medium containing TOCNs were investigated, respectively. As the results, apparent improvement of cell viability was observed in both cell adhesion and proliferation steps of the cells incubated in TOCN-containing culture mediums. However, no obvious distinction of cell density was found between experimental and control groups, which means the cell viability promotion does not come from the cell number difference. Some cell experiments will be reported for explaining the possible mechanism of the positive biological phenomenon. In the case of TOCN hydrogels, cell viability was suppressed on hydrogel surfaces, which may come from the proton acid that was introduced on nanofiber surfaces during the gelation step with hydrochloric acid.

CELL 200

Different size-unified cellulose nanocrystals obtained via a multistage separation

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Cellulose nanocrystals (CNCs) have a wide particle size distribution (9-1700 nm) when isolated by means of acid hydrolysis. This study reports on a facile and new approach to fractionate unseparated CNCs based on their particle size distribution into a series of narrower size ranges to obtain size-unified CNCs via a well-designed multistage separation process composed of layered filter membranes with different pore size cutoffs followed by a fast pressurized filtration. Fourier-transform infrared spectroscopy, thermogravimetric analysis, and X-ray diffraction results revealed that different size-unified CNCs exhibited particular thermal stabilities and crystallinities even though their chemical and crystalline structures remained unchanged. CNCs are perfect rod-like nanofibers that can self-assemble and form a chiral nematic phase. Different self-assembling morphologies of CNCs could be formed by different size-unified CNCs. The smaller size-unified CNCs readily self-assembled into polish chiral nematic phases with larger pitch value as compared to larger size-unified CNCs. Such a distinction amongst different chiral nematic phases and pitch values as functions of size is addressed by a mathematical equation, which suggested that the reduced volume fraction of the anisotropic phase as function of both increased ionic strength and reduced crystallinity of rigid rod-like CNCs are critical factors. The discrepancies in physicochemical characteristics and self-assembly chiral nematic behavior among different size-unified CNCs may explored for specific functionalization of cellulose materials using size-unified fibers instead of raw CNCs containing mixed small and large nanocrystals.
Nanocellulose- Silver hybrid structuration for stable suspension and transparent conductive material design

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Nanocellulose has gained increased attention during the last decades. Two kinds currently exist: the cellulose nanocrystals (CNC) and the cellulose nanofibrils (CNF). Nanocellulose is an interesting renewable, biodegradable, and biobased material for many applications in such fields as: composites, papermaking, food, or more recently for electronic purpose. This studies aims at developing new conductive inks based on nanocellulose and silver nanowires for transparent and conductive applications. This study has evaluated on one hand the ability of using tubular rigid CNC as template for producing...
silver nanorods, prior their formulation into conductive inks. On the other hand, the ability of using flexible and entangled CNF to stabilize commercial silver nanowires, usually unstable in suspension, was investigated. The results of this project lead to the patented formulation and commercialization of one low silver content conductive ink based on silver and CNC and two conductive transparent ink based on CNF and silver nanowires. Physico-chemical interactions and colloidal stability of such hybrid suspension have been scientifically studied meanwhile printing process adapted formulation have been successfully designed and tested at laboratory scale but also industrial scale.

CELL 202

Control of the surface properties of cellulose nanocrystals by acylation with functional vinyl esters: Application to the design of innovative fillers or Pickering surfactants

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Cellulose nanocrystals (CNCs) are nanometer-sized rod-like particles, which are increasingly considered as nanoscale building blocks for the elaboration of functional materials with applications in areas as diverse as biotechnology, electronics, optics, energy, packaging or catalysis. The potential benefits of these nanoparticles rely in particular on their high strength, low abrasiveness, high aspect ratio, biocompatibility and inclination for chiral nematic ordering. The application field is a priori vast, but the engineering of innovative functional materials from CNCs requires a fine control of their self-assembling properties and interaction with surrounding materials or in-use environment. This control is generally achieved by chemical functionalization of the CNCs surface, in particular using reactions based on alcohol chemistry. In this context, we report a versatile method for the surface tailoring of CNCs building blocks by acylation with functional vinyl esters. CNCs decorated with different chemical functionalities were accordingly prepared by reacting the nanoparticles with a selection of vinyl esters bearing various functionalities. Reactions were performed in various solvents (DMF, DMSO or water) and monitored by FT-IR and 13C CP-MAS NMR spectroscopy. The impact of the treatment on the supramolecular structure of the CNCs was controlled by atomic force microscopy (AFM) and X-ray diffraction (XRD). The potential of acylated CNCs as nano-filler in PDMS matrices or Pickering surfactant was later investigated. For some of the surface treatments, the incorporation of low amounts of CNCs in PDMS aerospace coatings was found to improve significantly the thermal and photo-stability of the composites. The tuning of the hydrophilic/hydrophobic balance at the CNCs surface by the acylation method also allowed preparing stabilized monomer-in-water Pickering emulsions, which could be subsequently polymerized to form micro and nano polymer beads with low dispersity.

CELL 203

Click-Thiols as an approach to implement novel functionalities within bio-derived scaffolds

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As a result of dwelling fossil resources and pressing environmental issues, the utilization of sustainable materials gains more impact nowadays. Among various natural resources, lignocellulosic materials will certainly contribute to the future challenges in the building sector and in the design of advanced materials as a sustainable alternative to petroleum-based materials. The benefits of this green material are numerous: besides an attractive appearance, light weight, low cost and excellent mechanical properties make it a very attractive material. However, working with wood also bears some drawbacks. Mostly when it is used as an engineering material: due to its hygroscopic and anisotropic behaviour. In order to improve the intrinsic properties, chemical modification can be used. In this study, we report on a novel modification, using a fully green approach, with the goal to obtain a clear hydrophobization. The aim is to
avoid or to retard water penetration, by the development of a superhydrophobic surface. Thiol-ene click chemistry is a well-established method, and the individual components of the wood cell walls can be functionalized with the technique. However, this method was never applied on lignocellulosic materials, and because of its versatility, it may open new modification pathways. Additionally, the chemistry can be done in mild conditions, and in the case of hydrophobic compounds, it can be catalysed by a natural molecule, cyclodextrin. Therefore, keeping in mind the templates’ natural origin, and in order to propose a fully green product – both in terms of resources used, and processing conditions – we have developed a straightforward protocol in environmentally friendly conditions. Using EDX mapping, AFM and FTIR, we have been able to show that pre-modified surfaces can be grafted by our simple click thiol approach. According to the thiol used large contact angles were reached. In a clear analogy to natural surfaces such as the lotus leaf, the superhydrophobic character of the new surfaces is the result of the low surface energy grafted thiols, and the surface roughness generated during our modification. By combining a natural material with a bio-inspired concept, we aimed to extend the service time of the material by creating a smarter material, which synthesis is a very green and yet versatile process. Given the availability of more complex alkene containing structures, there is a large potential for further modification by click-thiols.

CELL 204

Cellulose nanocrystals and surfactants as mini emulsion polymerization stabilizers

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Cellulose nanocrystals (CNCs) are nanoscale, crystalline, rod-shaped particles derived from wood pulp, plants, and other renewable sources. The inherent orientation of cellulose chains in each individual CNC results in an amphiphilic nanoparticle with a hydrophobic edge, a property that allows for CNCs to effectively stabilize emulsions and foams. In this work, we studied the interactions between CNCs and surfactants and their use as stabilizers for mini emulsion polymerization. Anionic CNCs in their acid form, or neutralized to have sodium counterions, and cationic trimethylammonium-modified CNCs were investigated with anionic sodium dodecyl sulfate and cationic cetyl trimethylammonium chloride surfactants. We observed an increase in CNC size and a decrease in absolute surface potential when oppositely charged CNCs and surfactants were mixed, implying electrostatic binding. Colloid probe atomic force microscopy also indicated that the adsorption and structuring of surfactants at CNC interfaces is strongly dependent on the surface charge and counterion. Mini emulsion polymerization reactions were performed in the presence of CNCs and surfactants, with and without hydrophobe, to understand the role of CNCs at the interface during polymerization. Poly(methyl methacrylate) (PMMA) latexes were produced giving PMMA nanoparticles when there was no interaction between the CNCs and the surfactant, and PMMA microparticles when the CNCs and surfactant acted as co-stabilizers (as measured by dynamic light scattering and MasterSizer, respectively). The size and morphology of the latex particles were further confirmed by scanning electron microscopy. Surface potential measurements showed that the charge of the PMMA particle was governed by the location of the CNCs. The glass transition temperature of PMMA remained constant among samples, suggesting that the polymer is not tethered to the CNCs. This work provides new insight into the use of CNCs in surfactant-based systems, such as in mini emulsion polymerization, and may extend CNC applications to new areas including adhesives, coatings, and cosmetics.

CELL 205

Fundamental differences due to deposition method in ultrathin films of cellulose nanofibres

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This work presents the electrophoretic (EPD) of TEMPO-oxidised nano-fibrillated cellulose (TEMPO-NFC) coatings. Mechanism of anodic deposition of TEMPO-NFCs was analysed based on the results of atomic force microscopy (AFM), ellipsometry and quartz crystal microbalance (QCM). The ability of the EPD technique to deposit films from relative dilute solutions (0.01%) was demonstrated. Additionally, the structures produced by EPD were compared to those produced by dip and spinning coating methods to determine differences in nanotopographic surface roughness and hydrophilicity. Overall, NFC-TEMPO coatings produced using the EPD method offer a potential starting point for the next generation of biobased coatings.

Figure 1. Surface topography of deposited CNF-TEMPO films as measured by AFM

CELL 206

Tailor-made 3D printed scaffolds from cellulose nanofibrils for guided growth and development of a neural tissue

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Today millions of people around the world suffer from neurodegenerative disorders which mostly refer to Alzheimer’s disease (AD), Parkinson’s disease and spinal cord injuries. It is estimated that over 35 million people in the world suffer from AD only, while the global costs of care reach nearly $805 billion in 2015. In order to solve this expanding public health problem, scientists continue to develop neural tissue engineering (TE) methods that allow regeneration of individual patient’s tissues with the help of supportive scaffolds. Previous studies showed that biocompatible cellulose-based materials are low-cost sustainable candidates for TE scaffolds. The aim of the present work is to 3D print tailor-made conductive
scaffolds for neural TE using cellulose nanofibril (CNF)-based inks, and to evaluate these scaffolds in terms of their ability to guide proliferation, growth and differentiation of neural cells into desired directions. 3D configuration is achieved through the excellent shear thinning properties of the CNF ink, while scaffold’s electrical conductivity is the result of the carbon nanotubes addition. Conductivity enhances transmission of interneuronal signals, which is essential for a mature neural tissue. The results of cell culturing showed that 3D printed conductive patterns provide clear guidelines for good cell attachment, growth and networking already within few days after cell seeding, and within two weeks first signs of neural differentiation are observed.


CELL 207

3D-printing of cellulosic materials – properties and suitability on cellulosic fabrics

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Utilizing cellulosic materials for textile modification and functionalization was based on the theory of combining materials with structural similarities in order to facilitate adhesion without external glues, confirming the material suitability for skin contact and simplify recyclability. Material application by 3D-printing enables e.g. affordable modifying, mass customization and material processing without the generation of waste. In this work, different cellulosic materials such as dissolved cellulose acetate (CA), hydroxypropylated cellulose acetate (HPCA) and cellulose linters dissolved in 1-ethyl-3-methylimidazolium acetate ionic liquid were tested for 3D-printing using direct ink writing –method. CA and HPCA were also mixed with pulp fibres to adjust material properties. Here, the suitability of the cellulosic materials for 3D-printing in textile applications was evaluated and material interactions were further studied. The applicability for the textiles products was examined by studying adhesion using mechanical peeling tests and material washability after printing. Material interactions were further
elucidated using QCM-D and SEM. In addition, successful textile modifications were demonstrated by introducing visual effects or functionalities on existing textile fabrics.

CELL 208

Cellulose macro-sheets with PTFE nanocoating and cellulose nano-sheets

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Cellulose macro-sheets with polytetrafluoroethylene (PTFE) nanocoating could be prepared by solventless mechanical ball milling in the PTFE vessel and it was found that the friction transfer of PTFE molecules from vessel wall to the cellulose particle surface occurs during the milling. Nanoscale cellulose sheets (nanosheets) could also be formed by ball milling plus the sonication in ethanol, with typical size of 0.1-10 µm in width and 4.2 nm in thickness. It was found that the cellulose macro- or nano-sheets can be formed only by milling with hydrophobic substances. The PTFE-coated cellulose macro-sheets are highly hydrophobic, incompletely repelled from water, with water contact angle of 110~121°. There is a nearly continuous coverage of PTFE layer with 10 nm in thickness on cellulose sheet surface. The PTFE-coated cellulose sheet show potentially applications such as hydrophobic material, lubricant, painting, cosmetics, composite element, etc.

Chemistry & Physical Chemistry of Thermal Processes for the Circular Carbon Economy
H. Mayes, Organizer; C. J. Pope, Organizer; H. Mayes, Presiding; C. J. Pope, Presiding Papers 209-216

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Hydrothermal carbonization and the circular economy

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Hydrothermal liquefaction has promise as a chemical-free means of converting biomass feedstocks into simple sugars for fermentation; hydrothermal carbonization occurs in parallel with liquefaction to produce a carbonaceous solid. Depending on the feedstock and reactor conditions, the hydrothermal char byproduct can represent as much as about 25% of the mass of the original feed and an even greater fraction of the original carbon and energy content. For a circular economy based on renewable biomass, the hydrothermal char must be valorized. Fortunately, many promising applications have been developed for hydrothermal char in the past several years, including as a catalyst or catalyst support, adsorbent, gas storage material, and soil amendment. A major gap in current understanding of hydrothermal char is how to connect feedstock properties to optimized carbonization conditions and hence to performance in targeted applications. Moreover, simultaneously optimizing hydrothermal char properties and carbohydrate recovery through feedstock selection and reactor design is not yet fully understood. In this talk, we will describe recent work performed in our group and with collaborators at Brazil’s UNICAMP to study the influence of feed material and hydrothermal liquefaction processing conditions on the chemical composition of the resulting hydrothermal char. For feedstocks, we have examined sugarcane bagasse, sugarcane straw, and two different coffee factory wastes. For reactor conditions, we have examined a range of temperatures and flow regimes; in particular, we have studied hydrothermal char composition resulting from batch processing (which is the most commonly studied technique), packed bed flow conditions (which has promise for maximizing sugars yield), and two-stage flow conditions. We have used Raman microscopy, infrared spectroscopy, and thermal analysis to study the composition of the
carbonized materials produced under different reactor conditions, identifying carbonization, formation of acids, extraction of lipids, and hydrolysis of hemicellulose and amorphous cellulose. Data will be presented on the use of the hydrothermal chars for heavy metal cation adsorption, a promising application for hydrothermal char especially given its high capacity and the need for new drinking water purification technologies.

CELL 210

Utilisation of microwave irradiation in the catalytic upgrade of cellulose and hemicellulose derivatives: Hydrolysis and hydrogenation reactions

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The selective hydrolysis of lignocellulosic biomass constituents still represents one major challenge for the sustainable exploitation of biomass feedstocks towards chemicals and fuels. Despite advances in biotechnology and biocatalytic methods, there is an inherent attractiveness about utilising thermochemical methods for biomass upgrade. However, these processes are typically slow and offer little selectivity. The utilisation of microwave reactors for biomass hydrolysis and pyrolysis is now known among the field, and there is some agreement that it offers substantial advantages in terms of efficiency. However, there is very little being done on combining mirowaves with catalysis in biomass upgrade. Furthermore, the hardest challenge of obtaining high selectivity towards sugars in hydrolytic processes and their direct upgrade towards high-value molecules is still receiving little attention and we believe that it requires innovative approaches. In this presentation, we will present how the combined effect of catalysis and flow microwave reactors can result in highly selective reactions and yields in the selective hydrolysis of biomass, to the extent that it is comparable to biocatalysis and fermentation methods. Additionally, high-pressure microwave reactors produce several times faster hydrogenation reactions (i.e. furfural, glucose, starch) in the upgrade of biomass-derived sugars as compared to conventional heating and they represent a very exciting technology for the development of the bioeconomy and new one-pot processes today.

CELL 211

Biomass vapor upgrading to produce hydrocarbon fuels

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The production of renewable transportation fuels from biomass has received increasing interest from governments, industry and the scientific community because of the potential for decreased carbon emissions compared to fossil fuels, the development of local agricultural economies and better control of national energy security. Fast pyrolysis is an attractive technology for converting biomass to hydrocarbon fuels because it can produce up to 75 wt% carbonaceous oil, called bio-oil, which with upgrading can be used as a fuel blending material or a feedstock for further processing. Bio-oil that has not been upgraded has limited applications because of the presence of oxygen-containing functional groups (organic acids, aldehydes, ketones, phenolics) derived from cellulose, hemicellulose and lignin, which give rise to high acidity, high viscosity, low heating value, immiscibility with hydrocarbons and aging during storage. The quality of bio-oil can be improved by removing oxygen from the bio-oil. This can be achieved through catalytic fast pyrolysis (CFP) of biomass, a process where the biomass pyrolysis vapors are passed over catalysts at elevated temperature and near-ambient pressure before condensation. Microporous materials, HZSM-5 in particular are used for upgrading biomass pyrolysis vapors to produce
hydrocarbons. However, the yields of hydrocarbons are low due to high CO and CO₂ gas production and coke deposits on the catalyst, which results in rapid catalyst deactivation. The goal is to increase bio-oil yield by decreasing coke and light gas formation, while maintaining low oxygen content. In this study we will report results from studies conducted with transition metal catalysts and compare them those from HZSM-5. The effect of catalyst on product yields, product composition, deactivation and reactivation will be discussed.

**CELL 212**

**Oceans of plastic converted to liquid fuels via small scale thermal depolymerization reactors**

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An estimated 10 to 28 billion pounds of plastic waste has entered the oceans annually since 2010, beyond the 500 million pounds already floating there, causing irreparable damage to the marine life and environment. Both remediation and prevention of further migration of plastic into the oceans are imperative. Clean Oceans International (COI) offers an innovative and sustainable long-term global solution to plastic pollution on land and sea. That plastic stream can be diverted from the ocean and converted to 20-50 million barrels of liquid fuels annually by Plastic to Fuel (PTF) reactors developed by Eco-Fuel Technologies (EFT) and in concert with Clean Oceans International. Each of these small-to-medium-scale reactors can convert 100-10,000 pounds of plastic per day via catalytic thermal depolymerization technology. EFT's reactor size allows its placement aboard vessels on or near ships actively engaged in floating plastic retrieval, solving key logistical problems in remediation. Storage and transport of plastic waste to land-based sites is no longer needed, saving money and reducing environmental impact. Best of all, plastic wastes are converted to liquid fuels to be directly used by these vessels. Mobile land-based PTF reactors are optimal for converting plastic waste at remote sites, such as plastic sheeting used in agriculture, from which transport to a central location is unfeasible. The PTF reactor design must be sufficiently robust to process floating plastic wastes of varying shapes, sizes, concentrations, and chemical composition. The resulting feedstock is a salt-water soaked mix of several plastics, including polyester, polyethylene, nylon, and others. COI's vision of global plastic remediation and energy production provides a world of environmental and economic benefits.

**CELL 213**

**Data science tools for biomass pyrolysis – application to thermochemical conversion of lignin**

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Lignin has great potential use as a feedstock for thermochemical processes to produce biofuels or other aromatic chemicals. It is a highly cross-linked amorphous polymer accounting for up to 40 wt% of dry biomass, which significantly complicates the understanding of molecular or mechanistic scale chemical reaction networks governing conversion. Empirical and global models of lignin pyrolysis using overall apparent kinetics derived from TGA studies are well established and often adequately predict yields of lumped products within a small range of experimental conditions. The main limitations of these models are their inability to predict the composition and distribution of product tars and gases, or to cover a wide range of heating rates and temperatures with one set of kinetic parameters. A fully mechanistic model of lignin pyrolysis would be of great interest for these reasons, but developing such a model has proved challenging due to the random structure of lignin polymers and complex kinetics involved. As a step toward a more mechanistic model, we explore the use of a semi-detailed kinetic model for lignin pyrolysis to predict the compositions of gases and tar components from the fast pyrolysis of lignin over a wide range of conditions. The model combines elementary and lumped reaction steps to track approximately
100 real molecules, radicals, lumped heavy species, and functional groups linked to the degrading polymer. The sensitivity of permanent gases and tar precursor molecules to experimental conditions is examined, and using this model we are able to explore new mechanistic details about the evolution of functional groups. In the first part of the talk we will present the model as well as a tool for looking a high dimensional sensitivity analysis of kinetic modeling data. The second part of the talk will present efforts to address a standing challenge in using mechanistic modeling schemes within more complicated numerical optimizations (e.g., spatiotemporal reactor models like fluidized beds or global optimization schemes that are limited on the solution time of the kinetic model). We introduce a scheme using neural networks to enable fast solution of the kinetic model on timescales up to 4 orders of magnitude faster than a stiff ODE solver. Implementation of the model for lignin pyrolysis and results will be discussed.

**CELL 214**

Mechanistic modeling of fast pyrolysis of hemicellulose extracted from cornstover

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Hemicellulose is one of the major components of lignocellulosic biomass and has potential for the production of renewable drop-in transportation fuels and multiple commodity chemicals.[1] Previously, however, the successful modeling of fast pyrolysis of hemicellulose was hampered by lumped kinetic models, which failed to describe the heterogeneous structure of hemicellulose and cannot predict the bio-oil composition. In this work, a structural model for hemicellulose extracted from corn stover that captured the experimentally measured properties was proposed, and a mechanistic model for hemicellulose pyrolysis was constructed based on the reaction family approach that we used for cellulose pyrolysis.[2] The model described the decomposition of hemicellulose chains, reactions of intermediates, and formation of a range of low molecular weight compounds at the mechanistic level. Rate constants were specified for each elementary reaction with Arrhenius format. Overall, more than 500 reactions of 144 species were included in the mechanistic model for fast pyrolysis of hemicellulose. The mechanistic model was able to closely match experimental yields of all the major products (with yield ≥ 1 wt%) from hemicellulose pyrolysis at 500 °C reported by Shanks and coworkers[3] at Iowa State University. The model predicted about 4 s residence time for complete thermo-conversion of hemicellulose. Model results showed that both degree of polymerization (DP) and polydispersity index (PDI) of hemicellulose had an insignificant effect on the pyrolysis products distribution. The mechanistic model of extracted hemicellulose is extendable to fast pyrolysis of native hemicellulose, which will be also discussed in this work.

**CELL 215**

On the importance of inorganics composition on biomass gasification

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Important efforts have been carried out by the authors to connect the forestry and agricultural biomasses chemical (organic and inorganic) composition and their behavior during different thermochemical processes. This work focus on the effects of inorganics composition on the gasification kinetics. Due to the limited availability of biomass, gasifiers will have to cope with various feedstocks, of different species, coming from different places and hence of variable nature. Isothermal experiments were carried out in a thermobalance in chemical regime of very different biomass (wooden, agricultural, short rotation
forestry and algae) chars produced under the same conditions. The reactivity obtained varied of a factor of more than thirty (Fig.1). This large difference appeared to be correlated with the biomass inorganic elements. Three different types of rate evolution versus conversion could be observed depending on the ratio K/(Si +P) : (1) When biomasses are rich in potassium in comparison with silicon and phosphorus, a law of zeroth order enables to give a satisfactory approximation of time conversion, with a kinetic parameter correlated with potassium content. (2) When biomasses are very rich in silicon or phosphorus in comparison with potassium, they seem to follow the same kinetics, which is correctly described by a first order law. (3) Lastly, when the content of potassium is close to those of silicon and phosphorus, the situation seems intermediate, and time conversion appears to be satisfactorily estimated both by a zeroth order law and a first order law. (4) Conversion could be satisfactorily predicted versus time through simple models taking into account the influence of inorganic elements and thus further useable in simulation of industrial gasifiers fed by various biomass types.

CELL 216

Computational studies of lignin chemistry and structure

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Lignin is a heterogeneous aromatic polymer found in abundance in plant cell walls, where it imparts structure, provides defense against pathogens, and facilitates water and nutrient transport. Lignin conversion to value-added fuels and chemicals is an oft cited objective of biorefineries, but it remains challenging due to the inherent recalcitrance and heterogeneity of lignin. Computational studies of lignin are an important component of understanding its reactivity and structure, and have provided valuable insights into experimental lignin valorization efforts. This talk will describe our ongoing computational studies in lignin reactivity including (1) understanding inherent bond strengths in diverse lignin structures including in traditional lignin dimers, hydroxycinnamic acids, flavonoid-lignin complexes, and the recently
discovered C-lignin based on caffeoyl alcohol units, (2) the reactivity of lignin in various catalytic environments of relevance to biorefineries, and (3) the development of a robust, general lignin force field for molecular mechanics studies.

MONDAY AFTERNOON

Design & Control in Polysaccharide Chemistry: Anselme Payen Award Symposium in honor of Kevin J. Edgar
P. E. Fardim, Organizer; O. J. Rojas, Organizer; C. M. Buchanan, Organizer; P. E. Fardim, Presiding Papers 217-222

CELL 217

Chemistry with activated polysaccharide derivatives – an efficient and simple path to novel structures

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Usually polysaccharide chemistry is focused on the hydroxyl groups applying esterification and etherification. While the commercial heterogeneous chemistry is limited due to the low reactivity of polysaccharides and reaction media applied, homogeneous chemistry is difficult to carry out and special solvents and even dissolution procedures must be applied, which is in particular true for cellulose. To make polysaccharide chemistry more attractive for organic chemists and to design novel structural- and functional materials, reactions with activated and organo-soluble polysaccharide derivatives are interesting alternative paths. Besides cellulose tosylates (1), polysaccharide phenylcarbonates (PPCs) with different substituents in the aromatic ring have proved to be a versatile class of starting materials to get novel products with amazing structures easily. The preparation of PPCs of cellulose, dextrans, and hemicelluloses applying different reaction media will be discussed. It was found that the degree of substitution (DS) can easily controlled and even a complete or regioselective functionalization is possible. The PPCs dissolves in common organic solvents and can be efficiently transferred with a broad variety of amines, amino alcohols, amino acids and various other nucleophiles yielding products with interesting properties including novel zwitterionic polymers, self-healing polymers, and polymer for biofunctionalization, e.g.

CELL 218

Using mixtures of ionic liquids and molecular solvents in cellulose chemistry

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The use of ionic liquids (ILs) as cellulose solvents is advantageous because their structure can be “fine-tuned” for a certain end-use of the resulting solution, e.g., fiber regeneration, biopolymer shaping and derivatization under homogeneous conditions. The viscosity of some ILs is high; cellulose dissolution increases this viscosity and eventually leads to formation of anisotropic solutions gel. The use of mixtures IL-MS (molecular solvent) decreases the viscosity and reduces solvent cost. The physico-chemical properties of IL-MS mixtures and cellulose solutions therein are, however, not ideal (i.e., not linear in solvent composition) because of the mutual interactions of solvent components, and of these with
dissolved cellulose. Therefore, choosing the best MS and the optimum IL-MS composition requires probing solvent-solvent and solvent-biopolymer interactions. We address these interactions by studying the rheology (macroscopic property) and solution empirical polarity, basicity, and acidity (microscopic properties, determined by perichromic probes) of mixtures of 1-methyl-3-allylimidazolium chloride and acetate with acetonitrile, N,N-dimethylacetamide, dimethylsulfoxide, and sulfolane. Additionally, kinetic data on acylation of cellulose in these IL-MSs show how the reaction rates and activation parameters depend on the nature of the MS. We corroborate our conclusions with results of molecular dynamics calculations.

**CELL 219**

**LB film preparation of regioselectively substituted cellulose cinnamates on nematic ordered cellulose templates**

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Monolayers of regioselectively substituted cellulose cinnamates having photo-sensitivity were prepared on the water surface. Then, they were deposited onto nematic ordered cellulose (NOC) templates having unique surface properties to successfully induce establishment of ordered three-dimensional, hierarchical structures of bacterial cellulose nanofibers secreted from _Gluconacetobacter xylinus_, epidermal cells as well as a biomineral of calcium phosphates by the attachments and subsequent culture for their growth. In this article, the regioselectively substituted cellulose cinnamates as a molecule was employed to compress the monolayer on water surfaces, before it was deposited onto NOC in comparison of glass slide surfaces. The result at first indicated that the structure of each solid monolayer was different depending on regioselectivity of the substituent. In particular, the 2,3-O-substituted derivative was found to form a homogeneous monolayer. In addition, the molecular orientation on the surface was induced by NOC templates, similarly to the previous cases above. This paper also refers to a UV-irradiation effect to the oriented structure.

**CELL 220**

**Take advantage of what Nature creates and utilize biomass**

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Natural polymers and monomers are used today to create environmentally friendly materials for a sustainable society. We have shown that it is possible to modify hemicellulose and transform it to hemigels that are elastic, homogenous, soft, transparent and easily swollen in water (1). The same biomass could be modified also to give good oxygen barrier materials (2). By using crude biomass with both hemicellulose and lignin, some of the properties created by nature are preserved, and environmentally friendly materials with improved properties are generated (3,4). A wide range of pathways have been used to vary and control properties and functions. However, if we want a total control and high reproducibility it is necessary to start from monomers. One main possibility is to synthesize aliphatic polyesters from monomers available in nature (5).
Enzymatic control of the acetylation pattern in chitosans

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Chitosans, partially N-acetylated polyglucosamines, are perhaps the most promising and most versatile functional biopolymers. Chitosans are a family of biomolecules differing in their degree of polymerisation (DP), degree of acetylation (DA), and pattern of acetylation (PA), and these factors have been shown (DP, DA) or are likely (PA) to influence their material properties and biological functionalities. Commercially available chitosans are derived by chemical processes from chitin typically sourced from crab or shrimp shell wastes. While DP and DA can be controlled rather well in these processes, the chitosans obtained invariably have random PA. In contrast, natural chitosans which are known to occur in some fungal cell walls are thought to be synthesised from chitin by the action of chitin deacetylases. Such natural chitosans have not been analysed in detail, and the fungal chitin deacetylases have proven difficult to obtain as recombinant enzymes. Recently, we have been successful in heterologously expressing a few fungal chitin deacetylase genes in different prokaryotic and eukaryotic expression systems, yielding active recombinant enzymes for detailed characterisation of their substrate specificities and of their products. Interestingly, we found that of the three chitin deacetylases analysed in detail so far differed in both aspects, yielding oligomeric and polymeric chitosans as products which differ in their pattern of acetylation. When fully acetylated chitin oligomers are used as substrates, the enzymes yield partially acetylated chitosan oligomers with different, defined sequences of acetylated and deacetylated residues, as revealed by mass spectrometric sequencing. Fully acetylated chitin polymers were poor substrates for the enzymes, but partially acetylated chitosan polymers with high DA (and random PA) were good substrates for all three chitin deacetylases which, however, were not able to fully deacetylate them. When we analysed the PA of the resulting chitosan polymers with low DA using enzymatic / mass spectrometric fingerprinting, they turned out to differ in their PA. While one of the enzymes yields a...

Studying the reactivity of cellulose by oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation

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Accessibility and reactivity of cellulose to solvents and reagents are key factors on the production of cellulose derivatives. Different parameters such as, crystallinity, microfibril aggregation, size of pores, and solubility of cellulose influence on their reactivity. Several indirect methods, such as fiber saturation point (FSP), water retention value (WRV) and surface area have been developed to characterize the reactivity of cellulosic samples. Here we report on using oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium (4-AcNH-TEMPO*) cation as a probe reaction to quantify the accessible methylhydroxyl group of cellulose. In fact, 4-AcNH-TEMPO* easily oxidized hydroxymethyl groups of cellulose into carboxylate groups. An iodometric titration method was introduced to calculate the concentration of the oxoammonium component during oxidation reaction. Finally the 4-AcNH-TEMPO* reactivity was correlated with several pulp characteristics, including WRV, FSP, surface area, chemical composition, crystallinity.
Orientation and interfacial stress transfer of cellulose nanocrystal nanocomposite fibers

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Orientation and interfacial stress transfer in cellulose nanocrytals (CNC) reinforced polyacrylonitrile (PAN) nanocomposite fibers were obtained by Raman spectroscopy. The 1095 cm\textsuperscript{-1} Raman band was used to quantify the orientation of CNC in composite fiber. Under VV (vertical/vertical) mode, polar plots of all composite fibers showed a two-fold symmetry. Under VH (vertical/horizontal) mode, it showed a four-fold symmetry. These suggest that CNCs are highly oriented in the composite fiber, which is confirmed by second and fourth order orientation parameters. The 1095 cm\textsuperscript{-1} Raman band shift under uniaxial deformation was used to characterize the interfacial stress transfer between PAN matrix and CNCs. All composite fibers showed a clear 1095 cm\textsuperscript{-1} Raman band shift. Fibers with 29x draw ratio exhibited a higher shift rate of 1095 cm\textsuperscript{-1} Raman band than the 4x draw ratio fibers. The interfacial shear strength ($\tau_i$) of the PAN-CNC interface was determined to be $\sim$ 20 MPa.
Understanding nanoconfinement and nanoscale interfaces in nanocellulose composites

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Nanocellulose based composites offer microphases that are confined in nanoscale dimensions to achieve potentially remarkable mechanical properties. However, the emergent performance of these materials depends strongly on both the chemistry of the interfaces and the microstructure of the material system, which complicates their design. In this talk, I will present a new computational materials-by-design paradigm based on molecular simulations for understanding phenomena occurring at such disparate scales in nanocellulose based materials. I will discuss several cases where the coupling between microstructure and chemical structure will lead to intriguing phenomena at polymer-cellulose interfaces. Drawing an analogy between thin films and nanocomposites, I will illustrate how understanding thin film simulations help us design better load-bearing nanocomposites cellulose nanocrystal fillers.

Enhancing supramolecular interactions in aromatic polymer/cellulose nanocrystals nanocomposites

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Cellulose nanocrystals (CNC) are classically use in nanocomposite. This study is inspired from wood structure and supramolecular interactions. CNC were grafted with an aromatic amine (4-phenylbutylamine) thanks to a new green grafting process. This grafting process was a success as ATR-FTIR and C13-NMR confirmed it. Composites of styrene butadiene rubber (SBR) with 10wt% of functionalized and unfunctionalized CNC, with and without hexafluorobenzene (HFB) were prepared through solvent casting and thermopressing. The aim of this project was to investigate the role of grafted CNC and hexafluorobenzene in the composite and the impact of supramolecular interaction in composite properties. SBR composites containing aromatic grafted CNC and HFB had shown promising results regarding the mechanical properties improvement: an increase of 230% and 360% in Young’s modulus and storage modulus at 25°C, respectively. This strong mechanical improvement is due to π-π interactions between the aromatic rings of the polymeric chains, the phenyl rings grafted on CNC and the hexafluorobenzene.

Excellent dispersion and property enhancements in polymer composites made with biobased filler from cellulose nanocrystals and waste paper to lignin and agro-waste to rice husk ash and eggshell

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Solid-state shear pulverization (SSSP) is a continuous process that consists of a modified twin-screw melt extruder which achieves excellent dispersion in polymer of fillers and nanofillers that cannot be well dispersed in polymer by conventional melt processing. By operating at relatively low temperature in the solid state, SSSP avoids problems associated with poor thermal stability of some biobased fillers and the inability to do sufficient work (via shear stresses, compressive forces, etc.) to deagglomerate and
disperse nanofiller using melt processing. Here, we will overview several years of studies in which a variety of problematic biobased fillers and nanofillers were well-dispersed in polyolefins (e.g., polypropylene (PP) and polyethylene), sometimes leading to the largest property enhancements for such polymer-biobased filler composites reported in the literature. For example, effective dispersion of 10 wt% unmodified cellulose nanocrystal in low density polyethylene (LDPE) leads to a ~70% increase in Young’s modulus relative to neat LDPE. The LDPE/CNC composites also exhibit superior creep performance with modest increment in yield strength compared to neat polymer and retain elongation at break values equal to that of neat polymer. Comparable enhancements in properties of polymer composites made with biobased but waste materials, including lignin, waste paper, agro-waste, rice husk ash, and eggshell, are also observed when the composites are made by SSSP.

What is Solid-State Shear Pulverization?

Unparalleled Dispersion with an Industrially Scalable Process

- Deformation energy stored & released by creating new surfaces
  - Break up of agglomerates leading to fine dispersion of nanofillers

Process Variables

- Screw Design
- Screw Speed
- Feed Rate (Output Rate)
- Barrel Temp
- Material Format, Hardness, Size, etc.

Previous Benefits

- Intimate mixing free from viscosity ratio and thermodynamics
- Mechanochemistry leading to block copolymer formation and compatibilization of blends
- Nanostructured blends

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Amyloid reinforced rubber nanocomposites

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Natural rubber (NR) has superior properties to synthetic rubber (SR), which partially originates in the ca. 2% protein found in NR. NR rubber elongation factor (REF) protein has been shown to aggregate into a high performance beta-sheet containing nanostructure called an “amyloid”. Amyloids have moduli of several to tens of gigapascals and so an amyloid phase in NR would confer a significant property advantage to NR advantage over SR. Here, proteins are aggregated in SR during rubber compounding to realize an amyloid nanophase. Modulus increases of several hundred percent result from amyloid reinforcement of SR. Fourier transform infrared (FTIR) spectroscopy shows the formation of beta-sheets in the protein phase and x-ray diffraction (XRD) reveals the crystal structure of the beta-sheets. Energy dispersive x-ray spectroscopy (EDX) performed during scanning electron microscopy (SEM) analysis shows the amylloids to be isotropic and evenly dispersed throughout the rubber matrix after compounding. Differential scanning calorimetry (DSC) shows no change to the rubber glass transition temperature upon addition of protein indicating weak hydrophobic interactions between the two phases.

**CELL 228**

**Melt mixing cellulose nanocrystals and industrially relevant polymers**

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The incorporation of small amounts of high-stiffness, high-aspect-ratio nanometer-sized fillers into polymers is a design approach that has rapidly emerged as a broadly exploited framework for the creation of new materials with tailored mechanical properties. Crystalline cellulose nanocrystals (CNCs) are attracting significant interest in this context, mainly due to their intriguing mechanical properties and the abundance of cellulose in the biomass. These nanocomposites show dynamic mechanical behavior, which is achieved through regulation of the molecular interactions, and therewith the stress transfer, between adjacent nanocrystals. We will present our experimental research, targeting the design and processing of CNCs directly into industrially relevant polymers, without the use of surface functionalization. We investigated how different processing methods affect the morphology and mechanical properties of nanocomposites made from poly(vinyl acetate) (PVAc), nylon 12 or polyethylene and cellulose nanocrystals (CNCs). Comparisons are made between traditionally made solution cast samples, and materials were post-processed by mixing in a roller blade mixer (RBM) or a twin-screw extruder (TSE) and subsequent compression molding.
CELL 229

Cellular mechanisms of CESA trafficking and delivery to the plasma membrane

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While progress has been made in understanding the mechanisms by which the components of the cell wall are synthesized, less is understood about the molecular and cellular mechanisms that deliver these materials to the apoplast and that direct the spatial organization of the cell wall; how the delivery of wall materials are targeted and how the assembly of diverse components may be coordinated. I will review published work investigating the functions of the microtubule and actin cytoskeletons in CESA delivery to the plasma membrane, then present unpublished data on the roles of two proteins in CESA trafficking and delivery, the SM protein KEULE and a newly characterized protein, TRANVIA1 (TVA1). Transient accumulation of KEULE protein marks individual sites of CESA secretion, and KEULE mutation results in a 50% decrease in CESA delivery rate and significant delay between vesicle capture at the cell cortex and observation of CESA complex motility. Together with what is known about SM protein function in mediating SNARE function, these data indicate that KEULE plays an important role in the efficiency of CESA vesicle fusion at the plasma membrane, and that tagged KEULE protein can be used as a discreet marker for secretion. TVA1 is a previously uncharacterized transmembrane protein that co-localizes with markers for the trans Golgi network and also to small organelles that do not share these markers. Importantly, among the latter organelles are apparent vesicles that deliver CESA to the plasma membrane. TVA1 mutants are reduced in cellulose content and are deficient in the rate of CESA delivery to the plasma membrane. Taken together, these data suggest that that TVA1 plays a role in anterograde CESA trafficking, likely in one or more steps from the TGN to vesicular interaction with the plasma membrane.

CELL 230

Does cortical microtubule array guide the orientation of cellulose deposition or not?

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In higher plants, cellulose microfibrils are synthesized at the plasma membrane by protein complexes known as cellulose synthase complexes (CSCs). Cortical microtubules are long known to guide the direction in which cellulose microfibrils are deposited. Recent discovery of cellulose synthase interacting proteins (CSIs) begin to reveal mechanistic details underlying the co-alignment between cellulose microfibrils and cortical microtubules. We demonstrated that CSIs bind both to microtubules and isoforms of CESA in CSCs, thus bridges the CSCs and cortical microtubules. We have also shown that CSI1 and CSI3 regulate cellulose biosynthesis in both microtubule-dependent and microtubule-independent fashions: CSI1 plays a major role in the guidance of CSCs along microtubules whereas CSI3 is dispensable for co-alignment of CSCs and microtubules. The identification of CSIs now poises us to dissect the molecular details of the intimate relationship between cellulose microfibrils and microtubules. We used spectroscopic tools including field emission scanning electron microscopy (FESEM) and atomic
force microscopy (AFM) to observe cell wall structure in loss-of-function csi1 mutants. Our results indicate that cellulose microfibrils can still adopt transverse orientation independent of CSIs. We will discuss the implications of these findings.

CELL 231

Myosins XI are involved in cellulose synthase complex dynamics and delivery

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Cellulose microfibrils, the major tensile components of the plant cell wall, play an essential role in plant growth and development. In higher plants, cellulose is synthesized at the plasma membrane (PM) by large cellulose synthase complexes (CSC) consisting of multiple cellulose synthase (CESA) proteins. Cellulose production is influenced by the rate of intracellular trafficking of CSCs and their lifetime at the PM. CSCs are believed to be assembled in the Golgi apparatus and delivered to the PM via small microtubule-associated transport vesicles, and their uptake into the cytosol is mediated by clathrin-based endocytic machinery. Both processes are likely to involve the actin cytoskeleton serving as tracks for vesicle or organelle transport, as well as clathrin-coated vesicle formation. Myosins XI are motor proteins that move diverse organelles and vesicles along actin filaments, thus playing a critical role in organelle trafficking in plant cells. However, the molecular mechanisms by which actin and myosin contribute to CSC trafficking or cellulose deposition remain obscure. In this study, measurements of cellulose content demonstrate that cellulose biosynthesis is significantly reduced in a myosin xik xi1 xi2 triple knockout (3KO) mutant. By quantitative image analysis of living epidermal cells expressing a functional YFP-CESA6 reporter in both the xi3KO mutant and myosin inhibitor-treated cells, we show that myosin regulates the abundance of PM-localized CSCs and determines the rate of delivery of CSCs to the PM by mediating the transport and exocytosis of small CESA-containing compartments. These are the first data implicating myosin in cellulose production in higher plants.

CELL 232

Real-time imaging of cellulose microfibril and biosynthesis

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The challenges of characterizing plant cellulose stem mainly from three facts: (i) Cellulose fibrils are small. The size of the microfibril has been reported to range from 2 nm to 50 nm based on observations by various microscopic and/or spectroscopic techniques. (ii) The cellulose microfibril is a composite structure that may contain multiple cellulose elementary fibrils (CEFs) and hemicelluloses. (iii) It is structurally inhomogeneous. The CEF is as long as several micrometers; disordered regions are expected in such long fibrillar structures with nanometer dimensions. Cellulose structure may change during plant development while the cells are expanded, elongated, sometimes lignified, senesced and dehydrated. Isolation of cellulose from plant materials results in shorter fibrils, further aggregation, and disordered structures. All above-mentioned factors affect data interpretation in many spectroscopic and microscopic approaches. Our research focuses on characterizing the native structure of cellulose using atomic force microscopy (AFM), specifically the nascent CEFs and their arrangement in the primary and secondary cell walls, combined with real-time tracking of cellulose synthase complex (CSC) using super-resolution fluorescence microscopy. In addition, AFM is used to image the ultrastructural changes of cellulose during chemical treatment and enzymatic hydrolysis.
Understanding the mechanism of (1,3;1,4)-β-D-glucan synthesis in cereals

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Mixed linkage (1,3;1,4)-β-glucan (MLG) is a major non-cellulosic polysaccharide of the commelinid monocot cell walls and an important soluble dietary fibre component found in abundance in cereal grains. Despite its importance, relatively little is known about the molecular mechanism involved in the synthesis and assembly of this polysaccharide. Using functional genomics, the commelinid-specific Cellulose Synthase-Like (CSL) F, CSLH and CSLJ multi-gene families within the larger CAZy GT2 family have been identified as encoding the catalytic components of the MLG synthase enzyme. We have adopted a multi-disciplinary approach, including molecular, cell biological, biochemical, and computational techniques to study CSLF6, the major MLG synthase in grasses. We have generated homology models of various GT2 enzymes based upon the recently crystallised bacterial cellulose synthase BcsA and have used molecular dynamics (MD) simulations to shed light on what protein features play a role in determining the specificity and sequence of the glycosidic linkages within this polysaccharide synthase family. We will present computational findings as well as experimental data relating protein structure to function and regulation.

A 3D model of the barley CSLF6 protein with its major features indicated.
Characterizing and utilizing CSLF6 to improve MLG synthesis

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Up to 20% of the cell wall in grasses is composed of mixed-linked glucan (MLG). The MLG carbohydrate is an important plant-based energy source for human consumption and potentially a readily accessible carbon source for biofuel production. MLG synthesis depends on two cellulose-synthase-like gene families (CSLH & CSLF). Although importance of CSLF family in the grasses during MLG synthesis has been reported, relatively little is known about how and where CSLF proteins produce MLG in the cell. We have investigated the topology of CSLF6 by expressing a CSLF6 gene found in the model grass Brachypodium (BdCSLF6) in both tobacco epidermal cells and the yeast Pichia. Using a combination of live cell imaging, immuno-electron microscopy, and protease protection assays, the catalytic domain BdCSLF6 was mapped in the cytoplasmic face of Golgi membranes, demonstrating that the Golgi localization is sufficient for MLG biosynthesis. To better understand localization and regulation of CSLF6 during MLG synthesis, we have expanded our research using transgenic Brachypodium expressing YFP-CSLF6. In addition, we have generated mutated version of CSLF6 to manipulate the localization and production of MLG in order to generate plants with high level of MLG. These analyses are poised to provide valuable information for designing new bioenergy crops with altered cell wall properties for improved bioenergy production.

Cellulose bio-inspired hierarchical structures

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Complex hierarchical architectures are ubiquitous in nature. By designing and controlling the interaction between elementary building blocks, nature is able to optimize a large variety of materials with multiple functionalities. Such control is however extremely challenging in man-made materials, due to the difficulties in controlling their interaction at different length-scales simultaneously. Here, I will discuss how to fabricate hierarchical cholesteric architectures by the self-assembly of cellulose nanocrystals within shrinking, micron-sized aqueous droplets. This confined, spherical geometry drastically affects the colloidal self-assembly process, resulting in concentric ordering within the droplet, as confirmed by simulation. This provides a quantitative tool to study the interactions of cellulose nanocrystals beyond what has been achieved in a planar geometry. Our developed methodology allows us to fabricate truly hierarchical solid-state architectures, from the nanometer to the macroscopic scale using a renewable and sustainable bio-polymer. Biomimetic with cellulose-based architectures enables us to fabricate novel photonic structures using low cost materials in ambient conditions and allows us to understand the biological processes at work during the growth of these structures in plants.
Driving forces for cellulose nanocrystal alignment in drying droplets: Center versus edge

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Drying droplets of cellulose nanocrystals have been reported to suffer the "coffee drop effect", where particles are transported from the center of the droplet to the edge in the drying process [1, 2]. This presentation will demonstrate that cellulose nanocrystals near the center of the droplet have a different orientation than cellulose nanocrystals near the edge and discuss the driving forces for these orientations.
**CELL 237**

In-situ small angle X-ray scattering of a levitated cellulose nanocrystal droplet

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Aqueous dispersions of cellulose nanocrystals (CNC) produced by acid hydrolysis from plants and bacteria, can form a chiral nematic liquid crystalline phase. While the rod packing in CNC dispersions has been investigated at concentrations up to 9.0 vol% by small angle X-ray scattering (SAXS) and laser diffraction, the self-organization at high CNC concentrations (above 10 vol%) has not been probed. Here, we will present our recent work where SAXS was applied to explore the time-dependent and evaporation-driven assembly of CNC in levitating aqueous droplets. By correlating estimates of the CNC concentration from measurements on the dimension for the shrinking droplet with analysis of the SAXS data, we find that the average spacing between the CNC rods decreases from 47 nm to 1.4 nm, as the volume fraction increases from 1.5 to 38 vol%. The chiral nematic order is improving up to CNC concentration around 10 vol%, where the dispersion starts to be arrested and the drying front moves into the droplet. The competition between percolation gelation of CNC rods and chiral nematic liquid crystal assembly eventually results in the formation of a hollow CNC sphere. Quantitative exploration of CNC colloidal assembly at high concentrations provides important insight into the competition between gelation, aggregation and self-assembly that can be used in the fabrication of advanced nanocellulose-based materials.

**CELL 238**

In situ Rheo-SAXS study of cellulose nanocrystals suspensions

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The ability of cellulose nanocrystals (CNC) to modify the rheology of the medium they are dispersed in is a very important property that paves the way to a large number of applications. Parallely, shear flow can be considered as a way to obtain macroscopically oriented CNC dispersions that could be used to design materials with controlled architecture and degree of alignment. The understanding of the effect of shear flow on the structural and rheological behavior of cellulose nanocrystals (CNC) is therefore a prerequisite for the development of new bio-based materials with better performances and controlled structural organizations. In order to access to this understanding, it is necessary to link the mechanical responses under flow (shear stress, shear rate) to structural observations at different length scales: from the nanometer length scales of the CNC to upper length scales corresponding to their mutual organizations. In this aim several in situ structural characterization techniques have been combined to rheometric measurements. Firstly local birefringence measurements under shear have been performed thanks to specific shear flow cells. Secondly a combined rheology and small angle X-ray scattering (Rheo-SAXS) setup available at the European Synchrotron Radiation Facility (ID02 High brilliance beamline) have allowed us to access to in situ and time-resolved CNC orientations and structure properties in the volume of the dispersions under flow. Analysis of transient and steady-state regimes revealed the main characteristics of the shear flow properties of the CNC dispersions as a function of the volume fraction. The changes in viscosity as a function of shear rate has been linked to the birefringence and to the order parameter deduced from the scattering intensity of the SAXS patterns. In transient states, time-dependent changes in the order parameter made it possible to identify the timescales at which the CNC become aligned in the shear flow and over which they relax after the cessation of shear.
**CELL 239**

**Effect of the size of the charged group on the properties of alkoxylated NFCs**

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The impact of the size of the charged group on the properties of alkoxylated NFC was studied by two chloroalkyl acid reagents. It was found that the employment of the larger 2-chloropropionic acid reagent leads to improved properties, e.g. higher fraction of nano-sized materials, and significantly better redispersion as compared to when the smaller monochloroacetic acid was employed. The differences in the impacts of the different reagents were hypothesized to be due to a more efficient disruption of the cohesion between the nanofibrils when a larger charged group was employed.

**CELL 240**

**Interaction of β-(1-4) xylan with cellulose surface in biomimetic reconstructed models**

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Microfibrils prepared from sulfite and kraft pulps were studied by sugar analysis and 13 CP-MAS spectroscopy, revealing the presence of hemicelluloses in interaction with the cellulose surface. A pure linear homopolymer of β-(1-4) xylan, was extracted from microfibrilated cellulose from birch kraft pulp using DMSO. The xylan exhibited a three-fold helix conformation in wet conditions. This polymer was readsorbed onto cellulose surfaces of aerogels with controlled specific surface area prepared from lyophilized microfibrils in order to build biomimetic reconstructed materials. 13C CP-MAS spectroscopy revealed that the conformation of the xylan molecules changes in contact with the cellulose surface, most probably in a two-fold conformation similar to the state in native microfibrils. An excess of added β-(1-4) xylan resulted in the presence of chains in the three-fold helix conformation corresponding to the bulk polymer. The quantity able to adopt two-fold conformation corresponded to a monolayer of polymer, calculated from the measured specific surface. MD simulation showed that the interaction for xylan with cellulose surfaces in the three-fold conformation was less favorable that the two-fold one, confirming the experimental observation. When in contact with the cellulose surfaces, the xylan chains remained in two-fold conformation and extended parallel to the chain axis.
**CELL 241**

**Periodate oxidation and chemical modifications of cellulosic backbone**

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Cellulose is an attractive candidate to replace oil-based polymers because of its bio-renewability and biodegradability. However, its melt-processability in the native form is impossible as such due to its degradation before melting. The idea here is to chemically modify the cellulose to increase the mobility and the free volume around the chains to make it processable. The oxidation of cellulose with sodium metaperiodate allows the selective cleavage of the C2-C3 bond and the formation of two aldehydes groups. This cleavage of the sugar rings gives a large increase in the mobility of the chains and the newly formed aldehydes allow further grafting onto the chain and free volume increase. To avoid the classical but heterogeneous and non-quantitative oxime titration due to hemiacetal formation, a new quantitative method based on solid-state NMR was developed to obtain an accurate measurement of the degree of oxidation (DO). Based on this method, a number of kinetic studies were performed to create a 3D quantitative map relating the DO with the reaction time and amount of oxidizing agent. A linear relationship between the mass yield of the water insoluble fraction and the DO, making the yield independent to the oxidation conditions but only proportional to the DO, was also revealed. Further modifications such as a simple reduction to dialcohol cellulose was performed and used as a reference for its thermo-mechanical properties. More advanced reactions were carried out using reductive amination.

**CELL 242**

**Designer molecules for one-step modification of cellulosic materials in aqueous and organic media through the triazine chemistry**

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Interest in the incorporation of renewable, environmentally friendly materials, e.g. nanocellulose, into consumer products has progressed rapidly because these materials could lead to nanocomposites with enhanced functionality and mechanical properties. However, a key challenge that prevents nanocellulose from being widely used is that cellulose is insoluble, relatively inert, and difficult to disperse in non-aqueous solvents and polymeric matrices. Available methods for the surface modification of cellulose to make it dispersible in polar and non-polar systems are complex and difficult to implement on a large scale. To address these challenges, we report a simple one-step surface modification approach for tuning the interfacial properties of cellulosic materials. We use triazine chemistry as a modular handle to install various functionalities and chemistries onto filter paper, cellulose microfibrils, and cellulose nanocrystals (CNCs). The ability to carry out surface modification at room temperature in aqueous and organic media is demonstrated. This novel method allowed us to directly graft C18, allyl-PEG, benzyl and propargyl dichlorotriazinyl derivatives onto cellulose via aromatic nucleophilic substitution. These aliphatic, polymeric, alkyne chains and aromatic rings were successfully confirmed to be stable and covalently linked to cellulose. Thus, the modified cellulose/CNCs exhibited hydrophilic/hydrophobic properties depending on the grafted functionality which resulted into colloidal suspensions in aqueous/organic solvents with improved stability. Additionally, atomic force microscopy images of
modified nanocellulose showed no observable change in the geometry and individualized character of CNCs after surface modification. X-ray diffraction analysis confirmed that the modification happened at the CNC interface whereas the bulk crystalline core remained unmodified. Finally, the propargyl moiety grafted onto cellulose fibres was used as a modular handle for further modification through an azide-alkyne cycloaddition reaction. In this way, azido-fluorescein molecules were grafted onto cellulose microfibrils, and fluorescence imaging showed labelling along the entire fibre. The developed modular chemistry provides the ability to tune the interfacial properties of cellulosic materials, improving their compatibility and dispersion in a wide range of solvents and solid matrices.

CELL 243

Dissolution of cellulose in NaOH/zinc nitrate at low temperature

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The effect of zinc nitrate on the cellulose dissolution in NaOH was clarified herein. The cellulose solubility of in NaOH increased from 15 to 88 % with the zinc nitrate content increased from 1 to 5 wt%, indicating the improvement of the cellulose dissolution by zinc nitrate, which was a physical process and no chemical reaction happened. Dynamic light scattering tests demonstrated the ordinary solution property of cellulose in NaOH/zinc nitrate, as well as extended chain conformation. On the other hand, the zinc nitrate also enhanced the stability of the cellulose solution in NaOH, indicating the zinc nitrate not only improved the dissolution, but also prevented the cellulose from aggregation, leading to potential applications. Furthermore, regenerated cellulose microspheres with ZnO crystals were successfully fabricated via emulsion approach, demonstrating potentials in various fields.

CELL 244

Novel robust and selective solvent for biomass fractionation

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We have developed an economic, robust and environmentally friendly process for biomass fractionation. The core of the process is biomass dissolution in aqueous ZnCl2- based solvent. The technology is feasible as the first step for a variety of biomass feedstocks in a large range of biomass based plants. Depending on the conditions (ZnCl2 concentration; solvent acidity; temperature and time) biomass main components – hemicellulose, cellulose, lignin - can be selectively separated. Due to mild process conditions (T<90 C) biomass sugar, glucose and xylose, are produced with very little degradation. Further, they are isolated from the solvent as rather concentrated aqueous solution, up to 25 wt.% sugars. The sugar stream is a nice starting material for almost endless options for further conversion: fermentation to bioethanol; hydrogenation/dehydration to monomers, etc. If desired, polymeric cellulose of nanoscale range can be produced in a simple process, by precipitation using an antisolvent. Most of lignin is not dissolved in the solvent and is recovered by filtration and washing. The process makes possible further selective conversion/utilization of all lignocellulosic biomass components. In contrast with today's high acidity processes, no special alloys are required.

CELL 245

Topochemical modification of nanocellulose in ionic liquids or gamma-valerolactone

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Topochemical modification of nanocellulose to give high degrees of redispersibility, in the absence of water, is very challenging due to the difficulty of removing water whilst avoiding aggregation. Practically, solvent exchange with dipolar aprotic solvents can allow for this. However, this typically requires 4* solvent exchange through centrifugation and resuspension cycles. In this abstract, we demonstrate that we overcome this problem by simple rotary evaporation of water directly from non-dissolving but surface stabilising ionic liquids, mixed with aqueous nanocellulose. We overcome the need to do laborious solvent exchange by taking advantage of the low volatility of ionic liquids, whilst surface stabilising nanocellulose. The process is illustrated by using acetylation as a model reaction. High degrees of redispersibility are demonstrated against controls. gamma-Valerolactone (GVL), as a novel dipolar aprotic solvent which is considered to be a modern bio-based green reaction media, is also demonstrated to do allow for the same process. While it is a volatile molecular solvent, it has a relatively high boiling point which allows for almost complete removal of water from nanocellulose, by rotary evaporation. These two solvent classes open the area to more sustainable water-free processing.

**CELL 246**

**Essential analytical approaches to characterization of lignin specifically targeting the abundant oligomeric fraction observed following a hydrotreatment**

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To provide essential understanding for lignin degradation mechanisms, we have focused on three main approaches: 1) mass balance closure using a newly developed thermal carbon analysis (TCA), 2) evaluation of main structural features through phosphitylation of OH-containing groups and ³¹P nuclear magnetic resonance (NMR) spectroscopy, and 3) molecular weight (MW) determination employing gel permeation chromatography with mass spectrometry (GPC-MS). TCA is based on carbon fractionation with increasing temperature (100–850 °C) without and with oxygen, respectively. This method allows to differentiate monomeric species evolving at low temperature steps (200–300 °C) from large MW compounds pyrolyzed at 400–850°C, and finally the “coke” fraction, which evolves only in presence of oxygen at high temperatures. The “coke” carbon cannot be observed with Py-GC-MS, as no oxygen is used. Our results support the need of using TCA for quantification demonstrating that the “coke” carbon represents a significant portion of all characterized samples including both raw and hydrotreated lignin. Moreover, the phenolic-oligomeric fraction is not amenable to GC. Yet, as we demonstrated, this potentially valuable mixture of nano-sized phenolic oligomers can be quantified using TCA with a complementary Py-GC-MS speciation. Phosphitylation followed by ³¹P NMR spectroscopic analysis allows for identification and quantification of the majority of OH-containing compounds formed during lignin hydrotreatment. Particularly, this method readily identifies phenols, alcohols and carboxylic acids. Comparison of ³¹P NMR spectra of lignin before and after a hydrotreatment may also provide useful information on possible repolymerization of degradation products, i.e., structure of nano-size oligomers. The application of GPC is limited due to lignin and its oligomers’ heteropolymeric nature and lack of representative standards. Thus, standards were synthesized and a protocol for their analysis was optimized. We confirmed that GPC methods are affected by the superposition of the molecular sieve effect and unwanted analyte-column interactions. The study was carried out using a time of flight MS equipped with electrospray ionization (ESI). We have demonstrated advantages of detection with ESI-high resolution MS providing accurate masses for high MW species of the oligomeric fraction, however, detailed optimization is essential to prevent excessive fragmentation and loss of molecular ions.
Silylated lignin and copolymers with acrylonitrile: Flexible membranes and material precursors

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A highly efficient disilazane reaction was used to substitute 30% of kraft lignin hydroxyl groups with silicon-containing vinyl groups. The in situ exothermic reaction was carried out in the melt state utilizing a reactive extruder. The silylated lignin was further copolymerized with polyacrylonitrile (PAN) to develop coatings (oven dried), membranes (phase inversion), and carbon films (carbonization of hot-pressed films). The products of lignin reaction and PAN-lignin copolymers were characterized by FT-IR, and ¹H, ¹³C, ³¹P NMR, which confirmed successful modification. Glass coating via solution casting followed by oven drying yielded films that were tested via SEM, TGA and DSC. A good compatibility between silylated lignin and PAN was determined. Copolymers with 30% of silylated lignin displayed a Young modulus of 486 MPa, an ultimate stress of 18 MPa and strain of 55 % (DMA). Overall, the introduced SiC and SiOC bonds improved lignin macromolecular mobility, facilitated its processability due to remarkably lower viscosity and is expected to open opportunities for its utilization as precursor in the synthesis of copolymers, as illustrated here with PAN, towards flexible films, porous membranes and carbonized films.

Grafting-from cellulose via photoinduced Cu-mediated reversible deactivation radical polymerisation

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The modification of cellulose through polymer grafting is highly desirable. Whilst cellulose is renewable and exhibits excellent mechanical properties, disadvantages mainly stem from its hydrophilic nature, resulting in limited barrier properties and poor miscibility with hydrophobic polymer matrices. Here, the modification of cellulose has been accomplished by covalent grafting via a grafting-from method. We demonstrate the surface initiated polymerisation of methyl acrylate (MA) from filter paper (FP) and cellulose nanocrystals (CNC) applying the recently reported photoinduced Cu-mediated RDRP technique. Initial experiments with FP proved successful, and the polymerisation of diethylene glycol acrylate inferred thermoresponsive behaviour to the FP. Utilising the same technique with CNCs resulted in high grafting amounts in short reaction times with simple purification procedures. Polymer-grafted CNCs may have potential in nanocomposite and emulsion applications.
Graphical representation of the Cu-mediated photoinduced surface-initiated polymerisation of methyl methacrylate from cellulose nanocrystals

**Valorization of lignin in 0D and 1D advanced systems: Particles for emulsification and fibers for energy storage**

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We demonstrate the valorization of technical lignins into advanced materials. First, 0D systems, namely lignin micro and nanoparticles were developed for stabilization of oil-water interfaces. We introduce spherical particles with sizes ranging from 30 nm to few microns and that were synthesized in an aerosol flow reactor with in-situ fractionation. This method allowed, for the first time, high throughput and high yield production of dry lignin particles. By varying the lignin source, systems with different surface energy were obtained and, as demonstration, the particles were used to stabilize oil-water interfaces, particularly, in Pickering emulsions. Depending on the particle size and hydrophobicity, emulsions with different morphologies and stability were obtained. We extended our work to 1D systems: Highly mesoporous carbon fibers were obtained from lignin aqueous solutions and used as webs for conductive electrodes with supercapacitance. Polyvinyl alcohol (PVA) was used as sacrificial polymer to facilitate electrospinning of lignin and, note, to produce microphase separation that induced high surface area and mesoporosity. An optimized sequential thermal treatment that included a stabilization step allowed the formation of a lignin-continuous structure in the as-spun fibers upon carbonization, while PVA evolved to the gas phase. The resultant mesoporous carbon fiber networks yielded flexible freestanding films. Their main morphological and chemical characteristics were assessed by SEM and Raman spectroscopy, respectively. Nitrogen gas adsorption revealed extremely high surface area (> 2000 m²/g) and pore volume (0.7 cm³/g). The carbon fiber networks were used directly as electrodes with electrochemical double layer capacitance as elucidated. The excellent electrochemical capacitance was demonstrated, including a high rate capability, and long-term cycling stability. A specific capacitance as high as 205 F/g in 0.5M Na₂SO₄ electrolyte was delivered, one of the highest recorded for electrodes obtained from
biopolymer precursors. Besides providing a route to enable nano-manufacturing, this work shows two examples of lignin valorization into organic and safe nanomaterials.

CELL 250

Synthesis, properties and carbonization of different types of ligneous aerogels

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Following our previous works on hydro- and aerogels from different lignins cross-linked with oligo(alkylene glycol)-α,ω-diglycidyl ethers and on the preparation of phenol-formaldehyde (PF) adhesives of high lignin content, this paper reports the preparation of mechanically stable, monolithic aerogels from ligneous precursor materials that have been brought to gelation by either step-reaction or chain reaction polymerization. Dialysis and subsequent thermo-induced gelation of ligneous resole resin pre-condensates (LPF, 40% replacement of phenol by lignin, ν = 1000 mPa s) in ethylene glycol afforded freestanding, homogeneous gels. Incremental replacement of ethylene glycol by ethanol and scCO2 drying produced aerogels that suffered from comparatively little shrinkage and perfectly maintained the initial cylindrical shape even at bulk densities as low as 25 mg cm⁻³. Scanning electron microscopy, nitrogen sorption at 77 K and thermoporosimetry using o-xylene as probe solvent revealed a largely homogenous internal mesoporous morphology featuring accessible specific surface areas as high as 527 m² g⁻¹. Chain reaction polymerization of consecutively Fenton-oxidized and per-methacrylated lignin in toluene using a suitable radical source turned out to be an efficient means to produce entirely lignin-based aerogels (apparent density 32-222 mg cm⁻³) that had an internal surface of up to 370 m² g⁻¹. Carbonization at 1300°C maintained the shape of the respective aerogels and interconnectivity of pores, however at significant shrinkage.

CELL 251

Fiber-based foams for papermaking

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Processing cellulosic fiber-based materials using foams as suspended media can resolve issues related to unwanted fiber flocculation, as well as to save water and energy consumption in conventional papermaking. Foam forming is a process involving complex colloidal interactions. Fundamental understandings of the physicochemical interactions taking place at the interface of air bubbles, aqueous phase and fiber surfaces still remains a challenge. Moreover, it is difficult to correlate the published data due to the different preparation methods of foam-laid sheets, as well as the different fiber types and foaming agents used. In order to investigate the mechanisms relevant to foam forming and to elucidate the effect of processing variables, fiber and surfactant species, we prepared handsheets both from water and foams with different surfactants (anionic, cationic, nonionic and amphoteric) and cellulosic fibers (chemical and mechanical). We compare the physical-mechanical properties of the produced handsheets in relation to the foaming process. The structure of the obtained fiber networks are proposed to explain the changes in physical properties. Overall, this study contributes better understanding of the capabilities and limits of foam forming in papermaking.
Towards a better understanding of alkali-lignins isolated from three kinds of non-woody materials

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Lignins are complex and heterogeneous natural polymers that play essential roles in the development of plant cell walls and affect their use as renewable biomaterials. As highly abundant natural aromatic polymers, isolation and application of lignins from lignocellulosic materials remain most challenging because of their complexity and heterogeneity, as well as their association with cellulose and hemicelluloses. Selective isolation of lignins from biomass therefore still plays an important role both in understanding its biosynthesis and structure and for optimizing the value for potential applications.

In this study, we report the structural characterization of alkali-lignins extracted from three kinds of non-woody materials including rice straw, bagasse and bamboo by aqueous alkali pretreatment at various temperatures (20, 80, 120, 140, and 160 °C). For the isolation of alkali-lignins, alkaline extracts were acidified, the precipitates were then extracted with 1,4-dioxane-H\textsubscript{2}O (96/4, v/v) and purified by cyclohexane-EtOAc (5:1, v/v) precipitation to remove hemicelluloses, p-coumaric acid and other kinds of low molecular weight impurities produced during the treatment. A total of 15 purified alkali-lignin preparations were obtained and analyzed by NMR. Considering the isolated yields, it was found that alkaline extraction was a suitable method for producing lignins from bagasse and rice straw with isolated yields ranged from 28.4% to 55.8% and from 20.71% to 64.97% respectively, but was not particularly efficient for bamboo with yields from 8.86 to 31.08%. From the NMR study, we found that most of the main characteristic linkages in lignins, such as $\beta$–O–4-, $\beta$–5-, and $\beta$–$\beta$-linkages, were all well preserved in alkali-lignins. Additionally, $\beta$–1 structures (spirodienones) that were originally found in MWLs (milled wood lignins) were observed in alkali-lignins extracted at or below 140 °C by NMR for the first time. The results showed that the temperature for alkaline extraction of bamboo and bagasse should not be higher than 140 °C, whereas the temperature for rice straw should be lower than 120 °C in order to minimize the degradation and/or structural modifications of alkali-lignins, which could be beneficial for their structural characterization. Compared with kraft lignins, non-wood alkali-lignins, structurally more closely resemble their original lignins, and could therefore be more attractive renewable resources for future industrial applications.

MONDAY EVENING

Sci-Mix


TUESDAY MORNING

Design & Control in Polysaccharide Chemistry: Anselme Payen Award Symposium in honor of Kevin J. Edgar

P. E. Fardim, Organizer; O. J. Rojas, Organizer; C. M. Buchanan, Organizer; O. J. Rojas, Presiding Papers 253-260
CELL 253

Control of optical anisotropy of cellulose derivatives

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Some cellulose derivatives are employed in optical functional films because of its good transparency with high glass transition temperature. Since the main chain of cellulose has low level of optical anisotropy, orientation birefringence of a stretched film can be easily controlled by chemical modification such as esterification. Moreover, good miscibility with various plasticizers for cellulose derivatives widens the material design to control the birefringence. In this presentation, material design of a multi-band quarter-wave plate, one of the optical retardation films, is presented using cellulose derivatives.

CELL 254

Design of optical films for liquid crystalline displays by control of cellulose ester structure

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Cellulose esters have long been used in the manufacture of films for liquid crystalline displays. Historically, these cellulose esters were prepared by traditional methods that provide little or no control of regioselectivity and these cellulose esters can be classified as random copolymers. Early research showed that type of acyl substituent and degree of substitution of the cellulose esters were the primary structural features influencing optical properties. In this account, we present esterification of cellulose dissolved in ionic liquids as an approach for the preparation of regioselectively substituted cellulose esters. Placement of substituents is in part dependent upon which ionic liquid is utilized for the reaction medium and in part upon selection of reaction conditions. By comparison of these regioselectively substituted cellulose esters and conventional cellulose esters, we show that cellulose esters with unique optical properties can be obtained via control of regioselectivity and can provide novel performance.

CELL 255

Nano- and micropatterns of cellulose - from lithography to microphase separation

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In the last two decades, an enormous progress has been made in the generation of patterned surfaces and films. This progress is particularly visible in the field of microelectronics, where miniaturization of the components has often been achieved by more effective patterning methods of the used photoresists. For polysaccharides, however, a limited amount of lithographic techniques is available, most of them harming the polysaccharide material due to the destructive nature of the used approaches (e.g. by laserwriting). As a consequence, degraded material at the edges of the polysaccharide patterns leads to limitations in performance and subsequently to a loss of the intrinsic properties of the cellulosic support. In this contribution, we give an overview on recent developments in the field of nano- and microstructured cellulosic materials. Different patterning approaches such as photolithography, two-photon absorption lithography, electron beam lithography as well as microphase separation are presented and it is demonstrated how common concepts employed in polymer chemistry can be easily transferred to cellulose. Major differences between the used techniques and the resulting properties of the cellulosic
materials are discussed and opportunities for the creation of new advanced patterned cellulosic substrates are provided.

CELL 256

Photo- and biodegradable thermoplastic elastomers containing cellulose and polylactide

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Thermoplastic elastomers (TPEs) are block copolymer structures comprised of hard and soft segments. With the properties of both thermoplastics and elastomers, traditional TPEs are used widely in the automotive, medical, and consumer products industries, but they are made from petroleum-based monomers (e.g., styrene and butadiene) and not degradable. We present here a method for synthesizing TPEs based on an ABA triblock polymer structure that contains a central, photodegradable soft block and renewable, biodegradable hard blocks. The core block is made by ring-opening metathesis polymerization (ROMP) of cyclooctadiene and an unsaturated cyclic ketone comonomer to yield polybutadiene with random ketone incorporation. This synthetic block can be degraded through Norrish fragmentation pathways upon activation with UV-C light. To complete the ABA triblock polymer structure, the alcohol chain ends on the core block polymers are used to initiate the polymerization of lactide. Cellulose derivatives can also be incorporated as the A blocks to make cellulose-based TPEs. These novel thermoplastic elastomers are both photo- and biodegradable, with tunable photodegradability depending on the level of incorporation of the ketone-containing comonomer in the soft block and tunable biodegradability depending on the choice of hard block monomer.

CELL 257

Heterogeneous catalysts for the regioselective modification of cellulose

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Cellulose is a substance that dominates terrestrial life and is resistant to degradation. However, nature has developed biocatalysts that work heterogeneously to modify and hydrolyze cellulose substrates.
Synthetic catalysts also have an important role in conversion of cellulose into derivatives with various substitution patterns. One example is found with nanocellulose materials that are produced using 2,2,6,6-Tetramethyl-1-piperidyloxy (TEMPO) mediated oxidation of cellulose pulp, converting C6 surface hydroxyls into carboxylic acid groups. The further advantage to this material are that carboxylic acid groups serve as “handles” that can be modified with a number of chemistries to enable functionalization for many applications. On the heels of this work, we developed a surprisingly efficient method of tethering catalysts to nanoparticles for the modification of cellulose pulp fibers. The efficacy of the catalyst is retained while nanoparticles enable recycling of the catalyst, as well as limits the release of it into wastewater effluent.

Supported catalysts for regioselective modification of cellulose

CELL 258

Control of cellulose chiral nematic structure

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Cellulose nanocrystals (CNC) form suspensions with chiral nematic order. This order can be preserved in films cast from the suspensions, raising the possibility of applications as photonic materials and templates. However it has proved difficult to generate uniform, well-ordered chiral nematic materials from CNC. Recently, the importance of kinetic arrest due to gel formation in the later stages of evaporation has been recognized as a key step in governing the structure of CNC films cast from suspensions. Recent developments regarding the organization of chiral nematic suspensions and films as monitored by polarized light microscopy are outlined, and attention is drawn to the importance of shear forces on the self-organization process.
Example of texture of solid film cast from 6 wt% CNC suspension between crossed polars with 530 nm red plate. The outer edge of the sample is close to bottom right of image. The lines are due to shear relaxation, not chiral nematic fingerprint texture.

CELL 259

Looking at the unwanted acetylation of polysaccharides by 1,3-dialkylimidazolum acetate ionic liquids: Analysis, acetylation agent, influence of water, and mechanistic considerations

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The acetylating action of ionic liquids frequently used in biomass and polysaccharide processing, namely 1,3-dialkylimidazolium acetates, on cellulose has been studied. Analysis was based on an accurate method to quantify even minute amounts of organic acetates in polysaccharides. The acetylation is caused by impurities in the ionic liquids, specially purified ionic liquids do not show an acetylating effect. 1-Acetylimidazole has been proven to be the actual acetylation agent, and its present in aged ionic liquids has been confirmed. Formation of the reagent, mechanism of its action – being an acetyl transfer rather than a typical esterification – kinetics of the acetylation and the effect of water in the system will be presented, and implications of processing of biomaterials in ionic liquids are discussed as well.
Peptide-cellulose conjugates for protease point of care diagnostics and treatment

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Peptide-cellulose conjugates containing Human Neutrophil Elastase substrate sequences with both colorimetric and fluorometric signal molecules have been synthesized on a variety of cellulosic and nanocellulosic substrates including cotton and wood nanocrystals, wood nanocomposites, cotton-based aerogels, and various forms of cotton-based materials (filter paper, print cloth). These peptide-cellulose conjugate materials have been designed with functional value as both point of care protease sensors, and protease sequestrant dressing materials. They are applicable to the detection and treatment of chronic wounds where high protease levels characterize chronic wound pathology. Critical to the efficacy of a combined sensor/dressing design is both the material’s sensitivity to detect levels of protease found in the chronic wound, and to remove them from the wound. The protease sensors sensitivity to protease levels was found to correlate mostly with the specific surface area of the sensors transducer surface, and in some cases is influenced by porosity and pore volume where whole material constructs were evaluated. Some of the peptide-cellulose sensors revealed an improved kinetic binding affinity constant (Km) over solution-based measurements, and models constructed of cellulose crystallites containing appended peptides help visualize the binding of protease to transducer surface. A linear correlation was found between both nanocellulosic and cellulosic material zeta potential values and the ability of the materials to remove protease from wound fluid. Thus, protease substrates linked to nanocellulosic and cellulosic platforms can be used to design ‘intelligent wound dressings’ by virtue of their combined detection sensitivity and protease binding performance.

Processing & Properties of Biobased Composites & Blends
J. R. Barone, Organizer; P. R. Navard, Organizer; J. R. Barone, Presiding; L. Averous, Presiding Papers 261-268

New biobased and sustainable epoxy and polyurethane materials and foams from vegetable and microalgal oil

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Vegetable oils come from various plants (soybean, palm, rapeseed, etc), cashew nutshell or microalgae and contain triglycerides molecules where the three hydroxyl functions of glycerin are esterified with fatty acids. These fatty acids could be saturated, with non-reactive aliphatic chains or unsaturated, with aliphatic chains bearing double bonds (oleic, linoleic, linolenic, ricinoleic acid, docosa hexanoic acid, etc.). These natural oils, and particularly the unsaturated ones, are of interest since various reactions could be performed from their different groups in order to obtain various building blocks for polymer chemistry. We report the synthesis of various building blocks from vegetable oils in one or two-steps syntheses. Thiol-ene coupling allowed to synthesize new biobased reactants with various function and functionality with reaction conditions in agreement with green chemistry principles: it does not use neither solvent nor initiator or need a simple purification step, feasible at industrial scale. We developed a real chemical toolbox based on thiol-ene coupling, epoxidation, amidification/esterification or carbonation to synthesize a library of biobased building blocks with various functions and functionality from vegetable and microalgal oils. The synthesized building blocks reported in this contribution are polyols, acids, amines,
epoxides and cyclocarbonates from vegetable and microalgal oils and from glycerin derivatives. These building blocks led to the synthesis of polymers such as polyurethanes, polyhydroxyurethanes and polyepoxides that were used for coatings, binders and foams. These materials present various properties: low Tg polymers for foams or high Tg polymers for composites.

CELL 262

Polylactide/ZnO nanocomposites: From improved functional properties for packaging to novel materials for biomedicine

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Here we develop nanocomposites based on polylactide (PLA) and zinc oxide (ZnO) nanoparticles for packaging and biomedical applications. Mechanically flexible films have been prepared by a simple scalable industrial process. We observe that ultraviolet light could be blocked by 61.2% for a concentration as low as 0.45 vol %, while the 95.9% of the visible radiation passes through the material.
Dynamic mechanical analysis exhibits a $T_g$ increase with nanoparticle loading arising from the chain confinement caused by the presence of ZnO interacting surfaces, while the structural relaxation of nanocomposites is reduced 3.6 times after the addition of 0.25 wt.% of zinc oxide. We further analyze the catalytic effect of zinc oxide during the in vitro hydrolytic degradation of PLA/ZnO nanocomposites. We observe that during hydrolytic degradation H$_2$O is dissociated on oxygen vacancy sites, giving hydroxyl groups that initiate the hydrolysis of ester bonds, and thus reducing PLA to soluble monomers. These findings are expected to allow the development of eco-friendly disposable polymeric waste by opening new possibilities in the use of naturally-available materials as efficient catalysts for feedstock recycling of biopolymers by common chemical processes. Overall, this work highlights the potential for these sustainable nanostructured functional materials to be used in packaging applications, where the use of non-biodegradable materials for short-term applications is extended. In view to biological applications, we further demonstrate that the system constitutes a dynamic surface in which nanoparticles are continuously exposed upon C2C12 myoblasts cell culture, activating the material surface and significantly driving cell differentiation. Moreover, we observe that PLA/ZnO scaffolds profile could be successfully modified by tuning both the amount of ZnO nanoparticles. Overall, results suggest that PLA/ZnO nanocomposites may serve to develop antibacterial porous structures with tunable degradation rates to be used as a substrate for the growth of different kind of cells and tissues.

**CELL 263**

*Green composites from hemp fibers and styrene-free soybean oil-based thermosets: Preparation and modification*

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A highly reactive vinyl monomer, $N$-vinyl-2-pyrrolidone (NVP), was used as a reactive diluent for acrylated epoxidized soybean oil (AESO) to fabricate styrene-free AESO resin and its composites with hemp fibers (HFs). Results indicated that the NVP has a good miscibility with AESO, and the obtained styrene-free AESO resin with 30 wt% NVP showed a slightly higher viscosity and activation energy than the styrene-AESO resin. The curing temperature of NVP-AESO resin was considerably lower than pure AESO and styrene-AESO resins. The HF composite of AESO with 30 wt% NVP demonstrated a much higher tensile strength, tensile modulus, flexural strength, flexural modulus, storage modulus, and glass transition temperature than the composite with styrene-AESO. To further improve the crosslinking density of AESO resins and the interfacial adhesion between HFs and AESO resins, the HF-AESO composites were modified with isophorone diisocyanate (IPDI). The results revealed that the isocyanate groups of IPDI would react with the hydroxyl groups of both HFs and AESO via forming urethane connections. The addition of IPDI into AESO resins resulted in the resins with reduced viscosities, activation energies, curing temperatures and reaction heatings. The dual functions of IPDI in the composites, i.e., crosslinking linker and coupling agent, contributed greatly to increasing the static and dynamic mechanical properties of the resulting composites.
Thermal superinsulating silica aerogels and xerogels reinforced with short cellulose fibers

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Silica-based aerogels are highly porous nanostructured materials with thermal super-insulating properties (i.e. thermal conductivity below that of air, 0.025 W/(m.K), in ambient conditions). Aerogels are obtained via drying in supercritical conditions. To overcome the latter step, drying at ambient pressure and slightly elevated temperature is used, leading to xerogels with similar thermal properties but not monolithic. One way to keep macroscopic monolithicity is to reinforce xerogels with non-woven fibrous mats.

We synthesized composite aerogels and xerogels with short cellulose fibers and demonstrated that a) mechanical properties of aerogels are strongly improved and b) it is possible to obtain monolithic xerogels with morphological and thermal properties similar to those of their supercritical-dried counterparts /G. Markevicius et al, Ambient-dried thermal superinsulating monolithic silica-based aerogels with short cellululosic fibers"Journal Materials Science, in press/. The proof of concept was demonstrated with model Tencel® fibers and extended to other natural fibers and paper waste.

Biopolymer-based multilayer nanocoatings that exhibit high gas barrier and flame retardant behavior

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Chitin, extracted from crustacean shells, is the second most abundant polysaccharide after cellulose. Alkaline deacetylation of chitin produces chitosan (CH), which is soluble in acidic aqueous solutions because of the protonation of its amino groups at pH < 6. In addition to its solubility, chitosan is biodegradable, biocompatible, and benign. Thin films prepared via a layer-by-layer (LbL) assembly were prepared with cationic CH and anionic montmorillonite (MMT) clay nanoplatelets. Thin-film assemblies prepared with CH at high pH are thicker, because if the low polymer charge density. A 30-bilayer nanocoating (~100 nm thick) reduces the oxygen permeability of a 0.5-mm-thick polylactic acid film by four orders of magnitude. Trilayer assemblies of CH/MMT/ carrageenan (CR) reduced the oxygen permeability of 179 um PET film by an order of magnitude with a thickness of just 40 nm. In an effort to create an environmentally-friendly flame retardant, ten bilayers of pH 6 chitosan (CH), as the cationic layer, and pH 10 montmorillonite (MMT) as the anionic layer, were deposited on flexible polyurethane foam (30 nm thick and added 4 wt%). When cut open after direct flame from a propane torch for 10 seconds, white undamaged foam was revealed under a thin black char layer. In related work on fabric, layers of chitosan and phytic acid rendered cotton self-extinguishing in a vertical flame test. Micro combustion calorimetry confirmed that all coated fabric reduces peak heat release rate (pkHRR) by at least 50% relative to the uncoated control. Fabric coated with pH 4 solutions shows the greatest reduction in pkHRR and total heat release of 60% and 76%, respectively. This superior performance is believed to be due to high phosphorus content that enhances the intumescent behavior of these nanocoatings. These environmentally-benign nanocoatings are useful for food packaging or as a replacement for environmentally persistent antiflammable compounds.

Polyurethane foam, coated with 30 nm of CH/MMT, after exposure to butane torch for 10 s.
Performance enhancing additives combined with protein-hybrid adhesives

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It has been well documented in the scientific literature that the incorporation of nanoclays into a polymer matrix produces enhancements in moisture resistance, physical properties, thermal distortion temperature, and rheological and processing properties. In this work we have incorporate exfoliated (or partially exfoliated) nanoclays, which have been exfoliated in an oil carrier, into aqueous protein dispersions that have the unique ability to disperse hydrophobic materials. These nanoclay/protein dispersions are then co-dispersed and cross-linked with PMDI. Data will be presented which shows that these unique water-based dispersion of pre-exfoliated montmorillonite/oil amalgams yield stable 2-part cross-linkable adhesives with enhanced properties for use as wood composites adhesives.

Comparative studies on miscibility and intermolecular interaction for cellulose ester blends with vinyl copolymers

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Polymer blending is practically useful to control the physical properties and functions of conventional cellulosics, readily at the lowest cost. This presentation surveys our studies on blends of cellulose esters (CEs), mainly cellulose acetate (CA), propionate (CP), and butyrate (CB), with vinyl copolymers containing an N-vinyl pyrrolidone (VP) unit. On the basis of thermal analysis data, a miscibility map for the respective blend systems was constructed as a function of the degree of ester substitution (DS) and copolymer composition. We summarize four factors contributory to the miscibility attainment of the CE/vinyl copolymer series explored. Attractive and repulsive interactivities between the CE and synthetic polymer constituents are quantitatively discussed, in terms of specific interaction parameters determined by solution viscometry. In addition to the basic characterization, some useful applications of the cellulosic blends to functional films are demonstrated. Especially, we highlight the molecular orientation and optical anisotropy in drawn films of some miscible CE/vinyl copolymer blends; the birefringence is widely controllable in both the degree and polarity.

Sustainable polymeric materials via strategic assemblies of renewable platform chemicals

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Thermoplastic and thermosetting materials are used in a wide array of applications, unfortunately many of the polymeric materials currently in use are derived from petroleum. Continued use of these materials will become increasingly expensive due to the dwindling petroleum reserves as time goes on. The need for viable alternatives feedstocks has driven the bio-refining industry to search for fuels and platform chemicals derived from abundant renewable resources such as lignocellulosics, agricultural wastes, and aquatic matter. A number of unique cyclic structures exists in these renewable resources that, thus far, shown promise for the development of novel polymeric materials that possess properties similar to those
found in the current marketplace. Work in our laboratories has focused on the development of new monomers and resins for sustainably developed high performance thermosetting and thermoplastic polymers. We present our Investigations that have primarily focused on the modification of lignocellulosic-derived platform chemicals into monomers and resins for high-performance polymeric materials applications.

Cellulose Structure & Biosynthesis
N. Carpita, Organizer; H. M. ONeill, Organizer; P. Langan, Organizer; D. Cosgrove, Organizer; J. Zimmer, Organizer; M. Doblin, Presiding; N. Carpita, Presiding Papers 269-276

CELL 269

Characterization of Arabidopsis CSLD cell wall synthase activities both in vitro and in vivo

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Plant cell expansion is governed by the deposition of new cell wall components, and cellulose microfibrils, the major load bearing components in plant cell walls, are deposited along one or more entire faces of a cell during diffuse growth. However, during tip growth, newly synthesized cell wall polysaccharides are deposited in a restricted region. Previously we have shown that the cellulose synthase-like D family protein, CSLD3, localizes to the tips of growing root hairs and provides essential cell wall synthase activity during root hair tip growth, and that fluorescently-tagged CSLD2/3/5 proteins localize to newly-forming cell plates in dividing cells. These results indicate that, in addition to their roles in cell wall deposition in tip-growing cells, CSLD proteins also provide essential cell wall synthase activity in cells undergoing cytokinesis. In both tip-growing cells and dividing cells, new cell wall deposition occurs in a highly polarized manner; either at the apex of the growing hair, or at the leading edge of the newly-forming cell plate. That CSLD proteins selectively localize to both these cellular regions may indicate that the cell wall polysaccharides synthesized by this class of cell wall synthases play important structural roles in these specialized zones of cell wall deposition. But what is the nature of the polysaccharide synthesized by CSLD proteins? We previously demonstrated that a chimeric CSLD3 protein containing the CESA6 catalytic domain rescues root hair defects observed in csld3 mutants, suggesting CSLD proteins may be glucan synthases. However, CSLDs have also been reported to have mannan synthase activities. In order to clarify the identity of the polysaccharides synthesized by CSLD proteins we have expressed CSLD and other plant glycan synthases in S. cerevisiae. CSLD3, CESA6, and CSLA9 were successfully expressed and purified using this heterologous expression system, and CSLD3 and CESA6 expressing microsomal membranes were determined to contain increased beta-(1→4)-glucan synthase activities. CSLD3, CESA6, and CSLA9 proteins were selectively extracted from yeast membranes using various detergents, and structural information regarding these protein complexes will be presented.

CELL 270

Golgi-localized STELLO proteins regulate the assembly and trafficking of cellulose synthase complexes

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Cellulose is produced at the plant plasma membrane by cellulose synthase (CesA) complexes (CSCs), which are assembled in the endomembrane system and trafficked to the plasma membrane. While several proteins that affect CesA activity have been identified, components that regulate CSC assembly and trafficking remain unknown. We have discovered and characterised STELLO1 and 2, Golgi-localized proteins that can interact with the CesAs and that control cellulose quantity. In the absence of STELLO function, the spatial distribution within the Golgi, secretion and activity of the CSCs are impaired indicating a central role of the STELLO proteins in CSC assembly. Point mutations in the predicted catalytic domains of the STELLO proteins indicate that they are glycosyltransferases facing the Golgi lumen. Hence, we have uncovered proteins that regulate CSC assembly in the plant Golgi apparatus.

CELL 271

Sphingolipid glycosylation in plants: Some implications for cellulose biosynthesis

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Glycosylinositol phosphorylceramides (GIPCs) are a class of glycosylated sphingolipids found in plants, fungi and protozoa. They are extremely abundant in the plant plasma membrane, estimated to form ~25-40 % of total lipids, but almost nothing is known about their function. GIPCs consist of a ceramide attached to a glycan headgroup via a phosphate group. Recently we have identified the first two proteins involved in the headgroup biosynthesis - IPUT1 (a glucuronic acid glycosyltransferase) and GONST1 (a GDP-Man transporter). Plants lacking functional copies of these proteins are either pollen lethal (iput1) or have extreme developmental defects (gonst1), despite the lipid portion of the GIPC being unaffected. This implies a critical function for the GIPC glycan headgroup in membrane function. Here, we describe a new Golgi-localized protein involved in GIPC headgroup biosynthesis - GMT1 (GIPC MANNOYLTRANSFERASE1). Plants lacking GMT1 show a phenotype similar to gonst1, including small stature, severe early senescence and poor seed set, as well as a constitutive defense response which is visible from the seedling stage. Heterologous expression of GMT1 in tobacco BY2 cells and yeast resulted in the production of mannosylated "Arabidopsis-like" GIPCs. Further investigation into the cause of the developmental defects showed that whilst the gmt1 cell wall has wild type-like matrix polysaccharides, it has a large reduction in crystalline cellulose, accompanied by an increase in lignin. We will present some possible hypotheses regarding the roles of these mysterious lipids in cellulose biosynthesis and membrane organization.

CELL 272

Functional differences between CESA protein classes

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CESA proteins form the catalytic subunits of the plant cellulose synthase complex. In higher plants, it is well established that three different members of the CESA protein family are required to synthesize cellulose. We have recently shown the CESA proteins are heavily modified by S-acylation and modifying the acylation of Arabidopsis CESA7 protein results in the cellulose synthase complex no longer being integrated into the plasma membrane. However, altering the acylation of CESA4 or CESA8 does not have the same effect, which prompted us to address the question of what determines the differences between
the CESA proteins, also known as CESA protein class-specificity. We have used bioinformatics, mutagenesis and comprehensive domain swaps to examine this question. We find a consistent trend where cellulose synthesis appears to be more sensitive to altering certain CESA classes than others. We will discuss our data in terms of what this might mean for how CESA proteins are organized in the plasma membrane.

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Brassinosteroids regulate cellulose biosynthesis in Arabidopsis thaliana by direct phosphorylation

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Cellulose is the most abundant biopolymer on the planet, and this complex polysaccharide is synthesized at the plasma membrane by large multimeric cellulose synthase complexes (CSCs) containing multiple non-redundant Cellulose Synthase A (CESA) catalytic subunits. Live-cell imaging has revealed that CSCs form motile puncta at the plasma membrane that move with a constant velocity along cortical microtubules, and the velocity of these puncta correlate with cellulose production rates. While the CSC composition is rapidly being elucidated, it is relatively unclear how cellulose biosynthesis is regulated. Large-scale phosphoproteomic surveys indicate that numerous CSC components, including the CESA subunits, are phosphorylated at multiple positions. We synthesized peptides mimicking the unphosphorylated state for each of these phosphorylation events and used these peptides as substrates to identify protein kinases that catalyzed potential CSC-regulating phosphorylation events. These assays identified BRASSINOSTEROID INSENSITIVE 2 (BIN2) kinase as a cognate protein kinase for CESA1. BIN2 phosphorylated a peptide derived from the N-terminus of CESA1, and subsequent phosphorylation site mapping studies identified CESA1 T157 as the BIN2 phosphorylation site. Furthermore, live-cell imaging studies indicated that CSC speeds were reduced in the hypermorphic bin2-1 background, suggesting that BIN2 is a negative regulator of cellulose biosynthesis. Phosphonull mutations in the BIN2 phosphorylation site restored CSC speeds in the bin2-1 background and partially complemented the mutant hypocotyl elongation phenotype. Additionally, CESA1 T157A mutants exhibited increased cell expansion compared to wild-type controls. Overall, these results suggest that BIN2 is a critical negative regulator of cellulose biosynthesis and that CSCs which are insensitive to BIN2 phosphorylation produce more cellulose, suggesting that CSC phosphorylation events can be manipulated for enhanced cellulose production in biomass and forage feedstocks.

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Ultrastructure of spruce secondary wall outer layers

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Due to the complex hierarchical structures of cellulose fibers, a heterogeneous swelling and dissolution can be observed along the fibers (e.g., ballooning effect) in various solvents. Many studies have suggested that the fiber ultrastructure along with solvent quality influence the fiber swelling and dissolution process. However, the ultrastructure of the secondary wall outer layers (i.e., S1 and S12) has not been studied thoroughly because of their small width. We have applied high-resolution cryo-transmission electron tomography for examining the ultrastructure of outer layers of the spruce secondary
wall. The detailed structure of elementary fibrils in native wood cell wall is visualized in three-dimensional electron tomograms. The resolution of the tomograms was further enhanced by computational means. Our observations increase the understanding of the complex organization of cellulose elementary fibrils and their aggregates in these cell wall layers. This knowledge is important in developing better ways to convert lignocellulose biomass into various products, through mechanical, enzymatic and chemical treatments. We believe that the structure of the fibril bundles will significantly contribute to the reactivity of cellulose in biomass.

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Investigating inter-fibrillar distance between crystalline cellulose microfibrils in plant cell walls using sum frequency generation vibrational spectroscopy

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Understanding the mesoscale structure of cellulose microfibrils in plant cell wall is important since cellulose is embedded in a matrix of polymers and any attempt to isolate cellulose from this polymer matrix could alter the orientation and packing of cellulose microfibrils. To circumvent the complications induced by the interference of matrix polymers, sum frequency generation vibrational spectroscopy (SFG-VS) was proposed as a nondestructive technique which can selectively probe crystalline cellulose in plant cell wall. To have a better understanding of how changing in cellulose packing can be detected by SFG, model samples with varying inter-crystallite distances were prepared. The SFG spectra show that when uniaxially aligned cellulose crystals, with no preferred polarity orientation, get closer to each other, the SFG peaks in the CH\textsubscript{2} stretch region get stronger substantially while the peaks in OH stretch region exhibit only minor changes. As cellulose crystals get closer to each other, the symmetry cancellation effect on OH dipoles among crystallites with opposite polarities gets larger, and this compensates the increase in the number of crystals per probing area. Therefore, the sum of these two opposite trends results in negligible changes in OH intensity. Using the outcome of this work, valuable information regarding the mesoscale packing and orientation of cellulose microfibrils in plant cell wall can be obtained.

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Bacterial cellulose: Self-assembly and reformatting

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Bacterial cellulose is an exopolysaccharide produced by various species of bacteria, with \textit{Gluconacetobacter xylinus} being the model organism to decipher the biosynthesis of cellulose. It has potential applications in food, pharmaceutical, and cosmetic industries due to its unique structure and mechanical property. The cellulose produced by bacteria is of high purity and crystallinity compared to those isolated from wood pulp due to the absence of lignin and hemicellulose. In this study, we examine the self-assembly mechanisms and microstructures of bacterial cellulose. Never-dried native bacterial cellulose produced from two \textit{Gluconacetobacter} species are disintegrated into individual fibres through TEMPO-mediated oxidation and mechanical treatment, obtaining transparent and viscous suspension. Although the main oxidant is NaClO, we find that mechanical treatment (ultrasonication) plays an important role in the disintegration process of the bacterial cellulose. The morphology of the disintegrated fibrils are observed by SEM and the crystallinity of the disintegrated fibers are analysed by XRD. The organic functional groups of the cellulose fibres are characterized in dry state and wet condition by FTIR and RAMAN, respectively. The birefringence of the fibre suspension is also investigated under polarizing
microscope. The oxidized cellulose fibres are expected to have physical interaction with metal ions. We will study this interaction in respect of forming conductive cellulose complexation. We further develop a method to synthesize bacterial cellulose hollow microparticles which is challenging to achieve using conventional methods. The reformatted bacterial cellulose has been shown to improve wound healing.

**Developments in the Fields of Celluloses & Lignocelluloses: In honor of Dr. Rajai Atalla**
U. P. Agarwal, Organizer; T. J. Elder, Organizer; A. Isogai, Organizer; T. Larsson, Organizer; A. D. French, Presiding; T. Rosenau, Presiding Papers 277-284

**CELL 277**

**Evolving models of lignocellulose structure: Do we need a plant cell wall interactome**

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There are more than one half-million published studies of cellulose, lignocellulose, or plant cell walls and the techniques employed range in scale from the submicroscopic to hectare scale. As shown by the decades-long debates over cellulose ‘structure’ or even limited to its crystalline structure, a fundamental problem is the evolution and frequent acceptance of models, which are derived from interpretation of data sets resulting from a single technique. Such models might be based upon crystallographic, enzymatic, spectroscopic, computational modeling, or other data, but a common thread is a tendency to over-interpret and extrapolate the limited data acquired by the investigators and ignore the wealth of data generated by studies using other techniques. Ideally, a single model consistent with all valid data should be the goal. A related problem is the use of treatments that alter the material for the sake of acquiring ‘better’ data. Better data for what? Are the models that we derive from this ‘better data’ helpful in understanding the problems that we seek to understand? Here we shall address these questions and look at an alternative approach to models that is attracting considerable attention in areas like molecular biology and its sub-disciplines like proteomics and bioinformatics. As an alternative or supplement, we think that the concept of an ‘interactome’ has merit for the study of plant cells and their cell walls. The goal, probably never fully realized, for any interactome is a complete description of all the interactions within a cell, or some limited area of that cell, such as the primary and secondary walls in woody plants and other dicots or specific cell types in monocots like grasses. At the cellular level, these tissues have many of the properties associated with composite materials. Any realistic, predictive model of cell/system properties must consider the spatial and energetic effects that arise from the interplay between proximate chemically distinct molecules with them.

**CELL 278**

**Chain polarity in polymorphic unit cells of cellulose, amylose, and chitin**

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The polymorphic structures of crystalline carbohydrate polymers such as cellulose, amylose, and chitin have been extensively studied using x-ray and neutron diffractions. However, the chain polarity, especially antiparallel polarity of polymer chains, within the unit cell determined from structural refinements of diffraction data was often challenged. Although spectroscopic techniques such as infrared, Raman, and nuclear magnetic resonance can distinguish the polymorphic differences, they could not provide the definitive answer for chain polarity within the crystalline unit cell. In order to resolve such disputes, we have applied vibrational sum frequency generation (SFG) spectroscopy which is intrinsically sensitive to non-centrosymmetric arrange of molecules in space and confirmed that cellulose II, alpha-
chitin, and V-type amylose have antiparallel arrangement of constituent polymer chains within the crystal unit cell. This talk will explain how such determination is possible with SFG.

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Enzymatic oxidation of carbohydrates: New applications and new paradigms for lignocellulose deconstruction

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With the discovery of the carbohydrate oxidizing enzymes Lytic Polysaccharide Monooxygenases (LPMOs) new dimensions of chemistry and applications of cell wall carbohydrates chemistry has emerged. The enzymes oxidize the glucosidic bonds of both cellulose and hemicelluloses creating oligomers primarily with an aldonic acid end group. LPMOs are widespread among both fungi and bacteria. Their role in biodegradation may be significant, highlighting the role of oxidative degradation also for carbohydrates. There is a strong synergy between LPMOs and cellulases, and the enzymes are an important component in commercial enzyme mixtures for conversion of lignocellulosic biomass to fermentable sugars. The LPMOs require an external electron donor to complete their catalytic cycle. The electron donor can be from a range of electron donating compounds among other lignin and light-excited photosynthetic pigments. Furthermore, the redox potential of the electrons has been found to regulate the activity of LPMOs, as light-excited photosynthetic pigments boosts the activity significantly compared to other known electron donors. In this presentation, the reactions and use of LPMOs for fuels and materials will be described and discussed. Furthermore, the fact the LPMOs interact with both lignin and photosynthetic pigments points toward a new paradigm for how biochemical redox reactions in plants link and connect cell wall structures and organelles which were believed to be separate. Could it be that the redox chemistry of cell wall degradation involves electron transfer reactions between cellulose, chlorophyll and lignin?

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13C NMR method for characterization of partially dissolved cellulose in aqueous media

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Industrial manufacturing of regenerated cellulose fibers relies on an initial step with cellulose dissolution. For environmental and economic reasons, there are current research efforts directed towards developing aqueous media that can dissolve cellulose without excessive chemical degradation. The well-known insolubility of cellulose in pure water can be improved by strong acids or alkali, as well as various additives such as zinc chloride. Rational design of dissolution media requires an understanding of the basic intermolecular forces acting between cellulose, water, and the additives. Contemporary theories emphasize the amphiphilic properties of cellulose, thereby suggesting strategies from surface and colloid science to overcome the insolubility. Critical testing of the theories requires experimental methods that have the capability for molecular-level characterization of cellulose in the solid, solvent swollen, partially dissolved, and completely dissolved states. Here we describe a novel 13C NMR-based approach appropriate for the hitherto rather neglected, but in our opinion critical, intermediate stages of dissolution. By combining features from solid-state and high-resolution liquids NMR, we are able to observe both solid and dissolved cellulose, as well as all organic additives, and even impurities and degradation products, in the native dissolution medium of typically very high viscosity, thereby giving information with sufficient detail to test the theories about the mechanisms for cellulose dissolution.
Disordered structures in plant cellulose microfibrils in terms of leveling-off DP and layer-by-layer surface peeling of microfibrils

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It is well known that cellulose microfibrils of plant cell-walls have disordered regions periodically present along each cellulose microfibril, which have been indirectly shown from the leveling-off degrees of polymerization (DP, 200-300) obtained from such cellulosics by dilute acid hydrolysis. However, it is unknown whether such disordered regions are originally present in nascent cellulose microfibrils formed by biosynthesis process or artificially formed during delignification and/or drying processes. In this paper, disordered regions of plant cellulose microfibrils are studied in terms of two aspects. One is dilute acid hydrolysis of wood meals, de-waxed wood meals, wood holocellulose and wood cellulosics for dried or never-dried samples, to study the conditions to form the leveling-off DPs and to determine DP values after dilute acid hydrolysis. The results showed that the leveling-off DPs varied, depending on the delignification and drying processes, indicating that such leveling-off DPs are formed artificially during pulping and drying processes. The presence of glucomannan was also the key factor to form the leveling-off DPs in the case of softwood cellulose. Another method was a layer-by-layer peeling of surface cellulose microfibrils, in which glucoronate units were densely and position-selectively formed on the microfibril surfaces by TEMPO-mediated oxidation. The surface molecules containing both glucose and glucoronate units present on each TEMPO-oxidized cellulose microfibril were removed by alkali treatment at a high temperature. Solid-state $^{13}$C-NMR, X-ray diffraction and AFM analyses were carried out to the layer-by-layer peeled TEMPO-oxidized cellulose samples. The results showed that algal cellulosics with larger cellulose microfibril sizes and higher crystallinities had rather perfect crystallites without any disordered regions on the microfibril surfaces. All the C6-OH groups in microfibril surface molecules, facing outside from the microfibril surface, had g-g conformation, whereas those facing inside the crystallite had g-t conformation. All the C6-OH groups present inside crystallites had t-g conformation. These different C6-OH conformations remained after repeated removal of the surface layers of algal cellulose microfibrils. In contrast, wood cellulose microfibrils indicated to have somewhat disordered structures from two layers from the microfibril surface, probably because of smaller microfibril widths.

Multifunctional cellulose derivatives for surface modification – an innovative nanostructural approach

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The modification of surfaces by different techniques like plasma- and ozone treatment or by chemical reactions forming covalent bonds are important tools to modify the properties of materials for a broad variety of applications. These modifications are connected with different problems; plasma treatment does not give a permanent modification and chemical reactions are hard to control at a surface, e.g., thus, novel approaches are of scientific and commercial interest. Based on our extended knowledge of chemical modification of polysaccharides, multifunctional cellulose derivatives, containing both stimuli-responsive, fluorescence active, or reactive functional groups as well as an amino- or ammonium (cationic) moiety, are advanced biopolymers for surface modification of different materials. Cellulose fibers are of particular interest, i.e., to modify the bulk material with a low amount of such biopolymer derivatives is an efficient and simple way to get advanced pulp fibers. The modification can be done simply in aqueous systems. The novel concept of fiber modification will be discussed based on various examples. Thus, bleached eucalyptus Kraft pulp fibers were modified by adsorption of novel multifunctional cellulose derivatives to generate light responsive surfaces. Cellulose backbone was decorated with both (3-carboxypropyl)-trimethylammonium chloride and photoactive 2-{(4-methyl-2-oxo-
2H-chromen-7-yl)oxy]acetate moieties. The adsorption was proofed by UV-Vis spectroscopy, SPR, and ToF-SIMS. The adsorption isotherms followed the Freundlich model and it turned out that the main driving force for the adsorption appeared due to electrostatic and hydrophobic interactions. The modified fibers underwent fast photo-crosslinking under UV-irradiation, as demonstrated by light absorbance and fluorescence measurements, yielding fibers with an increased mechanical stability.

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Fire protection of cellulose materials, procedures and mechanisms

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In the general strive towards a circular chemistry, wood and fibre-based materials are receiving an ever increasing attention as construction materials. The general nanocellulose hype has also strengthened this trend and new cellulose-based materials are being presented continuously today. As a building block, cellulose has many advantages but one major drawback is the inherent moisture sensitivity and another is the fire propensity of pure cellulose. If the new materials are to be used in for example interior decorations they need to be resistant to fire and the ban on many commonly used fire retardants has increased the need for new treatments of the cellulose to make products from fibres/fibrils fire resistant/retardant. We have been using two different strategies for preparing fire resistant/retardant materials. In the first strategy we have been preparing phosphorylated cellulose nanofibrils (P-CNFs) to be used as fire-retardant building blocks in high density composites and low-density cellular materials. By using high resolution spectroscopic techniques we have been able to establish on which structural level the fibrils have been chemically modified and this has assisted in the understanding of the underlying mechanism for their fire-retardant action. In the second strategy we have been using a layer-by-layer (LbL) technique for modifying macroscopic cellulose fibres with nanometer thin LbL films and been able to create fire resistant/retardant papers. By combining these techniques we have also been able to prepare fire-retardant, thin all-cellulose films by using P-CNF and cationically modified CNF (C-CNF). The fire retardancy has been evaluated by horizontal flame tests, flame penetration tests and cone calorimetry and the mechanisms behind the action of the different have been studied by free-standing films of the active components.

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Use of raman microscopy in elucidating the structure of cellulose

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The Raman microprobe was introduced in the early 1970’s as a molecular analogue to Castaing’s electron microscope. For a variety of reasons it reduced significantly the presence of fluorescence from minor contaminating species that limited the application of Raman spectroscopy to the study of real world materials. For the study of cellulose this was particularly important because in the bulk samples are often intractable. Consequently Professor Atalla was able to take advantage of the technology to study cellulose. Because of the polarization characteristics of the scattering phenomenon it is possible to monitor orientation as well as molecular configuration and crystallinity. In combination with XRD, TEM, electron diffraction, FTIR, Raman has provided information to characterize the state of cellulose which Professor Atalla will certainly review. In this talk, instrumental design characteristics that have potentiated this work will be reviewed. This will include the introduction of multichannel detectors and consequential redesign of the spectrographs to take advantage of the characteristics of the detectors; the result was a significant reduction in the time to acquire spectra. In addition the advantages of confocality in the
microscope optics and a wide selection of laser wavelengths will be described. Finally advances in data
treatment following the introduction of powerful, inexpensive desktop computers will be described. In
recent years tools for statistical analysis of spectra have been developed, and areas where they could
impact cellulose research will be mentioned.

Functional Lignocellulosics & Nanotechnology
M. K. Ek, Organizer; E. Filpponen, Organizer; T. Nypelo, Organizer; S. Peresin, Organizer; S. Spirk, Organizer; S.
Peresin, Presiding; E. Filpponen, Presiding; S. Spirk, Presiding; M. K. Ek, Presiding; T. Nypelo, Presiding Papers
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Nanoscale self-assembling properties of hybrid materials obtained from hemicelluloses oligomers
and fatty acids in polar and non-polar media

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Hybrid conjugates have been obtained by "click chemistry" (azide-alkyne coupling) of well controlled xylo-
oligosaccharides (XOS), obtained by mild hydrolysis of hardwoods xylans, and two model fatty acids,
namely methyl ricinoleate (MeRic) and methyl oleate (MeOl) (Figure 1). Evidences of self-assembling of
the conjugates were firstly obtained by recording NMR in polar (D₂O) or non-polar (CDCl₃). XOS protons
signals were not visible in CDCl₃ spectra, while those of fatty acids were only poorly resolved in D₂O.
Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to point out the
nature and dimensions of objects formed by dissolving the two conjugates (XOS-MeRic and XOS-MeOl)
either in water or chloroform, in different concentrations (from 0.1 to 10 g/L). The results obtained show
that the nature of the self-assembly properties considerably depends on the polarity of the solvent, the
solution concentration and the chemical structure of the fatty acids. Both conjugates form nano-objects
whose dimensions increases with concentration in chloroform (∼700 nm at 0.1 g/L, ∼1500 nm at 1 g/L,
and ∼2500 nm at 10 g/L as measured by DLS), clearly demonstrating the formation of aggregates.
However, at 1 g/L the combined use of TEM and DLS allows observing that the size and populations of
the objects depends on the fatty acid moiety. XOS-Ol presents important concentration of aggregates.
After the elimination of these later over a 0.45 µm filter, regular objects of diameter between 40 and 90
nm are observed. For XOS-MeRic, no differences were observed before and after filtering. Spherical
nanoparticles of around 30 nm diameter were evidenced by TEM. In water, XOS-Ol also form aggregates.
After filtering, poorly controlled particles measuring around 30 nm diameter were obtained, whereas for
XOS-MeRic, very well controlled spherical nanoparticles of 30 nm diameter were evidenced by TEM
before and after filtering. An overview of the different objects obtained from the two different conjugates in
both polar and non-polar solvents is also presented in Figure 1. These observations will be useful for the
future different applications (encapsulation, emulsion stabilizers, coatings, etc) envisaged for these hybrid
systems.
Xyloglucan functional block-copolymers: A modular platform for cellulose modification

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The current demand for advanced functional materials from sustainable resources has converged attention to the superior properties of cellulose, emphasizing the cellulose nanofibers currently available at tons’ scale. The utilization of cellulose in advanced material applications can only be realized if efficient and environmentally friendly procedures are developed, enabling the modification of a variety of cellulose surfaces under benign and aqueous conditions. Herein, a modular platform for versatile and multifunctional modification of cellulosic (nano)fibers through a biomimicking approach is presented. The base of the platform is the polysaccharide Xyloglucan (XG), a hemicellulose with an exceptionally high natural affinity for cellulose. Utilizing XG as a macroinitiator, a plethora of block copolymers have been produced by controlled radical polymerization methods, i.e. Reversible Addition Fragmentation chain Transfer (RAFT). In a first part of the project, XG-latex nanoparticles were synthesized in water-borne systems by RAFT-mediated emulsion polymerization of methyl methacrylate (MMA), where the particles formed through Polymer Induced Self-Assembly (PISA). The XG functioned as a MacroRAFT agent and the molecular weight of the hydrophobic PMMA block was varied. The method resulted in highly defined and tailored nanoparticles of XG-co-PMMA, controlled in terms of size and distribution, which were colloidally stable despite the absence of charges. The particles were adsorbed to cellulose model surfaces using Quartz-Crystal Microbalance with Dissipation (QCM-D) which showed that increasing mass of the particles were adsorbed with increasing length of the PMMA block. The particles were also successfully adsorbed to neutral cellulose, i.e. filter paper, and the modified surfaces were analyzed by FT-IR and SEM. In a second part of this work, block copolymers of XG and a zwitterionic polymer, poly(sulfobetaine methacrylate) (PBSA), were synthesized by RAFT. The resulting XG-b-PBSA exhibited an Upper Critical Solution Temperature (UCST) of 20-30 °C. The block-copolymers were adsorbed to cellulose nanofibrils (CNF) both in the QCM-D as well as in water dispersions. CNF composite films was achieved utilizing vacuum filtration and the swelling properties of the films were investigated. These results highlight the advantage of using a XG block for the biomimetic modification of cellulose to form new cellulose composite materials.
Spruce galactoglucomannans stabilize emulsions against physical breakdown and lipid oxidation

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Materials manufacturing industries seek efficient, economic, and sustainable compounds for stabilizing dispersed systems such as emulsions. In this study, abundantly available hemicelluloses, spruce galactoglucomannans, were obtained from forestry biorefinery processes and characterized as versatile novel stabilizers. Aqueous galactoglucomannan solutions were used as the continuous phase of rapeseed oil-in-water emulsions. Oil droplet size distribution, zeta potential, and morphology of emulsions was investigated, the presence of galactoglucomannans at the oil-water interface was determined [1], and the rheological properties of emulsions with varying oil volume fractions were characterized [2]. The visual appearance of the emulsions as well as the droplet size distribution over storage revealed that galactoglucomannans greatly enhanced emulsion formation and efficiently stabilized them against physical breakdown. Galactoglucomannans lowered the surface tension of the oil–water interface and increased the viscosity of the continuous phase, although much less than commercial polymeric stabilizers. The physical emulsion stabilization mechanism of galactoglucomannans was deduced to be steric repulsion assisted by Pickering-type stabilization [1,2]. Furthermore, the oxidative stability of emulsions was evaluated through the formation of hydroperoxides, volatile oxidation products, and polymerized lipids. The free and bound phenolic residues associated with plant polysaccharides were determined to explain the differences in the oxidation pathways of emulsions stabilized with galactoglucomannans [3]. Galactoglucomannans showed an exceptional capacity to inhibit lipid oxidation and act as multifunctional stabilizers, enhancing both the physical and oxidative stability of emulsions. Wood hemicelluloses are versatile and show great potential for use in industrial applications involving colloidal systems and soft materials.

Parametric analysis and mechanism of dispersion of single-walled and multi-walled carbon nanotubes by cellulose nanocrystals

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Carbon nanotubes (CNTs) have been the focus of great interest due to their unique optical, mechanical and electronic properties. These properties give them the ability to be used for many applications in various areas such as material science, electronics and biotechnologies. However, the poor solubility of CNTs in water, due to the hydrophobicity of the carbon surface and the highly attractive van der Waals forces between them, limit their application range. Among the different strategies that can be used to overcome this limitation, non-covalent functionalization appears to be one of the most promising since it makes possible to maintain the optoelectronic properties of CNTs. In a previous paper, we have shown that CNCs can efficiently disperse single-walled carbon nanotubes (SWNTs) in water to form colloidal dispersions that remain stable for months. In this work, we show that multi-walled carbon nanotubes (MWNTs) can be efficiently dispersed in water by CNCs as well. The dispersions are highly stable, showing that irreversible adsorption and high yields are obtained with more than 70 wt% of nanotubes dispersed (either SWNTs or MWNTs). A parametric analysis shows that the sonication time plays a key role in the dispersion process. A minimum power density is required to initiate the dispersion, which is higher for SWNTs than for MWNTs. Conversely, the association between CNCs and nanotubes is faster for MWNTs than for SWNTs. These results can be explained by their different initial state, bundling vs.
entanglement for SWNTs and MWNTs, respectively. AFM images and TEM micrographs show that hybrids between CNCs and nanotubes are formed. We argue that the association between both nano-objects is due to hydrophobic interactions between the hydrophobic (200) crystalline planes of the CNCs and the highly hydrophobic graphitic surface of the nanotubes, leading to the alignment of the CNCs along the tube axis in the CNC/SWNT hybrids. Such an alignment is not observed for CNC/MWNT hybrids. A stoichiometric model is proposed to fit the dependence of the dispersion yield with the initial concentrations of CNCs and nanotubes.

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Exclusive surface modification of cellulose nanopapers by adsorption of polymers from non-aqueous solvents

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Due to the hydrophilic and hygroscopic nature of native cellulose, hydrophobic surface modification is required in several materials applications. For instance, such modification is often seen as a necessity of obtaining even distribution of cellulose within hydrophobic composite matrices. In this work, modification of CNF nanopapers via polymer adsorption from non-aqueous solvents is introduced as a straightforward method for tuning the wettability of the cellulose surface. Whereas polysaccharide adsorption from aqueous solutions is a well-established route for cellulose surface modification, adsorption of hydrophobic polymer from non-aqueous solvent has been hardly investigated. It is shown that the level of surface modification is affected by the choice of polymer, its concentration in solution as well as the solvent quality. Unlike cellulose surface modification by polymer grafting typically utilized for composites, the presented modification method affects the surface only, allowing the high strength of the native nanofibrillar network within the nanopapers to remain intact.

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New insights on the effects of chemical structure on the properties of cellulose nanofibrils: Characterization, mechanical performance and barrier properties

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The interest in cellulose nanofibrils (CNFs) has increased significantly over the past decades and emanates from features such as high abundance, high mechanical strength, intriguing colloidal properties and excellent oxygen barrier properties as films. However, depending on the final application of the CNFs, a tuning of their properties is usually needed. This can be achieved, for example, through specific chemical modification. In this study, water-based modifications strategies have been used to achieve eight differently modified CNFs. The first step of all modifications consisted of a 25% oxidation of the C2–C3 bonds of the cellulose using sodium periodate to form dialdehyde cellulose. After the initial step, three different reactions, and combinations thereof, were used: borohydride reduction, chlorite oxidation or reductive amination. TEMPO oxidation was also used and combined with other modifications (see Figure 1). The use of one single cellulose source in combination with different modification methods facilitates elucidation of the influence of charge, chemical structure and crystallinity on the mechanical and structural properties of films made of each type of CNF. Prior to film preparation by a filtration procedure,
the CNFs were characterized by atomic force microscopy and the films were subsequently characterized in terms of crystallinity, mechanical strength, dynamic mechanical properties and oxygen barrier properties. The results of the characterization show that the properties of the different films vary greatly, emphasizing the importance to know what types of CNFs that are being used and the used pretreatment procedures. Furthermore, this work shows that chemical modification offers a tool to tune properties and expand the potential of modified CNFs in various applications.

Figure 1. Chemical modification procedures and the structure of chemically modified CNFs.

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Tannic acid – A transformative additive when combined with cellulose nanocrystals: From hydrophobic nanoparticles to dried oil powders

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Polyphenols, such as tannic acid, are widely distributed in plant tissues where they are involved in diverse biological functions including structural support, pigmentation, chemical defense, and prevention of radiation damage. The high catechol and gallic acid content of plant polyphenols recently received
attention in the context of nanoparticle surface modification, as catechols are known to strongly bind to
surfaces and are prominent constituents of marine polyphenolic-protein adhesives. Furthermore, tannic
acid is known to form complexes with a wide range of macromolecules including carbohydrates, proteins,
enzymes and other synthetic polymers. This work presents two examples of the synergistic interactions
between tannic acid and cellulose nanocrystals (CNCs): 1. Hydrophobic modification of CNCs – CNCs
are promising renewable nanoparticles with unique mechanical properties, however, the major challenge
limiting the design of commercial products is the inability to disperse them in non-polar materials (both
liquids and solids) due to the innate hydrophilicity of cellulose. We demonstrate a simple water-based
modification route where a CNC suspension is mixed with tannic acid (the primer) followed by the addition
of alkylamines or alkanethiols (the hydrophobe). Specifically with tannic acid and dodecylamine we
achieve CNCs that are well dispersed in toluene but retain the positive characteristics of CNCs. 2. Dried
and redispersible oil-in-water emulsions – The addition of tannic acid enables the freeze-drying of
Pickering emulsions stabilized by CNCs and water-soluble cellulose derivatives, without emulsion droplet
coalescence or oil leakage. The dried emulsions have oil contents of 94 wt.% and can be readily
redispersed in water with gentle shaking (with the same oil droplet size as before drying). We view this as
a new encapsulation method to protect oils and oil-soluble compounds and believe that these processing
abilities will likely extend the use of these surfactant-free, “green” and potentially edible emulsions to new
food, cosmetic and pharmaceutical applications.

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Cellulose nanoparticles stabilized in a hydrophobic polymer matrix through synthetic
functionalization

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Cellulos nano-materials are sustainable high-strength nanoparticles with potential to enhance the
mechanical properties significantly of polymeric composites. However, due to intrinsic hydrophilicity, it is
necessary to incorporate surface functionalization at the particle-polymer interface to promote dispersion
and bonding at the nanoscale. In this work, amine functionalization is used to form a link between lignin
coated cellulose nanocrystals (CNCs) and polypropylene. Diethylenetriamine (DETA) was combined
with the maleic anhydride polypropylene (MAPP), polypropylene and CNCs in high-shear mixing. MAPP
acts as a compatibilizer between the DETA, cellulose, and polypropylene matrix. The above reactions are
also confirmed using FTIR spectroscopy by observing the conversion of amine groups to amide and imide
groups. The DETA/MAPP treatment lead to stiffened CNC-PP composites with 75% improvements in
elastic modulus over neat PP and untreated CNC-PP composites. The treated composites also improved
tensile strength by 32% over neat PP and by 28% over CNC-PP composites without DETA treatment.
The composites were produced using an organic solvent-free, scalable, high volume manufacturing
approach. Lastly, DETA-treated CNC-PP composites have a lower density than many competitive
systems which will allow for this technology to compete with existing composites used in automotive,
additive manufacturing, construction materials and consumer product applications.
Dissolution and processing of lignocellulose using an ionic liquid solvent: Towards the production of high performance materials

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To date, there is only a limited number of established technologies to dissolve and process cellulose into various shaped products. Typically, an intermediate chemical derivatization is required to render cellulose soluble, with xanthation and the corresponding viscose process being the most widespread. However, this does not allow for the production of composite fibers as other biopolymers such as lignin cannot be solubilized in the same manner. This impedes the formation of homogeneous hybrid products in which various (bio)polymers are evenly embedded in a cellulose matrix. Direct cellulose solvents such as recently promoted ionic liquids can bypass this limitation and offer the possibility to valorize all wood constituents which allows for an alleviation in preceding refining processes. Herein we report the use of 1,5-diazabicyclo[4.3.0]non-5-enium acetate as direct solvent for cellulose, hemicelluloses, and lignin to produce hybrid filaments with excellent mechanical properties. We show that the intensity of pulp refining processes can be decreased drastically due to the high tolerance of the solvent towards different biopolymers. This allows to incorporate lignin and other functionalities into the cellulose matrix. Using a dry-jet wet spinning technique, continuous filaments of high mechanical performance were produced that are suitable for composite materials and could offer a sustainable alternative to currently overly used glass fibers.

Enzymatically produced lignosulfonate based paper coatings for substitution of petroleum based additives

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A process for enzymatic modification of lignosulfonates from the black liquor of a Mg-sulfite pulp mill to substitute oil-based binders like styrene-butadiene (SB) latex in conventional paper coating formulations was developed. Polymerization of lignosulfonates with laccase led up to a 13 fold increase of the molecular weight from an average of 5.5 to 170 kDa as indicated by SEC analysis. Coating formulations were prepared with the resulting enzymatically modified lignosulfonates (2 parts lignosulfonate substitute 1 part SB-latex) leading to rheological properties comparable to conventional latex formulations. The coating formulations were optimized regarding binder penetration using ultrafiltrated lignosulfonate prior to enzymatic modification, which led to a water retention value of 150 to 200 g/m², comparable to reference latex (168g/m²) formulation. Printing properties were determined based on offset suitability to investigate the binding power of modified lignosulfonates compared to latex. This new process demonstrates the potential of renewable resources combined with biotechnical strategies for substitution of petroleum based products.
Surface wrinkling phenomena in spherical lignin nano- and micro-particles obtained by aerosol flow synthesis

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Facilitated by worldwide efforts to further valorize bio-based materials, lignin surface and colloidal behaviors have become subjects of numerous research efforts, which have consequently shed light on their physicochemical properties and drastically expanded their relevance as nanomaterial building blocks. In this presentation, we report on lignin nano- and micro-particles with smooth and wrinkled surface morphologies prepared by using the aerosol flow method that we introduced recently. The morphologies of the lignin particles were characterized by electron tomography, which allowed access to the surface features and to quantitatively analyze their characteristics in terms of spherical harmonic decomposition. Other supporting inquiries include surface roughness and mechanical strength. Together with dynamic light scattering measurements and scanning electron microscopy, we describe the relationship between wrinkling and processing parameters and indicate the prospects for surface functionalization into advanced materials.

Wood waste: Resource of biopolymers and high value materials

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The MDF (Medium Density Fiberboard) fraction of post-consumer wood waste is currently under-utilized. However the annual quantity of MDF waste generated world-wide is estimated to be over 40 millions m³. Currently, there is no viable way to transform MDF into other materials. When MDF is chipped it creates a lot of dust and fibrous particles and these are not suitable for particleboard manufacture. Also, the presence of contaminants (e.g. coatings, paints, varnishes and resins) mixed with wood fibers makes the particles unsuitable for animal bedding and landscape uses. Therefore, the main users of recovered wood do not accept MDF. The research presented here aims at transforming fiberboard waste into valuable materials. Wood contains three major components: cellulose, hemicelluloses and lignin. These biopolymers could be used as raw materials for various applications such as nanocomposites, additives in resins, natural-based hydrogels or building-block polymers. Nevertheless, the presence of contaminants in MDF waste could have a negative impact on the extraction and selling of these value-
added elements. First research was made on the extraction of cellulose nanocrystals (CNC) from MDF wood waste, showing that a multi-step chemical fractionation was able to separate the resin and the other constituents used to make MDF from the wood fibers. This successful extraction led to CNC with a yield of approximately 13%, based on the initial amount of wood in MDF waste. The obtained nanocrystals possess comparable morphological and physical aspects to those recovered from pure wood fibers and have close characteristics, with length and width of 164.7 nm and 6.7 nm respectively, and a crystallinity of 71%. The absence of remaining contaminants in the CNC suspension was confirmed by Transmission Electronic Microscopy, elemental analysis and X-Ray Fluorescence measurements. The second part of the research was the study of the hemicellulosic fraction, which is a co-product of the previous chemical fractionation process. Hemicelluloses consist of a wide variety of monosaccharides arranged in different proportion and with various substituents. These polysaccharides could be used as polymers in the preparation of hydrogels. A graded-ethanol precipitation was applied to the alkali-recovered hemicelluloses in order to evaluate the composition of the different precipitation sub-fractions and choose the most suitable for the preparation of hydrogels.

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Valorization of lignin and cellulose in acid-steam-exploded corn stover by a moderate alkaline ethanol post-treatment based on an integrated biorefinery concept

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Due to the unsustainable consumption of fossil resources, great efforts have been made to convert lignocellulose into bioethanol and commodity organic compounds through biological methods. The conversion of cellulose is impeded by the compactness of plant cell wall matrix and crystalline structure of the native cellulose. Therefore, appropriate pretreatment and even post-treatment are indispensable to overcome this problem. Additionally, an adequate utilization of coproduct lignin will be important for improving the economic viability of modern biorefinery industries. The effectiveness of moderate alkaline ethanol post-treatment on the bioconversion efficiency of cellulose in the acid-steam-exploded corn stover was investigated in this study. Results showed that an increase of the alcoholic sodium hydroxide (NaOH) concentration from 0.05 to 4% led to a decrease in the lignin content in the post-treated samples from 32.8 to 10.7%, while the cellulose digestibility consequently increased. The cellulose conversion of the 4% alcoholic NaOH integrally treated corn stover reached up to 99.3% after 72 h, which was significantly higher than that of the acid steam exploded corn stover without post-treatment (57.3%). In addition to the decrease in lignin content, an expansion of cellulose I lattice induced by the 4% alcoholic NaOH post-treatment played a significant role in promoting the enzymatic hydrolysis of corn stover. More importantly, the lignin fraction (AL) released during the 4% alcoholic NaOH post-treatment and the lignin-rich residue (EHR) remained after the enzymatic hydrolysis of the 4% alcoholic NaOH post-treated acid-steam-exploded corn stover were employed to synthesize lignin-phenol-formaldehyde (LPF) resins. The plywood prepared with the resins exhibit satisfactory performances. An alkaline ethanol system with an appropriate NaOH concentration could improve the removal of lignin and modification of the crystalline structure of cellulose in acid-steam-exploded corn stover, and consequently significantly improve the conversion of cellulose through enzymatic hydrolysis for biofuel production. The lignin fractions obtained as byproducts could be applied in high performance LPF resin preparation. The proposed model for the integral valorization of corn stover in this study is worth of popularization.

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Functional materials from spruce hemicelluloses: Crosslinkable xylans and glucomannans

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Key characteristics such as renewability, abundance, biodegradability, relative ease for modification and their inherent physical and chemical properties make hemicelluloses suitable polysaccharides for development of new materials. Glucomannans and galactoglucomannans are the main hemicelluloses found in softwoods (up to 23 wt. %), while xylans represent up to 10 wt. %. The current biorefinery processes separate hemicelluloses as side-streams, making them a resource ready for new material applications. In this research we functionalize hemicelluloses, isolated from spruce, via esterification with acryloyl chloride and succinic anhydride. Acryloyl chloride enables the introduction of vinyl groups that can be used for free radical polymerization of vinyl monomers, (i.e. acrylic acid, methyl methacrylate, HEMA, etc.), capable to create cross-linked three-dimensional networks. Succinylated hemicelluloses are versatile materials that can be tailored for several applications, such as metal binding and formation of interpenetrating networks with other hydrophilic polymers, which can be used as binders, thickeners in food, disintegrants in excipients and coatings in paper. Glucomannans were succinylated and characterized regarding the degree of substitution and film forming ability. Further conjugation with tyramine allows fast enzymatic crosslinking.

**CELL 299**

**Cellulose-Reinforced carbon fiber/graphene nanocomposites for PEM fuel cell electrode**

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In our study graphene-based nanocomposites have been proposed as the electrode structure for green and renewable energy production systems such as fuel cells. Polymer electrolyte membrane (PEM) fuel cell is very promising due to its pollution free by products that are heat and water. PEM fuel cell electrodes consist of two main layers as gas diffusion layer (GDL) and catalyst layer (CL). Today, the most used GDL layer is the carbon paper since carbon paper provides higher porosity for oxygen transport while preventing the water accumulation that results in higher lower oxygen concentration on the CL. In the tradition of the carbon paper fabrication, it is necessary to have carbonization and graphitization processes that require high temperatures (up to 2500°C) and toxic phenolic resins as binder. Among the reported methods to overcome the mentioned issues, paper wet-laying was shown to be more eco-friendly, easy to handle, and cost effective in comparison with conventional approaches. During wet-laying process, aqueous slurry of chopped carbon fiber (CF)/cellulose microfibers was prepared by vigorous mixing, followed by paper preparation via a commercial paper sheet molding colum. Following the spraying of the graphene nanoparticle dispersion in iso-propanol on the prepared papers to improve the electrical conductivity, the insulating cell binder was removed via phase inversion process using an ionic liquid solution, providing an electrically conducting substrate. The effect of phase inversion treatment on the morphological, mechanical, and electrical conductivity properties of samples was studied via scanning electron microscopy, universal testing machine, and 4-point probe conductivity analysis devices, respectively. By using this method, the preparation cost and production of hazardous byproducts were minimized and a robust conducting composite layer was formed that can be used for fuel cell applications.
Olefin cross-metathesis: Mild, efficient and modular pathway to a new world of polysaccharide derivatives for drug delivery applications

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Water solubility is a key parameter for oral drug delivery: 40% of the top 200 oral drugs marketed in US and 90% of new chemical entities suffer from poor aqueous solubility. Amorphous solid dispersion (ASD) is an effective formulation for improving water solubility and bioavailability of crystalline drugs by creating a truly miscible dispersion of polymer and drug. The concentration of drugs dissolved within the dispersion can thus be substantial, and the energy barrier for drug dissolution can thereby be overcome. However, current polymers for ASD applications (e.g. HPMCAS) are not designed for this particular purpose and development of new drug formulations with high drug loading largely depends on the innovation of polymeric materials. Olefin cross-metathesis (CM) has been proven a powerful tool for modification of polysaccharides including cellulose esters and ethers. This mild and modular reaction has offered a broad collection of polysaccharide derivatives with various functionalities including carboxylic acid, different esters and amides, enabling promising candidates for applications like ASDs. In this work, we will present a tandem olefin CM/thiol-Michael addition modification of cellulosic polymers, leading to products with a series of diverse structures. We will also demonstrate the versatility of this "clickable" chemistry by showing CM conjugation of polysaccharides with bile salts and cholesterol derivatives. These conjugates are promising amphiphilic polymers for ASD matrices and P-glycoprotein inhibition. Successful conjugation of bile salts onto a cellulose backbone validates the concept of CM as a useful strategy for complicated polysaccharide conjugates, and its potential use for prodrug synthesis.
Overview of TEMPO-mediated oxidation of polysaccharides

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TEMPO-mediated oxidation is a unique and characteristic reaction for polysaccharides. The C6-primary hydroxyl groups of polysaccharides are almost selectively oxidized to C6-carboxylate groups in aqueous media. In our laboratory, TEMPO-mediated oxidation of various polysaccharides has been studied, and chemical and crystalline structures of the oxidized polysaccharides were studied in terms of oxidation conditions. When regenerated, mercerized and ball-milled native celluloses are subjected to TEMPO/NaBr/NaClO oxidation in water at pH 10 under suitable conditions, beta-1,4-linked polyglucuronate Na salts (CUAs) are obtained as water-soluble polymers through complete oxidation of C6-OH groups to sodium C6-carboxylate groups. Even though CUAs are artificially prepared, they are degraded to low-molecular-weight compounds by a lyase-type enzyme present in commercial crude cellulases. These results indicate that there may be a pathway in nature to degrade crystalline and stable native celluloses; they are first oxidized at the C6-OH groups by some C6-oxidation enzymes to add hydrophilic nature to native celluloses followed by the above-mentioned enzymatic degradation. When native celluloses with cellulose I crystal structures are subjected to TEMPO-mediated oxidation, the original fibrous morphologies remain even after harsh oxidation conditions. For example, the carboxylate content significantly increases from 0.01 to 1.70 mmol/g, when softwood bleached kraft pulp is used as a starting material and oxidized under suitable conditions. The original cellulose I crystal structure,
crystallinity and crystal size are unchanged before and after the oxidation, showing that such a large amount of C6-carboxylate groups are formed position-selectively and densely on the cellulose microfibril surfaces. When the fibrous TEMPO-oxidized celluloses (TOCs) prepared from wood celluloses with carboxylate contents of >1 mmol/g are mechanically disintegrated in water, highly viscous and transparent gels are obtained. The gels consist of individually dispersed TEMPO-oxidized cellulose nanofibrils (TOCNs) with homogeneous ~3 nm widths and high aspect ratios of >100. The TOCN elements have high Young’s moduli and tensile strengths, and form self-assembled structures in water. These characteristic nature of TOCNs results in unique mechanical, optical, thermal, gas-barrier and other properties of TOCN films and fibers, TOCN-containing composites, TOCN hydrogels and TOCN aerogels.

CELL 302

Synthesis, properties, and applications of cellulosic diblock copolymers

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Diblock copolymers have received considerable attention because of their micro-phase separation behavior in solid phase and self-assembly to form nano objects in solutions. We have prepared cellulosic diblock copolymers with regioselective functionalization patterns. Aqueous solutions of diblock methylcellulose and its analogues have exhibited lower critical solution temperature (LCST) under body temperature, thereby forming thermo-responsive hydrogels. We found that ribbon-like supramolecular nanostructures played critical roles in the formation of thermo-responsive hydrogels. The talk will include a versatile pathway to end-functionalized cellulose ethers, their solution properties, and some applications of the thermo-responsive hydrogels.

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Self-healing materials from cellulose

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Remendable materials were synthesized by thermoreversible crosslinking of a cellulosic diene with a flexible bis-dienophile by Diels-Alder (DA) reaction. Hydroxyethylcellulose was reacted with both furoyl chloride and acetic anhydride, leading to a processible polymer with pending furane substituents. Crosslinking of the cellulose derivatives was achieved by heating with 1,6-bis(N-maleimido)hexane to 80°C to initiate the [2+4]-cycloaddition. Further heating to higher temperatures (120°C) gave rise to the back reaction, called retro-DA reaction. Thermo-cycling between 120° and 80°C allows self-healing of these cellulosic materials. Remendable crosslinked cellulosic materials were als synthesized by RAFT copolymerization of ethyl acrylate M with small amounts of a thermolabile bis-methacrylate DA-X starting from a cellulosic chain transfer agent (Cell-I) as shown in the Scheme. The cellulose derivative Cell-I was obtained through esterification of commercial hydroxpropyl cellulose with a trithiocarbonate equipped with a reactive carboxylate group. The thermolabile bis-methacrylate crosslinker DA-X was synthesized through esterification of the Diels-Alder-dimer of furfuryl alcohol and hydroxyethyl maleimide with methacrylic anhydride. The resulting cellulosic material indeed showed thermo-reversible Diels-Alder reaction as demonstrated by IR-spectroscopy.
Polysaccharides are highly potential renewable resources for several applications. Modifications, affecting the structure of polysaccharides are used to improve functionality and applicability. Enzymes are useful sustainable and specific biocatalyst for targeted polysaccharide modifications. We have recently developed a technique for aerogel preparation of galactose containing polysaccharides applying enzyme-mediated crosslinking with galactose oxidase. Galactose oxidase uses molecular oxygen as the electron acceptor, and catalyzes the oxidation of primary C6 hydroxyl group in terminal galactosyl residues of polysaccharides to a corresponding aldehyde. The reactive carbonyl functionality obtained induces hemiacetal crosslinking between the polysaccharide chains resulting in hydrogel formation. Lightweight and stiff aerogels were further obtained by lyophilizing the hydrogels. The morphology and load-bearing properties could be tailored by freezing technique. Stiffness of aerogels was further increased by the addition of nanofibrillated cellulose prior to oxidation and gel formation to ensure its even distribution in the matrix. We have also looked other enzyme mediated oxidation techniques to create functional aldehydes in polysaccharides with no terminal galactosyl residues. TEMPO is a well-known mediator used in the selective oxidation of primary hydroxyl groups of carbohydrates. Laccase enzyme can regenerate TEMPO and in mild and slightly acidic reaction conditions, the TEMPO/laccase -catalyzed oxidation produced primary aldehyde derivatives and hydrogels were formed from several polysaccharides. Arabinoxylan-based aerogels, which showed high mechanical strength and interesting morphology, were produced successfully for the first time applying TEMPO/laccase system.
pattern. Glycosynthases are mutant retaining glycoside hydrolases (GH) in which the catalytic nucleophile has been removed rendering an inactive hydrolase but able to catalyze transglycosylation reactions from activated glycosyl donors with opposite anomic configuration to that of the natural substrate of the parental hydrolase.\textsuperscript{1,2} We here report on the application of the glycosynthase technology to the preparation of artificial polysaccharides by enzymatic self-condensation of simple glycosyl donors leading to polymers with defined structure. The methodology is applied to the preparation of mixed-linked \(\beta\)-glucans with regular distributions of \(\beta\)-1,3 and \(\beta\)-1,4 linkages,\textsuperscript{3,4} modified cellulosics with regular functionalization pattern\textsuperscript{5}, and chitosan analogues with defined patterns of acetylation. Key aspects to be discussed are: 1) the control of the degree of polymerization which is dependent on the ratio between the rate of enzyme-catalyzed polymerization and the rate of product precipitation, and 2) the introduction of modified glycosyl donors in the glycosynthase-catalyzed polymerization which will lead to functionalized polysaccharides with a regular pattern of derivatization.

**CELL 306**

**Design and control in polysaccharide chemistry**

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Natural polysaccharides are remarkably abundant and diverse, renewable, and typically are benign. Their diversity of structure leads directly to enormous diversity of function, from hydrogel formers, to composite reinforcement, to energy storage, to adhesion, communication, and exquisitely selective interactions with proteins to drive natural processes. Our understanding of how they work, how their structures are controlled, and how we can modify them lags badly however, and in part for those reasons they are overall quite poorly utilized vs. fossil fuel based polymers. We will discuss the work in our lab directed towards key issues in polysaccharide chemistry that are intended to enhance that utilization, including control of chemo-, regio-, and sequence-selectivity of polysaccharide derivatives. We will also discuss our work on new chemistries for modification of polysaccharides, and our work to exploit those chemistries to design polysaccharide derivatives for high performance in demanding applications such as drug oral bioavailability enhancement, protein delivery, thermoplastics, and others.

**Processing & Properties of Biobased Composites & Blends**

J. R. Barone, Organizer; P. R. Navard, Organizer; J. R. Barone, Presiding; J. Bras, Presiding Papers 307-312

**CELL 307**

**Comparison of biobased multiphase systems based on different thermoplastic polysaccharides (starch, chitosan and alginate) obtained by thermomechanical mixing**

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In the last 20 years, our team has developed a large range of innovative multiphase systems based on different plasticized polysaccharides (aka “thermoplastic polysaccharides”) using conventional plastic processing techniques such as extrusion or injection molding .... In this long story, starch has been the first carbohydrate to be deeply studied through different elaboration protocols, and multiphase systems such as blends, composites or nanocomposites. Corresponding physico-chemical, physical, mechanical properties and behaviors have been fully analyzed [1-3]. During the last decade, we have been the first team (as far as we know) to report the elaboration of thermoplastic chitosan by thermo-mechanical mixing [4-5]. Very recently, to the best of our knowledge, we have also been the first team to publish on the
elaboration and the behavior of thermoplastic alginates obtained by thermo-mechanical input [6-7]. This talk will be a brief overview of these different systems. Since these polysaccharides-based systems present some clear similarities and some differentiations concerning their elaborations and their respective properties, these last elements will be more particularly highlighted.

CELL 308

Melt processing of functional protein/polymer blends

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Biopharmaceuticals are the main growth area in pharmaceutical research and development and, most often, proteins are the active pharmaceutical ingredient. Recombinant protein production can be inexpensively scaled to multi-kilogram scales with the rapidly improving molecular biotechnology field. One technological hurdle, however, is the formulation of functional proteins into therapeutic reservoirs, also known as depots. Solvent based processes lose significant portions of the therapeutic protein (up to 70%) and proteins may lose potency due to processing conditions. This talk will describe melt-processing of several protein candidates and the effect on macromolecular structure and enzymatic activity of the processed proteins. Melt processing is exceptional scalable, with commercial extruders reaching throughputs of 1000 kg h⁻¹ and 100% of the active protein is encapsulated. Melt processing is thought to be possible because of the reduced hydration state in the melt, thus eliminating the driving force to form amorphous protein aggregates. The primary focus of this seminar will be a discussion of virus like nanoparticles (VLPs) derived from bacteriophage Qβ. Qβ is a combinatorial vaccine platform that has seen success in vaccine development for influenza, HIV, and hypertension. Melt processing conditions, physical models of processing, and biological data will be described in which Qβ is processed into slow-release depot delivery formulations.

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Compression molded composites from waste polyester and cotton textiles

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Composites were developed from waste polyester and cotton textiles. Plasticization effectively reduced processing temperature and improved mechanical properties of composites. Every year, substantial quantities of textile wastes are disposed into landfills over the world, leading to environmental problems and waste of valuable materials. Recycling and reuse of textiles especially those containing colored non-degradable PET textiles remain technologically and economically challenging. In this research, composites of polyester and cotton were developed from waste polyester and cotton textiles. Effects of plasticization on compression molding process and mechanical properties of the composites were investigated. With plasticization, melting temperature of polyester was reduced by up to 20 °C, leading to decreased processing temperature and improved mechanical properties of relevant polyester/cotton composites. Degree of polymerization, morphology and other properties of cotton after processed at different temperatures were analyzed and correlated with the performance properties of composites. It could be predicted that, waste cotton and polyester textiles might be effectively reused via compression molding with plasticization.
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Crucial role of processing regimes and compatibilization for toughening highly lignin filled polyethylene blends

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Although efforts have been reinforced on an industrial scale to isolate lignin from the cooking liquors accruing in the pulping industry, mass applications of Kraft lignin not utilizing its caloric value are still sought. One possibility in this respect might be the use of lignin as a filler in commodity thermoplastics creating partially bio-based and inexpensive commodity polymer blends. In the present paper suchlike blends from softwood Kraft lignin and high density polyethylene (PE) with lignin loads up to 70 wt% will be presented. Both kneader and twin-screw extruder techniques have been employed under various processing regimes to produce the blends and testing the mechanical properties after injection molding. It turned out that (i) good interface adhesion generated by the use of a coupling agent (maleic anhydride grafted PE), (ii) spherical lignin phase morphology and (iii) fine lignin spheres below 1 micrometer in diameter, are all beneficial for the blend mechanical properties, the latter two points implemented by appropriate compounding conditions. Under these an increase in tensile strength and modulus is noticed with increasing lignin content from 25 MPa and 1.2 GPa of pure PE to 35 MPa and 2.6 GPa for the 70 % lignin blend, respectively. The most striking result is the improvement (compared to pure PE) of the impact properties for 50 % lignin blends. Values as high as 8 kJ/m² (compared to 6.4 kJ/m² for PE) were found for the notched Charpy impact strength and no break in the un-notched test. Obviously, lignin is more than a simple filler if appropriate compounding conditions and coupling mechanisms are observed. Envisaged applications of this inexpensive partially bio-based polymer blend could be in the building and construction sector or other outdoor uses in agrí- or horticulture.

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Morphological and structural investigation of cellulose I and II nanocrystals

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Cellulose nanocrystals (CNCs) have been produced from eucalyptus wood pulp using three different methods: (i) classical sulfuric acid hydrolysis (CN-I), (ii) acid hydrolysis of cellulose previously mercerized by alkaline treatment (MCN-II), and (iii) solubilization of cellulose in sulfuric acid and subsequent recrystallization in water (RCN-II). The three types of CNCs exhibited different morphologies and crystalline structures that were characterized using complementary imaging, diffraction and spectroscopic techniques. CN-I corresponded to the type I allomorph of cellulose while MCN-II and RCN-II corresponded to cellulose II. CN-I and MCN-II CNCs were acicular particles composed of a few laterally-bound elementary crystallites. In both cases, the cellulose chains were oriented parallel to the long axis of the particle, although they were parallel in CN-I and antiparallel in MCN-II. RCN-II particles exhibited a slightly tortuous ribbon-like shape and it was shown that the chains lay perpendicular to the particle long axis and parallel to their basal plane. The reinforcing effect of these nanoparticles in a polymeric matrix was investigated.
Thin ply bacterial cellulose-reinforced polylactide nanocomposites

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Cellulose is the most abundant polymer on earth and can be found in plants or animals but is also produced by the *Komagataeibacter* strain of bacteria in the form of a wet reticulated nanofibre network called bacterial cellulose. With an estimated tensile modulus and strength of 114 GPa and 1.6-3 GPa respectively, cellulose nanofibres, represent a high potential green alternative to conventional polymer reinforcement such as glass fibres. The use of the hydrogen bonding ability of cellulose nanofibres to form strong dense fibrous networks (nanopapers) is essential to manufacture high fibre loading fractions (>30 vol.-%) polymer composites capable of rivalling commercial plastic materials. Achieving impregnation of the nanopaper by the matrix is a critical step in utilising the single cellulose nano-fiber tensile properties. In order to improve the network impregnation, we investigate in this study the use of low grammage bacterial cellulose nanopapers to produce BC-reinforced polylactide composites.

Bacterial cellulose (BC) nanopaper-reinforced polylactide laminated composites containing 50 g m\(^{-2}\) of BC nanopapers were produced using 10, 5, 2 and 1 layer(s) of 5 g m\(^{-2}\), 10 g m\(^{-2}\), 25 g m\(^{-2}\) and 50 g m\(^{-2}\) BC nanopapers, respectively. The filtration of the 5 g m\(^{-2}\) nanopaper was found to be 3 times faster than for the 50 g m\(^{-2}\) and lead to networks with a high porosity (78%). Tensile properties of the nanopapers were found to decrease with lower grammages resulting in the 5 g m\(^{-2}\) BC nanopapers possessing the lowest tensile modulus and strength, at 2.4 GPa and 30 MPa respectively. The composite containing 10 layers of 5 g m\(^{-2}\) BC nanopapers (\(\nu_\text{f} = 38 \text{ vol.-%}\)), with a tensile strength and modulus of 95 MPa and 11 GPa respectively, possessed tensile properties comparable to that of the composite containing 1 layer of 50 g m\(^{-2}\) BC nanopaper (\(\nu_\text{f} = 52 \text{ vol.-%}\)), with a tensile strength and modulus of 110 MPa and 12 GPa respectively. The better tensile properties of the thin ply composite than its nanopaper reinforcement could be due to the increased porosity of the nanopapers, as grammage was lowered, that lead to an impregnation enhancement. A higher PLA crystallinity, due to an increased contact area with nanocellulose fibres, was also found partially responsible. A comparison between the tensile moduli of the composites and predictions from the rule of mixture and the Cox-Krenchel model is also discussed in the presentation.

**New family of cellulosic excipients for poorly-soluble actives**

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A new and versatile family of cellulosic excipients (AFFINISOL™, The Dow Chemical Company) has been designed and commercialized for delivery of pharmaceutical actives with poor water solubility. Some of these excipients are targeted for spray-dried dispersion (SDD) processing while others are targeted for hot-melt extrusion (HME) processing. The solution rheology of selected excipients is explored at spray-drying conditions to understand their performance and to accelerate selection of options (solvent, excipient, and excipient concentration) for new actives. Similarly, the rheology of selected excipients is
explored at HME conditions. These HME excipients are thought to be yield-stress fluids when processed at temperatures above their glass-transition temperature $T_g$. These stresses are easily achieved in twin-screw extruder setups often used for hot-melt extrusion by the pharmaceutical industry.

**CELL 314**

**New understanding of syneresis in cellulose ether hydrogels**

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Cellulosic ethers are used in a wide variety of pharmaceutical, personal care, food and construction applications. One of the unique and enabling characteristics of many of these materials is their thermal gelation and phase separation into polymer-poor and polymer-rich phases (syneresis). These transitions affect end-use properties such as mouth feel in food applications, workability of cement plasters as well as low temperature gel stability and water retention in a broad range of additional applications. The gelation transition can be characterized by rheological, spectroscopic or turbidity measurements, but these methods give little information on the formation or volume of syneresed water, or the mechanism of gelation. This paper illustrates a new small-scale robotic digital imaging technique that enables simultaneous quantitative measurements of both the gelation and syneresis transitions of aqueous solutions of cellulose ethers. Several factors are identified that control the onset and amount of syneresis of different classes of cellulosic hydrogels, including molecular structure and processing conditions. This information is being leveraged to drive the design of new cellulosic materials for multiple applications.

**CELL 315**

**Development of extrudable derivatives of Hypromellose Acetate Succinate (HPMC-AS) polymer excipient for use in drug solubilization enhancement**

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Cellulose ether-ester derivative hypromellose acetate succinate (HPMC-AS) is recognized within the pharmaceutical industry as an effective polymer excipient to form amorphous solid dispersions (ASDs) with poorly soluble active pharmaceutical ingredients (APIs) as a means to improve oral bioavailability. These ASDs are often produced by way of spray-drying organic solvent solutions of polymer and API. To avoid the costs and potential safety concerns associated with use of organic solvents, many formulators have turned to Hot Melt Extrusion (HME) as a more efficient and economical process for ASD production. Current commercially available HPMC-AS polymers show poor extrusion performance. We have studied alternative synthetic methods for preparing new analogs of HPMC-AS with varying chemical and material properties impacting polymer extrudability. In this presentation, we will describe the results of these studies which show the relationship of ester substitution, molecular weight distribution and glass transition temperature ($T_g$) to polymer melt rheology. In particular, weight average molecular weight ($M_w$) build of HPMC-AS can be controlled for all substitution ratios of acetyl and succinoyl. HPMC-AS analogs of $M_w < 50,000$ g/mol having a $T_g < 120$ °C, also have a unique distribution of acetyl and succinoyl substitution at the C(6) and C(3) hydroxyl positions of the HPMC backbone. Melt rheology studies were performed on these low molecular weight analogs to identify candidates with a desired melt rheology profile suitable for HME evaluation. Preferred HPMC-AS derivatives were extruded with several model API’s and showed improved extrusion performance relative to available commercial grades. The resulting ASD extrudates of these new grades of HPMC-AS also exhibited favorable drug dissolution properties in biologically relevant systems.
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Bacterially derived medical devices: How commercialization of cellulose requires redefining standard industrial practice

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As novel biomaterials are introduced into the commercial medical device market, manufacturers face new challenges related to incompatibilities with current industrial standard manufacturing practice. A recently launched dura mater repair medical device product is a strong example of overcoming traditionally established production methods in order to introduce a disruptive technology to benefit patients and clinicians. A unique polysaccharide derivative has been transformed via a robust manufacturing method to produce SYNTHECEL® Dura Repair the first saleable implantable medical device based on Nanocellulose. Cellulose produced with *Gluconacetobacter xylinus* is characterized by a highly crystalline three-dimensional network consisting of pure nanofibers that are stabilized by inter and intra hydrogen bonds. The created fibrillar network displays unique characteristics such as high strength, high water holding capacity, and conformability to irregular surfaces which makes it particularly well suited for diverse medical applications. The techniques implemented for the manufacture of this product include a proprietary blend of media, propagation and fermentation of bacterial cells, purification, and dehydration steps that ultimately create a ‘wet’ ready to implant device. The techniques implemented were optimized so that production specifications such as cellulose content, burst strength, and endotoxin were in an optimal state of control. The manufacturing process was created without specific manufacturing guidance; however, this presentation will discuss the development and application of manufacturing technology for the production of this novel material.

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Development of cellulose-based bioplastic featuring high optical characteristics of traditional Japanese lacquerware: Urushi black bioplastic

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New cellulose-based bioplastics have been developed which realize elegant black (Urushi black) of traditional Japanese lacquerware. In order to apply bioplastics to various durable products, a new additional value, “decorativeness” was aimed at, in addition to environmental friendliness and durability. Although “Urushi black” of high-grade lacquerware is highly regarded internationally, mass production of the lacquerware is difficult. The new bioplastics, in contrast, can be mass-produced into products of various shapes using the molding process for ordinary plastics. The development process involved, first, fabrication of a high-grade Urushi craft model (lacquerware model) by a top-level lacquerware artist. The model was found to show an extremely low brightness (about 1) and an exceedingly high glossiness (about 100). Aiming at the optical characteristics of the model, bioplastic composites were produced by mixing a short-side-chain cellulose resin (cellulose acetate propionate) and specific additives, and were molded by injection molding using mirror-finished metal molds. Low brightness was found to be achieved by specific surface-treated carbon particles. High glossiness was realized by adding particular high-refractive-index aromatic organic compounds. Although there is usually a trade-off relationship between low brightness and high glossiness, optimization of the surface structures of the carbon particles and molecular structures of the aromatic organic compounds lead to resolution of the trade-off. The bioplastic composites realized low brightness and high glossiness close to the model, and furthermore, “depth” and “warmth”, which are unique to high-grade Japanese lacquerware.
New approaches to measure domain sizes in multi-component cellulosic derivatives using NMR

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Elucidation of the morphology of multi-phase blends remains a formidable challenge in material science. We have developed three new NMR methods to determine the structures and domain sizes in mixtures of ethyl cellulose (EC) and hydroxypropyl cellulose (HPC), which are important and used widely in the pharmaceutical industry, e.g., as binders or film coatings. The first method is based on proton detected spin diffusion experiments, previously used in the characterization of semicrystalline polymer morphologies. We have developed a ¹³C-edited mobility-filtered ¹H spin diffusion experiment in which magnetization in well-defined domains is selected and its diffusion over the sample is monitored. Modelling the spin diffusion process with the diffusion equation then allows us to obtain the domain sizes of the various components in the film coatings. The second and third methods make use of alternative ways of introducing a non-equilibrium state of polarization in the solid formulation through the addition of stable radicals, so-called surface-enhanced DNP (Dynamic Nuclear Polarization) and local PRE (Paramagnetic Relaxation Enhancement). We have applied these methods to controlled release pharmaceutical formulations without the need for any advanced sample preparation. The data has helped us to fine-tune the formulation in terms of drug release characteristics and control the in vivo plasma concentration of a drug over time.
Monitoring structural changes during fibrillation of cellulose pulp into cellulose nanofibrils

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With the growing industrial importance of nanocellulose production from pulp, it is critical to establish quantitative tools for monitoring the transformation from wood pulp fibers to cellulose nanofibrils (CNF). Generally the structure, geometry and morphology of CNFs are assessed with direct or indirect measures of dimensions (microscopy), crystallinity index (X-ray diffraction), viscosity, light transmittance etc. However, defining and measuring a degree of fibrillation for CNFs remains elusive. In this study, we attempt to establish parameters from various X-ray diffraction and scattering approaches to comprehensively describe the structure and morphology of cellulose pulp during fibrillation. Such parameters shall contribute to quantifying the degree of fibrillation in CNFs. Clear correlations between the X-ray derived parameters and other bulk properties of CNFs are further established.

Use of in vitro biosynthetic systems to understand cellulose formation and properties

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Cellulose synthase is an enzyme complex that largely determines the structure and properties of cellulose. This biosynthetic machinery is embedded in the plasma membrane where it extrudes cellulose chains to the plant cell wall or, in the case of bacterial cells, to the extracellular medium. The chains coalesce to form microfibrillar structures that may aggregate with each other and/or interact with other carbohydrate polymers present in the immediate environment to form complex natural composites. The understanding of cellulose biosynthesis has been stymied by the instability of the cellulose synthase complex upon extraction from the plasma membrane. However, significant progress has recently been made through the use of in vitro systems that allow preservation of cellulose synthase activity and the analysis of its biochemical properties. This presentation will review the different in vitro biochemical approaches used to study cellulose formation in vitro as well as the structural analytical methods available to characterize the cellulose formed in vitro by isolated cellulose synthases. The presentation will also discuss the structural properties of cellulose formed in vitro with that of cellulose isolated from plant cell walls.
Structure-property relationships of nanocellulose fibrils

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Cellulose in nature shows a rich phase behavior with complex superstructures, chirality and chiral inversions over different length scales. This has inspired work to engineer cellulose materials with tailored mechanical and optical properties using cellulose nanoparticle (nanocellulose) constituents. Even though many of these materials show great potential for a wide range of applications, the fine structural details of their nanocellulose components have so far not been fully elucidated. By gaining detailed knowledge of the nanocellulose chirality and fine structure, new strategies for advanced bottom-up nanotechnologies and self-assembly of new helical nanomaterials may become available. In this contribution our latest results, using high-resolution microscopy and statistical polymer physics, aimed at understanding structural properties of single nanocellulose fibrils will be discussed. Specifically, the origin and structural role of nanocellulose kinks will be examined and compared to the existing state of the art.

Cell wall formation of wood: The roles of cortical microtubules

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Wood has been used for thousands of years as a raw material such as timber, furniture, pulp and paper, chemicals and fuels. Therefore, there is still great demand for wood as a renewable bio-material and source of bio-energy. Wood is produced by the cambium of stems of living organisms, namely trees. Therefore, wood quality varies significantly depending on environmental and genetic factors. Differences in wood quality are largely due to differences in wood structure. Wood structure is determined by the process of xylem differentiation of cambial derivatives, such as cell enlargement, cell wall thickening, and formation of modified structure. However, its precise process is not yet fully understood. Therefore, in order to create new woods with desirable quantities and qualities by biotechnological techniques, more detailed cellular information is needed on cell wall formation of wood. The secondary xylem cells such as tracheids, wood fibers and vessel elements have cell walls with a highly organized structure. Continuous deposition of the secondary wall increases the thickness of the cell wall. During the formation of secondary walls, successive changes in the orientation of cellulose microfibrils occur in differentiating tracheids or wood fibers. Therefore, the secondary wall consists of multi-layers. The texture of the secondary wall, in particular the orientation of cellulose microfibrils of the secondary wall, is closely related to the physical properties of secondary xylem cells. Cellulose is synthesized by terminal complexes in the plasma membrane. Observations in a wide variety of plant cells have revealed that cortical microtubules, one of cytoskeletons, play an important role in the orientation of newly deposited cellulose microfibrils. It has been postulated that cortical microtubules that are closely associated with the plasma membrane guide the movement of terminal complexes. In addition, localized cortical microtubules might control the localization of terminal complexes in the plasma membrane, thereby the localized deposition of cellulose microfibrils in cell wall, such as pits and helical thickenings, in secondary xylem cells. In this symposium, I introduce evidences that the dynamics of cortical microtubules are closely related to the orientation and localization of newly deposited cellulose microfibrils in the differentiating
secondary xylem cells and the well-developing secondary xylem-like tracheary elements from cultured cells of trees.

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Changes in the supra-molecular structure of cellulose I during TEMPO-oxidation. Bringing together NMR, MD, and XRD results

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Some controversies still remain regarding the supra-molecular structure of cellulose I isolated from wood. Emphasis is here made on the concept of isolated cellulose meaning a cellulose rich, typically above 95 % glucose, cellulose I material with a low content of charged groups, typically below 30 micromoles per gram. Cellulose I isolated in the form of cellulose rich pulp fibres can be used as the starting material for chemical modifications, for example carboxymethylation and TEMPO-oxidation. Although there are several models used for describing the supra-molecular structure of the smallest cellulose I building-block, here called a fibril, common to all is the limited lateral dimension of the fibril. Cellulose fibrils isolated from wood typically have lateral dimensions in the range of 3 nm to 5 nm. These fibrils contain a core, normally considered as crystalline, surrounded by surface polymers possibly of a lesser degree of order. With an estimated crystalline density of 1500 kg/m^3 to 1600 kg/m^3 fibrils are considered dense enough to be impenetrable to most molecules, e.g. water. During heterogeneous reactions, chemical modification of cellulose is a process initially occurring at the fibril surface. Depending on the chemistry involved, fibril surfaces can be more or less accessible depending on how the fibrils are packed together, aggregated, one aspect of the complex supra-molecular structure. In this work the focus was on the changes occurring in the supra-molecular structure of cellulose during TEMPO-oxidation. When combining existing results from solid state NMR (CP/MAS 13C-NMR), atomistic molecular dynamics simulations and x-ray diffraction (XRD), a coherent picture was found in agreement with one of the proposed fibril models. The consistency between the experimental and computational results added support for a square or close-to-square cross-section fibril model with fibril surfaces are parallel to the (1 1 0) and (1 -1 0) crystallographic planes.

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Mechanical performance of CNF films revealed by Raman spectroscopy

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Films prepared using cellulose nanofibrils (CNF) possess high density and smoothness; they are lightweight with good mechanical performance and thus, can be considered as potential material alternatives for several application areas ranging from packaging to electronics. Strategies to produce CNF films have been developed allowing larger scale film production using industrially relevant unit operations. The film performance with respect to structural uniformity and strength can be improved by adding plasticizers and other strength additives. Here we present how the addition of sorbitol influences the mechanical performance of the CNF films prepared using cast coating. The role of the individual fibrils as well as the role of sorbitol as plasticizer on the evolution of the strength performance is revealed using Raman spectroscopy. A Raman band located at 1095 cm^{-1}, associated with the C–O ring stretching of the cellulose backbone, was used to quantify molecular deformation. Molecular strain in CNF films was measured by following a shift in the peak position of the Raman band at 1095 cm^{-1}, which is then related to the sorbitol content in the films.
Functional Lignocellulosics & Nanotechnology
M. K. Ek, Organizer; E. Filpponen, Organizer; T. Nypelo, Organizer; S. Peresin, Organizer; S. Spirk, Organizer; A. King, Presiding; T. Nypelo, Presiding Papers 325-330

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Structural evaluation of cellulose-coated oil-in-water emulsions formed from solution

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Cellulose is the most abundant renewable material in nature, yet only a minute fraction of its annual natural production is utilized as raw material for fabrication of synthetic products, or as source for biofuel production. Its processing requires harsh solvents or procedures considered to be detrimental to the environment and are increasingly regulated. Our previous research has shown that cellulose molecules are dissolved essentially as individual chains in mixtures of an ionic liquid and a polar organic solvent. Furthermore, the dissolved cellulose chains readily form a unique encapsulation coating in oil-in-water or water-in-oil emulsions. This coating exhibits a continuous amorphous structure which differs significantly from the distinct nano-crystalline nature of the cellulose coating in Pickering emulsions. The amphiphilic character of cellulose is supported by molecular dynamics simulations of its mixture with oil and water that indicate its propensity to form a thin amorphous coating at the oil-water interface rather than a nano-crystal. A more practical alternative is to form a hydrogel from the cellulose/ionic liquid solution by coagulation with water and applying it to homogenized oil/water mixtures. The emulsion particles were imaged by cryogenic electron microscopy and fluorescence microscopy, and their size was analyzed by light scattering. Structural information on the nature of the cellulose coating itself, in particular its thickness, density and inner structure, was achieved by small-angle neutron scattering experiments. For this purpose deuterium oxide was used as the aqueous medium, and deuterated or hydrogenated oil were used for shell contrast or full contrast of the emulsion droplets, respectively. The structure of the coating shell is relevant for specific applications such as controlled release of functional hydrophobic compounds, encapsulated phase-change materials for thermal control in textiles or insulation. It was also found that cellulose in the form of a coating layer in emulsions exhibits significantly higher rates of enzymatic hydrolysis, which is relevant for alternative fuel production from biomass.

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Organisation of cellulose ester monolayers on solid substrates upon Langmuir-Schaefer deposition

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Extensive research of molecular self-assembly patterns have led to the development of innovative applications utilizing surface modification via the deposition of organized macromolecules. Polymer brushes and self-assembled monolayers, for example, have been implemented in technologies including anti-fouling, controlled wetting, corrosion resistance and surface passivation. A key issue in developing these nano-scaled technologies is a comprehensive understanding of the parameters affecting their organizational behaviors during thin film deposition. Here, a systematic study of the monolayer organization of cellulose esters, with varying acetyl contents, on solid substrates during Langmuir-Schaefer deposition was carried out. Monomolecular layers of three different cellulose esters – cellulose triacetate, cellulose acetate butyrate and cellulose acetate propionate – were deposited onto substrates of varying surface energy ranging from highly hydrophilic to highly hydrophobic (hydrophilic silica, mica, highly ordered pyrolytic graphite (HOPG) and hydrophobized silica). To further analyze monomer
assembly, deposition of each cellulose ester onto HOPG was also carried out at three different surface pressures (5, 10 and 15 mN/m). Additionally, the behavior of the monolayers at the air/water interface upon two different rates of compression were monitored with acute precision. Results showed that, contrary to popular belief, the morphology of the deposited monolayers were highly dependent on the surface chemistry of the substrate, which resulted in a number of interestingly patterned ultrathin films. Deposition was also controlled and inhibited by the composition of the cellulose esters. It was found that the degree of substitution and length of substituent chain, and residual hydroxyl content had a significant role on the transfer rate of the polysaccharide from the air/water interface to the solid substrate, and on its’ consecutive assembly. Furthermore, polymer conformation at the air/water interface was directly related to the speed at which the monolayer was compressed before film deposition. The results provide a comprehensive insight into the molecular ordering of cellulose esters as the result of a wide array of varying parameters.

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Photo-induced thiol-ene functionalization towards superhydrophobic and slippery lubricant-infused nanocellulose films

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Films prepared from cellulose nanofibers (CNF) have recently been considered as promising substrates for the utilization in electronic devices including displays, transistors, organic light-emitting diodes (OLEDs), touchscreens, lithium ion batteries, solar cells, transparent conductive electrodes and antennas. However, a significant drawback for the use of CNF films in such applications is their high sensitivity to moisture. In this work, a novel and facile process to tailor the wettability of CNF film was developed. Firstly, transparent and reactive porous silicone brush-like nanolayers were introduced onto the CNF film surface by polycondensation of trichlorovinylsilane. Next, the pre-modified CNF films were converted superhydrophobic by introducing low surface tension thiolated fluorine and alkyl molecules via thiol-ene chemistry. Water contact angles (WCA) of 167° and WCA hysteresis < 3° were determined and found to change little after extensive rubbing cycles. Moreover, slippery lubricant-infused CNF film displaying repellency against liquids with surface tension as low as 18 mN×m⁻¹ was demonstrated.

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Effect of cellulose nanocrystal chirality on the stereochemistry of surface-tethered polymers

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Within the context of precision polymer synthesis, stereochemical control is highly desirable, as it affects many properties, such as crystallinity, solubility, thermal transitions and mechanical strength. In combination with controlled radical polymerization (CRP), stereoregular (helical) polymers also have well-defined molecular weight and dispersity, which provide a number of potential applications in materials science, including asymmetric catalysis, enantioselective separations and nonlinear optics. Moreover, chiral amplification is believed to be the second step in the evolution of homochirality, a fundamental property of life. The fact that a small number of chiral molecules (“sergeants”) can induce a preferred handedness in macromolecules consisting of achiral units (“soldiers”) raises the question as to whether or not solid chiral interfaces can induce a preferred handedness in surface-grown polymer chains. Individual cellulose nanocrystals (CNCs) and nanofibrils (CNFs) exhibit consistent right-handedness and thus offer a unique interface for macromolecular chirality induction. Here we present the results of recent
experiments involving surface-initiated atom transfer radical polymerization (SI-ATRP) of achiral monomers from CNCs in aqueous media. ATRP initiators were either unselectively attached to CNC hydroxyl groups via esterification or selectively attached to the reducing end groups via N-hydroxysuccinimide/carbodiimide-mediated chemistry. Following SI-ATRP, surface-tethered polymers were cleaved from CNC interfaces and analyzed by ¹H NMR spectroscopy, gel permeation chromatography (GPC) and circular dichroism (CD). CNC reducing end-initiated CRP may not only provide a new route to chiral amplification, but also novel anisotropic patchy colloids for complex self-assembling systems.

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Tailoring the surface wettability of cellulose paper/nanopaper via photo-induced click reactions

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We demonstrate that the wettability of cellulose paper/nanopaper can be tailored by a rapid and efficient thiol-yne click reaction. Firstly, the paper/nanopaper was functionalized with 4-pentynoic acid via well-known and scalable esterification procedure. Degrees of substitution (DO) of 0.2 and 0.3 were obtained for the paper and nanopaper, respectively. Next, the alkyne-bearing cellulose substrate was subjected to photo-induced click reactions with various thiol-containing molecules to yield either hydrophobic or hydrophilic cellulose surfaces. Finally, micropatterning of the cellulose surfaces was demonstrated by using a photomask-assisted approach. Scanning electron microscopy (SEM), contact angle measurements (CAM) and X-Ray photoelectron spectroscopy were applied to characterize the main morphological and chemical features of the produced materials. Main results and possible applications for such systems will be discussed.

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Nanocellulose as rheology modifier of drilling fluids – Thermostability of nanocellulose dispersions

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Cellulose nanofibrils (CNF) have potential as rheology modifiers of water based fluids, e.g. drilling fluids for use in oil wells or as additives in injection water for enhanced oil recovery (EOR). The temperature in oil wells can be high (> 100 °C), and the retention time long; days for drilling fluids and months for EOR fluids. Hence, it is important to assess the temperature stability over time of nanocellulose dispersions to clarify their suitability as rheology modifiers of water based fluids at such harsh conditions. Dispersions of CNF produced mechanically, by using TEMPO mediated oxidation and by using carboxymethylation as pretreatment, in addition to cellulose nanocrystals (CNC), have been subjected to heat aging at temperatures ranging from 110 to 150 °C. Additives that either stabilize pH or act as radical scavengers have been used in order to shed light over the degradation mechanisms. The results indicate that ORD is the main mechanism as addition of the radical scavengers cesium formate or sodium formate reduced thermal degradation considerably. The analyzes show clearly that the nanocelluloses start to degrade already at 110 °C, which is at a much lower temperature compared to experiments described in literature performed in dry state. Comparison of the nanocelluloses showed that there are differences between the nanocellulose qualities tested; Mech-CNF and CNC were the most stable qualities, being stable after heat aging to 140 °C for three days when using formate as additive. All the nanocelluloses assessed in this
study had better temperature stability than guar gum and xanthan, which indicates that nanocelluloses show promise as rheology modifiers for drilling fluids in oil wells.

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. J. Rojas, Organizer; C. G. Hunt, Presiding; O. J. Rojas, Presiding Papers 331-336

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Potential use of pulp and paper industry side streams in composites

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European pulp and paper industry generates eleven million tonnes of waste annually, of which 70 % is derived from the production of deinked recycled paper. The solid waste streams from paper mills include rejects, various types of sludges and ashes. Global demand for sustainable products is increasing and new environmental concerns and waste disposal laws with increasing treatment costs are pushing the pulp and paper industry to find new and alternative uses for waste residues. Utilisation of pulp and paper industry side streams for plastic composites would decrease waste generation, improve resource efficiency, reduce the environmental footprint and add value of the side streams that would otherwise discarded in the landfills. Various side streams components from paper industry using recycled paper as raw material were demonstrated as feedstocks for new low-cost plastic composites with good appearance. These side streams can be of different qualities and thus various end uses exist. The tensile properties and water adsorption of such composites are on a good level and their environmental benefits are clear, since they reduce need to landfill these streams. This is also supported by chemical analysis of the sludge. This approach can also bring additional revenue from the same raw material stream, improving the overall economy. Side streams which include a high amount of fibres have a reinforcing effect in polypropylene composites. They enhance the tensile strength, stiffness and heat resistance of the composites. Side streams with high inorganic content such as deinking sludge, total sludge and fly ash can be used as cheap fillers in polypropylene composites. They lead to stiffer but more brittle materials. [The research leading to these results has received funding from the European Community's Seventh Framework Programme under grant agreement n° 604187.]

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Experimental test of limited oxidant diffusion mechanism of decay resistance in acetylated wood

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The pathways by which chemical modifications, specifically acetylation, improve the decay resistance of wood are a topic of active research. In the early stages of decay, fungi secrete low-molecular-weight oxidants or oxidant precursors. These oxidants diffuse through the wood cell wall and oxidize cell wall polymers, which enable to decay process to proceed. One hypothesis states that acetylation stops decay by dramatically inhibiting the diffusion of these oxidants through the cell wall. In order to effectively stop decay, the reduction in diffusion rates would need to be substantial – probably several orders of magnitude. Because the Fenton reaction is widely believed to be a significant contributor to wood decay by brown rot, we ask the question: “How much is the diffusion rate and saturation concentration of iron in wood changed by acetylation, and can that change explain its decay resistance?” We probed the Fe uptake over time in wood acetylated to 0, 10, and 20 weight percent gain while exposed to a large excess of solution mimicking the conditions of brown rot: 1mM oxalate, 0.1mM FeIII, and pH 3.9, with FeII
(Oxalate)$^{3-}$ as the dominant iron species. The hypothesis predicted that acetylated wood would take up Fe at a far lower rate and saturate at a lower concentration than control wood. Results of ICP measurements of total Fe content, as well as quantitative X-ray fluorescence images of the Fe distribution in the wood will be presented and implications on the hypothesis discussed.

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Biocatalytic films based on lignin, cationic polymers and immobilized lipase layers

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Lignin is being studied as a renewable resource for chemicals and materials. Layer-by-layer (LbL) deposition technique offers a controlled way to fabricate coatings or thin films with precise sheet thickness and properties. In the present study, LbL films from industrial kraft lignin in combination with different cationic polymers were deposited on cellulose nanofibrils (CNF) substrates. Quartz Crystal Microbalance with dissipation monitoring (QCM-D) was used to follow the kinetics of layer formation with aqueous alkaline lignin solutions. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to compare the surface morphologies of the films. Cationic starch and chitosan induced the highest adsorption of lignin. Furthermore, the adsorption of lignin increased with increasing molecular weight of chitosan. Based on the QCM-D results, those two cationic polymers were chosen for the preparation of biocatalytic systems and further material development. Multi-layer films containing alternating lignin, cationic starch, the enzyme lipase and suberic acid were deposited on cellulose filter paper using the conventional solvent casting method. Suitability of these bioactive films is being studied for applications such as separation of chemicals from water and to be applied as selectively permeable coatings. Possibilities to develop large-scale manufacturing of lignin-based bioactive multi-phase materials to industrially attractive applications is discussed.

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Identification of accumulated carbohydrate degradation products during the processing of cellulose using an ionic liquid solvent: Towards solvent recycling

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The production of man-made cellulosic fibers via the Ioncell-F process is a novel environmentally-friendly and safe technology based on an ionic liquid solvent. With the production of high performance fibers, proof of concept of the spinning process has been achieved. However, for further commercialization, it is necessary to develop a cost-effective and eco-friendly solvent recycling system. The ionic liquid can be recovered from the spin bath solution by vacuum evaporation of water. Yet, slight cellulose depolymerization has been shown to occur during spinning. With a recycling loop, the resulting degradation products may accumulate and affect the process. The purpose of this study was thus to identify accumulated cellulose degradation products. The analysis of carbohydrate degradation products in ionic liquid solutions requires to address several challenges. To begin with, the chemical nature of the carbohydrate degradation products is not known. A first assumption was that of alkaline-type degradation and formation of hydroxy carboxylic acids, since the ionic liquid solutions are typically slightly alkaline. Secondly, the presence of ionic liquid limits the selection of analytical tools and may interfere with the analysis. Thirdly, the concentration of the impurities is low and their detection thus requires high sensitivity. To overcome these challenges, our approach was to separate the ionic liquid using solid phase extraction (SPE) and to concentrate the samples, which were then analyzed by LC/MS and CE. In addition, prolonged dissolution times were tested to increase the concentration of the degradation products. The removal of ionic liquid using SPE was successful, leading to the identification of some
degradation products. The results will support the selection of a solvent purification method for closed-loop fiber production process.

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Industrial biorefinery of lignocellulose for production of biomaterials in China

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A combination of hydrothermal pretreatment and alkali fractionation of cereal straws for fractional utilization of lignocellulose for production of biomaterials in China industry will be reported. During the hydrothermal pretreatment, only the polymeric hemicelluloses were degraded into oligosaccharides and monomers, which were subsequently converted into furfural or xylitol for the food ingredient and pharmaceutical sectors. Three commercial products from the degraded hemicelluloses have been produced on a large industrial scale in China today. Residual lignin was removed by post-treating with aqueous 1-2% NaOH under a mild condition. The recovered lignin, which is a significant source of CO₂ emissions if burned, has a high purity, and was activated under alkaline conditions and used to produce lignin-phenol-formaldehyde (LPF) adhesives for partially replacing the expensive phenols (50%) in the commercial production of biocomposite boards for construction. Finally, the cellulose-rich fraction, which has a large surface area and total pore volume, is enzymatically hydrolyzed and then fermented into bioethanol with a high yield (3 tonnes of the cellulose-rich fraction can produce one ton of bioethanol). The value-added biomaterials from hemicelluloses- and lignin-derived products have greatly improved the economy of both lignocellulose conversion and bioethanol production in industries.

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Wood component separation by dilute acid prehydrolysis with p-cresol

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Dilute acid process typically hydrolyzes hemicellulose and is working as pretreatment of lignocellulosic biomass for efficient enzymatic saccharification. However, lignin obtained in this process is not available as a functional material because the structure of lignin becomes complicated during the prehydrolysis. Therefore, the structural control of lignin during prehydrolysis is significantly important to make it useful. In this study, we conducted dilute acid hydrolysis of wood with sorption of p-cresol and attempted to bind p-cresol to the alpha carbons of lignin for preventing the self-condensation. In this prehydrolysis process, we expected that the structural control of lignin would be achieved while hemicellulose is hydrolyzed into the compositional sugar or furfural (Figure). The acid insoluble lignin prepared from the hydrolysis residue was dissolved in organic solvents, indicating that the self-condensation of lignin was successfully suppressed by the presence of p-cresol grafted to lignin. Most of lignin was extracted from the hydrolysis residue by alkaline cooking with NaOH. Furthermore, a specific aromatic dimer with phenyl coumarane type structure was found in the black liquor, indicating that the sorped p-cresol was linked to the alpha carbon of lignin during the dilute acid prehydrolysis. Our results demonstrated the potential to separate useful lignin from lignocellulosic biomass as well as carbohydrate derivatives like furfural, monosaccharides, and cellulose.
**WEDNESDAY MORNING**

**Bio-based Gels & Porous Materials**
T. Budtova, Organizer; F. Liebner, Organizer; R. Sun, Presiding; N. Abidi, Presiding Papers 337-344

**CELL 337**

**Insight into mild condition dissolution of high molecular weight cellulose in ionic liquid based solvent system**

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Cotton is a major source of highly structurally ordered (crystalline) and high molecular weight cellulose. Since significant portion of cotton is discarded in the textile industry as waste because not all the fibers meet the length and strength criteria needed in the manufacturing of the textiles, waste cotton could be utilized in preparation of regenerated cellulosic materials. However, effective dissolution of cellulose in energy efficient, cost effective, and environmentally friendly conditions still remains a challenge. In this study, room temperature dissolution of high molecular weight cotton (DP > 4000) at different concentrations in 1-Butyl-3-methylimidazolium acetate ([Bmim]OAc)/N,N-Dimethylacetamide (DMAc) (([Bmim]OAc)/DMAc) was investigated using Polarized Light Microscopy (PLM). PLM images of the fibers in the solvent were acquired at different time points after the start of the dissolution to obtain the information on progression of dissolution with time. Rheological properties of the solutions of cellulose dissolved at different concentrations in ([Bmim]OAc)/DMAc at room temperature were studied by
temperature ramp tests and steady state flow measurements. The physicochemical properties, namely surface morphology, chemical composition, crystallinity, and thermal behavior of regenerated cellulose were characterized by Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, X-ray diffraction, and Thermogravimetric Analysis. The results showed that 3% concentration of cellulose appears to be the maximum concentration that can completely dissolve in ([Bmim]OAc)/DMAc at room temperature. Viscosity of the solutions decreased with the increasing temperature. Solutions of 1 and 3% cellulose concentration displayed shear thinning behavior. However, solutions of higher cellulose concentration showed instabilities in flow behavior probably due to increased amount of undissolved cellulose in the solution. Characterization of regenerated cellulose for material properties showed that hydrogen bonding and structure of the cellulose was impacted during the process of dissolution and regeneration. Native crystalline structure of cellulose transformed from cellulose I to cellulose II after regeneration and crystallinity in regenerated cellulose lowered as compared to cotton cellulose.

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Soft gelation of cellulose/DMAc/LiCl solution

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The mechanism the process of gelation are critical in the preparation of gels as well as the fabrication of the properties of gels. In this paper, the gelation process cellulose/ DMAc/LiCl solution in acetone was investigated by using nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) measurements. The gelation process of cellulose/DMAc/LiCl solution in acetone was compared with that in water. It was found that acetone molecules replace part of the DMAc molecules in the solvation shell of Li+ ions. Therefore, the solvation of Li+ ions was weakened and the association between Li+ and Cl– was strengthened, by which to detach the Cl– ions that form hydrogen bonds with the proton of the hydroxyl groups of cellulose from the solvation shell of cellulose. The intermolecular hydrogen bonds was reconstructed, which leads to the gelation. MRI results indicate that there is no dense gel layer formed at the interface between cellulose solution and acetone. The apparent diffusion coefficient of the acetone is 3 time as that of water, which indicated that the penetrating rate of acetone into cellulose solution is much faster than that of water. The results suggested that soft gelation process occurred in the coagulation of cellulose/DMAc/LiCl in acetone.

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Cellulose gels and cryogels via physical and chemical cross-linking

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Wet and dry cellulose gels and cryogels were prepared via cellulose dissolution in 8 wt% NaOH-water, physical gelation or chemical cross-linking with epichlorohydrin (ECH), coagulation in water and lyophilisation /Ciolacu et al, Physically and chemically cross-linked cellulose cryogels: Structure, properties and application for controlled release, Carbohydrate Polymers 151 (2016) 392–400/. Cellulose and cross-linker concentrations were varied. The rheological behaviour of gelling solutions, of gels upon coagulation and the swelling of cryogels in water were analysed. An anomalous high swelling at a cross-linker concentration around stoichiometric molar ratio with cellulose was observed. The influence of chemical cross-linking on cellulose swelling was explained by suggesting that ECH acts as a spacer preventing cellulose chains tight packing during coagulation. Cellulose cryogel morphology, crystallinity and density were studied. Gels were loaded with a model drug, procaine hydrochloride, and the kinetics of its release was investigated.
New cellulosic sponge and foam made from cellulose fibers through a simple freezing/thawing method

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This work describes the development of a new crosslinked cellulosic material obtained from cellulose fibres through chemical derivatization followed by cryogenation and thawing processes. The treatment produces a shape-memory, pH-resistant cellulosic sponge which can be dried in a conventional oven to become a light (δ=0.035g/cm³) open porous material exclusively made of cellulose fibres. The remarkable properties of those two products allow them to be modified in numerous ways, such as layer-by-layer deposition on the shape-memory sponge or chemical vapour deposition on the open-pore foam, which provide them with functionalities ad hoc (fire protection, super-hydrophobicity, biocidal activity, etc.). Taking into account the nearly infinite possibilities of derivatization, the new materials can find application in a number of uses, including insulation, packaging, separation technologies, and many others.

Rheological behavior of thermosensitive hydrogel suspensions based on Cellulose Nanocrystals with adsorbed thermo-responsive polymer

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Nanocellulose, and particularly Cellulose Nanocrystals (CNC), is of high interest for several applications. Biomedical hydrogels are one of these promising applications, especially in the field of injectable hydrogels. In order to create these hydrogels, CNCs are decorated with thermo-responsive polymers.
Some previous work shows interesting rheological results but often with “grafting from” chemistry and harsh organic solvents (Like Yaman BOLUK and Justin ZOPPE team). Our proposed approach investigates the creation and characterization of thermo-sensitive bio-compatible, bio-based, and renewable hydrogel suspensions for medical applications. Our approach is advantageous because of the non-use of organic solvents, and is completely aqueous based. These are obtained by adsorption of polymers on CNC by green chemical methods. Well-known for their Low Critical Solution Transition (LCST) at the interface between room and human body temperature, Poly(N-isopropylacrylamide) (Pnipam) has been chosen for such use. To complete the work, block copolymers PDEGMA-PDMAEMA have been also tested. Physico-chemical interactions with CNC have been investigated by Small Angle Neutron Scattering (SANS), Quartz Cristal microbalance (QCM-d) and Surface Plasmon Resonance (MP-SPR). CNC hydrogel rheological properties and structuration under shear flow present very promising results with similarities between the hydrogel with CNC modified by absorption and previously reported CNC based hydrogels fabricated by “non-green” methods.

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Nanocellulose based electrospun membranes for water purification: Tailoring of porosity and functionality

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The use of nanocellulose as functional entity for water purification is a relatively new area of research in biobased nanotechnology and has attracted significant research and commercial interest in the recent years. Nanocellulose is a promising object for biosorption because of its generally increased surface area and availability compared to cellulose while keeping the same well-known surface chemistry.[i],[ii],[iii] The key challenge is however the tailoring of porosity without compromising on the functionality, water permeability and mechanical stability of nanocellulose based membranes in moist conditions. We present the potential of electrospinning as one processing route for developing membranes mechanically enhanced electrospun cellulose acetate (CA) membranes functionalized with cellulose nanocrystals (CNC) or chitin nanocrystals (ChNC). The developed impregnation process route resulted in CA fibers coated with nanocrystals (5 wt%) resulted in mechanically enhanced membranes with superhydrophilic surfaces and high water flux (27900 Lm⁻²h⁻¹bar⁻¹). [iv] Unique and interesting nanostructured surface patterning stable in moist environment was observed on CA fibers after nanocrystals coating. The electrospinning of CA-cellulose nanocrystal composites on the other hand resulted in lower functionality and mechanical stability than the coated membranes. The results confirm that use of biobased nanocrystals as functional coating can lead to a new generation of high flux, super-hydrophilic, anti-biofouling, ion exchange composite membranes, for water purification applications.
Robust, dynamic hydrogels with modified cellulose nanocrystals as crosslinkers

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Hydrogels are especially advantageous for delivering therapeutic cells and drugs for regenerative medicine. However, most of the artificial hydrogels are mechanically weak and lack of sophisticated structure. Although various toughened hydrogels have been reported, many of them were still suffering from the complicated preparation procedures, uncertain toxicity and the limitation of polymer selection. In this report, a novel type of dynamic hydrogels containing heterogeneous structures based on cellulose nanocrystals was reported. The polymerizable groups are grafted to the cellulose nanocrystals (CNCs) surface with pre-organized host-guest interaction, leading to autonomous dynamic nano-crosslinkers. Composite hydrogels are obtained after the in situ polymerization with these dynamic nano-crosslinkers and commoner. The hydrogels showed high toughness and stretchability. Furthermore, our dynamic hydrogels contain a heterogeneous structure. Thus, the extreme contrast in the mechanical properties of rigid nano-crosslinkers and soft flexible polymer phase also creates heterogeneity in stiffness and elastic modulus. The presence of these both components maintains the elasticity of hydrogels, which is favorable to resist fatigue under repeated work cycles. As the summary, we designed and introduced a kind of bio-inspired dynamic heterogeneous hydrogels with not only robust mechanical properties but also adjustable heterogeneity. Moreover, such robust hydrogels could be an ideal material platform for biomedical application.

Lignin-based hydrogels with super-swelling capacities

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Lignin is a complex natural polymer and one of the main constituent of the lignocellulosic biomass. It is a biorenewable material and available in large amounts as byproduct from the pulping industries. Lignin has been considered as a potential raw material in hydrogel production (1). Hydrogels are used in many technological applications, such as agriculture field (as soil conditioners and nutrient carriers), super absorbents in hygiene products (pads and diapers) as well as drug carriers and active principle control release devices for drug delivery. For the first time, lignin-based hydrogels with high swelling capabilities were prepared. Hydrogels were developed from three technical lignins: wheat straw soda, wheat straw organosolv (ethanol) and softwood kraft lignin. Optimization of the hydrogels formulations was optimized. They were fabricated utilizing 10% w/w lignin and 20% w/w of commercial crosslinking agent. Extensive characterization in terms of water up-taking capability, chemical structure, pore size distribution and mechanical and viscoelastic properties was performed. Lignin hydrogels were able to uptake water in up to 10 times its weight while being dimensionally stable in wet state. Controlled release properties of the hydrogels was tested using a model compound (Methylene Blue) to study the load capacity of the systems. The model absorption tests showed that the produced hydrogels have high adsorption capacity whereas only negligible desorption could be observed. Lignin origin and structure had a remarkable impacto on the structural and mechanical properties of the hydrogels.
Potential of cellulosic nanocomposites materials from cassava pulp

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Cassava (*Manihot esculenta*) is a staple food crop for more than 600 million people and is produced primarily by smallholders in developing countries. However, these crop has huge potential and could turn from a poor people's food into a 21st century crop, the FAO expects, if properly managed and grown according to a new environmentally-friendly farming model. Nowadays, most forms of cassava processing produce large amounts of waste, the type and composition of which are governed by the processing method and sophistication of the technology used. The cassava pulp, solid waste produced as a consequence of starch production, its often has no economic value which can make processing a marginal business proposition. This paper reports on the studies of the preparation of cellulose from cassava pulp for cellulosic nanocomposite materials development. The cassava-based cellulose was prepared from destarched cassava pulp, i.e. cassava pulp being previously hydrolyzed by α-amylase to remove the starch in pulp (% starch in cassava pulp and destarched pulp was 50-60 and 1% dry basis). The process included usual chemical treatment such as alkaline extraction, bleaching and acid hydrolysis. The chemical composition of fibers at different stages was analyzed and the results showed an increase in the cellulose content and a decrease in the lignin content. The Fourier Transform Infrared (FTIR) spectroscopy was applied to confirm the chemical structure of produced fiber and the spectrum suggests that lignin was almost entirely removed during alkali and bleaching treatment. In cellulosic nanocomposite materials, the cellulose component may provide the polymeric matrix for nanoparticles and/or the nanometer-scale constituent. Additionally, at a higher level, this report presents unique cellulose-based nanocomposites and examines the properties of these materials. The goal of the research project is to develop technologies to enable the economically viable production of cellulosic material from cassava pulp. New methodologies are required to achieve such an outcome, including the controlled, high level dispersion of cellulose due to a chemical reaction, and processing technologies that enable the cost-effective use of these procedure to convert cassava pulp to cellulosic materials. This will lead to expansion or opening of new market opportunities for new products and added value products generated from the waste of cassava.

Various shapes of chitosan based nanocomposites and their hemostatic ability

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An effective hemostasis can stop bleeding timely and avoid wound infections, which is important for saving the wounded in an accident or surgical treatment, especially the battlefield. In this study, various shapes of chitosan based nanocomposites including chitosan-nanoTiO₂ fibers (CT), chitosan-xylan-nanoTiO₂ powder (CXT) and chitosan-xylan-nanoTiO₂/PVA nanofibrous mats (CXT/PVA) were used for hemostasis and bacterial inhibition prepared via wet-spinning, grinding and electrospinning techniques, respectively. The results of SEM and TEM exhibited that CXT/PVA had uniform distribution and the
The diameters of the nanofibers were in the range of 50-150nm. In the hemostatic assessment, the commercial hemostatic sponge’s hemostatic time is 560s, and amount of bleeding is 1.695g. By contrast, CXT/PVA exhibited a hemostatic time of 353s decreased by 40.0% and an amount of bleeding of 0.415g decreased by 75.5%, while the CT showed 203s and 0.315g, the CXT manifested 110s and 0.18g. All kinds of chitosan nanocomposites had better hemostatic effects than the commercial hemostatic sponge whose main ingredient is medical gelatin as well as antibacterial activities, which may be related to the amine groups of chitosan which can interact with platelets, erythrocyte and fibrinogen to promote blood coagulation. CXT/PVA exhibited high levels of porosity, gas permeation, and a high surface-to-volume ratio, that would also promote cell respiration, skin regeneration, moisture retention, removal of exudates, and hemostasis. Such hemostatic material shows promising application in the surgical treatment and the battlefield.

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Degradation kinetics of compression-molded date pits composites

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Poly (lactic acid) (PLA) or polycaprolactone (PCL), date pits (DP), a byproduct of the date industry, were blended in a Haake Rheocord torque rheometer at 170°C for 10 min. Blends were compression molded and tested using thermogravimetric analysis (TGA). The TGA analysis of pure PLA or PCL showed a one line (one step) degradation profile with a one transitional temperature at 353.5 and 393.1°C, respectively as demonstrated by the derivative of the plot. Both PLA and PCL polymers exhibited higher thermal stability than DP because of the higher degradation temperature than DP which started at 286 and degraded completely at 799°C. DP showed a small degradation peak at 60°C which appeared to be a moisture loss peak. Although the degradation profile of pure PCL or DP was clear, the composite exhibited no clear distinction between PCL and DP degradation path where the profile showed gradual drop on weight versus sharp drop of the PCL which indicates the presence of a third component with different physical properties produced during blending of the two polymers. TGA was used to determine the degradation kinetics of the blends. Four heating rates, 10, 20, 30, and 40°C/min, were used to calculate the activation energy of degradation according to Flynn and Wall Walls. The degradation mechanism is considered a one-step process when all the points of Ea, as a function of percent conversions, fall on strait line regardless of heating rate. The data showed that neat PCL exhibited more than one-steps, whereas the addition of 10% date pits (DP) forced a one-step indicating some sort of interaction between PCL and date pits.

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Fiber, a wonderfull from plantain crop residues. Alternative for human sustainable development

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The project on its origins was oriented to determine uses and agregated values to plantain crop residues as fertilizers and ethanol production; however the research process led to the extraction of the stem and pseudostem plantain fibers of the varieties of Dominican Harton and Harton, and to determine its resistance qualities for industrial purposes. Additionally, it was found that there are difficulties in the productive zones to access to education, health and decent housing, and susceptibility to violence. For this reason the research results become in a social innovation project allowing the communities to generate revenues from the manufacture of crafts and decorative elements from plantain fibers.
Cotton-based cellulose nanomaterials for applications in composites and electronics

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A modern society demands development of highly valued and sustainable products via innovative process technologies and utilizing bio-based alternatives for petroleum based materials. This research demonstrates the applicability of the use of recycled cotton as promising sustainable material to be utilized as a substrate for electronic application and a reinforcing agent choice that can be produced without any intensive purification process and be applied to synthetic-based polymer nanocomposites in melt-processing. Low density polyethylene (LDPE) was used as the polymeric matrix and it was loaded with different cellulose reinforcing agent types and content including micro/nanofibrilated cotton, cotton nanocrystals, bleached and unbleached softwood. The morphology, crystallinity, thermal stability and specific surface area of cellulose nanoparticles were determined and used to interpret the nanocomposite behavior. Nanofibrillated cotton reinforcing agent in LDPE films resulted in the highest toughness as well as highest stiffness compared to cotton nanocrystals and wood originated nanofibrils. Thermal analysis of low density polyethylene polymer nanocomposites using DSC, TGA showed higher thermal stability of the NFC loaded material as compared to same loading of CNC.

Interfacial thickness for tailoring the reinforcing properties of nanocellulose in polymer matrix

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Material properties of nanofiller-reinforced polymer composites are governed by various phenomena such as stress transfer, fracture, thermal diffusion, and light scattering etc., which occur at the interface between nanofillers and polymer matrix. Thus, it is important for composite materials to control the
interfacial structure. In the present study, contributions of the interfacial thickness and the interfacial
density to the composite properties were investigated using TEMPO-oxidized cellulose nanofiber (TOCN)
and cellulose triacetate (CTA). To control the interfacial thickness, the surfaces of TOCNs were modified
by grafting amine-terminated poly(ethylene glycol) (PEG-NH₂) with different molecular weight. Neat
TOCN or PEG-grafted TOCN was compounded with CTA to prepare the nanocomposite films with
different interfacial thicknesses. As a result, the thinner interfaces enhanced stiffness of the
nanocomposite films, while the thicker interfaces enhanced toughness. In the neat TOCN/CTA composite
films, a rigid network of TOCNs was formed and contributed to the increase in Young’s modulus and
tensile strength. In contrast, in the case of PEG-grafted TOCN/CTA composite films, the network of
TOCNs was loosened by the soft PEG layer, which is responsible for the increase in toughness. The soft
and thick PEG layer on the TOCN surface is likely to show large deformation and thus prevent brittle
fracture at the interface. High light transmittances and a low haze value of CTA films were preserved
even with the addition of neat TOCN or PEG-grafted TOCN. This result can arise from the small width
and high dispersibility of the TOCNs. The coefficient of thermal expansion (CTE) of CTA films decreased
by incorporating neat TOCN or PEG-grafted TOCN. The CTE of the composites with the thicker interface
was higher than that of the composites with the thinner interface. In fact, PEG-NH₂/CTA composite films
had higher CTE than PEG-grafted TOCN/CTA composite films which consist the corresponding amount
of PEG. Therefore, the PEG layer on the TOCN surfaces had a negative impact on the restraint of
thermal expansion of the composites. These results show that an appropriate thickness of the interface is
required to efficiently improve material properties of the composites.

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Transparent, macro to nano moldable composites reinforced by cellulose nanofibers

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Transparent plastics are increasingly used in the advanced applications such as in smart and wearable e-
appliances, solar cells, and parts of vehicles. Cellulose nanofibers (CNFs) have gained a recent
enormous attention as the “green” reinforcing elements of these plastics because of their excellent
strength and stiffness, drastically low thermal expansion, and strong network forming ability via H-
bonding. Furthermore, nanoscale cellulose fibers in a plastic composite do not scatter the visible light
much. However, the processing of CNF-reinforced composites suffers from the difficulty of dispersing
native hydrophilic CNFs in the hydrophobic resin or plastic matrix (most commercial resins are
hydrophobic). Of note, a uniform dispersion of nanofillers defines the final properties of a nanocomposite.
To defeat this difficulty, previously, entangled CNF-networks, e.g., nanopaper or gel, have been prepared
first followed by impregnation with a curable transparent resin such as epoxy or acrylic resin to replace
the air or liquid in the network. The CNF-network greatly enhanced the strength and stiffness of the resin
and bestowed drastically low thermal expansion. Because of the high stiffness and low strain-to-failure,
these high-performance transparent composites cannot be molded into the 3D-curved materials such as
lenses, substrate for curved displays and so on. In this study, we resolved those problems by employing a
simple Pickering emulsification technique. The native CNFs have been used to stabilize an acrylic resin-
in-water emulsion. The emulsion contains numerous droplets of acrylic resin that are covered by and
trapped into the CNF-network. The emulsion was dewatered by vacuum-filtration to obtain a nacre-like
CNF/resin mat that was molded easily by hot-pressing into a high-performance optical lens, or a precisely
micro- or nano-patterned material.

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Functional cellulose nanocrystal reinforcing fillers in polymer nanocomposite films

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Short cellulose nanocrystals (CNCs) are promising lightweight materials with high strength and the potential to serve as reinforcing agents in many polymeric materials. The chemical pretreatments of cellulose fibers can be regarded as potential route to both promote nanocellulose fabrication and to adjust the surface properties of CNCs. Sequential regioselective periodate oxidation and partial chlorite oxidation can be utilized to obtain reactive cellulose nanocrystals (RCNCs) with carboxyl and aldehyde functionalities and further used as reinforcements to prepare acetal-bonding cross-linked poly(vinyl alcohol) (PVA) films. With the addition of 10% acetal-bonding RCNCs with respect to PVA weight, the tensile strength and Young’s modulus were up to 2-fold greater than those of pure PVA film. In addition, PVA’s effective oxygen barrier and thermal properties were preserved when RCNCs were introduced into the films. Significantly lower reinforcement effect was obtained when aldehyde groups of RCNCs were reduced to hydroxyl groups prior addition into PVA. Periodate oxidation can also be used to produce UV-absorbing CNCs after “click-type” reaction between aldehyde groups and p-aminobenzoic acid followed by mechanical disintegration. In the solution state, CNCs exhibit very high UV-absorption properties, especially in UVA and UVB regions and high transparency in the visible light region. Complete UVA and UVB opacity of the nanocomposite was achieved using 10% of CNCs in PVA while simultaneously retaining over 80% transparency over the whole visible light spectrum. In addition, improved tensile strength and modulus were achieved using UV-absorbing CNCs compared to pristine PVA.

Advances in Polysaccharides: Practice & Applications
A. Biswas, Organizer; H. Cheng, Organizer; G. W. Selling, Presiding Papers 353-360

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Chemo-enzymatic synthesis and functional properties of well-defined human milk oligosaccharides

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Human breast milk is rich in a family of structurally diverse unconjugated glycans, which have many health benefits. These compounds are not digested by the infant, but serve as metabolic substrates for beneficial bacteria thereby shaping the intestinal microbiome of the breast-fed neonate. Human milk oligosaccharides (HMOs) can also serve as soluble decoys for receptors of viral, bacterial or protozoan parasite pathogens thereby preventing attachment to the infant mucosal surface. These compounds can also modulate epithelial and immune cell responses, and reduce excessive mucosal leukocyte infiltration and activation. A major stumbling block in HMO research is a lack of well-defined glycans needed to unravel the underlying biological mechanisms of action of these compounds. We have exploited the redundant nature of HMO biosynthesis to develop a synthetic methodology that can easily give a wide variety of highly complex symmetrical and asymmetrical branched HMOs by exploiting inherent substrate specificities of a limited number of mammalian glycosyl transferases. The power of the new strategy is demonstrated by the synthesis of a library of 60 linear, bi-, and tri-antennary HMO structures, which were used to create a glycan microarray. Screening studies with a number of glycan binding proteins such as galectins, microbial toxins and viral adhesion proteins uncovered that glycan complexity contributes greatly to binding affinities and selectivities.
**CELL 354**

**Chemo-enzymatic synthesis of homogeneous hyaluronan polysaccharides and their biological applications**

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Hyaluronan (HA) is a unique linear polysaccharide that plays critical roles in various physiological processes. However, due to the inaccessibility of homogeneous HA polymers, the structure/activity relationship (SAR) of HA remains largely unknown. Here we present a general synthetic strategy for enzymatic synthesis of homogeneous HA conjugates. Nascent HA oligosaccharides were firstly prepared via HA synthase (PmHAS)-catalyzed step-wise synthetic route and HA trisaccharide (GlcA1-3GlcNAc1-4GlcA) was proven to be the necessary and minimum acceptor for the subsequent one-pot synchronized homogeneous HA polymerization. High-and low-molecular weights of HA polymers with definite chain lengths were synthesized with high yields. Benefiting from flexible substrate specificity of PmHAS, the strategy was also used to enzymatically produce various HA-biotin and HA-drug conjugates. The relationships of HA chain length and the corresponding biological functions are exploited. This strategy provides a general approach for enzymatic synthesis of homogeneous glycosaminoglycans polysaccharides for potential biological applications and therapeutics.

**CELL 355**

**Chemoenzymatic synthesis of carbohydrates and glycoconjugates**

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Carbohydrates are the most abundant organic materials on earth. They also play important roles in biology. Obtaining these structures in pure forms will help to elucidate their functions and explore their potential applications. We have developed highly efficient one-pot multienzyme (OPME) systems for synthesizing various carbohydrates and glycoconjugates from suitable glycosyltransferase acceptors and simple monosaccharides as donor precursors. These OPME systems have been used in sequential for large-scale production of various oligosaccharides and glycoconjugates as well as in glycan modification of glycoproteins. Our efforts on enzyme identification, characterization, mutagenesis and their application on the synthesis of carbohydrates including repeating units of bacterial capsular polysaccharides using sequential OPME systems will be presented.

**CELL 356**

**Structure and property of new dextrans obtained by enzymatic synthesis**

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Due to their carbon-neutrality and renewability, biosourced polymers are seen as attractive alternatives to polymers issued from fossil carbon for producing a wide range of materials with plastic and elastomeric properties. Notably, the bio-based material is entering the plastic market at a growth rate of 30% annually. In particular α-glucans are widely employed in industry for their functional properties: starch is used in food and bioplastics whereas pullulans and dextrans are only used for pharmaceutical and medical applications. Previous study has shown that dextrans synthesized with different dextransucrase mutants have interesting mechanical properties for potential application in bioplastics, which depend on their
structure. In order to determine more deeply the structure properties relationships of this biomolecule, dextrans with controlled and various architectures were synthesized in vitro from sucrose by mutants of dextransucrase from \textit{Leuconostoc mesenteroides} NRRL B-512F, obtained by combinatorial engineering and a branching enzyme. They exhibited α(1→2) or α(1→3) branching points with a branching rate ranging from 2 to 50%. The solubility, the macromolecular characteristics, the film-forming ability, and the thermal and mechanical properties of these new macromolecules were investigated. Their macromolecular structure and size were determined by \textsuperscript{1}HNMR and by using asymmetrical flow field flow fractionation (AF4) coupled with multi-angle laser light scattering (MALLS). Their weight average molar masses and radii of gyration ranged from 10^9-10^{10} g.mol^{-1} and from 10 to 1000 nm respectively. Mechanical analyses show that the storage modulus depends on the type and degree of branching. These results open new perspectives for the design of biosourced materials.

**CELL 357**

**Enzymatic production of oligosaccharides and polysaccharides for food ingredient applications**

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Glucosyltransferases (glucansucrases) convert sucrose to D-glucose polysaccharides (glucan) or oligosaccharides, together with fructose as co-product. The anomeric linkage composition of the polysaccharide or oligosaccharide products is dependent on the particular glucosyltransferase, and the solubility, viscosity, digestibility and fermentability of the carbohydrate products are each related to the anomeric linkage composition of the polysaccharide or oligosaccharide. A variety of glucosyltransferases have been screened for production of polysaccharides or oligosaccharides, where the products were subsequently evaluated for functionality and flavor in food products such as yogurt, beverages and food bars. Further modification of one or more of the properties of these polysaccharides or oligosaccharides was accomplished using a glucan endo-1,3-alpha-glucosidase or a glucosyltransferase having alpha-(1,2)-branching sucrase activity.

**CELL 358**

**Synthesis of well-defined unnatural polysaccharides by phosphorylase-catalyzed enzymatic polymerization**

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Natural polysaccharides are widely distributed in nature and thus considered as the very important biomass resources. The efficient methods for synthesis of functional polysaccharides have attracted much attention to provide new materials employed in application fields such as biomedical field. Enzymatic approaches have increasingly been important to precisely synthesize functional polysaccharide materials. Phosphorylase is one of the enzymes, which have been practically employed as catalysts for polysaccharides with well-defined structures. This enzyme catalyzes enzymatic polymerization of glucose 1-phosphate (Glc-1-P) as a monomer initiated from the nonreducing end of maltooligosaccharide primer to produce amyllose. The author has reported that by means of the phosphorylase-catalyzed enzymatic polymerization using analog substrates as monomers, well-defined polysaccharides with functional groups such as amino and carboxylic acid groups are efficiently obtained. For example, phosphorylase isolated from thermophilic bacteria, \textit{Aquifex aerolicus} VF5, catalyzed the enzymatic polymerization of glucosamine 1-phosphate (GlcN-1-P) as a monomer from maltotriose primer. The enzymatic reaction was accelerated in ammonia buffer containing magnesium ion, owing to the precipitation of inorganic phosphate, giving the high molecular weight aminopolysaccharide, which corresponded to chitosan stereoisomer (Figure 1). The thermostable phosphorylase-catalyzed enzymatic copolymerization of Glc-1-P with GlcN-1-P from maltotriose primer was also performed to produce
unnatural glucosaminoglucans composed of α(1→4)-linked Glc/GlcN units. The enzymatic polymerization manner was applied to synthesize amphoteric block polysaccharide having both amino and carboxylic acid groups.

![Chemical structures](image)

Figure 1. Thermostable phosphorylase-catalyzed enzymatic polymerization of GlcN-1-P under conditions with removal of inorganic phosphate as precipitate.

**CELL 359**

**Combined enzymatic-ionic liquid treatments to increase the accessibility and reactivity of pulp fibers**

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Cellulose is the most abundant renewable biopolymer in the World and cellulosic pulp fibers have excellent mechanical properties which are utilized in various products. However, the low solubility of cellulose in conventional solvents and its tight crystal structure limit the reactivity of cellulosic fiber materials for many applications. Certain ionic liquids are known to dissolve cellulose, or to swell cellulose when appropriately diluted with water, which may offer a new means for activating the fiber surface structures. Likewise, endoglucanase treatments of pulp fibers are also known to increase their reactivity in e.g. the viscose process and to reduce ballooning during dissolution. In our work, we have studied the combination of ionic liquid and endoglucanase treatments of a dissolving grade pulp and a bleached kraft pulp. In the first part of the work, different endoglucanases, representing different endoglucanase families and of different thermostability, were screened in a set of seven cellulose-swelling or –dissolving ionic liquids for ionic liquid tolerance. Several combinations of ionic liquid type and endoglucanase were found which allowed a relatively high endoglucanase activity in the screened 15 and 40 % ionic liquid solutions. The ionic liquids were also tested as fiber swelling and dissolving solvents. In the second part of the work, sequential ionic liquid and endoglucanase treatments were attempted on the studied pulps. The degree of hydrolysis, depolymerization, water retention value and fiber characteristics as analyzed by a fiber analyzer were determined for the pulp samples. As a measure of reactivity, the dissolution speed and mechanism were studied in CED solution. As a further measure of chemical reactivity, the degree of oxidation by reaction with TEMPO+ was studied. Overall, few synergistic effects were observed for sequential ionic liquid and endoglucanase treatments under the applied conditions. The endoglucanase treatments were effective in increasing the pulp dissolution speed, but the enzyme dosage needed to be carefully optimized to avoid excessive hydrolysis losses of the pulp. Ionic liquid treatments generally had slightly increasing or neutral effects on the water retention value, whereas the endoglucanase treatments clearly decreased this parameter.
Dendrimer-like biopolymers: A new arena for biomaterial development

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Dendrimer-like biopolymers (DLBs), which constitute a fundamentally new group of functional biomaterials, include both naturally occurring, dendritic or dendrimer-like glucan macromolecules and their derivatives. While native DLBs are essential components in biological systems, Dr. Yao's lab has been leading the scientific explorations to engineer these biomaterials for various applications that cover food, nutrition, and pharmaceutical areas. In this talk, Dr. Yao will review his studies on the molecular and particulate structure and functions of native DLB as well as their efforts in generating DLBs that can: (1) form Pickering emulsions to protect lipophilic compounds and deliver antimicrobial peptides, (2) dissolve poorly water-soluble drugs and other active ingredients, and (3) perform as high-efficacy vaccine adjuvants. Some thoughts on using DLBs as a set of powerful new tools to address scientific and technological challenges will be discussed.

Cellulose crystallinity: What does it mean?

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The concept of crystallinity has been a long-standing pillar of the characterization of cellulose and has led to many conceptual theories alongside some remarkable empirical observations that relate crystallinity with certain behaviors of cellulose. And although it has proved a highly useful concept in predicting digestibility of biomass in particular, there are multiple methods of quantifying crystallinity that rarely agree quantitatively and have very little strong connection to the molecular or structural nature of the cellulose they are measuring. With this motivation, we have embarked on a mission to connect simple x-ray diffraction patterns to molecular structure with the aim of interpreting patterns from a library of possible structures. We present here the results of creating a library of putative cellulose fibril structures and their associated patterns and how those patterns can combine to interpret patterns obtained from cellulose samples including treated and untreated plant cell walls. We also will present recent findings on modeling and simulation of fibril formation from individual gluten chains.

Visualization of dynamic changing in formation of cell wall cellulose and callose along with arrangements of microtubules with GFP on surfaces of protoplast cells

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We have been extensively studying bottom up processes to fabricate b-1,4 or b-1,3 glucan nano/micro-objects using protoplast cultured under a stressed condition. As a native nanoglucan-producing system, we found previously that a fiber bundle of hollow nano-fibrils composed of (1→3)-b-glucan (callose) was secreted from protoplasts of white birch (Betula platyphylla) leaves callus in an acidic medium containing high concentration of Ca\(^{2+}\). The stress culture condition for the fiber secretion was severe not to be found at the present environment. Instead, formation of cell wall was inhibited due to such an environmental stress response. The two phenomena might be corresponded with each other. In this paper, we attempt first to visualize cell wall cellulose formation with dynamic arrangements of microtubules with GFP (Green Fluorescent Protein) on surfaces of protoplast cells by time-lapse video using confocal laser microscopy. The results indicated that cell walls were formed along with the orientation behavior of microtubules in the normal culture condition. In the stress condition, cellulose was synthesized as disordered aggregates accompanied with production of callose hollow fibers.

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Explicit modeling and underdetermined (scattering) data to approach a complex reality

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A number of characterization tools are available today as routine to partially assess the structural characteristics. X-ray/neutron scattering (diffraction), resonance spectroscopy or vibrational spectroscopy are among them. Often in practice, structural parameters based on assumption of simplified models are extracted. However, since the data are inherently underdetermined, the resulting description can significantly depart from the reality. In principle, given an explicit model, we are able to predict the data that can be directly checked by simple experiment. Wave scattering is among the simplest to relate an explicit model to the data at any length scale, from atomic resolution to micrometric length scale, based on the same simple formalism. Thus a rational construction of realistic models is crucial to fully exploit the information contained in the scattering data. Examples of successful and unsuccessful discrimination of competing models will be presented.

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Folding of xylan onto cellulose fibrils in plant cell walls revealed by solid-state NMR

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Exploitation of plant lignocellulosic biomass is hampered by our ignorance of the molecular basis for its properties such as strength and digestibility. Xylan, the most prevalent non-cellulosic polysaccharide, binds to cellulose microfibrils. The nature of this interaction remains unclear, despite its importance. Here we show that the majority of xylan, which forms a 3-fold helical screw in solution, flattens into a 2-fold helical screw ribbon to bind intimately to cellulose microfibrils in the cell wall. \(^{13}\)C solid-state magic angle spinning NMR spectroscopy, supported by \textit{in silico} predictions of chemical shifts, shows both 2- and 3-fold screw xylan conformations are present in fresh Arabidopsis stems. The 2-fold xylan xylan is spatially close to cellulose, and has similar rigidity to the cellulose microfibrils, but reverts to the 3-fold screw conformation in the cellulose-deficient \textit{irx3} mutant. The discovery that induced polysaccharide conformation underlies cell wall assembly provides new principles to understand biomass properties.
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Cellulose II formation by cellulose synthase: Negative data can make themselves positive?

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Cellulose synthase is the enzyme responsible for synthesizing the cellulose microfibril. This enzymatic reaction is twofold of β1→4-glucan synthesis (polymerization) and microfibril formation (crystallization). Mechanism of the polymerization starts to be clarified based on the three dimensional molecular structure of the enzyme, while the crystallization mechanism still remains to be clarified. For investigating the crystallization mechanism as well as polymerization, we conducted the reconstitution of bacterial cellulose synthase to synthesize cellulose in vitro and in vivo, either of which will be a useful platform to analyze the crystallization process of cellulose synthase. Crude enzyme preparation of Acetobacter solubilized by mild detergent like alkylmaltoside successfully produced cellulose from UDP-glucose in vitro. Weight-averaged degree of polymerization (DPw) of the synthesized cellulose was as high as 300, which is higher than the celloligomers synthesized by reversing hydrolase or phosphorylase reaction. This highlights that our crude cellulose synthase preparation has polymerization function. However the synthesized cellulose is globular aggregation and crystallized into cellulose II after washing SDS, meaning that this enzyme preparation is unable to form the microfibril by assembling a bunch of cellulose chains, despite a significant polymerizing activity. We also have conducted in vivo synthesis of cellulose by heterologous expression of Acetobacter cellulose synthase in Escherichia coli. It was successful to produce cellulose polymer as long as 700 of DPw by the recombinant E. coli, which we designated as CESEC (Cellulose synthesis in E. coli). However the product obtained after washing by SDS and dilute NaOH was cellulose II aggregation as well. This indicates that the cellulose synthase expressed in living E. coli cell is not enough for the native activity to produce cellulose I microfibril. We could not, to date, accomplish the reconstitution of the native activity of bacterial cellulose synthase. However these enzyme preparations maintain polymerizing activity, one of the essential functions of cellulose synthase. It then should be possible to recover the native activity of cellulose synthase by supplementing the missing factor(s). We believe that either system, in vitro or in vivo (CESEC), is a useful experimental setup to find out key factors for the microfibril formation of cellulose synthase.

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Towards an improved understanding of cellulose swelling, dissolution and regeneration at the molecular level

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The exact structure of the hydrogen bond networks and the changes of these networks upon swelling and dissolution processes are current ‘hot topics’ in cellulose research. H-bonds are responsible for the allomorphism of cellulose, for the typical properties of cellulose, and for reactivity and chemical behavior. The use of isotopic labeling with modern solid-state NMR techniques in combination with X-ray crystal structure analysis is a powerful approach to obtain solid state and gel structural data of cellulose and cellulose model compounds, so that we now come close to an understanding of cellulose swelling and dissolution at a molecular level. In our studies we used 13C-perlabeled compounds in combination with special NMR experiments. The following cellulose solvents, which had to be synthesized in perdeuterated and 15N-labeled form beforehand, were selected: NMMO, DMAc, BMIM acetate and NaOH / urea. Swelling of cellulose is a reversible process, consisting of 3-4 distinguishable stages. Mainly hydrogen bonds to/from OH-6 and OH-2 are broken during swelling. Dissolution, by contrast, is irreversible, and it additionally involves H-bonds to/from OH-3. With the help of perdeuterated, 15N-labeled solvents, distances between solvent and solute carbons can be measured. In “early” swelling stages, only a few solvent molecules surround the cellulose (cellulose model compounds), these solvent species being mainly located around 2-OH and 6-OH, but being rather far from 3-OH. In “later” swelling stages, more
solvent molecules surround 6-OH and 2-OH – not 3-OH – but they do not come much closer than in the early state. In the final swelling state, just prior to dissolution, more solvent molecules per AGU are approaching, also coming closer to 3-OH. Upon dissolution, the solvent has closely approached also 3-OH. Intriguingly, upon dissolution, cellulose solvents form non-conventional C-H…O H-bonds with cellulose, in addition to the common and well-known O-H…O hydrogen bonds. The C-H hydrogen bonds are formed regioselectively at C-1 and C-3, but not at any other positions. Formation of those C-H H-bonds might be a (crucial?) prerequisite to cellulose dissolution, and might also be a special feature that defines the nature of cellulose solvents. The lecture will present and discuss approach, experiments and results.

CELL 367

Evolution of our understanding of native celluloses

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If we begin with Anselme Payen’s finding that cell wall polysaccharides are a form of “dextrose”, it is good to reflect on progress in our understanding of celluloses and its correlation with advances in investigative methodologies, as well as the evolution of conceptual frameworks for interpretation of experimental observations. After an extended detour into colloid science during the second half of the 19th century and early decades of the 20th, the homo-polymeric nature of celluloses was accepted in the 1930s. In the next five decades the needs of cellulose based industries such as cotton textiles, pulp and paper and cellophane and rayon industries, led to interpretation of observations in terms of paradigms developed for the synthetic polymer industries, in large measure because they became available. In the 1970s and 1980s it was recognized that native celluloses are, after all, biological tissues optimized for their function in living organisms. With the advances in biotechnology, and the opportunities to enhance the properties of crops and advance modern agriculture, our paradigms must be adapted to acknowledge the hierarchic organization of the nanoscale structures of living systems.

Functional Lignocellulosics & Nanotechnology

M. K. Ek, Organizer; E. Filpponen, Organizer; T. Nypelo, Organizer; S. Peresin, Organizer; S. Spirk, Organizer; T. J. Elder, Presiding; S. Peresin, Presiding Papers 368-375

CELL 368

Hydrolysis assisted by hydrogen chloride vapor on different cellulose polymorphs

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Cellulose hydrolysis catalyzed by acid originating from hydrogen chloride vapor was recently published by one of the authors. Rapid hydrolysis was shown to occur at room temperature, utilizing the water that resides on fibers under ambient conditions. Gaseous HCl adsorbs on the fibers, dissociates when in contact with water, and proceeds to catalyze the hydrolysis of cellulose down to levelling-off degree of polymerization (LODP). Here, we present what happens when different cellulose polymorphs are treated under HCl vapor. Cellulose II, cellulose III and cellulose III exhibited all distinct degradation behaviors that were markedly different from the previously published results with cellulose I. Unlike with native cellulose, the kinetics of the other polymorphs did not correspond to those in a conventional liquid/solid system. Furthermore, it appeared that their degradation did not halt at the LODP value.
Crosslinking as a facilitator for novel (nano)cellulose-based applications

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The water-liking nature of cellulose is not only a prerequisite for its biological function in the tree, but also for its processing into manmade products such as paper, packaging and absorbency products. However, for many applications, and for further functionalisation and use in more complex materials and applications, moisture and water sensitivity is a severe shortcoming and wet-durability is often a necessity. This durability can, for example, be achieved by mixing the cellulose with polyfunctional molecules that can bridge the individual particles, but this type of approach often involves some kind of curing and one or several washing steps to remove unreacted molecules. Over the last few years, our laboratory has developed a platform based on aldehyde-containing cellulose which during material processing presumably self-associate through hemiacetal bonds, and under certain conditions possibly even acetal bonds. This paper demonstrates how this modified cellulose (where the aldehyde groups introduced also acts as highly potent reaction sites for further functionalisation), as fibres or nanofibrils, can both be used to make light-weight materials, without involving any freeze-drying step, suitable for further functionalisation and excellent high-density barrier films suitable for not only packaging applications but also suitable for pharmaceutical applications where it is desirable to have a tuned and controlled diffusivity.

Biomimicked low density stiff materials from self-organized cellulose nanofibrils

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Cellulose nanofibrils (CNFs) are bio-based, nontoxic and renewable nanomaterials exhibiting excellent mechanical properties. Due to their high aspect ratio and unique surface chemistry, CNFs can be assembled to produce ultra-light, highly porous, wet stable and biocompatible aerogels. These structures are commonly found in nature where stiff, strong and highly porous structures are widespread in cellular materials such as toucan and hornbill foams¹. Characterization of their morphology has shown that most of these structures are made of a light, soft and porous core surrounded by a stiff shell to meet the necessary requirements for their practical use. In this work, a bio-mimicking approach has been used to produce low density stiff and natural materials from self-organized CNFs. A recently developed freeze-linking method was used to cast wet-stable CNF aerogels into molds of a defined-shape. Stiff coatings based on natural materials were then applied to the aerogels to provide them with a high stiffness. The preparation procedure, the structure characterization and the mechanical properties of the porous materials were studied for different core and shell compositions.
**CELL 371**

**Oriented all-cellulose film based on ramie fiber with high mechanical property and transparency**

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All-cellulose composites are typically prepared using a partial cellulose dissolution approach, here an all-cellulose film based on ramie fiber was prepared using a water-based hot pressing process. The original ramie fiber was properly degummed, mercerized, and aligned before mounted into a designed mold. After optimizing the temperature and pressure, the still wet ramie fiber “cake” was pressed into a transparent film. The structure, mechanical properties and optical properties of the film were investigated using scanning electron microscope (SEM), X-ray diffraction, tensile tests and integrating sphere devices. With ultimate strength of 620 MPa and Young’s modulus of 37 GPa, the final all-cellulose film also has a transmittance above 80%. Additionally, the degree of orientation and Herman’s orientation parameter were calculated to be above 0.9 and 0.8 based on X-ray diffraction data. Apart from being eco-friendly, the strong and transparent film may find applications in building materials and optical devices.

**CELL 372**

**Sample geometry dependency on the measured tensile properties of cellulose nanopapers**

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A prerequisite to producing high performance nanocellulose-reinforced polymer composites is to incorporate high loadings of nanocellulose (typically > 30 vol.-%) into the polymer matrix. In this context, high performance cellulose nanopapers can be used directly as reinforcement for polymers. Various researchers have reported the tensile properties of cellulose nanopapers. The reported tensile moduli and strength of between 3.2 - 22.5 GPa and 84 - 515 MPa, respectively, with various miniaturised test specimen geometries used. Cellulose network in the form of cellulose nanopapers represents a conceptually important material structure for various applications. Therefore, an accurate method for determining the mechanical properties of cellulose nanopapers is of upmost importance. In this work, we report the influence of test specimen geometries on the measured tensile properties of cellulose nanopapers. 4 different test specimen geometries for both nanofibrillated cellulose (NFC) and bacterial cellulose (BC) nanopapers were studied: (i) miniaturised dog bone test specimens, with gauge length and width of 10 mm and 2 mm, respectively, (ii) miniaturized rectangular test geometry, with gauge length and width of 25 mm and 5 mm, respectively, (iii) standard dog bone test specimens with gauge length and width of 25 mm and 5 mm, respectively and (iv) standard rectangular test geometry with gauge length and width of 70 mm and 15 mm, respectively. It was found that the tensile moduli of both NFC and BC nanopapers were not significantly influenced by the test specimen geometries as long as an independent strain measurement system was employed. The tensile strength of cellulose nanopapers, on the other hand, is influenced by test specimen geometries. It was observed that the smaller the specimen width, the higher the measured tensile strength. The measured tensile strengths of NFC nanopapers decreased from 182 MPa (2 mm width) to 157 MPa (15 mm width) and BC nanopapers decreased from 149 MPa (2 mm width) to 120 MPa (15 mm width). This is attributed to the weakest link theory, whereby probability of defects in cellulose nanopapers increases with increasing test specimen width. The effect of independent strain measurements, as well as the fracture resistance of cellulose nanopapers are also discussed in this work.
**CELL 373**

**Enzymatic and chemical modification of nanosized colloidal lignin particles**

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In this work cross-linking of nanosized colloidal lignin particles (CLPs) from softwood kraft lignin (Lignoboost™) using high redox potential *Trametes hirsuta* (ThL) and low redox potential *Melanocapus albomyces* (MaL) laccase was studied by varying enzyme dosage and incubation time. Oxygen consumption method was used to study reactivity of laccases on CLPs including visual detection of red-brown colour due to oxidation of phenolic groups to quinones. Changes in the zeta potentials towards more negative values verified oxidation of CLP surfaces due to carboxyl group formation. Dynamic light scattering measurements showed clear changes in the profiles of CLP size distributions showing cross-linking of the particles after laccase treatments. Changes in surface morphology of enzymatically cross-linked CLPs was studied by atomic force microscopy (AFM). Redispersion of ThL and MaL treated CLPs in tetrahydrofuran (THF) verified that covalent cross-links were formed in CLPs as nanolignin dispersions were stable in organic solvent even overnight. Finally, potential to exploit ultrasound treatment under alkaline conditions with H₂O₂ for the decolourization of CLPs dispersions was evaluated. It was concluded that enzymatic cross-linking at optimal pH combined with chemical oxidation is an attractive green methodology to prepare spherical, pale and non-smelling CLPs that are stable in organic solvents. As the scale up of both modification methods is feasible, it is anticipated that in the near future CLPs may be exploited as additives in different bionanomaterial applications varying from techno-chemicals to medical sector.

**CELL 374**

**Partial dissolution as a reinforcing chemistry for CNF films**

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The aim of this work was to improve the mechanical performance of CNF film with a post-crosslinking chemistry leading to a fully cellulosic film structure. Typically, pure CNF films have poor wet-strength performances due to the inherent hygroscopicity of cellulose nanofibrils (CNF). This wet-performance can be improved with added polymeric materials that can mechanically bridge fibrils, or with added substances that can glue or coat the film matrix. The all-cellulose concept is a vital approach to increase the extent of permanent fibril-fibril linkages in a CNF film, when it is targeted to a fully cellulosic film structure. In this study, we utilize the partial dissolution approach with N-methylmorpholine-N-oxide (NMMO), which is a powerful cellulose solvent. NMMO was impregnated into the CNF film structure from a methanol solution followed by a heat activation in dry conditions using simple hot-calendering approach. The study shows that the fibril structure of the CNF film existed after the NMMO dissolution. It was observed that a simultaneous heating and compression step was required to achieve embedding of fibrils during regeneration. After heat activation, the treated CNF films were purified with methanol to remove NMMO from the film structure. The used treatment elevated the mechanical performance of the CNF-films significantly. The dry strength of the reinforced CNF film was increased from 122 MPa up to 195 MPa. The wet strength of the reinforced CNF film was up to 75 % from the dry strength of a pure CNF film. The investigated robust and fast method can be utilized to produce CNF films for applications where improved water resistance and fully cellulosic structures are required characteristics.
Cell 375

Water-resistant nanocellulose films with inter-fibrillar interactions via multivalent metal ions

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Nanocellulose films exhibit excellent physical properties such as high strength and low oxygen permeability under dry conditions. However, these material properties become impaired drastically under humid conditions. In the present study, water-resistant nanocellulose films were prepared using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-oxidized cellulose nanofibrils (TOCNs) with multivalent metal carboxylate groups. The counterions of carboxylate groups on the TOCN surfaces were exchanged to multivalent metal ions from the sodium ones in as-prepared TOCN films by immersing the films into multivalent metal chloride solutions. Wet, high-moisture-content (300–500%) films of TOCNs with aluminum or iron (III) carboxylates showed high Young’s moduli of about 3 GPa and tensile strength values of 30–40 MPa. Furthermore, TOCN films with aluminum or calcium carboxylates exhibited very low oxygen permeability of about 0.1 mL μm m⁻² day⁻¹ kPa⁻¹ even at high relative humidity of 80% RH, which is an outstanding value compared with those for nanocellulose-based materials reported so far. These results are explained based on high densities of the films and the strong interactions between surface-carboxylated TOCNs via multivalent ions.

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. J. Rojas, Organizer; J. Lopez-Sanchez, Presiding; M. L. Auad, Presiding Papers 376-383

Cell 376

Wood-derived hemicelluloses as green binders in wood adhesives

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Wood adhesives of today are generally both inexpensive and perform well. However, most of them are based on petroleum-derived chemicals, which is a limited and non-renewable resource. Furthermore, some of these chemicals, for example formaldehyde, also have a negative impact on the environment and on human health. Increasing environmental concern also increases the motivation to find alternatives derived from bio-based resources that can replace petroleum-based polymers. To enable this transition it is important that the new adhesives are equally good in terms of bond strength, water resistance and heat resistance, and that the alternative can compete in terms of cost. It has proved difficult to find bio-based alternatives that fulfill all requirements; they are often too expensive or have poor water resistance. Proteins, for example, have shown very good results and a lot of research is today focusing on protein-based wood adhesives. However, protein is also a valuable food source, and therefore not an ideal candidate for the production of adhesives. Motivated by the wood-biorefinery concept of utilizing side-streams from the forest-products industry, and by the surprisingly good results from our previous studies on other polysaccharides in this type of applications, we are now, as a follow-up, investigating the possibility for using hemicelluloses derived from the forest-products industry as binders in wood adhesives. The hemicelluloses were extracted using a pilot-scale model for pre-hydrolysis and sulfate cooking of hardwood and softwood wood chips at Holmen AB, to simulate the industrial process. Water dispersions of the hemicellulose were prepared and evaluated as adhesives for wood veneers. However, the hemicellulose cannot be used as a wood adhesive by itself, due to its limited bonding performance,
especially regarding the water resistance. Therefore, the addition of different dispersing agents was evaluated, as well as the variation of different parameters, such as wood type (hardwood or softwood), solid content, pH, and preparation and application methods. Several of the hemicellulose dispersions demonstrate very good bond strength and surprisingly good water and heat resistance, even in comparison with commercially available wood adhesives.

CELL 377

Novel thermoset polymeric networks from fast pyrolysis bio-oil

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Wood biomass is the most promising bio-based resource of raw materials due to its abundance. Through fast pyrolysis as a thermochemical conversion process, it can be transformed into more utilizable liquid fraction called fast pyrolysis bio-oil. Several attempts have been done to polymerize fast pyrolysis bio-oil. Present research is focused on the development of graft networks of fast pyrolysis bio-oil derived polymers. In the initial phase, formaldehyde was used to polymerize the phenol derivatives present in the fast pyrolysis bio-oil with varying proportions of phenol in acidic medium to form bio-based novolac polymer (BioNovolac). The BioNovolac polymer was chemically incorporated with epoxy resins synthesized from α-resorcylic acid, a naturally occurring dihydroxybenzoic acid. Fourier Transform Infra Red (FTIR) spectroscopy was used to monitor the synthesis of BioNovolac as well as bio-based epoxy resins. Crosslinking of epoxy resin was carried out by anionic polymerization route in immediate presence of BioNovolac to give novel thermoset networks. Fast pyrolysis bio-oil was also epoxidized in order to form another type of epoxy networks. The characterization techniques mainly included thermomechanical performance by Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC).

CELL 378

Development of clay-like extrudable wood fiber material

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According to the Paris Agreement, we have to hurry up to develop 100 \% plant-based materials which could substitute oil-based plastics. Although many bio-based plastics have been industrialized, the durability is not good enough in most cases. In this study, learning from the long life of wood, we considered to create novel bio-based materials with any shape using wood fibers. Unfortunately, wood fibers are not able to be molded by injection or extrusion like plastics. In order to extrude wood fibers without using any oil-based plastics, water and a cellulosic derivative were mixed to increase viscosity. The extrudability and shape retention of the resultant clay-like wood fiber materials were studied. The extruded materials were naturally or mandatorily dried to give molded products. Their bending and tension strength were measured using a testing machine. Recyclability was also studied by addition of water. The ratio of wood fiber to cellulose derivative and the water content were searched to give sufficient extrudability, recyclability and characteristics required.
Synthesis and characterization of bio-oil-based self-curing epoxy resin

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The purpose of this study was to investigate the utilization of bio-oil obtained from hydrothermal liquefaction (HTL) of loblolly pine for the synthesis of bio-based epoxy resin. In addition, the effect of ethanol, which is used as a co-solvent in the HTL process, on the properties of resulting bio-oil-based epoxy resin (BOBER) was studied for the first time. Quantitative ³¹P-NMR analysis of HTL-bio-oil showed that addition of ethanol in HTL process resulted in increase in the concentration of aliphatic type OH groups. It was found that not only the total hydroxyl (OH) number of HTL-bio-oil had an effect on the yield and epoxy equivalent weight of BOBER, but the distribution of OH groups within bio-oil (aliphatic, phenolic and acidic OH) also played an important role for the determination of the optimum amount of catalyst to be used in the synthesis of BOBER. Differential Scanning Calorimetry (DSC) analysis proved the self-curing phenomena of BOBER, and the activation energy for curing was calculated to be 95 – 98 kJ/mol, using Kissinger model of kinetic analysis. Fourier Transform Infrared Spectroscopy (FT-IR) and curing kinetics analysis suggested that etherification reaction was the dominating reaction during the self-curing of BOBER. Glass transition temperature, crosslinking density, and the storage modulus of self-cured BOBER were calculated to be 63.6 – 96 °C, 8.5 – 58.7 mol/m³, and 425 – 845 MPa, respectively, using Dynamic Mechanical Analysis (DMA). The BOBER system developed in this study provided promising results to replace HTL-bio-oil with the petroleum-based phenolic resource for the synthesis of epoxy resins.
Valorization of starchy, cellulosic, and sugary food waste into value-added chemicals

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Approximately one-third of the food products, i.e., over one billion tonnes per year go to wastage globally. This study aimed to produce value-added chemicals from catering remains through a high-throughput catalytic thermal process. Using pre-consumer food waste (sugary, starchy, and cellulosic), a range of metal chlorides were evaluated to produce hydroxymethylfurfural (HMF) and levulinic acid in dimethyl sulfoxide (DMSO)/water (1:1 v/v) under heating at 120-160°C for 20-40 min. The results showed that cooked rice as a surrogate of starchy food waste produced 8 wt% HMF and 65 wt% glucose over SnCl₄ under heating at 140°C for 20 min. The hydrolysis of starch was acid-catalyzed by protons released from metal hydrolysis and acidic by-products, as well as the Lewis acid site of metal. Yet the subsequent isomerization of glucose was rate-limiting so a longer time was required to improve the HMF yield to 23 wt%. An increase in temperature to 160°C could promote the further rehydration of HMF to yield 17 wt% levulinic acid. Kiwifruit that represented sugary substrates yielded 14 wt% HMF over SnCl₄ mainly from the naturally present sugars. However, the pre-existing organic acids in the fruit may hinder the Fe-mediated fructose dehydration. In comparison, the conversion of raw mixed vegetables i.e., cellulosic waste was not satisfying under any conditions in this study due to the limited hydrolysis of crystalline cellulose, which may be improved by thermal pretreatment. The experimental results of this work demonstrate a good potential of catalytic valorization of sorted food waste to HMF and levulinic acid in real-life applications.

Microcellular foaming of arabinoxylan with scCO₂

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Commercial foamed materials used in packaging, wound care and hygiene products are today produced mostly from fossil-based raw materials. From a sustainability perspective, foams for various applications should be based on renewable materials. The hemicellulose arabinoxylan can be extracted from barley husk, today an agricultural by-product. Characterization of the extracted hemicellulose gave a composition consisting mainly of 62.1% xylose, 26.2% arabinose, and 10.5% glucose, giving an Ara/Xyl ratio of 0.42. The arabinoxylan also contained 9 wt.% lignin. Arabinoxylan foam was produced using a microcellular batch foaming process. The gas, here scCO₂, dissolves by diffusion into the polymer and when the pressure is released forms foam cells inside the material. The morphology of the foams produced are determined by several factors, such as amount of gas dissolved in the polymer and heat. Foaming was performed at set temperatures (120°C, 130°C, 140°C, 150°C, 160°C, and 170°C) and solubilization time was 2 hours with a CO₂ pressure at 10MPa. Arabinoxylan foams could be produced at temperatures above 150°C.
The chemistry and processes involved in transforming biomass offer many challenges that continuously tantalise scientists in the search of more efficient and creative ways to minimising the energy required and overall environmental footprint. We have seen the consolidation of biotechnology as a fundamental tool in biomass transformations, particularly due to the mild conditions typically required by enzymes and microorganisms. Thermochemical transformation technologies offer many advantages over biotransformations, however, the high energetic requirements is still a draw-back. The utilisation of alternative energy vectors and *stimuli* to transform biomass, such as in the utilisation of microwave technology, sonochemistry or mechanochemistry offer some promise. However, could we possibly carry out demanding biomass transformations at very mild conditions without microorganisms or enzymes?

The answer is yes, using light and catalysis. We have the vision that solar light will one day be used as the driving energy source to carry out the highly demanding upgrade of biomass under conditions similar to biotransformations, without requiring the feed microorganisms do. Our experiments recently demonstrated that it is possible to convert glucose to a range of partially oxidised products with 100% carbon mass balances with solar light even on a cloudy day in Liverpool (UK) using cheap and unmodified TiO$_2$ as photocatalyst. We also found that plasmonic gold, silver and gold-silver alloyed nanoparticles promote the activity of titania in this reaction towards oxidation products. And more
recently, we have demonstrated that selectivity can also be achieved when directly reacting cellobiose in one single process that breaks down the cellobiose glycosidic bond to yield glucose, but also formic acid in substantial yields using light at room temperature. In this presentation, we will critically review recent advances in this area and highlight the opportunities we have experimentally identified on the more challenging direct cellulose conversion and the utilisation of high-pressure reactive gases during the photocatalytic transformation.

CELL 383

Agricultural and industrial residues: Cellulose fiber and its nanocrystals

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The growing demand for more sustainable products and production processes, has contributed to the development of new materials that contribute to the lower generation of environmental impacts. In this sense, biodegradable composite production route has been gaining attention, in particular by enhancing use of natural fiber or cellulose nanocrystals (CNC). The fiber contains cellulose microfibrils, held together by a matrix formed of lignin, hemicellulose and cellulose. However, these levels vary with the variety of sources of cellulose, natural or industrial fibers, and thus provide different studies, most recently, aimed at modification of the ligno-cellulosic structure and can obtain nanocrystals. In this study we addressed the reuse of cotton fibers (cellulose type I) and paper residue from industrial process for production of paper (cellulose type II) by obtaining CNC’s by acid hydrolysis. This study compared its thermal properties by thermogravimetric analysis (TGA), chemical structure by spectroscopy in the infrared region using Fourier transform (FTIR), scanning electron microscopy (SEM) and dynamic light scattering (DLS) to check the size of the obtained nanocrystals, aiming the reuse and minimization of discards materials. The results showed that cotton residue has higher thermal stability and fewer impurities than the industrial residue. The obtaining nanocrystals both cotton residue and paper industrial further differentiate the cellulose type (I and II) of pulp for each fiber. It revealed that the cotton had smaller CNC (120nm) with great water level (80 wt.%) and industrial residue had larger CNC (160nm) with improved stability.

WEDNESDAY AFTERNOON

Bio-based Gels & Porous Materials
T. Budtova, Organizer; F. Liebner, Organizer; F. Liebner, Presiding; H. Mansur, Presiding Papers 384-391

CELL 384

Green synthesis of superabsorbent carboxymethylcellulose-based hydrogels with tunable physicochemical properties by citric acid crosslinking for wound dressing applications

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Skin, as the largest organ of body, is a complex tissue and an efficient barrier against external factors, such as UV radiation and pathogenic microbial agents. Skin loss can be caused by accident, burn, trauma, chronic wounds, and diseases, which has become one of the most serious problems in clinic.
Hence, skin damages require a regenerative strategy based on the use of appropriate wound dressing supports to facilitate the regeneration of tissue and repair the lost or damaged tissue [1-3]. Thus, this study focused on the preparation of new environmentally friendly hydrogels based on carboxymethylcellulose originating from renewable and sustainable natural resources and extensively investigating their physicochemical properties and non-toxicity. Sodium carboxymethylcellulose (CMCel) biopolymer with two degrees of substitution (DS=0.77 and 1.22) were used for the green synthesis of superabsorbent hydrogels with citric acid (CA) as crosslinker for tailoring the matrix network properties. In addition, 10 wt.% of polyethylene glycol (PEG) was blended to CMCel in the synthesis to compare the effect as network plasticizer. These hydrogels were characterized by swelling measurements, thermal analysis (TGA/DSC) and Fourier transform infrared spectroscopy (FTIR) to access the degree of crosslinking (DC) with different concentrations of CA with each of the polymers. The results demonstrated that superabsorbent hydrogels were produced capable to absorb large amounts of water through a swelling process with weight gain typically ranging from 10–30 times higher than their initial one (i.e., 100%–3000%), which was strongly dependent of the concentration of CA crosslinker and the addition of PEG. Moreover, insights on the mechanism of crosslinking were suggested based on the FTIR results of the characteristic bands of –COOH and –OH as reacting chemical functional groups. All of the CMCel-based hydrogels investigated were biocompatible considering the cell viability responses by MTT assay (≥95%). Thus, these novel superabsorbent CMCel-based hydrogels with designed tunable properties were biocompatible and eco-friendly biomaterials to be potentially used for wound dressing and skin tissue engineering applications.

CELL 385

Multifunctional hydrogel dressing material for treatment of chronic wound

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One-step enzymatic crosslinking approach was used to synthesize multifunctional hydrogels for chronic wounds from thiolated chitosan and gallic acid. Stable at physiological conditions hydrogels with tunable physicomechanical and functional properties were generated with the aid of the oxidative enzyme laccase. The potential of these hydrogels as wound dressing materials was evaluated in vitro against major factors governing the chronicity in wounds, such as myeloperoxidase (MPO) and matrix metalloproteinases (MMPs) activities, reactive oxygen species (ROS) and bacterial contamination. The study revealed a decrease of the MPO and collagenase activities by up to 98 % and 23 %, respectively. The hydrogels showed significant antioxidant activity, scavenging the free 1,1-diphenyl-2-picrylhydrazyl radical up to 94 %. In addition, the hydrogels reduced by 2 logs the bacterial population of both S.aureus and E.coli strains. Ex-vivo studies with a wound exudate collected from a patient with a venous leg ulcer confirmed the inhibitory capacity of the hydrogels against MPO and MMPs. The hydrogels showed up to 99 % biocompatibility over 24 and 168 hours of incubation. This new dressing material combines in a unique design several beneficial to wound healing properties – control over the MMP/MPO activity, antioxidant and antimicrobial effect, coupled to high swelling capacity for exudate retention.

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Hierarchically porous nanocellulose materials for cartilage applications

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Recently, the use of nanocellulose has garnered outstanding interest in biomedical applications due to high surface area, high mechanical properties, hydrophilicity, good cytocompatibility, moisture stability,
and ability to form porous structures. In the current study, we present nanocellulose based porous materials processed via freeze-drying technique with potential use for cartilage applications. In the first approach, 3-dimensional porous scaffolds were prepared using cellulose nanofibers (70-90 wt%) as functional additive and/or reinforcement. In room conditions, the mechanical performance of the produced materials in compression mode was found to be comparable with natural cartilage and in phosphate buffered saline (PBS), the mechanical properties were found appropriate for chondrogenesis. In the second approach, oven-drying was used prior to freeze-drying to achieve improved mechanical performance and stability in simulated body conditions. Cellulose nanocrystals (50 wt%) with carboxyl group on the surface were used as reinforcement, which resulted in synergistic mechanical properties comparable to natural cartilage in high humidity conditions. Both approaches resulted in highly porous structures with interconnected pores and nanoscaled pore wall roughness favorable for chondrocyte attachment and potential use in cartilage applications.

CELL 387

Cellulose-based hydrogels with encapsulative cyclooligosaccharides to enhance the efficient release of hardly soluble drugs

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Cyclooligosaccharides have been recently used as a suitable encapsulative complexation agent to enhance the solubility of drugs that are hardly water-soluble via supramolecular complexation. In this study, we prepared cellulose-based hydrogels with encapsulative cyclooligosaccharides such as cyclophorase (Cys) and β-cyclodextrin (β-CD) where Cys is a cyclic β-1,2-glucan and β-CD is a cyclic-
α-1,4-glucan. Those hydrogels were prepared from cellulose or carboxymethylcellulose and cyclooligosaccharides using epichlorohydrin as a cross-linker. The structure and morphology of the those hydrogels were characterized using Fourier transform infrared (FT-IR) spectroscopy, solid-state nuclear magnetic resonance (NMR) spectroscopy, field-emission scanning electron microscopy (FE-SEM). Galangin and tetracycline were chosen as hardly soluble model drugs for efficient release, respectively. Galangin was known to inhibit the activity of β-lactamase directly and to exhibit intrinsic antibacterial activity, and tetracycline is a wide range of spectrum antibiotic used for the treatment of infections. The results revealed that the cyclooligosaccharide contributed to the change of pore sizes and the adsorption ability for target drugs with its strong encapsulative complexation ability in the hydrogels. In case of Cys containing hydrogel, it had antibacterial activity against S. aureus with growth inhibition maintained up to 72 h in an efficient release of galangin. Throughout the study, the cyclooligosaccharides containing hydrogel showed potential advantages as an efficiently release of hardly soluble drugs.

Scheme for the cellulose-based hydrogels with encapsulative cyclooligosaccharides.

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Biomass-derived highly stretchable and elastic hydrogels with effective antimicrobial activity

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Hydrogels are attractive for their wide applications as scaffolds for tissue engineering, vehicles for drug delivery, actuators for optics and fluidics, and model extracellular matrices for biological studies. The performance of hydrogel applications, however, is often severely limited by their poor mechanical
behavior. Herein, we present a scalable methodology to create highly stretchable, interpenetrating structured hydrogels by combining a green biomass—alginate and polyacrylamide. Our approach causes the naturally abundant and sustainable alginate to assemble into elastic hydrogels with tunable water-content and desirable shapes on a large scale. The resulting hydrogels exhibit high water content of > 90 wt%, rapid recovery from 20 times deformation, efficient energy absorption, and high transparency. Moreover, by incorporating antimicrobial materials such as halamine and light active anthraquione derivatives, highly antimicrobial hydrogels can be facilely achieved. The successful synthesis of such fascinating materials may provide new insights into the design and development of multifunctional hydrogels for various applications.

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Preparation of cellulose and chitin-CdTe quantum dots films and antibacterial effect on Staphylococcus aureus and Pseudomonas aeruginosa

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Novel chitin–cadmium-tellurium quantum dot (Chitin-CdTeQD) and cellulose-CdTeQD hybrid films combining chitin and CdTe quantum dots (CdTeQDs) were prepared via a facile aqueous synthesis route at room temperature. Films were characterized by field emission scanning electron microscopy and energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis. Antibacterial activity was studied on both gram positive (Staphylococcus aureus) and gram negative (Pseudomonas aeruginosa) bacteria. Antibacterial properties were tested with agar diffusion testing assay and with confocal laser scanning microscopic image analysis. Chitin–CdTeQD films exhibited an excellent antibacterial activity against both gram-positive and gram-negative bacteria. Chitin–CdTeQD films might be a desirable antibacterial material that could have potential in biomedical applications such as in wound dressing, burn treatment, drug delivery systems, ophthalmology and implants.

CELL 390

Cellulose aerogels via self-assembling and electrospinning

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This paper presents novel cellulose aerogels created by optimizing self-assembling and electrospinning approaches into unique cellular and pore morphologies and tunable surface hydrophobicity and hydrophilicity for versatile applications including polar/non-polar liquid separation, water purification, catalysis, and ion diffusion. Cellulose nano-fibers and sub-micron sized fibers have been electrospun with varied pore and sheath-core structures as well as chemical functionalities. 1D nano-arrays of highly crystalline nanocellulose in varied geometries and surface chemistries have been derived from the waste streams of our food system. These nanocelluloses are not only amphiphilic but can also be tuned to be surface charged to act as surface active agents, coagulants for microbes, templates for nano-particles and nano-prisms and to self-assemble into various porous structures. Cellulose aerogels have been facilely engineered from either nanocellulose or electrospun cellulose nanofibers alone as well as in combination to exhibit super-absorbency, wet-resiliency, dry strength and tunable amphiphilic-to-hydrophobic characteristics.
Nanocellulose composite hydrogels – Tailoring of mechanical properties of tissue scaffolds

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Hydrogels are promising scaffold candidates for tissue engineering, as they exhibit excellent biocompatibility and physicochemical properties similar to those found in the early stages of wound healing. Among these hydrogels, nanocellulose based materials have shown promising characteristics for tissue engineering. In combination with other biomaterials (e.g. alginate and gelatine), promising composite hydrogels can be produced. Structure-function relationships in the composite hydrogels are of current interest, and can be used to tailor the mechanical properties of the composite systems. In this presentation, the combination of biopolymers and how the combinations affect mechanical properties (e.g. elastic properties and swelling/syneresis) will be highlighted.

Reactive extrusion of zein with glyoxal and polyethylene maleic anhydride

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In order for zein, a potentially significant co-product of the bio-ethanol industry, to be used in new markets, improved zein based products are needed. These products need to be produced by the most economical means possible, and extrusion techniques meet these requirements. It has been shown that the processing window for zein on an extruder is quite large, up to 160 °C. This suggests that various reactive reagents can be employed to provide a modified zein protein using reactive extrusion techniques. We will report on our efforts to modify zein using either glyoxal or polyethylene maleic anhydride (PEMA) in solution and in the melt state. As PEMA is polymeric it is orders of magnitude safer than other crosslinking technologies. The zein modification was undertaken in melt batch processes and using reactive extrusion. Final melt processed articles were produced by compression molding and by injection molding. The articles produced had improved physical properties and improved solvent resistance.
Melt-processing of cellulose pulp and polycaprolactone composites: Wet feeding approach to improve the filler dispersion

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Poly(ε-caprolactone) (PCL) is a biodegradable and biocompatible commercially produced thermoplastic with unique properties similar to low-density poly(ethylene) (LDPE) such as high elongation at break, and facile melt-processing. However, despite vast progress in producing PCL based materials, PCL suffers from low tensile strength (16-27 MPa), Young’s Modulus (250-420 MPa) and higher cost compared to LDPE and Polypropylene (PP). To produce a high strength composite while maintain biodegradability, PCL has been melt blended with Cellulose Nanocrystals (CNC) and Cellulose Nanofibres (CNF). Melt blending of cellulose in a traditional fashion is not only energy and time consuming, it also results in cellulose agglomeration due to polysaccharide aggregation and large interfacial energy, and therefore poor dispersion leading to inferior mechanical properties. The “wet-feeding” strategy is already an industrial compounding reality for clay-based composites and recently it has been reported also for CNC/poly(lactid acid) nanocomposites that not only prevents polysaccharide aggregation but also in which the drying takes place during the extrusion. This method may also lead to a three-dimensional percolating cellulose network in the composite after melt processing. This work reports the development of a wet feeding method to prepare biodegradable cellulosic fibers/PCL composites. A cellulosic pulp was selected for this study. The concentration of cellulosic fibers in the composites was varied from 0-20% and the resulting thermal-mechanical properties of the composites were investigated by DSC, TGA, Tensile testing and DMA. The effect of the wet feeding on the composite morphology was assessed by SEM and microtomography. The effect of the shear stress on the shortening and dispersion of the cellulose fibers is reported. With the addition of 20% cellulosic fibers, the Young’s Modulus was increased from 240 MPa to 1500 MPa for the composite produced by using the wet feeding strategy, while for the dry feeding one the value was 710 MPa. The morphological analysis confirms a better dispersion of the fibers in the polymeric matrix for the composites prepared by using the wet feeding extrusion strategy in comparison to the dry feeding one.

Reactive extrusion compatibilization of cellulose acetate/water soluble polymer blends

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The production of fully biodegradable materials is receiving large attention in the research community and industrial sector as the way out to produce environmentally friendly products. Biodegradable polymeric materials are an important alternative because they diminish the consequences of plastic waste through composting. In this communication, the preparation and reactive compatibilization of biodegradable blends of cellulose acetate (CA) with two water soluble polymers; polyvinyl alcohol (PVOH) and the bio-sourced hydroxyethyl cellulose (HEC) will be presented. Like CA, HEC is advantageously both biodegradable and bio-sourced. The prepared blends were characterized in terms of morphology and
thermo-mechanical properties. The quality of blend interface was enhanced by reactive compatibilization using maleic anhydride grafted-polylactide (MAgPLA). An original procedure was conducted using two extruders connected in a T-configuration to prepare various plasticized CA-PVOH blends compositions. This advantageous set up allowed for in situ plasticization of CA which significantly reduces its thermo-oxidative degradation. The water-response of these blends was evaluated to settle on their potential as new water-dispersive biodegradable materials.

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**Reactive compatibilizers in the creation of wood fiber plastic composites**

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This work investigates the production, mechanical, thermal properties, water resistance and microstructure of a plasticized starch (PSA) modified wood plastic composite (WPC), which were made by low density polyethylene (LDPE), hardwood fiber (HW), plasticized starch (PSA), and polyethylene grafted maleic anhydride (MAPE). The addition of MAPE by 5 wt% in the composite formulation significantly increased both tensile strength and modulus. This can be attributed to the reactive interaction between the MAPE and the carbohydrates present in the composite materials. The addition of 25 wt% plasticized starch mixed with MAPE further improved the benefits of the MAPE. This allowed for increased amounts of natural based materials to be used in the composite and also improved both the tensile strength and the modulus of the composite materials. Microstructure analysis of PSA modified WPC indicated that bonding does take place between the wood fiber, starch and polyethylene with the reactive interaction of the MAPE. WPC modified with addition of PSA absorbed more water than unmodified WPC in the same amount of time. Thermal degradation and transition properties were also studied. This project has shown that the use of starch modified with MAPE as a binder in wood plastic composite can give improved strength and modulus while still be relatively stable in water and providing traditional thermoplastic benefits of moldability and durability.
液态辅助挤出过程的 cellulose 纳米复合材料

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制造 cellulose 基础纳米复合材料的困难在于在热塑性聚合物中分散纳米纤维或微晶，同时不致使其降解。最常见的方法是溶剂浇铸，其中首先在溶剂中分散 cellulose 纳米纤维或微晶，随后与溶解的聚合物混合。然而，使用非水溶性聚合物会带来困难，如纳米纤维或微晶的分散以及溶剂的蒸发。本文介绍熔体挤出和通过液体喂入分散 cellulose 纳米纤维或微晶在熔体聚合物中的可能性。这种方法在 PLA 聚合物中分散了纳米纤维并改善了性能。挤出是一个能源效率高且成本低廉的加工方法，可以被扩大为工业规模。

新见解于熔体加工的 cellulose 纳米材料基纳米复合材料

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使用湿法（溶剂浇铸）加工 cellulose 纳米材料支撑聚合物纳米复合材料已经广泛研究和报告。此模式的加工允许保持纳米颗粒的分散，从而提高材料的机械性能。然而，如果工业和大规模制造 cellulose 纳米材料支撑聚合物纳米复合材料是最终目标，熔体加工肯定是更感兴趣的技术，因为最终产品可以很容易地通过挤出、注射-模压、吹模或压缩模压来成形，但也是最具挑战性的。自我聚集和热降解问题已被清楚地识别为需要克服的主要挑战。然而，这些问题可以很容易地通过化学表面改性来解决，例如通过化学地改变纳米颗粒的表面。但是，共价功能化纳米填料通常涉及复杂且昂贵的步骤，这可能阻止大多数工业应用。因此，许多研究人员最近将研究重点放在最简单物理功能化 cellulose 纳米材料上，并且优先考虑使用水作为分散介质。事实表明，由此产生的材料的机械性能总是令人失望，与预期相去甚远。

挤出技术用于包含可再生 lignocellulosic 材料的纳米复合材料

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纤维是高性能复合材料中最重要的先进工程材料之一。在这一方面，从可再生和可持续植物来源获取 cellulose 和 lignin。为复合材料提供了纤维。一个主要挑战是 lignin 和 cellulose 与各种合成聚合物材料的不相容性。在这里，我们讨论开发挤出的纤维纳米复合材料的新方法，从聚合物。熔体挤出在塑料化剂的存在下使用 cellulose 纳米微晶。
of the CNC. The resulting structure of the nanocomposite and thermal, mechanical and physical properties are described. The approach successfully allows for melt extrusion of filament with high CNC loadings. With regards to using lignin as the matrix material in composites, we have evaluated several chemical modifications to the lignin to make it more thermally stable, have a lower processing temperature and improve compatibility with synthetic polymers. Chemical modifications to the lignin can be used to tune properties so that there are windows in which the lignin can be adequately processed. Results have shown that a variety of interesting blends of lignin with synthetic and other natural polymers can be produced.

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Processing of (nano)biocomposite foams by continuous supercritical CO₂ assisted extrusion

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Biobased polymers like biopolymesters (PHAs, PLA) or thermoplastic starch (TPS) are marketed as eco-friendly alternatives to the currently widespread non-degradable oil-based thermoplastics, due to their renewable origin, their biodegradability and biocompatibility. Their properties are similar to various synthetic thermoplastics like polypropylene, and hence can be used alternatively in agriculture, packaging but also biomedical applications. However, some drawbacks prevent their development on the market. In particular, this class of biobased polymers is often brittle with poor thermal stability and low crystallization rate. Current researches are focused on the control of their processing and structure by chemical / microstructural modifications or the design of new processes. The synthesis of copolymers or the use of plasticizers have been proposed to control mechanical properties, lower melting temperatures and extend processing windows. Improved thermal stability, mechanical or barrier properties can be obtained by the preparation of nanocomposite materials incorporating nanoparticles with high aspect ratios and specific surfaces. An innovative way to control polymer structures is the use of supercritical fluids assisted processes. Supercritical carbon dioxide (sc-CO₂) has favorable interactions with polymers and can be easily dissolved to act as a plasticizer hence modifying drastically their properties. sc-CO₂ can also act as a foaming agent during processing to generate porous structures of interest for packaging or drug release applications. In this study, a continuous sc-CO₂ assisted extrusion process has been used to prepare PHBV/organo-clays nano-biocomposite foams by the direct foaming of physical PHBV/clays mixtures, and the foaming of extruded PHBV/clays mixtures prepared by twin-screw extrusion. The structures obtained were characterized in terms of clay dispersion, matrix crystallization, and porosity. The influence of processing conditions and the clays/foaming interrelationships have been elucidated. By controlling the sc-CO₂ mass fraction in a narrow window, good clay dispersion appears to favor homogeneous nucleation while limiting the coalescence of the pores, and hence allowed to obtain nano-biocomposite foams with better homogeneity and porosity up to 50%. Perspectives in the use of such processes with amorphous biopolymesters such as PLA and its blends will be addressed.

Advances in Polysaccharides: Practice & Applications
A. Biswas, Organizer; H. Cheng, Organizer; W. J. Orts, Presiding Papers 400-407

CELL 400

Polysaccharide-surfactant association—basics and applications

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Formulations typically contain both polymers and low molecular weight amphiphiles, i.e., surfactants or lipids. Depending on polymer charge and polarity, intermolecular interactions, and, consequently, macroscopic properties are very different. Here we review on the basis of the fundamentals of interactions phenomena and applications of mixed systems of surfactants and polysaccharides. The latter may be anionic (alginate, carboxymethylcellulose...), cationic (chitosan, cationic hydroxyethylcellulose...) or nonionic (cellulose ethers...). For ionic polysaccharides, electrostatic interactions dominate the behavior and depending on the situation associative or segregative phase behavior may occur. For nonionic polysaccharides temperature dependent hydrophobic interactions dominate the phase behavior and other properties. In general there is a delicate balance between different interactions. Water-soluble polymers, which have hydrophobic groups, form physical cross-links, hence their important use as thickeners. The rheological behavior is strongly influenced by surfactants and both a decrease and an increase in viscosity can occur. For oppositely charged systems where the polysaccharide-surfactant interactions are particularly strong, an associative phase separation can occur. A similar behavior is shown for mixtures of two oppositely charge polysaccharides. This association is the basis for thickening formulations, for polysaccharide deposition on surfaces and different ways of producing particles in the nano- to micron size range. Furthermore, the behavior of these mixed systems on surfaces is discussed. In particular, we consider the adsorption of mixtures of ionic polymers and oppositely charged surfactants on polar and nonpolar surfaces. Depending on concentration, an ionic surfactant can either induce additional polyanion adsorption or induce desorption. Kinetic control of adsorption and, in particular, desorption is typical. Important consequences of this include an increased adsorption on rinsing and path dependent adsorbed layers.

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Creating cost-effective agriculturally-derived nanocomposites for commodity applications

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Recent strategies for expanding the commercial potential of lignocellulosic (bio)composites and nanocomposites are reviewed with the focus on processes that could compete economically in commodity markets. For example, the high cost of creating and separating nanocrystalline cellulose fibrils at a viable commercial scale has prevented their wide-scale adoption. This was addressed in a series of studies where nanofibrils were isolated using the enzyme-rich digestate from a commercial-grade anaerobic digestor – a “cost-free” source of (unspecified) enzymes. Fiber pulps which were incubated for 5, 10, and 20 days in the enzyme-rich liquid supernatant isolated from a mesophilic anaerobic digestor resulted in marked changes in morphology, crystallinity, and thermal stability of fibrils, eventually creating nanofibrils. Results from DSC, x-ray analysis and microscopy showed that enzymatic hydrolysis likely favored removal of amorphous domains. Another low-cost approach for making (nano)composites involved thermal-treatment of pulps. In a series of studies, fibrils from different biomass sources were heat-treated at 200-300°C in a process called torrefaction, and were used as fillers/modifiers in place of typical plastic additives with some unique results. Addition of 5% ground torrefied walnut and almond shells, for example, into commercial-grade polypropylene increased its heat distortion temperatures; i.e., its practical softening point, by 8–24°C compared with neat polypropylene. It also increased flexural modulus by up to 40%, accompanied by a moderate increase in glass transition temperature. In this review, we present several studies exploring how properties of thermally-treated fibrils vary by source and size (altered via grinding toward the nano-scale), making them uniquely applicable in various potential commercial applications including (1) as additive in commodity (bio)plastics, (2) in car tires as a carbon black displacement, (3) as filtering media for water treatment via activation, and (4) as an amendment in
soils. This presentation will explore processing methods that meet the low cost-points required to enter high volume commodity markets.

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Functional cellulose arabinoxylan fiber from agricultural biomass

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Water insoluble cellulose arabinoxylan fibers were prepared from low-valued agricultural processing by-products (corn fiber, wheat bran, sorghum bran, rice fiber, barley hulls, sugar cane bagasse, carrot pomace etc.), agricultural residues (corn stover, wheat straw, barley straw etc.) and energy crops (switch grass, miscanthus, biomass sorghum, etc.) by removing the alkali-extractable hemicelluloses and processing the alkali insoluble material under high temperature and high shear conditions. The yield of these fibrous plant materials varied from 14.3 to 59.90 % and most of them contained more than 90% insoluble dietary fiber. Sugar composition and glycosyl-linkage analysis show that they are composed of cellulose and arabinoxylans indicating that they have a typical cellulosic arabinoxylan structure. They have very high water holding capacity varying from 6.374 to 74.33 g/g (water/fiber), indicating their usefulness in many food system applications as moisture management aids and texturizing agents. Their ORAC values vary from 352 to 1560 µmole Trolox/100 gram showing that they have the ability to provide antioxidant activity in foods, as well as offering other functionality and health-promoting benefits of dietary fiber.

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Strategies toward cellulose nanofibers, porous fibers and hybrids

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This paper highlights top-down and bottom-up approaches to generate ultra-fine cellulose fibers of nanoscale dimensions, micro-porous, meso-porous and shealth-core hybrid structures as well as surface active fibrous materials. Dissolved cellulose derivatives have been facilely electrospun into homogeneous or 1D to 3D hybrid fibrous membranes that could be easily converted to cellulose, nanocomposites and porous fibers. Highly crystalline Ib nanocellulose in varied geometries and surface chemistries have been efficiently derived via diverse ways to exhibit unique dispersing and emulsifying properties for oil-water emulsions, coagulants for microbes as well as templates for nanoparticles and nanoprisms. These nanocelluloses could also be assembled into new fibrous structures, super-absorbent hydrogels and amphiphilic aerogels for applications, such as nano-composites, oil recovery and separation, water purification, etc. While these ultra-fine fibers from these two approaches share some similar fibrous morphologies, their crystalline structures, thermal behavior and chemical functionalities are distinctly different, offering a wide range of characteristics as novel functional materials.

CELL 404

UV-absorbing materials based on natural molecular sunscreens and chitosan

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To prevent the negative effects of ultraviolet (UV) radiations from sunlight (e.g., skin cancer), we have designed and prepared novel UV-absorbing materials inspired by nature and entirely based on molecular compounds from marine organisms. The unique physicochemical and structural properties of chitosan were combined with the remarkable UV-absorbing capacity of metabolites designated as mycosporine-like amino acids (MAAs). MAAs are known to act as natural sunscreens in marine organisms, namely cyanobacteria, algae, fungi and some fish species. Chitosan was used as a matrix to graft the MAAs. The resulting UV-absorbing materials retained the characteristic absorption properties of the MAAs in the UVA and UVB regions, and exhibited a strong capacity to absorb both types of UV radiations. The materials were also photostable and thermoresistant after exposure to drastic physical treatments. The biocompatibility of the materials was assessed using cell cultures of murine fibroblasts. The materials were shown to be non-cytotoxic and fully compatible with cell proliferation and adhesion. Thus, they present a high potential for use in medical devices and many other applications.

**CELL 405**

Higher value films prepared from poly(vinyl alcohol) and amylose-fatty acid derivatives inclusion complexes

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Water soluble amylose fatty acid and fatty ammonium salt inclusion complexes (AIC) were prepared by jet cooked high amylose corn starch with water soluble salts of long chain fatty acids or fatty amines. The formation of AIC was confirmed by X-ray diffraction of freeze-dried samples. After dissolution in water, AIC solutions were combined with solutions of polyvinylalcohol (PVOH) at various ratios. High clarity films, using glycerol as a plasticizer, were produced. Physical properties were determined and many PVOH/AIC films had improved properties versus traditional PVOH and corn starch blends where no complex was present. The surface tension of these films was determined versus water and surprisingly it was found that the films prepared from the water soluble AIC and water soluble PVOH had much higher water contact angles when compared to the control PVOH film. While PVOH films had a water contact angle of 32°, the PVOH/AIC films had contact angles of between 70 and 89°. The oxygen permeability of the films remained exceptional. These properties allows PVOH to be used in other markets and reduces the carbon foot print for PVOH articles by replacing PVOH with a starch complex providing a new revenue stream for corn starch producers.

**CELL 406**

Bio-based sources for p-xylene

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Bio-based terephthalic acid is becoming a commercial reality due to the support of brand-owners such as those of the Plant PET Technology Collaborative (Coke, Ford, Heinz, Nike, P&G) and PepsiCo announcing their goal for a 100% bio-based PET plastic. Micromidas is scaling up a chemical process to convert carbohydrate raw materials into the petrochemical precursor of terephthalic acid, with the goal of producing biobased p-xylene cost-competitively with the incumbent petroleum-based p-xylene. The process is feedstock agnostic, being capable of converting raw materials such as agricultural residues (corn stover and sugar beet residues), wood residues, glucose, sucrose and starch. It uses hydrochloric acid to simultaneously saccharify and dehydrate pentoses to furfural and hexoses to 5-chloromethylfurfural (CMF). These compounds are then reduced to 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), respectively, which are then converted to toluene and p-xylene by a Diels-Alder
[4+2] cycloaddition with ethylene. The Micromidas process gives industry-leading yields throughout and
has demonstrated that the p-xylene produced from this process meets the same quality specifications for
terephthalic acid production as petrochemical p-xylene.

CELL 407

Chemical platform for the production of Bio-PET

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Micromidas has developed a process to convert a wide variety of carbohydrate feedstocks to higher value
chemicals. For example, fossil based plastic, polyethylene terephthalate (PET), dominates the current
plastic bottle industry. To improve the carbon footprint of their packaging, and to reduce their reliance on
volatile priced oil, the plastic bottle industry desires to instead produce a biobased PET bottle. The
thermoplastic polymer, PET, is a product of the polymerization of monoethylene glycol (MEG) and purified
terephthalic acid (PTA). These two monomers are almost entirely sourced from fossil sources. To date
there are a few commercial efforts to produce bio-based MEG from ethanol; biobased PTA, however,
remains unavailable in the market. PTA is itself synthesized through the oxidation of isomerically pure
para-xylene, whereas para-xylene is a product of oil refining. Micromidas Inc. is a West Sacramento,
California, chemical company, which converts biomass to commodity chemicals and resins. They have
recently developed the technology, piloted the process, and are planning to build a first-of-a-kind
commercial demonstration plant that will convert biomass - not oil - to polymer grade p-xylene and other
monomers of interest.

Developments in the Fields of Celluloses & Lignocelluloses: In honor of Dr. Rajai Atalla
U. P. Agarwal, Organizer; T. J. Elder, Organizer; A. Isogai, Organizer; T. Larsson, Organizer; M. G. Laborie,
Presiding; N. Robitaille Brown, Presiding Papers 408-415

CELL 408

Single-sourced nanocelluloses: Process-linked characteristics and behaviors

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This paper presents the structural characteristics and behaviors of different nanocelluloses, all from rice
straw cellulose isolated via a facile extraction-NaClO2-KOH process. A variety of single-sourced
nanocelluloses have been generated using our newly developed coupled chemical-mechanical
approaches as well as the extensively reported methods of sulfuric acid hydrolysis, 2,2,6,6-
tetramethylpyperidine-1-oxy (TEMPO) mediated oxidation and shear forces. Both methods of derivation
and fractionation govern not only the yield but also the quality attributes of nanocelluloses. The
dimensional and surface attributes of these nanocelluloses, specifically, thickness, width, length and their
distributions, surface charge nature and charge densities have been closely analyzed and related to the
methods of derivation. 1H and 2D heteronuclear single quantum coherence (HSQC) NMR data confirm
that solution-state NMR detects nanocellulose surface carbons and protons primarily, direct
characterizing individual nanocellulose surfaces in a never-dried state. Nanocelluloses have also been
derived from less pristine cellulose to be longer and more thermally stable as well as self-assemble less.
Each of these nanocelluloses possesses unique properties that lead to vastly different behaviors,
promising for diverse applications.
CELL 409

Interactions between cellulose and random and block copolymers: Antifouling and friction

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Block copolymers of PDMAEMA and POEGMA as well as Pluronics-type were adsorbed on cellulose
surfaces with different anionic charge density and included regenerated cellulose, cellulose nanofibrils
(CNF) and TEMPO-oxidized cellulose nanofibrils (TOCNF). The extent and dynamics of adsorption were
determined by quartz crystal microbalance (QCM-D) and surface plasmon resonance (SPR). Other tools
such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used to
elucidate features of the adsorbed layer. The role of interfacial water is highlighted for the adsorption of
the cationic blocks but in all cases, the effect of hydration is observed to have a critical influence in the
interface. The observations are highly relevant to properties such as antifouling, friction and surface
modification. Some application examples will be discussed.

CELL 410

Conformational energy distribution for crystals of cellobiose and analogs

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The most important determinant of cellulose molecular shape is the range of likely values of the
interglycosidic torsion angles φ and ψ. Therefore it is of substantial interest to know the potential energy
surface for their variation. Such contoured surfaces, often called Ramachandran maps, indicate the
location in φ,ψ space where the energy is lowest, secondary minima, and the energy barriers between the
minima. Increasingly sophisticated maps for cellobiose have been computed since the 1960s. Some 68
relevant pairs of φ,ψ values are available from small molecule crystal structures; they can be plotted on
the map as well. Our studies with B3LYP/6-31+G(d) theory, with and without aqueous SMD continuum
solvation, have three main minima, all of which are occupied by observed experimental crystal structures
or the vacuum-phase structure observed in a very low-temperature experiment. Unlike some other
modeling studies, our vacuum map supports the anti-φ, syn-ψ conformation for the vacuum structure and
the SMD map supports the condensed-phase structures. The φ,ψ locations of cellulose crystal structures,
as well as the small analogs with and without intramolecular hydrogen bonding ability will be discussed,
with positive support for 2-fold screw axis symmetry in cellulose.
Portion of energy surface for cellobiose; magenta contour at 0.25 kcal/mol. Plotted points represent experimental crystal structure values. Orange triangles - cellulose polymorphs; black dots - cellobiose analogs that could make hydrogen bonds; cyan dots - analogs lacking hydroxyl groups. The dashed diagonal line indicates 2-fold screw axis symmetry (or pseudo symmetry).

CELL 411

Three-dimensional alignment of lamella single crystals of cellulose II using magnetic field

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Enzymatic synthesis of cellulose was performed using cellodextrin phosphorylase (CDP), sucrose phosphorylase (SP), sucrose, and 1-azido-1-deoxy-β-glucoside in 40 mM phosphate buffer (pH 7.0). The synthetic product was cellulose oligomers (DP ≈ 10) with azide groups at the reducing end. Lamella single crystals of cellulose oligomers with surface-reactive azide groups are expected to form by recrystallization of the synthetic products. The lamella single crystals were crystalline form of cellulose II, several hundred nm in width and several μm in length. The average thickness of the lamella single crystals was 5.1 nm, which is almost equivalent to the chain length of cellulose oligomers DP = 10. When suspensions of the lamella single crystals were cast under a horizontal 8 T magnetic field, films were obtained, in which the lamella single crystals were three dimensionally aligned.

**CELL 412**

**New model for untangling cellulose ultrastructure**

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In the field of cellulose materials, understanding of cellulose ultrastructure will benefit a wide variety of R & D activity. Areas as diverse as structure and function of plant cell walls, recalcitrance of biomass, and structure and properties of nanocelluloses are all likely to be advanced. But developing the understanding of the ultrastructure poses quite a challenge. The existing approach, based on solid state NMR spectroscopy, consists of deconvolution of a sample’s C4 region in terms of various possible sub-structures of cellulose (Iα, Iβ, paracrystalline, I(α + β), and accessible and non-accessible fibril surface cellulose). However, the deconvolution approach has limitations due to the fact that more than one possibilities exist to separate the overlapping 13C NMR signals. Our research based on Raman and IR spectroscopies has developed a new capability which indicated an alternate model wherein the cellulose ultrastructure can be seen as consisted of four fractions – consolidated (Co, k1), coalesced (Co, k2), hornified (Ho, k3), and crystallized (Cry, k4) - or for short, Co-Co-Ho-Cry. According to the model, cellulose in various materials will have different quantities of these fractions. In the presentation, as a test case, the Co-Co-Ho-Cry model will be applied to cellulose ultrastructure in hydrothermally treated poplar and, based on Raman and IR, it will be illustrated how to calculate the different fractions (k1, k2, k3, k4).

**CELL 413**

**Dynamic FTIR as a tool to assess the interaction of lignin in wood pulps**

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The complex heterogeneous structure of the wood cell wall have always provided for a challenge with regard to the understanding of how the wood polymers are organised and how they interact with each other to provide for the excellent mechanical properties of wood fibres. In particular the organisation and contributions with regard to the amorphous, matrix polymers of hemicelluloses and lignin has been debated. With the advancement of spectroscopic techniques it is now possible to obtain a deeper understanding of this structure. One such technique is dynamic FTIR or 2D-FTIR which has the possibility of detecting the degree of interaction between the constituents within a composite material. The possibility of utilising dynamic FTIR for wood fibre cell wall analysis is here presented. By using this technique the close interaction within the cell wall between cellulose and glucomannan has been possible to confirm. With regard to lignin, its contribution to strength properties has not been easily addressed, mainly due to the dominating effects of the cellulose. It has also earlier not been possible to detect an IR-response of lignin due to straining. However by the further development of dynamic FTIR it is now shown possible to follow the behaviour of lignin during mechanical straining of the wood fibre material. It is thus shown that by using sufficiently large deformations the contribution to the stress transfer of lignin in wood samples may be shown. However, by analysing the dynamic coupling in the 2D-FTIR experiments it is
clear that, although molecular lignin deformations are detected, the lignin do not directly contribute to the stress transfer in the wood fibre structure. By slight chemical processing, where sufficient amounts of lignin still remain in the cell wall, the interaction between lignin and cellulose may be altered which affects the coupling seen by 2D-FTIR. The implications of these new findings on the structure of the wood fibre cell wall are discussed as well as the implications for developing improved processes and products.

CELL 414

Modeling the mesoscale architecture of lignocellulose to elucidate its impact on transport phenomena and biomass conversion processes

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Lignocellulose is a continually mass-produced biopolymer composite that holds tremendous potential as a renewable source of fuels, chemicals, and materials that can displace large portions of fossil fuel-derived products. Realizing cost-competitive processes that convert lignocellulosic biomass into these desired products requires development of conversion strategies that specifically address its inherent complexity that spans multiple length scales. Such technological advances are informed by improving our fundamental understanding of the chemical, physical, and biological characteristics that govern the properties and functionality of lignocellulose in plant cell walls. Towards these goals, computational tools provide an excellent complement to experiment for the purposes of optimization and interpretation of experimental results. While much attention has been devoted to modeling biomass structure and behavior during conversion processes at the extreme length scales (i.e., the molecular scale and the bulk process scale), relatively little effort has been focused on understanding the role of lignocellulose mesostructure via computational modeling. Well established tools exist for modeling biomass at extreme scales, such as molecular dynamics simulation at the molecular scale and reactor models for the bulk process scale; however, few tools are available that can adequately account for the complex, highly variable geometry of lignocellulose at the mesoscale. In this presentation, I will describe our recent efforts towards elucidating the impact of lignocellulose mesostructure on physiochemical processes of great importance to many conversion processes, namely the transport of heat and mass throughout the cell wall. A general method based on constructive solid geometry will be presented that can be used to explicitly model lignocellulosic biopolymer assemblies on the length scale of ~ 100 nm. Several examples of how quantitative microscopy and chemical analysis can be used to parameterize the model for various scenarios will be included. Next, I will show how these structural models can be employed in finite element simulations to predict the transport behavior of heat and/or various chemical species throughout the material. Finally, I will describe how findings at this scale can be coupled to particle-scale simulations to provide estimates of useful parameters for the optimization biomass conversion processes.

CELL 415

Chemical microscopy of polysaccharide surfaces using TOF-SIMS

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Chemical microscopy methods combine information about chemical composition and spatial localization of different molecules and molecular nanosegments. Time-of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a unique technique able to combine mass spectrometry of organic and inorganic materials with imaging of molecules, ions and fragments with a lateral resolution similar to optical microscopy. In this work, we present state-of-the art applications of TOF-SIMS to characterize polysaccharides surfaces in wood tissues, fibres, papers, films, particles and polysaccharide derivatives. We show how chemical
microscopy techniques can be combined with adsorption methods for elucidating complex phenomena in biomass pretreatments, enzymatic hydrolysis, bleaching, modification of surfaces of biomaterials and interactions between multifunctional polysaccharides with native cellulose. Chemical microscopy with TOF-SIMS enables detailed understanding of polysaccharide interactions at the molecular level, facilitating processing and engineering of advanced biomaterials.

**Functional Lignocellulosics & Nanotechnology**

M. K. Ek, Organizer; E. Filpponen, Organizer; T. Nypelo, Organizer; S. Peresin, Organizer; S. Spirk, Organizer; S. Spirk, Presiding; E. Filpponen, Presiding

**Papers 416-423**

**CELL 416**

**Investigation of the thermodynamics of the interaction of (modified) cellulose nanocrystals with natural polymers**

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Controlling the interactions of nanocellulose with molecules and polymers is key to a more structured approach to developing materials with tailored properties and selective and efficient sensors. We thus started to look into the interaction of nanocellulose with natural polymers such as proteins and hemicellulose. Protein cellulose interaction studies will help us to understand the driving force and requirements for interaction with a view on biosensors and more effective enzyme-catalysis. Studying cellulose-hemicellulose interactions on the other hand may prove very helpful in designing moisture-insensitive natural fiber materials and high performance all renewable material nanocomposites. For our studies, we used unmodified and TEMPO oxidized cellulose nanocrystals as well as nanocrystals modified with positively charged pyridinium groups with varying level of surface charge. Isothermal titration calorimetric measurements showed that most interaction are entropically driven rather than enthalpically, with binding the result of the collapse of an ordered water molecule structure around the dispersed nanocellulose and the dissolved polymers. These findings indicate that our thinking of nanocellulose-polymer interactions in the presence of water is governed by the water molecules, and to a much lesser extent or even not by preferential interactions between nanocellulose and polymers. The details of the work will be presented as well as consequences of these findings.

**CELL 417**

**Cellulose-inorganic hybrid structures as promising thermoelectric materials**

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Hybrid materials containing nanoscaled cellulosic constituents can be an attractive choice for thermoelectric energy harvesting, since it is possible to fabricate layered hybrid superlattice structures in a way that the thermal conductivity is reduced, while the electrical properties are simultaneously maintained. The aim of the presentation is to introduce approaches to construct such structures using various nanoscaled cellulosic materials such as cellulose nanocrystals (CNC), cellulose nanofibrils (CNF) and TEMPO-oxidized CNF with ZnO, and Earth-abundant inorganic component. Superlattice structures have been built on the solid substrates and on flexible CNF films using spincoating or dip coating along with the atomic layer deposition (ALD) method. Several characteristic features with respect to
thermoelectric performance have been investigated which include for example resistivity, thermal conductivity and Seebeck coefficient of the hybrid materials. The results show that resistivity and thermal conductivity of the superlattice structures can be manipulated by the cellulosic thin layer nanoarchitecture.

CELL 418

Nanocellulose mediated layer-by-layer chip modification for cellular in-vitro diagnostics

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Microfluidics and the concept of lab-on-a-chip continue to gain traction as a successful emerging field that aims to integrate complex biochemical analyses into automated systems. One of the most promising applications for these microfluidic systems is in point of care blood diagnostics. Isolation of cells, such as circulating tumor cells from blood provides insights for diseases diagnosis, developing drugs and treatment. Several approaches have been used to capture cells using microfluidics devices. However, many of these approaches don’t yield viable cells and change the phenotype of cells by activating the cells, which negatively affects the downstream processing. Layer-by-layer (LbL) assembly offers an alternative method for surface modification, for the fabrication of uniform and stable coating of microfluidics devices. LbL is a highly versatile and simple procedure that has been employed in microfluidics in many applications and also for in-vitro assay for studying fundamental tissue and cell biology. Naturally occurring polymers are widely used in LbL coating. In this work, we introduce for the first time LbL coating of cellulose nano fibrils (CNF) in the microfluidic channel for efficient cell capture. We report here the efficient capture of viable cells. In addition, we demonstrate efficient release of the captured cells from the microfluidic devices. This LbL coating strategy is stable and may be used for capturing of different cell types from complex biological fluids, such as whole blood. Finally, we demonstrate proliferation of released cancer cells and cell viability, which opens up for applications in cancer biology

CELL 419

Multi-layered polysaccharide based nanofilms for the treatment of chronic venous ulceration

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Polysaccharide-based multilayer thin films enable storage and sustained release of controlled doses of different drugs, which is important in local treatment of chronic wounds (e.g. chronic venous ulcers). Due to possible control of such systems’ preparation procedures, we can study them in detail as in the case of model systems. Different performance testing of such thin films (e.g. in vitro drug release, cell testing) can be used as a wound dressing on their own or be correlated to commercial wound dressings, and hence boosting the development of advanced wound care solutions. Based on the mentioned, was the aim of our study the development of a platform for the design and testing of potential novel wound dressings. These were prepared in the form of multi-layered nanofilms consisting of oppositely charged polysaccharides with the target application being the treatment of chronic venous ulcers using
pharmacotherapy with pentoxifylline (PTX). Using a combination of biocompatible cationic trimethyl chitosan (TMC) and anionic alginate (ALG) polysaccharides, and the potent anti-inflammatory drug PTX, we prepared and characterized an advanced wound dressing for the treatment of chronic venous ulceration based on controlled delivery of a personalized dose of PTX. Among others, its high potential for future use, can be deduced from the in vitro cell testing on human skin cells, showing an improved cell viability after exposure to the developed system, indicating possible improved healing performance.

CELL 420

Graft modification of cellulose nanocrystals with carbon dioxide responsive polymers via living radical polymerization

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Cellulose nanocrystals (CNC) are readily dispersible only in very hydrophilic environments, such as aqueous media and very polar solvents. Different approaches have been attempted to alter/improve the surface properties and dispersibility of CNC in organic solvents (hydrophobic media), including functionalization with small molecules and grafting of polymer chains to the CNC surface. However, when hydrophobic polymer chains are grafted on the CNC surface, CNC are irreversibly altered toward increased hydrophobicity, which can be undesirable for some applications. Grafting stimuli-responsive polymers chains to the CNC surface may offer a solution to this problem, and surface-initiated nitroxide mediated polymerization represents a very versatile and robust technique to perform grafting polymerization on the CNC surface. In this study we present stimuli-responsive CNC whose surface properties can be reversibly switched using only carbon dioxide (CO2) and nitrogen as triggers to conduct the switching process. In recent years carbon dioxide has emerged as a new and innovative “trigger” for stimuli-responsive materials. In addition to being abundant, inexpensive, nontoxic and environmentally benign, CO2 does not accumulate in a system upon repeated cycles. Among the new CO2-switchable materials that have been developed, polymer-based materials are of particular interest. The change in properties result due to a transition from a neutral to charged state (or vice versa) on functional groups within the polymer (e.g. amidines or tertiary amines). The modification of CNC surfaces was performed using different CO2-responsive polymer chains will be presented.

CELL 421

Quantitative modelling of water transport in ultrathin cellulose nanofibril films

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Cellulose nanoparticles exhibit distinct water uptake behaviour in response to changing humidity conditions. Models that describe the associated phenomena, such as diffusivity and permeability, are needed for fundamental understanding of behaviour of cellulose nanoparticles. Cellulose thin films combined with surface-sensitive methods provide a unique platform for studying the fundamental aspects of water transport in cellulose nanofibril films quantitatively. We use the quartz crystal microbalance with dissipation monitoring (QCM-D) equipped with humidity uptake module to determine the water diffusivity and permeability of water in ultrathin cellulose nanofibril films. Additionally, we evaluate the relevance of the Langmuir-Flory-Huggins bimodal sorption model with regard to cellulose nanofibril films over the whole range of water activity. The model provides new insights into the peculiar behaviour of cellulose nanofibrils with respect to applications, such as membranes, barriers and sensors.
Impact of water vapor adsorption on physically treated cellulose thin films

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In this contribution, we present the impact of increasing humidity (0 %RH at 70 %RH (97 %RH) on amorphous cellulose thin films which serve as model systems for regenerated cellulose. The films were prepared by spin coating of two different trimethylsilyl cellulose precursors and converted to cellulose by simple hydrochloric acid vapor hydrolysis. Afterwards different physical treatments, such as swelling and drying, were performed and the consequences of the water vapor uptake were investigated. This process was examined in real time by XRR, GI-SAXS and QCM-D equipped with a humidity module to obtain information about changes of the thickness, roughness, electron density and pore size of the films.

Elaboration of cellulose nanocrystals CNC/Ge-imogolites multilayered thin films

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In the past decade, multilayer thin films drew the scientific community attention for their unique properties. Indeed, principally made of an association of polyelectrolytes and/or nanoparticles, of various morphologies and chemistries; they allow the design of a range of porous nanomaterials with amazing surface and optical properties, such as structural colors or anti-reflectivity. Less commonly encountered, thin films made of two nanoparticles of opposite charges are gaining interest since they open properties compared to polyelectrolytes/nanoparticles thin films. In this study, multilayer coatings were investigated for the association of two oppositely charged nanorods of well-controlled aspect ratio, i.e. anionic Cellulose Nanocrystals (CNC) and cationic Ge-Imogolites. CNC were obtained from hydrolysis of cellulose from cotton linters, and synthetic imogolite (Ge-Imogolite), an aluminogermanate nanotube, was synthetized from the hydrolysis of Al and Ge precursor salts in aqueous media. Here, elaboration of multilayered thin films from CNC and Ge-Imogolites nanorods, was studied in comparison with reference films incorporating CNC or Imogolites with polyelectrolytes bearing opposite charges of the nanorods. Multilayered thin films were assembled by the dipping procedure and various parameters (adsorption time, ionic strength, etc.) were varied to investigate the optimal conditions for the film growth. Linear growth until 10 bilayers revealed that interactions between CNC and Imogolites are strong enough to stabilize the film. Film porosities were investigated using Quartz-Crystal Microbalance with dissipation (QCM-D) with the H₂O/D₂O exchange procedure as function of film composition and of the aspect ratio of Ge-imogolites. Finally, optical properties of films were investigated by transmittance measurements.
Alkylation of unsaturated fatty compounds

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Alkyl-branched fatty compounds are of interest for industrial products in the cosmetics and lubricant areas. Electrophilic additions of alkyl carbenium ions generated by decomposition of alkyl chloroformates by ethylaluminum sesquichloride and hydride transfer to the adduct carbenium ion give well-defined alkyl-branched oleochemicals with good yields. Unfortunately, alkyl chloroformates are not easy to handle and are poisonous. Moreover, dichloromethane has to be used as solvent. We describe herein an important improvement of the synthesis protocol using bromoalkanes as alkylating agent in a solvent-free reaction. This new protocol can be performed with molar or higher amounts of substrates, gives higher yields and purer addition products. Secondary and tertiary bromoalkanes can be added giving the hydroalkylation product. The reaction protocol can be applied generally to alkenes with inner double bonds as well as 1-alkenes. Various polar substituents are tolerated. We are reporting on the hydroalkylation of methyl oleate, high oleic sunflower oil, methyl 10-undecenoate and other interesting fatty compounds.

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\text{methyl oleate : Et}_3\text{AlCl}_3 \cdot \text{2-bromopropane} = 1 : 1 : 1.1
\]
Valorization of industrial biomass ash in structural materials

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Throughout the developing world, incineration of lignocellulosic biomass is still one of the most prevalent methods of energy production, commonly used to power small- and medium-scale factories in countries with unreliable energy grids. While much of the carbonaceous material is consumed during combustion, inorganic phases remain in residual ashes, which are often subsequently discarded in nearby landfills. Inorganic composition varies with biomass feedstock, but typically includes contributions from Si, Al, Fe, Na, K, Ca, Mg, and other minor constituents. Biomass ashes rich in reactive Si, Al, and/or alkalis can be utilized in the synthesis of alkali aluminosilicate binders, typically called geopolymers or alkali-activated materials. The objective of this study has been to characterize the physicochemical properties of industrial biomass ashes from northern India for use in energy efficient binder materials, reducing both landfill burden and the carbon footprint associated with current cementitious binders. The ash being explored has been found to contain >80% silica content, much of which exists in reactive, amorphous form. Chemical activation has thus been the focus of this investigation, with specific interest aimed at understanding the formation and presence of sodium and calcium aluminosilicate networks in the resulting binder samples.

Adsorption and viscoelastic studies of gold Nanoparticles (NPAu) and Bovine Serum Albumin (BSA) complexes at chitosan-alginate-cellulose films

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Cellulose is a natural, harmless and biocompatible polymer, so it is considered a model material with a lot of uses. In addition it can be extracted from different sources, which include algae; the algae cellulose has the advantages of not having lignocellulosic complex in their cell wall and this facilitates its extraction and at the same time allows a particular structural characteristics [1]. On the other hand, gold nanoparticles (NPAu) are inert materials with an infinite number of therapeutic applications from antibiotic up to anticancer and have been widely studied. Finally bovine serum albumin (BSA) is a globular protein considered as a multifunctional carrier, i.e., serves as transporter protein model to protect and improve nanoparticles access to the active sites. In this work, with the intention to understand the mechanisms of interaction and surface adsorption of these materials and thus evaluate the potential applications that they may have together, we will present results on the formation of thin film cellulose coated surfaces as well as different functionalization strategies with chitosan and alginate, and compare their advantages as supports for immobilization of NPAu-BSA complexes. For this purpose, viscoelastic properties of cellulose or cellulose-chitosan/alginate surfaces are measured by frequency and dissipation shifts in a Quartz Crystal Microbalance at different physicochemical conditions, followed by adsorption of the hybrid nanomaterial. Also, preliminary results of the interaction and viscoelastic properties of cellulose-chitosan-NPAu-BSA films at the air-water interface using an Interfacial Shear Rheometer, will be presented.
Sustainable hybrid bio-composites for automotive applications

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Plastic parts for automotive applications today are normally loaded with high amounts of mineral fillers or synthetic fibers for property enhancement. The high density of these fillers increases the overall weight of the vehicles. Natural fibers are renewable and lightweight. However, their properties are often inferior to their synthetic counterparts. This work demonstrates that the property constraints can be overcome by the hybridization of natural fibers with synthetic or bio-based fillers such as carbon fibers, glass fibers, torrefied or pyrolyzed biomass. The hybridization improves the thermal stability of the composites, thus allowing wider processing windows. By using hybridization it is possible to keep relatively high loadings of natural fibers in the composites while achieving balanced mechanical properties including stiffness and strength as well as impact resistance. Furthermore, hybridization also impacts positively the moldability, which in essence helps to reduce cycling time during the injection molding of the parts. In addition, the use of pyrolyzed biomass as natural colorant eliminates the need for carbon black. Overall, up to 35% of the total weight of the synthetic fillers and plastics can be substituted by natural fibers through hybridization. This technology can greatly expand the application of natural fibers in the automotive sector.

CELL 428

Reactive film-forming maleimido dextrans for cysteine-containing surfaces adsorbing BSA

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Carbonic acid derivatives of dextran possessing furfuryl- and maleimido moieties were synthesized and processed into thin films by spin coating. First, products with different degrees of substitution (DS) of up to 3.0 and substitution patterns were obtained. Thin films possessing maleimide groups were obtained by spin coating of maleimido dextran (furan-protected) and dextran furfuryl carbamate that was converted with bismaleimide. The removal of the protecting group (furan) on the thin film was monitored by QCM-D and compared with gravimetric analysis of the bulk material. Thin films were obtained by spin coating and characterized by AFM, QCM-D, FTIR spectroscopy, and XPS. Surface morphology, hydrophobicity, swelling behavior, and reactivity of dextran furfuryl carbamate bismaleimide adducts are suitable for the preparation of surfaces containing cysteine. Up to 9 mg m⁻² of bovine serum albumin (BSA) are adsorbed on this nanorough, hydrophilized films at different pH values (4, 6, and 8.5). The BSA layer might resist nonspecific adsorption of biological molecules and could be interesting for prevention of biofilm formation on medical devices.
Morphological and thermo-chemical changes upon autohydrolysis and microemulsion treatments of coir and EFB residual biomass to isolate lignin-rich Micro and Nano Fibrillar Cellulose (MNFC)

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Autohydrolysis and microemulsion treatments followed by microfluidization were employed to isolate Micro and Nano Fibrillar Cellulose (MNFC) from coir fibers and palm tree empty fruit bunches (EFB) with residual lignin content of ~24 and ~31 wt\%, respectively. The fibers and associated MNFC were characterized in each treatment for their chemical (FTIR), structural (SEM, AFM, confocal microscopy and XRD) and thermal (TGA) properties. The most significant findings include the fact that two MNFC populations, with distinctive structural differences were produced, with characteristic lateral dimensions of 20-70 nm and 1-3 μm. The lignin distribution after possible re-condensation on the fiber walls or inside hollow fibers occurred in the form of nano-droplets. Finally, a correlation between thermal degradation of MNFC with the spatial arrangement of lignin is hypothesized and a defibrillation mechanism is proposed. The detailed structural and thermo-chemical analyses presented here are expected to facilitate further interest in the synthesis of new materials from MNFC isolated from coir and EFB, two abundant bioresources that are most suitable for their valorization.

Effect of cellulose nanofibril morphology on the strength and stiffness of macroscopic filaments

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Cellular architecture of wood is intended to provide ideal conditions to the trees, using a minimum of material. On the nanometer scale, the highly ordered arrangement of cellulose nanofibrils (CNFs) parallel to each other plays a crucial role in providing necessary mechanical structural performance of trees. Thus, these CNFs have the prospective of being a building-block for future high-performance materials, due to their exceptional mechanical properties, such as a modulus of up to 140 GPa in its crystalline form. However, the mechanical properties obtained to date are far from the maximum potential values speculated for individual CNFs, and it can be hypothesized that the fibrils must be aligned and assembled in a controlled manner to make full use of the potential of CNFs. Inspired from the arrangement of CNFs in trees, here we have tried to align and assemble the CNFs in the form of hydrocolloidal dispersions, with the help of an elongational flow field followed by the solidification using solidifying agents. We have used a double flow-focusing channel for the fabrication of strong and stiff filaments. Our results suggest that strength of macroscopic filaments is dependent on the surface charge density and length of nanofibrils. We further advanced our study by grafting the surfaces of CNFs with polyethylene glycol (PEG) to various lengths (10 nm to 200 nm) and densities and studied their effect on the mechanical performances of our filaments. Our filaments have exhibited up to 60 GPa stiffness and 900 MPa strength, which as per our knowledge never have been obtained before, with the artificial assembly of CNF into hierarchical filament or fiber structures.
Role of lignin on functional and physicochemical properties of enzymatic modified soy protein film

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Lignin, a byproduct of wood processing industry, was added to the enzymatically modified biopolymeric matrix to improve not only physicochemical, but also antioxidant properties due to the vast number of functional groups such as aromatic rings, methoxy groups, phenol and alcohol groups. Two types of lignin, alkali lignin (AL) and lignosulphonate (LSS), potentially carrying antioxidant activity, were added to the soy protein solution at different concentrations (2%, 4%, 6%, and 10% w/w of protein). Films incorporating lignins were characterized by physicochemical and morphological properties, along with radical scavenging activity and UV-blocking ability. Results revealed that AL material carried higher radical scavenging ability than that of LSS. However, films containing LSS showed slightly higher radical scavenging activity. It is attributed to the higher solubility and compatibility of LSS in the protein film matrix. The UV-spectroscopy test revealed that films containing AL showed high absorption range in UV region, and this UV-blocking ability increased with increasing the level of lignin. Thermal and mechanical analysis tests showed that the addition of lignin to the films improved tensile strength and thermal stability of films while it reduced the %E as a function of lignin concentration. Scanning electron microscopy pictures showed that films with LSS had smoother surfaces compared to those with AL. It resulted in lower differences in the contact angles between plateside and airside of films containing LSS. Lignin acted as a filler and reduced water vapor permeability of films compared to the control film. Consequently, the incorporation of lignin, which was relatively cheap, nontoxic, and naturally abundant, into biopolymeric film will bring additional functionality to apply in a wide spectrum of applications such as packaging of food products, pharmaceutical, and agricultural industries.
CELL 432

MS techniques in structure analysis of complex glycans

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Complex carbohydrates (‘glycans’) or polysaccharides are arguably the most structurally complex and heterogeneous family of biomacromolecules. They are typically built of different types of monomers (monosaccharides or “sugars”) linked to each other through a great variety of glycosidic linkages with rich stereochemistry. Glycans are often substituted and exhibit branched structures, which result in an extremely complex macromolecular architecture. The complete structural determination of the ‘primary structure’ of glycans is far from being implemented as it is routinely done for nucleic acids and proteins through common genomic, transcriptomic, and proteomic sequencing techniques. Determining the constituent sugars and substitution/branching patterns in glycans is fundamental to decipher the biological functions and their physico-chemical properties. In this tutorial we will discuss different mass spectrometric strategies for a comprehensive understanding of the molecular structure of complex glycans, focusing on their constituent sugars, glycosidic linkages and patterns of substitution. These mass-spectrometric based strategies (‘glycomics’) require the integration of biochemical approaches (e.g. selective enzymatic deconstruction and/or chemical derivatization) and hyphenation with different chromatographic separation modes (e.g. gas chromatography, hydrophilic interaction liquid chromatography, anion-exchange chromatography). Traditional GC-EI-MS has been used for decades to determine the average monosaccharides and linkages in complex glycans. The introduction of soft ionization mass spectrometric techniques (e.g. MALDI, ESI), alone or in combination with LC, has enabled the mass profiling of complex mixtures and the full sequencing of oligosaccharide structures in some successful cases by sequential fragmentation (MSn). Recent advances in ion mobility mass spectrometry (IMS) for high throughput glycan analysis will be as well presented. These different glycomic strategies need however to be adapted to the rich variety of glycan structures and the specific molecular information that is aimed at. The tutorial will be illustrated with several examples, focusing on the elucidation of the substitution patterns of heterogeneous native plant polysaccharides and chemically-modified polysaccharide derivatives.

CELL 433

Advancing glycopeptide characterization using high sensitivity HILIC-MS methods

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The analysis of glycopeptides spans many different areas of research, from investigators probing subtle changes of glycosylation due to pathological conditions to scientists characterizing biopharmaceutical products. However, glycopeptides present several unique analytical challenges in their overall characterization, including suppressed mass spectral (MS) ionization efficiencies when they are present as lower abundance components of complex mixtures. One approach to improve their MS performance is to first employ a state-of-the-art ultraperformance liquid chromatographic (UPLC) separation technique. Such separations are routinely performed as part of peptide mapping experiments as part of the overall characterization of biotherapeutic products. These experiments most frequently rely on reversed-phase chromatographic methods which separate analytes based on their hydrophobic characteristics. Unfortunately, the effectiveness of this technique to efficiently resolve the glycoforms of a single peptide backbone is limited and significant coelution analytes occurs. Alternatively, however, hydrophilic
interaction liquid chromatography (HILIC) is a technique that is widely used for efficient separations of both small and large molecules with hydrophilic characteristics. Using optimized mobile-phase conditions for an amide-functionalized UPLC HILIC column, the glycan becomes the critical component driving the separation. Using this mode of chromatography, different glycoforms of a single peptide backbone are well resolved. Thus, HILIC allows the glycan microheterogeneity of a specific site of glycosylation to be accurately mapped and quantitated if an optical detection technique, like tunable UV, is employed. In this presentation, we will discuss optimizing mobile phase conditions to balance chromatographic performance and MS sensitivity. We will also present glycopeptide mapping results for standard and biotherapeutic proteins which demonstrates the ability of UPLC/HILIC/MS to characterize specific sites of glycosylation.

CELL 434

Infrared spectroscopy integrated to mass spectrometry: An innovative platform for de novo carbohydrate sequencing

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Mass Spectrometry and spectroscopies (NMR, Raman ...) are both highly valuable analytical approaches in chemistry, and provide complementary information on molecular structure. Here we present an integrated platform offering simultaneous access to the mass and IR spectroscopic fingerprints of carbohydrates. While carbohydrate isomerisms remain ambiguous with mass analysis alone, this platform allows for rapid disambiguation of the monosaccharide content, regiochemistry, stereochemistry and functional modification patterns. A breakthrough consequence is that the sequence of saccharides can be fully resolved in "user-friendly" conditions, that is without MS standards, from relatively crude samples, and in small quantities.

CELL 435

Examining glycan structure and dynamics with NMR: A tutorial

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Nuclear Magnetic Resonance (NMR) has a long history of application in structural analysis of carbohydrates (glycans). It returns information on, not only composition, but conformation and dynamics. We will first review solution NMR methods for the determination of dominant structures of glycans in solution, with particular attention to sensitivity and resolution limitations of modern high-field spectrometers. We will then discuss how these methods can be augmented by structure prediction software and molecular dynamics representations of conformational sampling. However, glycans exist not just free in solution, but as integral parts of glycoproteins, protein-glycan complexes, and high molecular weight polysaccharides. Investigation of glycan structure and dynamics in these systems requires special techniques, including relaxation dispersion, paramagnetic tagging, and solids NMR methods. We will provide a brief introduction to these methods with some examples that point to prospects for the future.

CELL 436

Asparagine-linked glycosylation of immunoglobulin G and the Fc gamma receptors impacts immune system activation

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Immunoglobulin G1 (IgG1) is the major circulating human antibody and also the primary scaffold for therapeutic monoclonal antibodies (mAbs). The interaction between IgG-coated targets and membrane-bound Fc \( \gamma \) receptors (FcgRs) requires the presence of an asparagine-linked (N-) glycan on the Fc. Our laboratory used a combination of solution NMR spectroscopy, x-ray crystallography and molecular dynamics simulations to determine the Fc N-glycan stabilizes a single polypeptide loop in a conformation compatible with FcgR binding and explain how changes to the Fc N-glycan termini affect affinity. Further measurements also implicate an essential role for FcgR N-glycosylation in Fc binding.

**CELL 437**

**NMR Analysis of substituent distribution in polysaccharide derivatives**

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Polysaccharide-based materials are PROMISING for use in areas as diverse as coatings, flat screen displays, and biomedical applications. Numerous polysaccharide derivatives have been synthesized, characterized and used in many areas. Degree of substitution and position of substitution greatly influence derivative properties and utility. NMR, as a powerful characterization technique, has been demonstrated to be employed for analyzing and determining the structures of polysaccharides and their derivatives. In our work, 1D and 2D NMR has been employed to confirm structures, degrees of substitution (DS), and substitution regioselectivity of cellulose and other polysaccharide derivatives such as cellulose esters, curdlan derivatives and polysaccharide-based electrolytes. For example, we used NMR to study regioselectively substituted cellulose esters which were derived from TBAF deacylation. Commercial cellulose esters were also analyzed by NMR to determine positional DS of each ester group. In addition, it has been reported by us that the structures, DS and regioselectivity of water-soluble polysaccharide ionomers were successfully affirmed by NMR spectra. We will discuss powerful NMR techniques including \(^1\)H NMR, \(^13\)C NMR, HSQC, HMBC and DEPT, their use in effectively analyzing polysaccharide-based materials, and how they help us to study and develop structure-property relationships of polysaccharide derivatives.

**CELL 438**

**Solid-state NMR methods to determine glycan structure, intermolecular interactions and protein binding in plant cell walls**

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The polysaccharide-rich plant cell wall provides mechanical strength to plant cells and is loosened during plant growth. Structural investigations of the wall polymers at the molecular level are important for understanding these diverse functions of the wall. We have developed several solid-state NMR techniques to determine the polysaccharide conformations and intermolecular interactions in intact cell walls. A T1 relaxation-compensated proton-driven \(^{13}\)C spin diffusion experiment enables us to suppress intramolecular cross peaks in 2D spectra and selectively detect only long-range cross peaks. This allowed us to determine unambiguous spatial contacts between cellulose and pectins in primary plant cell walls. We have adopted a CHHC technique to measure the H4-H6 distances in glucose, which allows us to restrain the hydroxymethyl conformations of surface and interior cellulose in the cell walls of model plants. To determine how wall-loosening proteins bind to wall polysaccharides, we developed two methods. Under dynamic nuclear polarization to enhance the NMR sensitivity by 30 fold, we can selectively excite and transfer protein \(^{13}\)C magnetization to polysaccharides, thus determining the binding target of the protein. Using this approach, we showed that bacterial expansin binds xyloglucan-enriched regions of the cellulose microfibrils in *Arabidopsis* primary cell walls to loosen the wall. For proteins that
cannot be produced recombinantly, we developed a paramagnetic relaxation enhancement NMR technique whereby the naturally extracted protein is tagged by a paramagnetic ion to speed up nuclear spin relaxation to polysaccharides in close proximity to the protein. Using this method, we showed that β-expansin binds the non-covalent junctions between highly substituted and lowly substituted glucuronoarabinoxylan to loosen the cell wall. These novel solid-state NMR techniques enlarge the toolbox for molecular-structure characterization of complex polysaccharides in cell walls, and provide unique insights into the functionally relevant three-dimensional structure of the cell wall.

THURSDAY MORNING

Bio-based Gels & Porous Materials
T. Budtova, Organizer; F. Liebner, Organizer; C. Freire, Presiding; T. Budtova, Presiding Papers 439-446

CELL 439

Cellulose nanofiber - towards tailored release of small molecules

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The development of drug delivery systems with tailored drug release characteristics can be very challenging especially in the case of problematic drugs, such as poorly soluble drugs or drugs with a narrow therapeutic window. To address this problem, pharmaceutical scientists frequently use different preparation approaches and ingredient, often involving a complex and multistep preparation protocol. Cellulose nanofibers (CNF) is a very interesting and promising excipient candidate in pharmaceutical formulations that could be used to easily optimize drug delivery rates. CNF has interesting physico-chemical properties and a large surface area that can be used to stabilize poorly-soluble drugs in the amorphous state and hence enhance the solubility of these drugs. By preparing CNF/drug films the release is fast, typically completed within tens of minutes. At the same time, by combining CNF with a surfactant or in some cases certain drugs, it is possible to create very stable air bubbles and dry foams. Utilizing this property, it is possible to modify the kinetics to more sustained release. In this case, the release is prolonged to several hours or days. The sustained drug release is due to the presence of intact air bubbles present in closed cells, which impart a tortuous diffusion path. The diffusion coefficient, assessed using Franz cells, is shown to be more than one order of magnitude lower for the cellular solids compared to films in the wet state. The entrapped air bubbles in the foam also induced positive buoyancy, making them potentially useful as gastric retentive systems. Furthermore, applications may stretch beyond the use for pure pharmaceuticals and include areas such as forestry, agricultural or house-hold applications.

CELL 440

Nanocellulose aerogels with thermal superinsulating properties obtained by spray freeze-drying

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Aerogels are highly porous materials with very low density and a large specific surface. They are prepared by replacing the solvent of a gel with gas with very moderate shrinkage of gel solid network. They form a class of materials showing potential for a wide range of applications due to their unique
optical, mechanical, and thermal properties. Nanofibrillated cellulose aerogels were prepared by conventional freeze-drying (CFD) and spray freeze-drying (SFD) to compare their structural, mechanical and thermal properties. Spray freeze-drying is a drying technique consisting of two main steps: first the solution is sprayed in a cryogenic solvent and the drops are instantly frozen into micro granules. In the second step, frozen droplets are dried by sublimation. The monolithic aerogels prepared by SFD method show a fibril skeleton morphology, which defines a mesoporous structure. The compression properties were determined for materials prepared with both drying processes. Then, the thermal insulation properties were characterized. They are significantly improved for SFD materials compared to CFD aerogel, reaching values of thermal conductivity of 0.018 W/(m.K), which is actually lower than the thermal conductivity of air. SFD reduces the pore size of aerogels and thus results in improved thermal properties SFD aerogels compared to CFD ones.

**CELL 441**

Anisotropic cellulose ester aerogels with tunable mechanical properties via controlled solvent exchange

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The current synthesis procedures for polymeric aerogels do not offer the freedom to tune their structural or mechanical properties. The density and porosity of an aerogel is usually controlled by changing the polymer concentration. However, decreasing the polymer concentration reduces the number of interactions within the polymer gel that often compromises the mechanical performance of an aerogel. This study describes a novel approach to tune mechanical properties of an aerogel by controlling the swelling properties of the gel preceding the aerogel. The Hansen solubility parameter approach is applied on the cellulose acetate (CA)-acetone-water system to predict the swelling behavior of cross-linked CA gels. The swelled free standing gels are subjected to unidirectional freezing to produce aerogels. The synthesis approach provides a theoretical platform to control gel swelling and subsequently the density and mechanical properties of the aerogel. Using this approach, the density of CA aerogels can be tuned from 25.0 to 113.0 mg/cm3 without changing the polymer concentration, and the porosity of the corresponding aerogels ranges from 98.1 to 91.3 %. The fine control over aerogel density induces wide range of mechanical properties which are quantified by compression modulus (13-340 kPa), energy of absorption (4-103 kPa) and compressive strength (22-373 kPa). Furthermore, unidirectional freezing induces anisotropy in the aerogel which makes them behave elastic or plastic based on the direction in which the property is measured.

**CELL 442**

2,3-Dicarboxyl nano cellulose: A novel source material for transparent, birefringent and thermally superinsulating aerogels

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Periodate oxidation of cellulose can be an intriguing alternative to TEMPO mediated oxidation since periodate can be recovered and regenerated. In continuation of our previous work on preparation of birefringent, transparent aerogels from TEMPO-oxidized, nanofibrillated pulp, this study investigates the manufacture of cellulosic aerogels from 2,3-dicarboxyl cellulose (DCC) as obtained by consecutive treatment of dissolving pulp with periodate and chlorite in aqueous medium. Subsequent mechanical
fibrillation of the oxidized pulp (1 mmol g⁻¹ COO⁻, conductometric titration) afforded individualized DCC fibrils (nf–DCC) with uniform dimensions (AFM: diameter 2.08 ± 0.4 nm, n=35; length 525 ± 160 nm, n=8). Acid-induced gelation of aqueous dispersions of nf–DCC afforded nematic aquogels. After replacement of interstitial water by ethanol and subsequent scCO₂ drying (95 MPa, 40 °C), highly transparent aerogels of well-preserved nematic ordering were obtained. The self-aligned structure dominating the morphology of nf–DCC aerogels was unveiled by FEG-SEM imaging and was quantified by polarized light experiments using the modified Michel–Lévi chart. The calculated birefringence was about 1.75 x 10⁻⁴ for aerogels of a density of 19 mg cm⁻³. The prepared nf–DCC aerogels featured furthermore comparatively high internal surfaces of up to 500 m² g⁻¹, high transparency in the visible light range (~70% transmission at 600 nm for a 1 mm thick samples with a density of 25 mg cm⁻³) and specific moduli of around 9 MPa cm³ g⁻¹ which renders them interesting materials for high performance insulation and optical applications. In an attempt to improve the rather poor mechanical properties inherent to lightweight cellulosic aerogels, post-scCO₂-drying uniaxial-densification has been found to be a very surprisingly efficient means of strain-hardening and pore-size control as entirely mesoporous and mechanical strong nanocellulose aerogels at full preservation of nematic ordering, birefringence and transparence can be obtained.

CELL 443

**Functional aerogels based on nanocellulose and platinum nanoparticles/graphene oxide for catalytic applications**

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Nowadays, there has been an increasing search for alternative and effective functional bio-based materials for application in several areas, such as in packaging, catalysis, filtration, aeronautic and electronic industries. Cellulose, due to its ubiquitous nature, renewability, biodegradability, broad chemical-modifying capacity and unique mechanical properties, is among the most interesting sustainable resources that can be used for the development of innovative bio-based materials. In addition to conventional plant cellulose fibres, other forms of cellulose have gained considerable attention in recent years, namely different forms of nanocellulose. One example, is bacterial cellulose (BC) that due to its 3D network nanostructure, high water holding capacity, high crystallinity, and outstanding mechanical strength might impart improved, and in many cases new, properties to the final materials. This biopolymer can be combined with distinct nanofillers, as metal nanoparticles (NPs) and graphene derivatives as graphene oxide (GO), in order to obtain materials with unique structures and functionalities. Platinum NPs and GO are promising examples of nanostructures that can be used in sensors or to develop nanocomposites with catalytic properties. Furthermore, GO can work as excellent support for the homogeneous growing of the Pt NPs enhancing the properties of the final materials, namely their catalytic effect. This communication aims to report the preparation and characterization of original nanocomposite aerogels based on BC and platinum NPs GO. Different compositions and preparation methodologies were exploited aiming to address their effect on the morphology and stability of the aerogels. Furthermore, the catalytic activity of the final materials on thioanisol oxidation was accessed.

CELL 444

**Fabrication of functionalized aerogels from cellulose and whole biomass for absorbing formaldehyde from indoor air**

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Aerogel is an extremely light material with porous network structure, low density and high specific surface area. These properties bring it many prospective applications such as gas storing medium, gas sorbent,
and gas filter. In the present study, a novel method was developed to fabricate cellulose/biomass–
chitosan blended aerogel as functionalized biosorbent to remove formaldehyde from indoor air. The
aerogel was prepared from cellulose/biomass and chitosan in concentrated LiBr solution via a process
consisting of dissolution/dispersion, gelation, washing, solvent exchange, and drying. Because of the high
porosity, large surface area, and free amino groups, the resultant aerogel can react instantaneously with
formaldehyde and remove it irreversibly from indoor air. The results indicated that at cellulose – chitosan
ratio of 2:1 (w/w), the resultant blended aerogel had density of 24.5 mg/cm³ and specific surface area of
245.4 m²/g. In a stationary chamber with initial formaldehyde concentration of 24.5 mg/m³, the
functionalized aerogel adsorbed 85.5% and 97.46% of the formaldehyde within 1 and 4 h, respectively,
with a theoretical adsorption capacity of 53 mg formaldehyde/g aerogel.

CELL 445

Superhydrophobic nanocellulose-silica composite aerogels for efficient water-in-oil emulsions
separation

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Oil-water separation materials has attracted increasing attention due to expanding industrial oily
wastewater discharge and oil spill accidents. It is a challenge to develop a low cost and highly efficient
absorbent for oil-water separation. Herein, superhydrophobic nanocellulose-silica composite aerogels
were fabricated via immersing the nanocellulose aerogels into a silica microsphere suspension, followed
by a thermal chemical vapor deposition of methyltriethoxysilane (MTES). The as-prepared aerogels
showed porous structure with high porosity (≥ 99%) and low density (≤ 10.25 mg/cm³). The deposition of
silica microspheres and MTES resulted in the superhydrophobicity of the obtained composite aerogels
with water contact angle up to 153.4°. The composite aerogels could selectively absorb oils from the
mixture of oils and water with excellent absorption capacity (105 g/g for pump oil). Interestingly, the
composite aerogels could effectively separate surfactant-stabilized water-in-oil emulsions solely by
gravity, with high flux rate (maximum of 532 ± 15 L m⁻² h⁻¹) and superior separation efficiency (≥ 94.5%).
Great antifouling property and reusability were also achieved for the obtained aerogels, which match well
with the requirements for the oil-water emulsions separation. The simple, low cost, and environmentally
friendly fabrication method in this work provided a new pathway to prepare cellulose-based materials for
the highly effective separation of oils and water, exhibiting potential application in treating real polluted
water.

CELL 446

Cellulose Aerogel Reinforced Polymers (CARPs)

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Cellulose itself is a strong polymeric backbone that is highly accessible and renewable and therefore
predestinated to be a convenient fiber-reinforcement. Nonetheless, it is often hampered due to
sedimentation of the Cellulose fibers or for incompatibility reasons with respect to the resin matrix.
To overcome these obstacles Cellulose aerogels can be used instead of adding loose Cellulose fibers
aiming for the reinforcement of a desired thermoset. Cellulose Aerogels combine the strong cellulotic
backbone with an accessible and high porosity (>85%) resulting in a light yet stiff monolithic material.
These Aerogels can be prepared by numerous routes that all involve the dissolution of the original
Cellulose (e.g. in aqueous salt hydrate melts such as ZnCl₂) followed by regeneration and drying in
supercritical CO₂. The final network consists of randomly arranged Cellulose fibrils (7-20 nm in diameter)
that reveal a nano-felt like structure. In substituting the air in the obtained system with a thermoset matrix
yields strong nanofiber-matrix composites. While fiber matrix composites most often use fiber fractions of
more than 30% the nanoscale fibrils in the Cellulose aerogel show considerable effects on the
mechanical properties while only minimally adding to the composite density with less than 10wt.% fiber fraction. As a result, Cellulose aerogels are clearly suited to reinforce polymer matrices providing their open-porous network for a mechanical interlocking of the matrix resin to give performance-competitive composites.

Reactive Extrusion: Advances at the Nexus of Polymer Processing, Materials Technology & Green Chemistry
A. Ayoub, Organizer; L. A. Lucia, Organizer; A. Ayoub, Presiding Papers 447-453

CELL 447

Twin-screw extrusion: A versatile tool for the pretreatment of biomass

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For more than 20 years, the laboratory of Agro-Industrial Chemistry develops an ambitious and multiscale research topic on the use of twin-screw extrusion for the processing of biomass for non-food applications. This talk will give an overview of past and present projects, discussing specific operating conditions and their consequences on biopolymer native organization. For the production of agro-materials, compounding processes have been designed and in some cases industrialized integrating specific targeted actions such as the plasticization of primary cell-walls (sugar beet, tobacco), the "fusion" of storage polymers (starch, oilseed proteins) and/or the destructuring of secondary cell-walls (lignocellulosic fibers). In those cases, low moisture conditions, high shear screw elements and compression zones (in which water reaches the subcritical state) are necessary. For the pretreatment of lignocellulosic fibers, the conjugated use of chemicals is also discussed. In integrated biorefining processes, twin-screw extrusion may also be used simultaneously as a continuous liquid-solid extractor for oil, polysaccharides or proteins and as a pre-treatment of the fibrous raffinate. This is especially efficient for the processing of oilseed crops and the production of binderless fiberboards or to prepare technical fibers for composite applications. Finally, in the bioenergy field, a specific pretreatment process for the production of bioethanol from lignocellulosic feedstock has been developed and is actually in the up-scaling phase. Integrating the use of enzymes during the extrusion, this process enlightens the good mixing capacity of twin-screw extrusion.

CELL 448

Using reactive extrusion to manufacture greener products – from laboratory fundamentals to commercial scale

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Reactive extrusion (REX) is an efficient means of continuously polymerizing monomers as well as chemically modifying existing polymers – it offers “just-in-time manufacturing”. This presentation discusses the use of twin screw extrusion processing to manufacture biobased and biodegradable-compostable polymeric resins for a portfolio of commercial applications. We have developed REX for the ring opening polymerization of epsilon caprolactone and p-dioxanone (1,4-dioxan-2-one) to manufacture biodegradable-compostable polymer resins. The polymerization of monomer to high molecular weight polymer has been achieved in 2-3 minutes using special catalysts and specific screw configurations. Starch, an anhydroglucose polymer, exhibits strong hydrogen bonding and crystallization leading to poor thermal processing since the Tm is higher than the thermal decomposition temperature. We have developed a twin-screw reactive extrusion process in which glycerol transesterifies the starch polymer to
make it pseudo thermoplastic and flow. Biodegradable polyesters have been grafted onto this glycerylated thermoplastic starch to provide thermoplastic starch-polyester graft copolymers that can be readily used for blown films and molded product applications. We have designed and engineered a one step, reactive extrusion process using water as the plasticizer and blowing agent along with suitable polymer modifiers to generate cellular starch foams. Water and shear imparted in the extrusion process breaks down hydrogen bonds without significantly reducing molecular weight. Nucleating agents and process aids control the cell structure, and maintain flexibility of the foam material. Reactive extrusion processing has been developed to synthesize maleated and epoxy modified poly(lactic acid) PLA through transesterification and coupling chemistries. These functionalized PLA molecules can be reactively blended with PLA and other biodegradable polyester resins, such as poly(butylene adipate-co-terephthalate) (PBAT), to achieve properties not found in traditional PLA resins — strain hardening properties for blown-film applications, improved processability, heat and impact resistance.

CELL 449

Extrusion of protein plastics

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Proteins are interesting raw materials for plastics. They can be considered nature’s polyamides. Besides being a renewable resource they are in several cases available as cheap side streams from existing industrial processes. Examples are wheat gluten from wheat starch/fuel production, whey from cheese production and rape proteins from biodiesel production. Most proteins are stiff and brittle because of the many hydrogen bonds, but can be made softer and tougher by the use of a plasticiser. One of the most effective plasticisers for these is glycerol. Glycerol is also a side stream product, from biodiesel production. Hence it is possible to produce a tough protein plastic entirely made from by-products. A drawback with protein plastics, as well as oil-based polyamides (e.g. PA6, PA66), although to a lesser extent, are their moisture sensitivity. This limits their use to indoor applications. The most important issue to consider when replacing oil-based plastics with those that are protein-based is that the latter must be able to run on conventional plastic processing equipments. Hence they need to be extrudable, injection mouldable and compression mouldable. On obstacle here, in contrast to thermoplastics, is that the temperature range where they can be processed is narrow. If the temperature becomes too high the protein aggregates and cross-link to such an extent that the viscosity increases drastically. Compression moulding is in general more suitable for protein plastics but extrusion and injection moulding are more “important” production techniques. In this presentation the extrusion of wheat gluten and Crambe Abyssinica protein (industrial oil crop) is discussed and problems and possibilities highlighted.

CELL 450

Silicone-based cellulose materials: Processes & characterizations

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Cellulose represents a promising alternative regarding the development of new materials.1,2 In parallel, Silicone based materials and especially the poly(dimethylsiloxane) (PDMS) answers to the requirements of numerous and various applications owing the -Si-O- linkages that bring a chemical robustness, a high thermo-oxidative stability, a high moisture resistance as well as a low surface tension to the materials.
Thus there is a great interest for designing Silicone-based Cellulose Materials. However, there is in parallel a need for developing eco-friendly processes ensuring the compatibility and the homogeneous ligation between the two substrates. In a first part, we present a new method of cellulose fibers/polymer coupling consisting in a unique operation of reactive compounding, based on an original chemistry of organosilanes in the polymer melt. In this process, grafting on polymer chains and on cellulose fibres surface as well as formation of Si-O-Si network occur in parallel during reactive extrusion. In a second part, we discuss on the elaboration and characterization of alkynated-cellulose which constitutes a new building block for the elaboration of bio-based composites (Figure 1).

Figure 1: Silicone elastomer filled with 1 % Alkynated Microcrystalline Cellulose of Cotton (a) Hydrosilylation Coupling reaction (b) MEB observation

**CELL 451**

**Novel silicone recycling technology based on extrusion depolymerization**

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Manufacturing of silicone polymers starting from quartz is an energy intensive operation. Meanwhile the vast majority of silicone polymers produced eventually ends up in discarded wastes, representing a very significant net energy cost from cradle to grave. Recycling waste silicones can save greater than 95% of the energy needed for silicone production on a per unit mass basis. But the current recycling technologies are predominantly batch processes, less efficient than necessary for certain geographic regions, and often suffer from either a narrow set of material types and forms that can be handled, or labor intensive pre-sorting and processing. This paper will present findings on depolymerization behavior of silicone polymers in a high shear extruder under various conditions, and some of the characteristics of a novel reactive extrusion silicone recycling process. High shear extrusion processes offer the advantages of being able to handle virtually any material form with minimum pre-processing, being continuous, and easily scalable. But an efficient depolymerization reaction is needed to match the relatively short
Thermomechanical extrusion preteatment for production of ethanol and arabinoxylan from corn fiber

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Corn fiber is the hemicelluloses-rich bran from the corn hull and is generated during the wet milling of corn and contains approximately 17% residual starch, 18% cellulose, and 35% hemicelluloses. The production of bioethanol from renewable biomass depends largely on the development of environment-friendly and highly efficient enzymatic hydrolysis for economic cellulosic ethanol production. The present study reports the effects of thermomechanical extrusion, particle-size reduction and chemical pretreatment on ethanol production from corn fiber. Extrusion pretreatment and particle-size reduction resulted in a significant (p < 0.05) difference in physical properties and color value of extruded corn fiber as a result of accelerated degradation of corn fiber structure. Extruded corn fiber at particle size (0.3 to 0.15 mm) also significantly increased (p<0.05) ethanol yield (28.80 g/L) and conversion (68.18%) by increasing protein digestibility and free amino nitrogen, which are essential for higher fermentation efficiency. Significant removal of hemicelluloses and lignin was observed from extruded destarched corn fiber treated by sodium hydroxide. Extrusion also affected structural disruption such as microstructures, crystallinity and degree of polymerization. The optimum extrusion process conditions, feed moisture content, screw speed and barrel temperature for minimum crystallinity index for saccharification and fermentable sugar yields by enzymatic saccharification were optimized using response surface methodology with center control points. Minimum crystallinity index of destarched corn fiber was determined at feed moisture content of 25.96%, screw speed 247.90 rpm and barrel temperature of 137.55°C. The maximum total sugar of extruded destarched corn fiber was optimized at moisture content of 44.89%, screw speed of 249.62 rpm and barrel temperature of 141.45°C.

Optimizing high shear and other process parameters for reactive mixing and nanocomposite dispersion

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This work elucidates the effects of ultra-high speed twin screw extrusion (TSE) on homopolymer degradation reaction as well as its capability to provide improved mixing. Effects of rotation speed, screw profile and feed rate on molecular weight loss are determined for several polymers. A kinetic model of depolymerization is proposed to simulate the evolution of conversion reaction along the various screw profiles. This predictive kinetic scheme determines the relative contributions of temperature and shear rate on the extent of reaction inside the high speed TSE. The study is extended to explore the efficient processing of polymeric compounds that can benefit from the high shear of this reactive system. For this purpose, rotational rheometry, scanning electron microscopy (SEM), and X-ray diffraction (XRD) characterization techniques have been applied in conjunction with fluid dynamics simulation software to quantitatively describe the dispersion progress of PS/organoclay nanocomposites. The physical correlation between morphological/rheological properties of the nanocomposite and processing conditions is discussed with the aim of optimizing exfoliation and minimizing damage to the polymer. Thereby, the
application of extreme shear is explored for its potential in developing new polymeric systems with desired final properties for any specific commercial application.

Advances in Polysaccharides: Practice & Applications
A. Biswas, Organizer; H. Cheng, Organizer; A. Biswas, Presiding Papers 454-461

CELL 454

Design of new functional polysaccharide nanoparticles for biomedical imaging applications

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The applied science of Polysaccharides (PS) is on continuous evolution offering more and more complex synthesis strategies and new application areas. As the controlled synthesis of PS nanoscale particles advances, the need for protocols to develop complex PS materials with enhanced properties rises. In the last two decades, a lot of attention was devoted to novel multifunctional nanostructures based on magnetic nanoparticles useful as agents for Magnetic Resonance Imaging (MRI), Optical Imaging and Magnetic Fluid Hyperthermia, as contrast agents, carriers for drugs and molecular targeting vectors. In this vein, we will present PS nanoparticles as carriers of nuclei possessing quadrupole moments, which could be used as a new type of MRI contrast agents for molecular imaging (1). The focus will be on systematic design of PS nanoparticles (NPs) from various polysaccharides in order to control the size, chemistry and hydrophilicity of the prepared NPs. Several synthesis routes will be discussed ranging from charge complexation (chitosan with alginate shown in Figure 1, chitosan with tripolyphosphate, chitosan with carboxymethyl cellulose), solvent exchange precipitation (carboxymethyl cellulose, ethyl cellulose, cellulose acetate) as well as coacervation emulsification method (ethyl cellulose) resulting in tunable sizes and surface chemistries of PS NPs.

Figure 1. Chitosan-Alginate nanoparticles produced by charge complexation
Chitin-Glucan nanopapers from fungi in membrane and water treatment operations

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Next to cellulose, chitin is the second most abundant biopolymer on earth, serving as building block inside the crustacean exoskeleton, insect cuticles and fungal cell walls. The structural component of fungal cell walls is comprised of nano-sized fibers made of chitin and glucan, which are covalently cross-linked. These fibers form a ready-made nanocomposite fabric, which is useful in the development of nanopapers, potentially applicable as membranes in water treatment operations. Due to their high content of N-acetyl groups not only size-exclusion filtration but also adsorption of cationically charged contaminants, such as heavy metal ions, should be feasible. In this study, the chitin-glucan base-material was extracted from common mushroom fruiting body (Agaricus bisporus). Extracts from common mushroom were found to be readily disintegrated into nanofiber dimensions (10 to 20 nm wide, several μm long) without any mechanical treatment, thus already utilizable for direct nanopaper preparation. Nanopapers were prepared by vacuum filtration of homogeneous chitin-glucan dispersions. The membrane performance of these nanopapers was assessed with respect to their permeance and rejection of contaminants both in size-exclusion and adsorption mode. Furthermore, the applicability of these nanopapers in organic solvent nanofiltration was investigated. It was found that chitin-glucan nanopapers were efficient in rejecting dissolved macromolecules from aqueous and THF solution, respectively, in the range of several thousand Daltons, corresponding to particles sizes of around 10 nm. Furthermore, adsorption of metal ions was successfully achieved due to interaction of these ions with the N-acetyl group of chitin.

Cellulose functional materials with multiple stimuli responsive and their applications in sensors

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Cellulose is the most abundant, renewable, biodegradable natural polymer resource on earth. Nowadays the main uses of cellulose are for paper or cardboard, membranes, tissue, explosives, textiles and construction materials. Cellulose molecular chain is composed of β-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed 180° with respect to its neighbors. Cellulose is highly crystalline and generally insoluble, due to the intra- or inter-molecular hydrogen bond networks. An extensive scope of applications of cellulose is limited for insoluble in common solvents and by the lack of properties inherent to synthetic polymers. Chemical modification is a common method endowing cellulose with new functions to apply in the wider fields. In this paper, we designed and synthesized several cellulose functional materials with multiple stimuli responsive, such as thermal, pH and redox responses, through ATRP grafting polymerization and “click”chemistry. Based on the highly hydrophilic microenvironment of cellulose backbone for enzyme, they can be used as an excellent mediator for the fabrication of enzyme sensors, which exhibiting a good linear electroanalytic response.
Figure 1. (A) Cyclic voltammograms of HPC-Fc/HRP electrode at 100 mV/s in 100 mM PBS at pH 7.0, in the absence (a) and presence (b) of H₂O₂. (B) Current-time curve obtained at a HPC-Fc0.25/HRP film electrode upon successive addition of H₂O₂ solution to 100 mM PBS (pH 7.0) with an applied potential of 0.35 V. (C) Calibrated curve of the biosensor with successive addition of H₂O₂.

CELL 457

Adsorption of IgG antibodies on cellulose thin film surface

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Cellulose is a bio-friendly material and has a strong potential to engineer bio-diagnostics tool to identify pathogens and other biomolecules. Cellulose has three liable hydroxyl group per monomer which can easily be exchanged with other functional groups for specific purpose. Therefore, visualization and quantification of the adsorbed molecules on the cellulose surface is important to develop cellulose based devices. In the present work, cellulose thin films were made by using deuterated bacterial cellulose and cellulose acetate followed by different regeneration processes and used as a model surface for the adsorption of IgG antibodies. Atomic force microscopy measurement shows that the obtained films are smooth and have roughness of about 1.1 nm. Neutron reflectivity (NR) data analysis reveal that the initial cellulose film thickness is 10 nm and swells up to two to three times in the water. Moreover, NR experiments allow to visualize and quantify the adsorption of IgG molecules onto the cellulose thin film surface. The antibody blood typing efficiency and the surface hydrophobicity was measured using image analysis and contact angle measurement respectively. Results obtained from different investigations allow to understand and optimize the interaction mechanisms between cellulose and IgG molecules. The gained knowledge will contribute in the optimization and development of low cost and biodegradable diagnostic devices for biomedical applications.

CELL 458

Development of cellulose helicoidal architectures in nature

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Nature provides a multitude of nanostructures that have been finely tuned by natural selection and produce structural coloration that play a role in many biological functions such as mating, signalling or camouflage. A recurring design that is found both in the animal and plant kingdoms is the helicoidal structure, i.e. a multi-layer structure where adjacent layers rotate along a helical screw. Examples of such
structures have been found in different plant tissues and species. In this work, we study the assembly process of cellulose helicoids in the cell wall of a living plant. Polarization resolved spectroscopy allows to directly correlate the optical response measured from a single developing cell with the architecture of the cellulose in its cell wall. In parallel, by investigating the polysaccharides involved in helicoidal cell wall architectures, their interaction and their chemical and physical properties we try to underpin the design principles used by nature to produce such complex hierarchical structures.

The figure shows some fresh fruits *Margaritaria nobilis*. The intense metallic coloration of the fruits is the result of selective reflection from a helicoidal cellulose structure in the cell walls of the endocarp.

**CELL 459**

Free-standing multilayered membranes from renewable polymers, towards tissue engineering applications

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The incorporation of polymers from renewable resources on polymeric membranes has providing valuable properties in a wide-range of applications: besides being available on large scale, low cost and friendly-user, they have also been suggested as biodegradable and biocompatible. Such properties can be specially harnessed for tissue engineering, and for that the membranes should adapt to geometrical changes of the attached tissues and together with other factors induce the regeneration of different anatomic sites, such as periodontal membrane, skin, liver and cardiac tissues. In this context, we developed stretchable 2-dimensional multilayer constructs through the assembling of two bio-based polyelectrolytes, chitosan (CHT) and chondroitin sulphate (CS), using the layer-by-layer methodology. The morphology and topography of the developed membranes were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM); also the transparency of the films were evaluated. The influence of genipin, a natural-derived cross-linker agent, was also investigated in the control of the mechanical properties of the CHT/CS films. Changing the genipin concentration can tailor parameters like the water uptake ability, which influenced the young modulus and ultimate tensile strength. The maximum extension tends to decrease with the increase of genipin concentration, compromising the elastic properties of CHT/CS films: nevertheless, using lower cross-linker contents, the ultimate tensile stress is similar to the films not cross-linked but exhibiting a significant higher modulus. The interaction between cells and free-standing CHT/CS membranes was investigated in vitro. Better L929 cell adhesion and proliferation were obtained when using the cross-linked membranes and the non-cytotoxicity of the CHT/CS films was confirmed. The developed free-standing biomimetic multilayer made from renewable polymers could be designed to fulfill specific therapeutic requirements by tuning properties such as swelling, mechanical and biological performance.

**CELL 460**

**Structural features of polycarboxylic acids as crosslinking agents of cellulose**

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Polycarboxylic acids (PCAs) have been investigated as crosslinking agents for cotton due to the potential formation of multiple ester bonds with different cellulose chains. These acids all possess three or four carboxylic acids on adjacent carbon chains including 1,2,3,4-butane-tetracarboxylic acid (BYCA), citric acid, and even aromatic acids. BTCA is one of the very promising compounds, and has received a lot of attentions from many researchers. After evaluating many different acids as potential crosslinking agents, it was found that all of polycarboxylic acid treated cotton fabrics have demonstrated certain efficiency in crosslinking cellulose, reflected by pretty matching or even better wrinkle recovery angles of the treated fabrics compared to the performance of dimethyl-dihydroxyethyleneurea (DMDHEU) treated fabrics. However, durable press ratings of the PCA treated fabrics were always lower than that of DMDHEU treated one, even under optimized conditions. After analyzing the molecular structural features of the acids and their reactions with cellulose, as well as affinities to cellulose and water by using modeling programs and experimental studies, we identified several key factors that significantly restrict their efficiency in forming most effective crosslinks between cellulose chains. In this presentation, the potential determining factors of polycarboxylic acids will be discussed and compared with those of DMDHEU. We hope this study could provide useful clues to the development of novel environmentally friendly crosslinking agents for cellulose.
PEGylation of chitosan via nitroxide chemistry in aqueous media

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Chitosan is one of the most important biopolymers on earth, and is derived from the second most abundant natural polymer, chitin. Chitosan, valued for its biocompatibility, biodegradability, and biological tolerance, finds applications in the biomedical and pharmacy fields including for example with drug delivery systems. However its properties and applications in these fields could be improved if functional groups or polymer chains are covalently attached to modify its properties. PEGylation of chitosan has been used to enhance its solubility, biocompatibility and absorption since PEG has low toxicity and is biocompatible. In this research, PEGylation of chitosan with well-defined poly(poly(ethylene glycol) methyl ether methacrylate), polyPEGMA, via living radical polymerization using nitroxide chemistry and a “grafting to” approach is reported for the first time. Chitosan was first functionalized with glycidyl methacrylate (GMA) yielding CTS-g-GMA. Nitroxide-terminated polyPEGMA was then prepared via nitroxide-mediated polymerization (NMP) in water. These polyPEGMA chains were then grafted to the functionalized chitosan in aqueous media. PEGylation of the chitosan was carried out on the hydroxyl groups on the chitosan molecule, thereby preserving the amino functionality for subsequent reaction or functionalization. The grafting to procedure enabled grafting well-defined graft modified chitosan. The resulting properties of the PEGylated chitosan may be modified simply by the changing the molecular weight of the polyPEGMA made via NMP. A unique feature of our research is that both the graft polymer synthesis and grafting to step were performed in aqueous media, thereby avoiding the use of toxic solvents.

Developments in the Fields of Celluloses & Lignocelluloses: In honor of Dr. Rajai Atalla
U. P. Agarwal, Organizer; T. Larsson, Organizer; A. Isogai, Organizer; T. J. Elder, Organizer; T. Larsson, Presiding; Y. Hsieh, Presiding Papers 462-469

CELL 462

New development of wood chemistry promoted by TOF-SIMS

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Lignification is an important differentiation process in plant cell walls in which lignin is deposited in the polysaccharide matrix. The actual chemical structure of the lignin polymer is still unclear. The regulating mechanism of lignin biosynthesis is also still controversial. To overcome these problems, in this study, cryo-time-of-flight secondary ion mass spectrometry (cryo-TOF-SIMS) was used to investigate the tissue and cellular distribution of a monolignol glucoside of coniferin. Coniferin, the promising candidate of a lignin precursor is water-soluble and the actual distribution in living plants was unclear. The heterogeneous distribution of coniferin in the differentiating xylem would provide useful information about the storage and supply mechanism of lignin precursors. Two-year-old shoots of Ginkgo biloba was quick-frozen and used as a sample. After cutting to form a clean and flat surface in the glove box, positive ion images were obtained by cryo-TOF-SIMS, and subsequently the same region was observed by cryo-SEM. The lignification stage of the cells was confirmed by microscopic observations using visible, polarized, and UV light. Cryo-TOF-SIMS images were obtained for the transverse surface of freeze-fixed stem of G. biloba. The m/z 180.08 ion of coniferin fragment was largely detected in the differentiating xylem region. The cellular distribution of coniferin was compared with the twice-assimilation timing of
coniferin to lignin which was shown by 14C-labeled coniferin administration experiments previously. The report suggests that if coniferin exists in the lignifying cells, it is assimilated to lignin. The cellular distribution of coniferin revealed by cryo-TOF-SIMS was in consonance with the lignification stages of the cells. These results lead us to the conclusion that coniferin is stored in the cells of differentiating xylem and one of the uses should be a lignin precursor.

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Following in-situ hydrophobisation of plant cell walls by Raman imaging

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Around 10 years ago the coupling of Raman spectroscopy with Confocal microscopy evolved as a powerful imaging tool to get insights into cell wall chemistry and structure of the native wooden cell walls with submicron resolution\textsuperscript{1,2}. Two-dimensional spectral maps can be acquired and chemical images calculated by integrating the intensity of characteristic spectral bands or by using multivariate data analysis methods\textsuperscript{3}. The variability of cell wall composition is revealed, including changes in the orientation of the cellulose microfibrils\textsuperscript{4} as well as the spatial variation of lignin amount and composition in context with the cell structure\textsuperscript{5}. Due to the multicomponent nature of plant cell walls the Raman spectra usually comprise overlapping bands from cellulose, hemicellulose, lignin and extractives. Therefore especially multivariate approaches aiming in unmixing the multicomponent spectra, like vertex component analysis (VCA) and non negative matrix factorization (NMF) have potential to reveal new insights\textsuperscript{6}. VCA revealed that the lumen sided S3 layer as well as the pits, functioning as connection valves between the water conducting tracheids, have a different lignin composition than the main part of the secondary cell wall-layer (S2)\textsuperscript{5}. During heartwood formation of pine an additional hydrophobisation has been observed by impregnation with stilbenes in a similar pattern with accumulations in the S3 and pits (Fig.1) The different lignin composition and extractive impregnation of the surface layers and connection pathways is of relevance for plant cell wall processing as well as resistance against abiotic and biotic stresses and decay.

Fig.1. Raman image of pine heartwood based on vertex component analysis (VCA) revealing an almost pure stilbene endmember spectrum and abundance in the lumen-sided cell walls, connecting pits and rays (red).
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On the mechanisms of cellulose dissolution in aqueous media

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Cellulose is known to be insoluble in water and in many organic solvents, but can be dissolved in a number of solvents of intermediate properties, like N-methylmorpholine N-oxide (NMMO) and ionic liquids (ILs) which, apparently, are not clearly related. Cellulose can also be dissolved in water at extreme pHs, in particular if a cosolute of intermediate polarity is added. We review the main achievements in the dissolution area and discuss underlying mechanisms. Recent work has much emphasized the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions, rather than strong intermolecular hydrogen bonding between cellulose molecules as was suggested in some earlier work. Thus we argue that cellulose is significantly amphiphilic. In addition to presenting recent work on novel cellulose solvents we illustrate the association and precipitation of cellulose from rheology studies, and how they can be affected by other amphiphilic compounds. Cellulose has a strong tendency to re-assemble when dissolved; this process is strongly affected by surfactants and other additives affecting hydrophobic interactions. Cellulose dissolution and regeneration have had important applications for a long time. By dissolution in aqueous media further uses become possible.

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Construction of cellulose based nanofibrous materials via green route

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Herein, a series of nanofibrous materials were constructed from cellulose solution in NaOH/urea and NaOH/thiourea solvents at the low temperature, in which the extended semi-stiff chain of cellulose aggregated in parallel under fluctuation to form nanofibers. Thus, cellulose multifilaments containing nanofibers with mean diameter of 30 nm were fabricated, displaying an orientation microstructure and excellent properties. With a drawing process, the crystallinity and orientation factors of the fibers increased, as well as the tensile strength increased from 2.16 to 3.05 cN/dtex, superior to the commercial viscose rayon. Cellulose microspheres consisted of nanofibers also were constructed, which could be used as matrix for the in-situ synthesis of the organic or inorganic composite materials, and hierarchical co-doped carbon nanofiber microspheres were successively fabricated by pyrolyzing. Moreover, stronger and tougher cellulose hydrogels weaved with nanofibers were constructed via both physical and chemical cross-linking, showing specific properties. Therefore, we opened up a completely new avenue to construct the regenerated cellulose materials with nanofibrous architecture via a “green” and low cost route.
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Polymerization of cellulose and lignin on a chip: Morphological studies

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Several researchers in our group previously demonstrated that bacterial cellulose synthesis enzyme, Bcs A-B, bound on the surface of a chip, is capable of producing crystalline cellulose II. In this paper, we extended the work by incorporating lignin in the system. Lignin was polymerized on the chip either before or after cellulose synthesis, and morphological studies were conducted. Atomic force microscopy studies showed that cellulose microfibril morphology was altered after lignin incorporation. Cellulose crystal size, and also the crystallinity index, were also significantly affected by lignin polymerization, particularly when the polymerizations were conducted simultaneously, suggesting that lignin deposition and incorporation changes the nature of cellulose microfibril deposition. The implications and limitations of this work with regard to native lignocellulose synthesis will be discussed.

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Crystal deformation and transformation of cellulose allomorphs derived from stability of molecular chain sheets

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Microscopic observations of a native cellulose microfibril using atomic force and transmission electron microscopy have often revealed the formation of a right-handed twist. We have reported molecular dynamics (MD) simulations of finite crystals of the native forms in aqueous solution using the AMBER force field coupled with Glycam04 parameters, and the right-handed fiber twists were reproduced in the solvated cellulose Iα and Iβ crystal models with the Iα crystal models showing greater twisting. Just prior to our reports, Matthews et al. also reported the right-handed twist of the cellulose Iβ crystal in a similar MD study. As the cellulose allomorphs other than the native ones, cellulose III can be obtained by treatment of the cellulose Iβ form with liquid ammonia or amines, and is readily converted back into the latter form by hot-water treatment. Our MD study of the cellulose crystal models were then adopted to the cellulose III chain models in hot-water simulation at 370 K, exhibiting partial crystalline transformation of (1−10) chain sheets accompanied by irreversible rotation of the hydroxymethyl groups from gt to tg conformations and hydrogen-bond exchange from the original O3–O6 to cellulose-I-like O2–O6 bonds. The corrugated (1−10) chain sheet was converted to a cellulose-I-like flat chain sheet with a slightly right handed twist. Recently, the structural stabilities of the molecular chain sheets constituting the crystal structures of the cellulose allomorphs Iα, Iβ, II, and III were investigated by density functional theory (DFT) optimization of the isolated chain sheet models with finite dimensions. The DFT optimized chain sheet models of the two native cellulose crystals developed a right-handed twist with a similar amount of twisting. The DFT-optimized cellulose II (010) and (020) models twisted in opposite directions with right- and left-handed chirality, respectively. The cellulose III (1−10) model retained the initial flat structure after the DFT-optimization. Obviously, the structural features of the DFT-optimized chain sheet models were reflected in the structures of the parent crystal models observed in solvated molecular dynamics (MD) simulations described above.
Imaging mass spectrometry analysis of woody cell wall using $^{13}$CO$_2$ pulse labeling

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Green plants assimilate carbon dioxide (CO$_2$) in the atmosphere and convert it to sugars via photosynthesis. A part of the carbon incorporated to tree is retained more than decades or centuries in cell walls of woody xylem, which is composed of mainly cellulose, hemicelluloses and lignin. Carbon allocation is an important aspect of wood formation in trees. To better understand the process of xylem cell wall formation, we have investigated how photosynthetic products are incorporated to cell walls, by means of stable isotopic pulse labeling and isotopic imaging using secondary ion mass spectrometry (SIMS). Isotopic labeling is one of powerful tools to study the metabolic pathway or translocation of molecules in plants and animals. Carbon isotopes have been used to investigate xylem formation in trees. In this study, carbon isotopes are traced using SIMS with high lateral resolution, and this method revealed distribution of the carbon isotopes in subcellular scale. We produced $^{13}$C-labeled poplar tree by $^{13}$CO$_2$ pulse labeling. The $^{13}$C content of cell wall components in the samples was measured by an isotope ratio mass spectrometer. For ion imaging, the samples were fixed and embedded in resin according to sample preparation methods for transmission electron microscopy. SIMS analysis was performed on semi-thin sections, and ion images of $^{12}$C, $^{13}$C were acquired using a Cs$^+$ primary ion beam. The ion images revealed subcellular localization of the tracer $^{13}$C in various tissues. Remarkable accumulation of the tracer $^{13}$C to cell walls was detected in the developing xylem and a $^{13}$C-rich layer was observed. The layer had already appeared on the cell wall after 6 h from $^{13}$CO$_2$ feeding, indicating that assimilated carbon was rapidly incorporated to the cell wall. Based on the localization of the tracer $^{13}$C and its distribution to different cell wall components in various $^{13}$C-labeled samples, correlation between cell wall formation and carbon allocation will be discussed.

Immunocytochemistry gives new insight into cell wall formation in wood

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Major cell wall components in woody plants are cellulose, hemicelluloses, and lignin. Cellulose is synthesized by cellulose-synthesizing rosette complexes located on the plasma membrane and deposited at the inner surface of developing cell wall. Hemicelluloses are synthesized in the Golgi apparatus, secreted by exocytosis of Golgi vesicles, and deposited to the developing cell wall. However, how glucomannan and xylan are synthesized and processed in the Golgi apparatus, and how their transports to cell walls are controlled are still not clarified. Although lignification of cell wall and distribution of lignin within the cell wall have been studied, what type of linkage in lignin is located within the cell wall is not elucidated. Because the antibody raised against targeting substance is very specific and highly sensitive, immunocytochemistry is a useful technique to visualize the distribution of cell wall components. Immunocytochemistry revealed the deposition of glucomannan in normal wood starts at cell corner region of S$_1$ at the beginning of secondary wall formation in Japanese cedar (Cryptomeria japonica). Then the deposition appears all over the developing secondary wall. Glucomannan with more acetyl group is deposited at outer part of S$_2$. Acetyl group is gradually removed by aging. Density of labeling is slightly higher in S$_1$ than S$_2$, indicating glucomannan is deposited more in S$_1$. Deposition of xylan occurs during secondary wall formation. The labeling of xylan is slightly higher in S$_2$ than in S$_1$, indicating xylan is deposited more in S$_2$. The labeling appears in compound middle lamellae including cell corner region during secondary wall formation, suggesting intussusceptional deposition of xylan. The labeling is also observed in warty layer. Monoclonal antibodies, KM1 and KM2 were raised against dehydrodiconiferyl alcohol with 8-5' linkage and pinoresinol with 8-8' linkage, respectively, and used for immunolabeling of
lignin. Immunolabeling by KM1 is observed in the compound middle lamellae and secondary walls of Japanese cypress (*Chamaecyparis obtusa*). Weak labeling by KM2 is also observed in the compound middle lamellae and secondary walls. These labeling suggest the distribution of 8-5' and 8-8' linked structure of lignin in the cell walls.

**Functional Lignocellulosics & Nanotechnology**

S. Peresin, Organizer; T. Nypelo, Organizer; E. Filpponen, Organizer; S. Spirk, Organizer; M. K. Ek, Organizer; S. Spirk, Presiding; E. Filpponen, Presiding Papers 470-477

**CELL 470**

**First steps towards bio-based static true volumetric 3D displays: Transparent cellulose scaffolds equipped with photon upconverting rare earth metal doped nanophosphors (uc-NP)**

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Doping of nanoparticles from transition metal compounds with rare-earth metal ions, such as Eu$^{3+}$ affords nanophosphors which feature upconversion (anti-Stokes) photoluminescence (uc-NP). Homogeneous dispersion and chemical immobilization of uc-NP in a suitable transparent matrix allows to generate adressable «active elements» transparent in off state but either opaque or luminous in on state. Switching between these two states can be accomplished by pulsed IR laser light. The emission of photons from selectively activated ensembles of uc-NPs having different PL characteristics can be employed to create visual representations of any object in three physical dimensions as opposed to planar images of traditional screens, thus providing ultimate physiological depth cues. As the color gamut of uc-NPs is typically much greater than that of the common RGB standard, 3D color images of high brilliance can be obtained provided that a well-balanced mixture of uc-NPs capable of emitting in the whole range of the visible light is randomly dispersed within the transparent matrix. Following our previous works on transparent, monolithic aerogels from nematic liquid-crystalline, nanofibrillated carboxyl cellulose derivatives, their reinforcement by percolating networks of biocompatible polymers and covalent equipment with both semiconductor and carbon based quantum dots, this paper communicates the results of an ongoing study investigating approaches towards grafting of uc-NP onto the large internal surface of transparent, highly porous yet mechanically robust aerogels from nematic liquid-crystalline suspensions of nanofibrillated oxidatively modified cellulose.

**CELL 471**

**Phase separated bicomponent biopolymer thin films - enzymatic patterning and protein interaction**

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In this contribution, we present the fabrication of micro phase separated blend thin films, composed of PHB (poly-3-hydroxybutyrate) and cellulose in order to generate patterned polymer surfaces. This is of high interest due to the requirement of a variety of surface morphologies for thin film applications in various fields. Blend thin films were prepared in different ratios via spin coating of PHB/TMSC (trimethylsilyl cellulose) solutions followed by regeneration of TMSC to cellulose afterwards. The thin films were investigated in terms of thickness, surface free energy, surface roughness and morphology.
Moreover, the extent of nonspecific protein adsorption was tested for the herein examined films at the example of bovine serum albumin. Enzymatic structuring was performed with either PHB-depolymerase or cellulase. Atomic force microscopy studies of enzyme treated surfaces reveal complete removal of PHB or cellulose and display features in the nano and micro size range depending on the blend ratio. Additionally, enzyme-substrate interaction of PHB-depolymerase was studied by means of multi-parameter surface plasmon resonance spectroscopy, showing extremely fast PHB degradation compared to other enzymes of this kind.

CELL 472

Dye functionalized polysaccharide nanoparticles – From synthesis to bio-sensor applications in immunoassays

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Hydrophobic polysaccharide (PS) derivatives can self-assemble into spherical nanoparticles (NP) using facile dialysis or dropping-in procedures. These nanomaterials are of great interest for various applications, in particular in medicine and biotechnology, because they are easy to prepare and biocompatible. Moreover, it is possible to introduce desirable functions such as dyes, affinity ligands, and drugs by advanced polysaccharide chemistry. However, this can be a very laborious procedure depending on the number and type of functional substituents. In the present work, two facile approaches towards novel functional PS-NP are described. The overall aim of the project was to obtain bio-sensors in particular for immunoassay applications that carry dyes and reactive groups for an efficient coupling of antibodies. (I) Different hydrophobic dyes were physically entrapped within a cellulose acetate phthalate (CAPh) matrix by a co-self-assembling process. Depending on the preparation conditions and the chemical nature of the dye, spherical dye loaded PS-NP in the scale of 200-500 nm could be obtained. By electron microscopy and UV-vis spectroscopy, it was demonstrated that the dyes are well incorporated within the PS matrix and that spectroscopic properties are determined primarily by dye-dye interaction. The novel CAPh-NP feature reactive carboxyl groups that could be used for efficient coupling with antibodies. Thus, a lateral flow immunoassay for C-reactive protein (CRP) was constructed that was more sensitive than a reference test using nano-gold. (II) CAPh was chemically modified prior to the NP formation to quantitatively convert the carboxyl group into an activated N-hydroxy succinimide (NHS) ester. Four different reaction strategies were compared and the molecular structure of the products was characterized comprehensively. It was demonstrated that the NHS groups react quantitatively with amines and are not removed during the NP formation in aqueous media. Thus, it was possible to obtain activated PS-NP that could easily be functionalized with dyes and/or antibodies in one step.

CELL 473

Cellulose-based microcapsules: Bio-compatible vessels for packing, delivery and attachment of active species

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Microencapsulation technique can efficiently accommodate solid, liquid or gaseous substances within a shell of another substance, creating small sealed capsules. Diffusion of embedded material through the shell walls can be monitored with the structure of the capsule, resulting in controlled release under given
conditions of applications. With microencapsulation, a functional barrier is constructed between the packed species and the surrounding wall material, maintaining biological, functional and physicochemical properties of the active material and preventing chemical and physical reactions. Presented study delves into the design and construction of cellulose derivative-based microcapsules, which serve as (i) carriers of active species or (ii) possess functional shell surface. In the first instance, α-tocopherol-loaded ethyl cellulose microcapsules, applied as a functional coating for treatment of skin (α-tocopherol, i.e. vitamin E acts as a scavenger for free radicals, preventing skin damage), will be presented. Surfactant-assisted fabrication of microcapsules was carried out using different process parameters and a variety of surfactants, which results in differences in size, size distribution of particles and surface topography and effectively influences their packing and release properties. The second cellulose microcapsule system tackles the applications pertaining to isolation and separation of specific molecules, essential procedures in a variety of bioscience and biotechnology areas. Here, magnetic particle-based bioseparation is one of the most widely used; we have constructed capsules with magnetic shells, which serve as efficient platform for isolation of e.g. proteins.

CELL 474

Cellulose nanofibers used in the fabrication of energy storage devices

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The growing environmental awareness associated with the increasing use of electronic technologies in our everyday life has triggered the use of renewable materials in energy storage devices. In this perspective, materials extracted from wood, such as cellulose nanofibers (CNF), appear to be an interesting alternative. Among the remarkable properties reported for CNF, recent work has shown their ability to stabilize water-based dispersions of carbon nanotubes, and to build three dimensional networks which can further be surface treated into three dimensional energy storage devices. Taking advantage of those possibilities, we demonstrate in the present contribution how CNF can be used in the fabrication of Li-ion battery electrodes. More specifically, CNF has been used as binding agent in lithium iron phosphate cathodes and lithium titanate oxide anodes. The use of CNF allows for a water-based preparation of the electrodes, whereas conventional fabrication procedures involve toxic solvents such as N-Methyl-2-pyrrolidone. Different fabrication strategies have been investigated in order to tailor the properties of the CNF-Li-ion energy storage devices.

CELL 475

Cellulose as a template for generation, wireless transport and storage of electrical energy with conducting polymers

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Conducting polymers (CPs) may be seamlessly transitioned across a large range of electrical conductivities. This may be achieved on-the-fly by electrochemically changing their doping level. However, the processing of CP films has typically been constrained to thicknesses in the micrometer range which has hindered their adoption beyond a few niche applications. A composite containing a CP [viz. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate] with cellulose nanofibrils (CNFs) and high-boiling-point solvents is found to combine excellent electronic and ionic conductivities (up to 500 S/cm and 20 mS/cm respectively). We provide experimental results which suggest the CNFs are coated by the CP providing the electronically transporting phase. The solvents trapped in the interstitial nanovoids of the cellulose network act as the ion transporting phase. Moreover, the CNFs provide structural integrity enabling the fabrication of thick films with a high mechanical integrity. We use this material to prepare
solenoids with which we demonstrate the first organic (i.e. metal-free) electromagnetic generator. Furthermore, we use these organic solenoids in a resonant inductive coupling configuration to transmit electrical power wirelessly. Lastly, the electrochemical activity of the CP phase coupled with the fact that ions can be readily transported in the material is exploited to build competitive, reliable and environmentally-friendly energy storage devices that bridge the gap between batteries and capacitors. Ongoing efforts to scale up the manufacturing process is expected to benefit from the natural abundance of cellulose and the technological maturity of the paper production industry.

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Bacterial nanocellulose-based composites as ion exchange membranes for fuel cells

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The exploitation of raw materials from renewable sources is becoming a recurrent activity, aiming to contribute to a sustainable model of development, both in terms of energy/fuels and of chemicals/materials. Hydrogen fuel cells (FCs), and particularly the polymer electrolyte fuel cell (PEFC) technology, are the heart of the near-term sustainable energy paradigm having hydrogen as the energy vector. Albeit the research blooming about PEFCs, only a small number of studies have addressed the use of alternative and environmentally friendly materials to replace the state-of-the-art perfluorinated membranes like Nafion®. Bacterial nanocellulose (BC), a highly pure and crystalline form of cellulose with a tridimensional nanofibrillar structure, presents singular properties, such as good dimensional...
stability and mechanical properties, high water retention capacity and stability in alkaline medium, biodegradability, ability to be produced in the form of membranes with tailored size and form, and high potential as reinforcing element in composite materials, that makes it a very attractive solution for the development of bio-based ion exchange membranes for PEFCs. The present study describes a simple and easy method to produce both proton and hydroxyl ion conducting BC nanocomposite membranes by combination with different polyelectrolytes with suitable anionic, namely poly(4-styrene sulfonic acid) (PSSA), poly(methacryloyloxyethyl phosphate) (PMOEP), or cationic functional groups, such as poly(methacryloyloxyethyl chloride) (PMACC). All these membranes showed good thermal, viscoelastic and mechanical properties, and high ion conductivity, and therefore potential as bio-based alternatives to other polymer electrolyte membranes for application in fuel cells.

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Hydrogen bonding and polymer adsorption: A look at polyethylene glycol with cellulose and silica colloids

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Polyelectrolyte adsorption to cellulose is well understood, however adsorption of non-ionic polymers is less clear. Often hydrogen bonding is cited as a governing factor, yet recent work suggests that it does not play a significant role, and in fact non-ionic polymer adsorption is largely entropically driven. In this work we provide further insight into polymer adsorption by using polyethylene glycol (PEG) as a model non-ionic polymer and monitor adsorption to cellulose nanocrystals via quartz crystal microbalance with dissipation, dynamic light scattering and isothermal titration calorimetry. We compare adsorption phenomena to well-known hydrogen bonding interactions between PEG and fumed silica and additionally draw upon previous papermaking research to better understand the mechanisms involved. Unlike the strong acid-base interactions, which drive adsorption to silica surfaces, PEG exhibits limited or no interaction with cellulose nanocrystals either as thin films or dispersed particles. Our findings along with current literature suggest that hydrogen bonding does not occur between cellulose nanocrystals and PEG despite in aqueous media reports to the contrary. We emphasize that understanding these interactions is essential for the development of cellulose nanocrystals and cellulose-based materials as many applications contain a complex mixture of polymers and surfactants.

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems

M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. J. Rojas, Organizer; R. L. Quirino, Presiding; M. L. Auad, Presiding Papers 478-484

CELL 478

Activated polysaccharide nanoparticles derived from xylan phenyl carbonates – From synthesis to applications

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Xylan is a highly available bioresource present in hardwoods and non-wood lignocellulosic biomass. It can easily be obtained as a by-product of pulp production or by upgrading paper pulp to dissolving quality by cold-alkali extraction. However, valorization strategies for xylan are highly needed to justify the added costs for adopting xylan extraction and purification processes. Chemical functionalization of xylan to
derivatives and shaping into functional materials are very attractive approaches in this regard. The aim of the present study was to prepare novel activated nanomaterials from xylan phenyl carbonates (XPhC). It is demonstrated that the PhC group (i) is easily introduced by homogeneous derivatization, (ii) is hydrophobic and thus should enable facile self-assembling into spherical nanoparticles (NP), and (iii) can be converted with nucleophilic amines to introduce various functionalities (e.g., dyes, drugs, antibodies) prior or subsequent to the NP formation. XPhC with high degrees of substitution (DS) of up to 2.0 were prepared in completely homogeneous reactions using different reaction media. Spectroscopic characterization revealed different substitution pattern for the products: statistic (in ionic liquids) vs. preferential at position 3 (in dipolar aprotic solvent with LiCl). Xylans from different origin were included in this study to investigate the effect of molecular weight and monosaccharide composition on the xylan carbonate synthesis and likewise evaluate the potential for adding value to different processes in which xylan could be derived as a by-product. Finally, the quantitative conversion of the activated XPhC into carbamates was studied with different nucleophilic amines. Using a dialysis approach, spherical XPhC-NP were obtained with a Z-average diameter of ≈ 100-300 nm and a narrow polydispersity (PDI ≈ 0.1). It could be demonstrated that the activated PhC groups are not cleaved during the particle formation. Thus, it is possible to functionalize these “activated-NP” for specific applications (e.g., drug delivery, biosensing, immunoassays). Surprisingly, cellulose phenyl carbonates were not suitable for the preparation of NP, which clearly indicates the possibilities for integrating xylan into high-value added nanomaterials with unique fields of application.

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Emulsion polymerization of tung oil-based latexes with asolectin as a biorenewable surfactant

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Bio-based vesicles, with potential application in drug delivery and/or catalyst encapsulation, have been prepared by the free radical emulsion co-polymerization of tung oil, divinylbenzene (DVB), n-butyl methacrylate (BMA), and asolectin in a xylene/water mixture. The free radical polymerization was initiated by di-tert-butyl peroxide (DTBP) at 100°C in a convection oven. Molecular weights of approximately 11,000 Da were measured by Matrix-assisted Laser Desorption/Ionization-Time of Flight (Maldi-TOF) for tung oil-asolectin copolymers, verifying that significant polymerization occurs under the cure conditions employed. The cure of the co-monomer mixture employed in this work was monitored by Dielectric Analysis (DEA), while changes in the Raman spectrum of all co-monomers before and after the cure, along with differential scanning calorimetry (DSC) analysis, have been used to verify the need of a post-cure step and completion of the polymerization reaction. Transmission electron microscopy (STEM) images of the emulsion after polymerization indicate that vesicles were formed, and vesicle size distribution of samples prepared with different amounts of tung oil were determined using a Zetasizer.

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Bioactive nano-coatings from hyaluronic acid and a lysine-derived surfactant

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The biofilm formation triggered by uncontrolled protein adsorption, on medical devices is the leading cause of catheter-associated urinary tract infections (CAUTI) during implantation. Herein, we report a simple and one-step strategy to functionalize surfaces of silicone catheters, poly(dimethylsiloxane) (PDMS), with antifouling and antimicrobial substances. A novel formulation consisting of an anionic polysaccharide (hyaluronic acid, HA) and a lysine-derived biocompatible cationic surfactant (N-ε-myristoyl-lysine methyl ester, MKM) was prepared, resulting in the formation of nanoparticles (NPs, ca. 100 - 250 nm). Besides their high stability and long-lasting hydrophilicity in ambient and aqueous environments for 60 days, the nanometric layers (58 ± 2 nm) of HA-MKM NPs on the PDMS showed very low protein adsorption against BSA and lysozyme and significantly lower adsorption against fibrinogen as revealed by a quartz crystal microbalance with dissipation. In-vitro antimicrobial test with S. Aureus, E. Coli, P. Aeruginosa, P. Mirabilis C. Albicans microbes under dynamic conditions revealed that the microbes’ attachment was hampered by 85% when compared with the unmodified PDMS. Given the multiple functionalities and different physiochemical properties of polysaccharide-lysine-based surfactant mixtures, this approach can be easily extended for the development of novel coatings on other silicone-based materials, thereby broadening potential applicability of PDMS-based devices in microfluidics, diagnostic biosensors and others.

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Biomaterials based on polysaccharide conjugates

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Polysaccharides proteins and DNA are the main polymers determining and influencing the structure and function of living biological systems. Understanding and utilizing the interaction of these three types of biopolymers with each other is prerequisite for designing new and efficient biomaterials for tissue engineering or biosensors. Polysaccharide-amino acid conjugates are materials that possess properties of the acetal and peptide world. These materials are intended to mimic nature’s proteoglycans, glycoproteins and glycosylated enzymes in form and function and are expected to carry even unprecedented properties. Development of derivatization strategies for the conjugation of polysaccharides with amino acids are the crucial step for obtaining these materials. Subsequent processing into two and three-dimensional objects (particles, coatings, foams, fibers) allows for their use in bio-medical applications. Studying interactions of living cells with the described biomaterials gives insights into the mechanisms and applicability of this relatively unexplored group of semi-synthetic bioconjugates.

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Green approaches to preparation of amphiphilic soy protein microfibrils and films

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Soy proteins are vastly under-utilized byproducts of the largest edible oil and biodiesel production in US and represent readily available plant biopolymer resource for environmentally friendly materials. In this work, a green approach involving neither chemical additive nor heat has been established to produce stable aqueous soy protein colloids. Such soy protein colloids could be assembled and mass fabricated
into amphiphilic microfibrils that were 1.19-1.29 µm in average diameters. These microfibrils have been cast into films with either hydrophobic surfaces with 70.8° water contact angle or completely water wettable and hydrophilic surfaces. These facile approaches offer green alternatives for processing soy proteins into stable aqueous colloids, amphiphilic microfibrils and films with the aid of only water and another specific polar solvent but without any other chemicals, demonstrating soy protein based functional materials for potential biomedical and industrial applications.

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Improvement of BC production by a new reclassified acid-resistant strain using food supply chain waste in a two-stage fermentation

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This work summarizes the use of food supply chain waste (FSCW) namely, rotten banana and rotten mango, as a new and low-cost feedstock to produce bacterial cellulose (BC) films by a new reclassified acid-resistant strain, Komagataeibacter medellinensis. In this case, the two-stage fermentation strategy allowed increase biomass in agitated mode (first stage) in order to increase BC production in static mode (second stage). The production and the properties of BC films were different depending on substrate source used, especially mechanical properties and thermal properties. In order to understand why that happened, a modification of HS medium was done by adding MgSO4, KHPO4, CaCl2, due to importance of divalent cations (Ca2+, Mg2+) and potassium in BC metabolism. The results of this test proved that the presence of these cations in culture medium could improve BC production and its properties.

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Conversion of tomato paste by-product into a value-added fucose-rich polysaccharide

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Out-of-specification tomato paste, a by-product from the tomato processing industry, was used as the sole substrate for cultivation of the bacterium Enterobacter A47 and production of FucoPol, a value-added fucose-rich extracellular polysaccharide. Among the different tested fed-batch strategies, pH-stat, DO-stat and continuous substrate feeding, the highest production (8.77 g L-1) and overall volumetric productivity (2.92 g L-1 d-1) were obtained with continuous substrate feeding at a constant flow rate of 11 g h-1. The polymer produced had the typical FucoPol composition (37 mol% fucose, 27 mol% galactose, 23 mol% glucose and 12 mol% glucuronic acid, with an acyl groups content of 13 wt.%). The average molecular weight was 4.4×106 Da and the polydispersity index was 1.2. This study demonstrated that out-of-specification tomato paste is a suitable low-cost substrate for the production of FucoPol, thus providing a route for the valorization of this by-product into a high-value microbial product.
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Separation and characterization of polysaccharides by multi-detection size-exclusion chromatography and field-flow fractionation techniques

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Polysaccharides are renewable biomacromolecules that have potential (either in native form or after structural modification) in various industrial applications. Accurate characterization of the macromolecular properties of polysaccharides is an ongoing challenge, oftentimes due to structural complexity but also to the broad molar mass range and to the ultra-high molar mass of many polysaccharides. In this tutorial, different size-based separation techniques (namely, size-exclusion chromatography and flow field-flow fractionation) for polysaccharide characterization will be compared with each other and their benefits and challenges will be discussed. These techniques are powerful, especially when coupled online to multiple detectors, such as light scattering, differential refractometry (DRI), and viscometry detectors. The principles of these detection methods together with critical discussion on their applicability to polysaccharide analysis will be highlighted. Additionally, a technique in which hollow-fiber flow field-flow fractionation (HF5) is coupled on-line to both multi-angle static light scattering (MALS) and DRI detectors and employed to characterize various structurally different polysaccharides will be introduced. The detectors employed allowed the determination of molar mass across the peaks of the fractograms. Hydrodynamic sizes (hydrodynamic radius, \( R_h \)) of the polysaccharide samples were determined directly from the retention times of the HF5 experiments as well as by off-line using quasi-elastic light scattering (QELS) and the results from different approaches were compared. In general, good agreement was obtained between the off-line QELS determined \( R_h \) and the values of this same radius as calculated from HF5 theory. Comparison of the size data obtained from both methods provided information about the separation process itself. In cases where retention times deviated from those predicted by theory, the reasons for these differences were discussed.

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Determination of thickness, aspect ratio and size distribution of cellulose nanocrystals using asymmetric flow FFF and MALS

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Cellulose is the most abundant natural polymer which has been used mostly in the form of fibers in a wide range of products and materials. Acid hydrolysis of cellulose fibers yield rod-like crystalline by-products known as Cellulose nanocrystals (CNC). CNC has numerous applications in nanotechnology and nanomedicine, including nanocomposites, enzyme immobilization, antimicrobial and medical materials, green catalysis, bio-sensing, and drug delivery. CNC dimensions, such as length and width, may vary depending on the origin of cellulose fibers and the acid hydrolysis conditions. CNC exhibits a relatively broad distribution in length and width. The average length can vary from tens of nanometers to several micrometers, while width ranges from 3 nm to 50 nm. The morphology of the CNCs has been traditionally studied by bulk characterization techniques such as electron microscopy, atomic force microscopy, light scattering techniques including small angle neutron scattering (SANS) and dynamic light scattering (DLS). However, important size-dependent information can be overlooked in such measurements. Using a separation technique allows for more detailed investigation of distributed properties such as morphology and aspect ratio.
Field-flow fractionation (FFF) is an elution-based separation technique which is capable of rapid and high resolution separation of macromolecules, colloids and particles. The separation in FFF takes place inside an open channel where an external physical field is applied. Different types of separation fields can be implemented in FFF which result in realization of different FFF sub-techniques. The most prominent ones are Centrifugal (or sedimentation) FFF, Flow FFF, Thermal gradient FFF (Thermal FFF), Electrical FFF and Magnetic FFF. Each sub-technique separates sample species based on their specific properties, such as mass or density, hydrodynamic size, composition, charge and magnetization. In this presentation FFF separation principles and theory will be discussed. Advantages and limitations of different FFF sub-techniques in characterization of natural and synthetic polymers will be demonstrated. Data will be presented for the analysis of a CNC sample by Asymmetric Flow FFF interfaced with a multi angle light scattering detector. It will be demonstrated that in a run time of 30 minutes, valuable information on length, width and aspect ratio of the nanocrystals as function of hydrodynamic size can be obtained.

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Benefits of MALS, FFF and Viscometry in the characterization of polysaccharide molar mass, size, conformation and branching ratios

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Complex carbohydrates such as cellulose can be characterized for molar mass, size, conformation, and branching following fractionation by Asymmetric Flow Field Flow Fractionation (AF4) or Size Exclusion Chromatography (SEC) using multi-angle light scattering (MALS) and viscometry to measure these important physical characteristics. A multi-detector approach is beneficial for determining more than just molar mass distribution; characteristics such as intrinsic viscosity distributions and determination of conformation and branching characteristics can also be made. Examples of this type of multi-detector analysis will be presented to demonstrate the range and sensitivity that modern instrumentation is now capable of achieving with polysaccharides in solution when fractionated by SEC or FFF methods, including the use of hollow fiber technology with AF4. Recent improvements in on-line viscometry will also be discussed that enhance the sensitivity of detection and software improvements in data analysis to reduce issues from peak broadening and pump pulsations.

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Quantitating cellulose crystallinity: Approaches, problems, and perspectives

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This tutorial will emphasize studies of cellulose crystallinity in higher plants and products derived from them, areas where crystallinity studies are complicated by the small size of the crystalline domain, commonly only a few nanometers transverse to the fiber axis. While the goal of any crystallinity measurement/calculation is to determine the mass fraction of ‘crystalline’ cellulose, both the reason for making the measurement and the physical/biological basis of the chosen technique may vary. We will begin with an overview of different methods for measuring cellulose crystallinity including diffraction, NMR, and other methods. What are the physical bases of each approach, are they in fact measuring the same thing? Or, is this an example of the classic blind men and the elephant problem, where the answer is dependent upon the limited subset of data available to each observer? Next, is the issue of what one hopes to gain from the study? Is the goal to provide a marker for accessibility to enzyme action, or to provide batch to batch comparisons in a processing environment? Choices like these influence the relative importance of accuracy vs. precision in selection of methods of measurement and analysis. Finally, one needs to consider the kinds of samples that they are going to study. Native plant tissue is likely to have numerous impurities such as lignin, hemicelluloses, silicates and other inorganics, possibly
cutins and xyloglucans. The relative abundance of these will change in any purification process, and that may significantly alter the scattering profile of non-cellulosic material and therefore crystallinity measurements based upon diffraction. The small size of samples required for most techniques raises questions of how representative a sample is of the material from which it was obtained. If addressing all of this sounds like a very tall order, well it is, but we shall try.

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Simplified studies of cellulose crystallinity with a Rietveld program

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Researchers routinely want to know the crystallinity of cellulose samples. Powder X-ray diffraction (PXRD) is a way to study crystallinity because diffraction is intrinsically based on periodically repeated atoms, i.e., crystals. Other techniques typically measure signals from certain groups of atoms that are associated with crystals than from the crystals themselves. Park et al. describe three PXRD analyses. However, given the overlap of diffraction peak tails, the amorphous subtraction and popular Segal peak height methods have a fatal flaw: substantial intensity from crystalline material occurs in the areas ascribed to amorphous scattering. This was shown by our calculated PXRD patterns with different peak widths that are inversely related to crystallite size. Park et al.’s third method, peak deconvolution, considers peak overlap but most deconvolutions do not consider all the smaller peaks, and peak size and shape are not tied to known diffraction physics. The information content in cellulose PXRD patterns limits how much can be learned. One way to maximize the information is to use the known crystal structures for the different polymorphs of cellulose to calculate the diffraction patterns and fit those calculated patterns to the observed experimental data. The Rietveld method embodies that strategy. Essentially, it is curve fitting software that modifies peaks that arise from the input crystal structure in ways restricted to known diffraction physics. The lecture will demonstrate Lutterotti’s general purpose Rietveld program Maud for cellulose. Such programs have many options. However, analyses can be done quickly once the most likely variables are known. Follow-up with a spreadsheet is also useful.

Comparison of experimental observed pattern with calculated pattern for cotton fibers based on Rietveld refinement of background, cellulose Iβ, and an amorphous contribution that refined to give a cellulose II structure.
Vibrational spectroscopy study of crystalline cellulose – peak assignment, crystallinity, and non-linear optical responses

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Although cellulose crystallinity index (CI) has been used widely, its limitation may not be discussed adequately. In this talk, the CI values of a set of reference samples were determined from X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and infrared (IR), Raman and vibrational sum frequency generation (SFG) spectroscopies. The methods investigated show the same qualitative trends among samples, but the CI values differ depending on the determination method. The intensities of certain crystalline peaks in IR, Raman, and SFG spectra positively correlated to the amount of crystalline cellulose in the sample, but the correlation with XRD was non-linear due to fundamental differences in detection sensitivity to crystalline cellulose and improper baseline corrections for amorphous contributions. This talk will also address the assignment of vibrational peaks detected in IR, Raman, and SFG spectra of cellulose and how SFG peak intensities can be interpreted in terms of cellulose structure and assembly.

Raman spectroscopy in the analysis of cellulose: Addressing the issues of crystallinity, polymorphy, and ultra-structure

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Although in the studies of cellulose materials visible-Raman spectroscopy has been applied since early seventies, it was not until much later that the other Raman capabilities became available. For instance, Raman microprobe and FT-Raman methods became available in early eighties and mid-nineties, respectively. With the former, cellulose could be analyzed at micron and sub-micron levels and for the first time, Raman imaging of samples became feasible. With the development of FT-Raman, near-IR laser excitation of samples permitted acquisition of fluorescence-free spectra for most cellulose materials. Since then, many advances have taken place by the applications of Raman to cellulose R & D field. This presentation will focus on three such areas of activity, namely, crystallinity, polymorph, and ultra-structure of cellulose. Based on the work completed in our Group, it will be shown that in general, compared to other methods Raman generates superior results. In support, findings from the use of 380-Raman to measure crystallinity, quantitation of cellulose II and cellulose III polymorphs in presence of cellulose I, and the effort made to understand the ultra-structures of cellulose in various materials will be an important part of this address.
**Bio-based Gels & Porous Materials**
T. Budtova, Organizer; F. Liebner, Organizer; B. Cathala, Presiding Papers 492-499

**CELL 492**

**Nanocellulose aerogel beads: Structurable and printable energy storage**

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Cellulose from wood as a raw material has quickly been adapted and used in more and more advanced products such as 3D-batteries and supercapacitors. One family of cellulosic materials that have been used and has gained considerable interest is the nanocellulose family, predominantly named cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). CNFs are high aspect ratio nanoparticles, 4-5 nm in width and up to microns in length, with several desirable properties such as high mechanical strength and a high specific surface area which can be easily functionalized. CNFs can also be used to prepare wet stable aerogels using different chemistries for crosslinking and techniques for shaping the aerogels. Using a consecutive shaping-oxidation-freezing method it is possible to produce chemically crosslinked, wet stable and robust CNF aerogel beads with considerably reduced size (1 mm in diameter). These aerogels can later easily be functionalized by the Layer-by-Layer method where oppositely charged polyelectrolytes and/or charged nanoparticles are adsorbed alternately creating a multi-layered, functional structure on the entire surface of the aerogel. In this way aerogels with properties ranging from electrical conductivity, redox activity and antibacterial properties been produced. In the present work size-reduced CNF aerogel beads have been used as the template for incorporating electrical conductivity and redox active species using the LbL-method with carbon nanotubes (CNTs) and polyaniline nanofibers (PANi). The adsorption of the PANi and CNTs on the aerogel beads is straightforward and produces beads displaying high electrical conductivity and redox activity. Characterization of the obtained aerogel beads reveal that a single bead can act as an electrode in a pseudocapacitor displaying a good capacity and good cycling stability. As the beads have a significantly reduced size it is possible to structure them creating a unique design of the electrode after functionalization which is not possible with a pre-shaped aerogel. Furthermore, as the beads have a significantly reduced size they open up for the possibility of using them with different printing techniques where they are mixed with an appropriate ink making it possible to print energy storage devices.

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**3D interdigitated energy storage devices built inside aerogels using layer by layer assembly**

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Energy storage devices are being developed to power an increasingly diverse range of devices. Up to now, commercial energy storage systems, for example, lithium-ion batteries, are mostly limited to two-dimensional devices with highly compact multilayer structures which rule out their potential applications in which flexible, stretchable, or compressible batteries are needed, such as wearable or bendable electronic devices. Aerogels are suitable three-dimensional (3D) substrates for energy storage due to their very high specific surface which can allow for a much larger contact area between the active battery materials, and the electrolyte. In addition, the fine pore size of aerogels allows for effective mass and ion transport kinetics. Exploiting the third dimension of materials for energy storage can also provide unique properties such as mechanical compressibility. In this work, we employ Layer by Layer (LbL) self-
assembly to build 3D interdigitated energy storage devices, including supercapacitors and lithium-ion batteries inside cellulose nanofibril (CNF) aerogels. We have used wet-stabilized CNF aerogels that are prepared by freeze-drying followed by chemical cross-linking. We have then used a number of different polymers and electroactive nanoparticles, which all carry ionic charges and are dispersible/dissolvable in water, and assembled these materials onto the CNF aerogel surface using LbL assembly. We have successfully built 3D interdigitated supercapacitors with single-wall carbon nanotubes as symmetric electrodes. Cyclic voltammograms demonstrate that the supercapacitors have good cycling stability at different scan rates. Primary data suggest that LbL assembly is also feasible for building 3D interdigitated lithium-ion batteries.

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Processing and properties of elastomer covalently bound to nanocellulose aerogel

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The use of nanocelluloses as a reinforcing filler is the object of research efforts since several decades, and intensified those last years. In the particular case of elastomers, it requires both a good level of dispersion and a high density of covalent bonds, together with a simple melt process of mixing, like carbon black or silica. We designed first a drying process that allows the conservation of the individual fibrilar shape for both cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC) that lead to nanocelluloses aerogels with high specific surface area. We developed also a gas-phase modification procedure that allows to graft different acyl chloride with substitution degree from 0 to almost 3, depending on the operating parameters. Incidentally, we discovered also that difunctional reagents (diacyl chlorides, but also anhydrides...) are blocked at the surface of the nanocelluloses, allowing a gentle and controlled modification of the fillers. By choosing reactive grafting moieties, we obtained nanofillers with high surface area covalently bound to the matrix and easily dispersible. We prepared materials dispersing those fillers in a styrene butadiene elastomer by melt processing, and we characterized both the filler state of dispersion by transmission electron microscopy and the mechanical properties by tensile tests. When the filler interface create covalent bonds with the matrix, the resulting material presents a dispersion of nanometric rod particles and a strong mechanical reinforcement while preserving a large extensibility (Figure 1). This material is thus similar to silica or carbon black filled elastomer, and is an interesting achievement in the field of nanocellulose composite considering both the process employed and the properties obtained.

Figure 1: Left. TEM pictures of the nanocellulose filled materials at different filler volume fraction. Center. Tensile curves. Right. Linear modulus reinforcement
Functional polysaccharide hydrogels through chemical derivatization of agarose

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Agarose is the major component of agar, a polysaccharide (PS) from red algae that has been used for centuries as a traditional food gelling agent. Recently, agarose hydrogels received high interest for advanced applications such as cell encapsulation and tissue engineering because they are non-cytotoxic, show high mechanical strength, and are highly porous with a high water content ≈ 99%. However, agarose is bio-inactive and does not stimulate important cell processes such as adhesion, migration, proliferation, and stem-cell differentiation. Aim of the present work is to overcome this limitation by synthesis of well-defined agarose derivatives that are subsequently transformed into novel PS hydrogels. Two different homogeneous synthesis strategies were pursued in this context using dipolar aprotic solvents (with and without LiCl) and ionic liquids as reaction media: (i) Non-natural agarose sulfates (AS) were prepared under different reaction conditions. The derivatives showed a regioselective modification at the primary G-6 position and were either completely soluble in water or showed thermoreversible gelation depending on the degree of substitution (DSsulfate). Natural PS sulfates and materials derived therefrom are renowned for their bioactivity. Thus, it is evaluated how introducing sulfate moieties can influence the interaction of agarose hydrogels with cells. (ii) Tosylated agarose derivatives (TOSA) with $\text{DS}_{\text{tosyl}} \leq 1.8$ were prepared as activated intermediates. The derivatives showed a unique transition from regioselective G-6 to non-preferential G-6/LA-2 substitution depending on whether the reaction was performed in the absence or presence of LiCl. By quantitative nucleophilic displacement reaction, azido-deoxy-agarose derivatives were obtained that showed thermoreversible gelation at $\text{DS}_{\text{azide}} < 0.5$. The functional hydrogels obtained are highly versatile and it is studied how they can be further functionalized directly in the gel state (e.g., with dyes, drugs, affinity ligands) by exploiting "azide-alkyne click chemistry". The current approach is well suited to prepare novel highly porous PS materials. It is demonstrated how specific functionalities can be introduced into agarose based hydrogels and how the chemical derivatization affects the gel formation and properties. Based on the presented results, highly functional hydrogels for specific bio-applications can be tailored. Moreover, further conversion into organo-, xero-, and aerogels is feasible.

Guar gum as unique building block to generate elastic and conductive ionogels with ionic liquid-containing derivatives

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With the aim to generate non-conventional biobased solid electrolytes, we exploit the synergistic interactions between galactomannan chains and hydrophilic imidazolium ionic liquids (IL). More particularly, we selected guar gum as galactomannan related to - its abundance, -its renewable character, -its non-toxicity, - its peculiar structure, - its high thermal stability and the commercial availability of very high molecular weights. We recently demonstrated that the guar/IL association leads to solid-like gels with relevant rheological, thermomechanical and conductive properties. Based on these advanced research, we are now focusing on the development of ternary blends presenting a higher degree of sophistication by incorporating additional reinforcing building-blocks, such as imidazolium-based poly(ionic liquid) (PIL), in view of generating biohybrid materials with enhanced properties. We synthesized a series of PIL by RAFT polymerization and we particularly showed the excellent control of the polymerization. PIL are promising synthetic polymers which combine the unique attributes of ionic
liquids (thermal and chemical stability, non-inflammability, non-volatility and conductivity) with the ones of polymers in terms of mechanical reinforcement, and dimensional stability. Structure/properties relationships of the resulting multicomponent biobased systems were in-depth investigated. The rheological, thermal and conductive properties were methodically studied and correlated with the morphology of the biohybrids by means of synchrotron scattering measurements. The concept presented herein, based on biosourced polymer-containing multi-component systems represents a promising route for the design of advanced conductive materials.

Ionogels resulting from the addition of guar gum into a solution of poly(ionic liquid) in ionic liquid: viscoelastic and ionic transport properties

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**Biologically modified lignin for water purification**

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The biomodification of Kraft lignin was done by immobilized basidiomycetes fungi (*Coriolus versicolor*). Potential properties for water purification of this biomodified lignin were evaluated. Due to the biomodification, small molecules were removed, therefore the resulting product is seen to not leak lignin compounds in a water based environment. This biopolymer is also very stable when exposed to organic solvents, including dimethylsulfoxide and tetrahydrofuran. The buffering capacity of the biomodified Kraft lignin was found to be 9.5 % increased compare to unmodified Kraft lignin. Membranes which were
assembled from the biologically modified lignin show similar properties to graphene filters in salt retention. Chelating activity of the biologically modified lignin was also evaluated.

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Preparation of carbon aerogels from TEMPO-oxidized cellulose nanofibers for organic solvents absorption

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In this study, ultralight and hydrophobic carbon aerogels were prepared from 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-oxidized cellulose nanofibers (TOCNs) for the removal of organic solvents. The morphology structure, density and chemical composition of TOCN aerogels freezed at -56 °C or -196 °C followed by pyrolysis were examined. The obtained carbon-based aerogels possessed ultralight density of 8.8 mg cm⁻³ and excellent fire-resistant property. The high porosity (up to 99.5%) and hydrophobic property (contact angle of 139.6°) of the obtained carbon aerogels allowed them to adsorb various organic solvents with high absorption capacity (up to 110-260 g/g). After five absorption-combustion and absorption-distillation cycles, the absorption capacity of TOCN carbon aerogels exhibited excellent recyclability with up to 64-99% of its initial absorption capability, demonstrating potential applications in oil-spill cleanup field.

Fig. a and b TOCN aerogels on the left (T1, T2) and carbon aerogels on the right (C1, C2). c The TOCN carbon aerogels stand on the top of the grass stably. d The TOCN carbon aerogels immersed in water. e and f SEM images of carbon aerogels C1 and C2.
Value-Added biomaterials from lignocellulose based on biorefinery scenario

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Lignocellulose is mainly composed of lignin, hemicelluloses, and cellulose, which account for more than 90% of the total content of plant cell wall. However, from a biorefinery scenario, lignocellulose should be effectively separated into single component, such as lignin, hemicelluloses, and cellulose and then transformed the single component into value-added products. In my team, based on the well-isolated, well-defined composition and molecular structure of the single component (lignin, cellulose, and hemicelluloses), a series of biomaterials were prepared such as flexible nanocomposites prepared based on a cellulose-derived framework coated with polyaniline, highly recyclable superabsorbent for oil spillage cleaning prepared from renewable cellulose fibers, highly thermostable, flexible and conductive films prepared from cellulose, graphite and polypyrrole nanoparticles, conductive cellulose/graphene composite prepared by green fabrication, conductive cellulose paper based on gold nanoparticle–reduced graphene oxide and quaternized chitosan, Ag NP in xylan by green synthesis, a lignosulfonate-modified graphene hydrogel (LS-GH) with ultrahigh adsorption capacity for lead ion (Pb²⁺) removal, fabrication of high performance thin-film humidity sensor based on lignosulfonate and reduced graphene oxide, etc., which will be reported.

Melt extrusion of lignin carbon-fiber precursors: The path forward for low-cost fibers or unrealizable dream?

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Lignin’s carbon dense aromatic structure, potential abundance, and unique ability to behave as a thermoplastic/thermoset polymer has intrigued scientist and engineers for decades as a potential low cost and environmentally friendly replacement for polyacrylonitrile (PAN) based carbon fibers. However, the heterogeneous amorphous structure and difficulty isolating it in high purity from woody feedstocks makes processing into high quality fibers difficult. In this presentation, we will discuss our experience melt processing multiple lignin feedstocks from organosolv, kraft, and other fractionation technologies. Additionally, we will present our model discussing the assembly of lignin molecules into polymer fibers derived NMR, thermal analysis, and neutron scattering data. We will contrast the structure and properties of lignin based carbon fibers derived from melt extrusion with commercial PAN fibers and fibers produced by other means. Further, we will provide insight for using lignin based carbon fibers in additive manufacturing, thermal management, and other potential nonstructural applications.
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Melt extrusion of acrylonitrile based quad-polymer precursor for green carbon fiber technology

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Polyacrylonitrile (PAN) based polymers are wet spun for making carbon fiber precursors. This technique is associated with expensive solvent recovery and solvent recycling for hazardous solvents which have both economic and environmental impact. Use of low cost melt processable precursor can provide solution of this problem by replacing wet spinning with melt spinning. Here, in this study, a successful synthesis and melt extrusion method of a PAN based melt processable quad-polymer for carbon fiber precursor is presented. Unlike PAN, the new precursor polymer showed excellent melt extrusion ability to make thin fibers (~25 μm) that can be used to stabilize and carbonize to make carbon fiber with excellent properties. This new precursor polymer also has the advantage of low cost compare to the current technology.

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Rheology and modeling of complex food systems in reactive extrusion

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In reactive extrusion, thermomechanical stresses are explicitly applied to biopolymeric food materials to achieve the desired functionality and structure in the final food product. However, control of the extrusion process is very challenging due to strong interactions between mass, energy and momentum transfer, coupled with complex physicochemical transformations of the material, which govern its thermomechanical properties. With other words, material structure is not only the result but also a part of the process, as it affects the development of material properties and therefore processing conditions along the extruder. For understanding structural changes in extrusion, the processing conditions must be characterized on a local level by in-depth analysis of the thermal and mechanical stress profile together with the mixing characteristics in extrusion processing. Furthermore, material properties and their relation to the local processing conditions play crucial role on structural changes in extrusion processing. Therefore, the material properties (i.e. mainly reaction and rheological properties) under extrusion conditions must be characterized. Such information is essential to provide a mechanistic understanding necessary to move away from purely empirical approaches in designing complex biopolymeric systems. In this talk, we present a research approach and tools that practically enable us to gain an improved process understanding at a mechanistic level. The approach is based on the fractionation of the process into interrelated sections. These sections can then be investigated in defined manner using various experimental and numerical tools, including rheometry (inline slit-die rheometer, offline closed cavity rheometer), computational fluid dynamics simulation, and inline infrared sensors.
Polymerization of sugars by reactive twin-screw extrusion to produce soluble fibers for food and feed

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Lactose containing dairy co-products of cheese manufacturing are generally low value. The development of value-added products, such as prebiotic dietary fiber, is desirable. We have successfully polymerized mixtures of lactose and glucose into polylactose via extrusion using citric acid as a catalyst. The effects of extruder feed rate, citric acid concentrations, and the concentration of glucose have been evaluated for their effects on fiber yield, and extruder parameters (SME, motor torque, temperature). Product was extruded on a Buhler twin-screw 44mm twin-screw extruder. Process (temperature, motor torque and specific mechanical energy (SME)) and product (color, dietary fiber, degree of polymerization (DP), residual lactose and hydroxymethylfurfural (HMF)) responses were measured in response to the formula and process change. Generally, higher feed rates resulted in lower SME and higher motor torque. Higher feed rates resulted in less brown color, and more residual lactose and glucose. The citric acid catalyst concentration effects were more pronounced at a lower feed rate and higher concentrations lead to more brown color. Residual lactose decreased with higher citric acid concentrations. Surprisingly, brown color did not correlate with higher HMF concentrations but did correlate with higher temperatures in the early portion of the extruder and with SME. HMF can be removed via carbon filtration. The cleaned-up fiber material is currently being evaluated to see if it has prebiotic activity in rats, and this could pave the way for the generation of soluble fiber from lower-cost lactose-containing dairy co-products via a continuous process.

Advanced thermal analysis modelling for the characterization of active poly(lactic acid)/natural fibre food-packaging composite materials

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The future brings with it the ever increasing need to supply fresh and safe foods to the world’s population. There is also an increasing consumer demand for naturally-derived food-packaging products that produce minimal environmental impacts during their production and ultimate disposal to landfill. These realities have led to the search for novel active packaging systems based on natural resources that incorporate new materials that are not derived from the traditional petroleum-based sources but instead are derived from renewable sources such as biopolymers. Composites comprised of the renewable biopolymer poly(lactic acid) (PLA) filled with kenaf, a natural fibre, have been assessed in our laboratory in the context of their potential use as antimicrobial (AM) food-packaging materials. It has been found that the incorporation of the kenaf fibres enhances the physicomechanical properties of the PLA and its presence as a filler will also reduce the overall cost of the material. This paper discusses the latest work performed in our laboratory on the formulation and characterization of potential AM packaging systems comprised of PLA/kenaf and the natural AM agent thymol. The optimization of the performance of these materials with particular respect to controlling the release of the AM agent from the composite matrix will also be discussed. Differential scanning calorimetric measurements along with a novel approach to thermogravimetric analysis were used to characterize the interaction between the composite matrix and the AM agent and hence better understand the factors that influence the release of the AM agent from the matrix. The application of the long-established technique of non-isothermal thermogravimetric kinetic analysis is re-visited in the form of a novel computer-based iterative numerical method that was developed to process the experimental kinetic data by executing an integral approach. This advanced method enables the activation energies and Arrhenius factor parameters for these systems to be obtained without having to invoke the usual simplifying assumptions in solving the kinetic expressions. This is achieved via an algorithm that calculates from the experimental data a set of parameters that can be compared to corresponding characteristic parameters that pertain to a wide range of known kinetic models that were calculated theoretically in an independent study.

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Utilization of coffee wastes in biobased composite materials for food packaging uses

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The production and consumption of coffee, the most popular caffeinated drink in the world, generates a large amount of co-products and wastes. When coffee beans are roasted, the innermost skin floats free and is usually referred to as coffee chaff (CC). CC and the residue of the brewing process, spent coffee grounds (SCGs), are major contributors of organic wastes disposed in landfills. In this research, we explore the opportunities of utilizing CC and SCGs as low-cost renewable fillers in composite materials for food packaging uses. The first part of the work was a comprehensive characterization of the properties of the CC and SCGs. The compositional and elemental analyses of the two materials were carried out. The thermal stability was investigated to evaluate the materials’ suitability to be processed at high temperatures. The surface chemistry and morphologies were studied to assess their potential interaction with bioplastics. CC was found to have higher thermal stability and denser fibrous structure than the SCGs. In the second part, CC was combined with bioplastics to produce compostable biocomposites to be used in a commercial food packaging product. Maleic anhydride based compatibilizers were developed to enhance the interaction between the CC and the polymer matrix through reactive extrusion. After property and process optimization, the material has been successfully adopted in a coffee package and released in the market. The utilization of the byproducts of food production in food packaging can have profound impact on reducing the environmental footprint of the industry.
Extrudate bulk density model for crossing different recipes and extruders in aquatic feed extrusion cooking process

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For aquaculture sustainable development, people are searching all possible plant-based protein sources to replace fish meal in aquatic feed production. Thus, we have to setup an efficient method to determine suitable extrusion cooking conditions for different recipes. Modelling method is an efficient way to guide us to find out operation conditions for the often changed recipes processing. In this work, we have investigated a pellet bulk density model, developed from Buckingham-theorem, for its capability of crossing different feed recipes with four recipe extrusion trials. The rheological behaviour of the model is represented through Arrhenius type equation and combined into the bulk density model through energy input and output calculation in an extrusion system. The activation energy is used to evaluate a recipe characteristic. The modelling results show that the bulk density model can satisfactorily fit the feed pellet bulk density data with overall average absolute density 3%. Based on shear stress definition, a shear impact factor is derived from the bulk density model to explore a general indicator to describe the pellet bulk density behaviours crossing different recipes and extruders. The analysis results show that the shear impact factor can be employed to represent the feed pellet bulk density characteristics in some degree. As the extrudate bulk density is often the first value checked in extrusion operation and is also an indicator for pellet floating or sink property estimation, the modelling work will help us quantitatively understanding extrusion processing and setup a foundation to make a more efficient extrusion operation.

Preparation of water soluble oligosaccharides from sugar reversion reactions in acidic lithium bromide trihydrate

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Bioactive oligosaccharides are finding attractive applications as functional food, prebiotic compounds, immunostimulating agents, and pharmaceuticals. Oligosaccharides synthesis prevalently relies on biological methods such as enzymatic transglycosylation and partial hydrolysis. In this study, we demonstrated a novel chemical method to produce water-soluble oligosaccharides in acidic lithium bromide trihydrate via sugar reversion reactions, in which new glycosidic bonds were formed between the C1 oxocarbenium on a protonated sugar and the hydroxyl groups (C2, C3 or C6) of another sugar. Glucose was treated at varied loading concentration in LiBr 2-12H2O media with 10-160 mM HCl at 70-110°C, and the oligosaccharide products were analyzed using HPIC, MALDI-TOF/MS and NMR. The results indicated that up to 60% of the glucose was converted to gluco-oligosaccharides. Decreasing the hydrate numbers of the LiBr media significantly favored the reversion reaction. The yield of oligosaccharides was thermodynamically dependent on the sugar loading concentration and kinetically controlled by acid concentration and reaction temperature. The resultant gluco-oligosaccharides contain predominant α-1,6-glycosidic bonds and a minor amount of β-1,6-, α-1,2- and α-1,3-glycosidic bonds. The oligosaccharides could be recovered from the reaction media using anti-solvent precipitation using acetone, and the acidic lithium bromide trihydrate could be directly reused in next batch of reaction.
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Gradient separations and two-dimensional separations of cellulose derivatives

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The molar mass, the type and number of the substituents, the substituent pattern of the anhydroglucose units (AGU) as well as the substituent distributions among and along the cellulose chains influence application properties of cellulose derivatives. Consequently suitable characterization techniques for these parameters are essential to achieve a thorough understanding of structure-property relations. The molar mass distribution of cellulose derivatives can be conveniently characterized by SEC. The average number of substituents (degree of substitution, DS) can be obtained from NMR -measurements or by chain degradation followed by quantitation of the AGUs. However, only limited information is available on the distribution of the AGUs among the different chains (heterogeneity of 1st order).

By applying methods of interaction chromatography it was possible to separate intact carboxymethyl celluloses (CMC) and cellulose acetates (CA) according to the degree of substitution. This allowed gaining insight into heterogeneity of 2nd order. Furthermore separations in terms of DS and molar mass were achieved by two-dimensional chromatography (2D-LC). This approach allowed for deformulation of blends composed of cellulose derivatives differing in molar mass and DS.

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New insight into the gelation of Na-alginate aqueous solution

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Sodium alginate (SA) hydrogels have a wide range of applications including tissue engineering, drug delivery and formulations for preventing gastric reflux. The dynamics of sodium ions during the gelation process of SA solution is critical for clarification of the gelation mechanism. In this work, nuclear magnetic resonance (NMR) relaxometry and pulsed-field-gradient (PFG) NMR diffusometry were used to
investigate the dynamics of the sodium ions during the gelation of SA alginate. We find that sodium ions are in two different states with the addition of divalent calcium ions, corresponding to the bound-state and free-state. The sodium ions in free-state are those released from the alginate chains via the replacement of calcium ions during the crosslinking. The relative content of sodium ions in bond state decreased with the increase in the content of calcium ions in the system. The relaxation time $T_2$ of sodium ions in bond-and free-states shifts to shorter and longer relaxation time with the increase in concentration of calcium ion, which indicates the closer package of SA chains and the larger space for the diffusion of free sodium ions. This work clarifies the gelation mechanism of SA at molecular level.

**CELL 510**

**Electrospun polysaccharide based materials as modern wound dressings**

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Modern wound dressing materials can aid the wound healing through mechanical and antimicrobial protection, by providing optimal wound healing conditions, and through active pharmacotherapy. The trends in development of such materials are nowadays directed towards the use of renewable, natural polymers, like polysaccharides (cellulose, chitosan, alginate, and their derivatives) combined with green technologies for their preparation and modification. One of the most interesting techniques for the latter is the environmentally friendly electrospinning that is simple to use, has only minor technical/chemical limitations (e.g. related to formulation properties), uses no additional hazardous organic solvents, and allows for formation of nanofibrous matrices mimicking features and morphologies of the extracellular matrix. Such materials are therefore believed to stimulate cell proliferation and encourage wound healing. Electrospun matrices have also been shown to provide a high-surface area and micro-porosity, making them ideal for loading of drugs or other biomolecules. The focus of this presentation will be on the preparation of electrospun polysaccharide based materials with incorporated active substances; (i) incorporation of different natural extracts (chamomile, rosemary, marigold, yarrow, St John's Wort and purple coneflower) for the preparation of natural antimicrobial and antioxidative materials, (ii) preparation of multi-layered materials combined with local anaesthetic and non-steroid anti-inflammatory drugs for relief of wound pain, (iii) incorporation of probiotic bacterial strains from a healthy skin microbiome for prophylactic treatment of the diabetic foot.

**CELL 511**

**Hemicelluloses cationization: Comparison of liquid and solid phase preparation processes**

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Cationic hemicelluloses are interesting polysaccharides derivatives for different industrial applications. Cationisation of hemicelluloses is usually performed in aqueous alcohol or in water in the presence of NaOH and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) or 2,3- epoxypropyltrimethylammonium chloride (ETA) as etherifying agent yielding DS up to 1.6, depending on the conditions and hemicellulose type. In a previous studies, we have reported the optimization of hemicelluloses cationisation in aqueous media using ETA as cationic reagent. DS values from 0.1 to 1.3 have been obtained by varying reaction parameters. However, ETA is an expensive and potentially
carcinogenic chemical. In order to increase the reaction efficiency and decrease the consumption of ETA, it is possible to perform the reaction in a solid state, by using a minimum amount of solvent. This type of process is currently used for the cationisation of starch. In this work, the cationisation of two hemicelluloses (a galactomannan and a xylan) was studied both in liquid and in solid phase. By this method, the reaction efficiency was significantly increased for all hemicellulose types, up to 90% in the case of xylan. The consumption of reagents was reduced by ten compared to the reaction in liquid phase, while comparable DS values are obtained. DS values of 0.10 to 0.30 were obtained for the xylan type, and up to 0.44 for the galactomannan. These values are in agreement with the ones typically used in most of applications targeted for theses cationic polysaccharides. By reducing the number of purification steps, the consumption of solvents is limited, and high mass yields are preserved. These obtained cationic derivatives were then tested as additives to pulp in order to increase the resistance of paper. The cationisation of hemicelluloses had a beneficial effect on the mechanical properties of paper, compared to the native polysaccharides. Cationic derivatives of DS 0.3 gave the best results for both polysaccharides, the galactomannan ones being more efficient than the xylan ones with 90% of increase for the burst index. Therefore, the solid process constitutes an excellent improvement in terms of economy, environmental and safety for the cationisation reaction of hemicelluloses, compared to the liquid process.

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Use of polysaccharides from cashew gum in encapsulation applications

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Cashew gum is the bark exudate from the cashew tree (Anacardium occidentale L.), Anacardium occidentale, which grows wild in Brazil and many tropical and subtropical countries. Polysaccharides are isolated from cashew gum after removing impurities such as proteins, fibers, and tannins. Polysaccharides from cashew gum can undergo electrostatic interactions with other polysaccharides, proteins, or even guest substances that improve the encapsulation and retention efficiency of active ingredients. In this work, we will discuss the encapsulation of oils and dyes using modified and unmodified cashew gum matrix through complex coacervation and spray drying methods. Modification of cashew gum by crosslinking has resulted in superior encapsulation and retention efficiency. Thus, the crosslinked cashew gum is promising as a potential encapsulating agent and a carrier material for selected active ingredients.

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Electrosynthesis and characterization of polypyrrole/cashew gum composite

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One of the current trends in the design of electronic materials is the use of agro-based, renewable materials with a minimum amount of toxic substances present. Consistent with this trend, we investigated the electrosynthesis and the electrochemical, morphological, and topographical characteristics of two novel conducting composites: polypyrrole/cashew gum and polyaniline/cashew gum. Cashew gum is an exudate of Anacardium occidentale L., a plant native to Brazil and tropical regions in America, Africa, and Asia. It is a branched acidic heteropolysaccharide, comprising arabinose, galactose, rhamnose, glucose and glucuronic acid. The composite films were grown on gold surface by cyclic voltammetry and
chronoamperometry in an aqueous medium. They were characterized using FTIR-ATR, SEM, AFM and cyclic voltammetry. The conductive bio-based films have shown conductivity, charge storage capacity, morphologies and chemical stability when comparable to conventional polymers.

CELL 514

**Novel polyurethanes from Xylan and TDI: Preparation and characterization**

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Xylan is a hemicellulose which is found abundantly in nature. In this work a novel polyurethane was developed involving xylan and tolylene-2,4-diisocyanate (TDI). Polymer synthesis was achieved via conventional heat or microwave-assisted reaction in dimethylsulfoxide. Because xylan has multiple OH groups on each polymer chain, the TDI/xylan molar ratio had to be adjusted in order to produce a soluble polymeric product. The reaction products were characterized by \(^{13}\)C NMR, FT-IR, thermogravimetric analysis and differential scanning calorimetry. The xylan polyurethane was shown to exhibit improved thermal stability over xylan.

**Developments in the Fields of Celluloses & Lignocelluloses: In honor of Dr. Rajai Atalla**

U. P. Agarwal, Organizer; T. Larsson, Organizer; A. Isogai, Organizer; T. J. Elder, Organizer; A. Isogai, Presiding Papers 515-522

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**In situ Raman Microscopy to monitor changes in cellulose crystallinity during acid pre-treatment**

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Building on the work of Dr. Rajai Atalla and his co-workers, we have successfully used Raman microscopy to monitor changes in cellulose crystallinity that occur during acid pre-treatment. Abundant literature suggests that cellulose crystallinity correlates with observations of recalcitrance toward enzymatic hydrolysis. Using Raman microscopy, we found that acidic pre-treatment increased the apparent crystallinity of ball-milled microcrystalline cellulose as a clear trend in the crystallinity index over time was observed. Crystallinity index increases for approximately 60 min, at which time it ceases to change. Crystalline cellulose (filter paper) was subjected to temperature programmed hydrolysis, with crystallinity increasing at temperatures as low as 120 °C. We attribute these observations to preferential hydrolysis of amorphous cellulose, resulting in a residual solid enriched in crystalline cellulose. We tested this explanation by performing control experiments in the absence of acid and under dry thermal conditions. In the absence of acid, cellulose crystallinity index is stable over time; instead, distinct bands attributable to the O-H bending modes of water appear and grow over time. We attribute the appearance and growth of the O-H bending modes to swelling of amorphous cellulose by water; in the presence of acid, the O-H bending modes appear in the cellulose spectrum, but are significantly reduced in intensity compared to their appearance in the absence of acid. Under dry thermal conditions, we confirm that the bands used to track crystallinity index did not shift or broaden substantially, supporting their use under pre-treatment conditions. Furthermore, thermal conditions alone did not alter cellulose crystallinity (up to approximately 200 °C), again supporting the interpretation of the Raman spectra obtained under pre-treatment conditions. As supporting evidence, we performed cellulose hydrolysis experiments to track carbohydrate yield and infra-red spectroscopy under thermal conditions to complement Raman spectra.
These results provide new understanding of cellulose chemistry during pre-treatment and once again show the versatility and utility Raman spectroscopy to probe cellulose structures.

**CELL 516**

On the ionization of cellulose in aqueous alkali


Cellulose, one of the most abundant renewable resources, is insoluble in most common solvents but dissolves in aqueous alkali under a narrow range of conditions. To elucidate the solubilization mechanism, we performed electrophoretic NMR on cellobiose, a subunit of cellulose, showing that cellobiose acts as an acid with two dissociation steps at pH 12 and 13.5. Chemical shift differences between cellobiose in NaOH and NaCl were estimated using 2D NMR and compared to DFT shift differences upon deprotonation. The dissociation steps are the deprotonation of the hemiacetal OH group and the deprotonation of one of four OH groups on the non-reducing anhydroglucose unit. MD simulations reveal that aggregation is suppressed upon charging cellulose chains in solution. Our findings strongly suggest that cellulose is to a large extent charged in concentrated aqueous alkali, a seemingly crucial factor for solubilization. This insight, overlooked in the current literature, is important for understanding cellulose dissolution and for synthesis of new sustainable materials.

**CELL 517**

Structural factors affecting ¹³C NMR chemical shifts of C4 and C6 of cellulose: a computational study

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The doublet C4 peaks (centered at ~85 and ~89 ppm) and the doublet C6 peaks (centered at ~62 and ~65 ppm) in solid-state NMR spectra of cellulose have long been attributed to signals of C4 and C6 carbons from surface (solvent-exposed) and interior chains, designated as sC4/sC6 and iC4/iC6, respectively. (Ha et al., 1998, Newman, 1998) The relative ratio of sC4 and iC4 has been used to estimate the degree of crystallinity of cellulose as well as the number of glucan chains in cellulose microfibrils. (Wang & Hong, 2015, Park et al., 2009, Teeäär et al., 1987) However the relationship between the doublet C4 peaks or C6 peaks and cellulose structures are still elusive. Herein, we investigated four factors that could affect $^{13}$C4 and $^{13}$C6 NMR chemical shifts using computational methods. We found that C4 NMR chemical shifts are influenced by different conformation of exocyclic groups at C6 (TG, GT and GG), water molecules on the surface, glycosidic bond angles ($\Psi$, $\Phi$) and the position of the proton (HO3) of -OH group connected to the adjacent carbon C3. However, C6 NMR chemical shifts are only affected by different conformations of exocyclic groups at C6 and water molecules on the surface. Among these factors, the doublet C4 and C6 peaks are mainly due to different conformations of exocyclic groups at C6. The upfield C4 peak (~85 ppm) is dominated by residues with GG conformation, whereas the downfield C4 peak (~89 ppm) is dominated by GT and TG, regardless of whether the hydroxymethyl group is on the surface or within the interior of the model CMF. The upfield C6 peak (~62 ppm) is dominated by residues with GG and GT conformations, whereas the downfield C6 peak (~65 ppm) is dominated by TG. Therefore, it is possible to estimate the percentage content of each conformation (TG, GT and GG) in a cellulose sample using both C4 and C6 peaks of solid-state NMR spectra of cellulose.

**CELL 518**

**Effect of dilution-freezing-drying process on Cellulose Nanocrystals (CNCs) for Polylactic Acid (PLA)-CNC composite packaging**

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The trend toward bio-derived and biodegradable packaging materials has led to both consumers and manufacturers to alternative materials. The use poly(lactic acid) (PLA) has shown promise as a bio-derived and biodegradable packaging material but does not have good barrier properties. The addition of cellulose nanocrystals (CNCs) can improve barrier properties while maintaining film transparency. Therefore PLA-CNC composites are a sustainable alternative to reduce the environmental impact of packaging. One of the major challenges is the difficulty in dispersing dried CNCs in the polymer matrix. Poor dispersion can lead to film defects, lack of transparency, and decreased mechanical performance while not fully exploiting the improvements CNCs can impart. Our objective is to advance our understanding of the influence of the morphology of dried CNCs to the properties of the resulting PLA-CNC nanocomposites. In this study, CNC aqueous suspension was diluted from 10.7% to 1% with aid of sonication and followed by freeze drying (slow and flash). The particle size and morphology of the CNCs before and after freeze drying were determined by Atomic Force Microscopy and scanning electron microscopy, respectively. Nanomposites were tested for thermal and mechanical properties. Before freeze drying CNCs were in nano-scale, while agglomerations were formed after freeze-drying process. The sizes of particles/aggregates were reduced with increased sonication treatment time. By incorporating CNCs that were flash-frozen in liquid N2 from 1 wt% suspension, the mechanical properties of nanocomposites were increased as compared to neat PLA. CNCs dried from diluted suspension showed higher cold-crystallization temperature and lower cold-crystallization enthalpy than neat PLA and nanocomposites from CNCs dried from 10.7% suspension. This indicated delayed cold crystallization kinetics when compounding small aggregates of CNCs. This could be contributed to better dispersion of CNCs with smaller particle sizes which was dried from 1% suspension. The nanocomposites from CNCs
with smaller sizes also showed higher degree of crystallinity as determined by differential scanning calorimetry analysis. This demonstrated that smaller aggregates of CNCs would facilitate the crystallization of PLA polymer as a role of nucleation agents. By varying the morphology of dried CNCs the properties of nanocomposites can be tunable for packaging applications.

**CELL 519**

**Liquids NMR toolbox for the analysis of modified nanocelluloses**

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Recent developments in the area of ionic liquid electrolytes for cellulose or biomass dissolution has allowed for high-resolution \(^1\)H and \(^{13}\)C NMR on very high molecular weight cellulose. This should lead the way for the development of advanced liquid-state quantitative NMR methods for characterisation of nano-structured celluloses, before and after chemical modification. As such, we present the use of tetrabutylphosphonium acetate ([P\(_{4444}\)][OAc]):DMSO-d\(_6\) electrolytes for 1 and 2D NMR characterisation of nanocelluloses. Special attention is put on poly(methylmethacrylate) (PMMA)-grafted CNCs, as a difficult to analyse model. CPMG T2 and diffusion filtered HSQC was shown to be effective in the discrimination between polymer graft and low molecular weight peaks, arising from the solvent system. Bulk ratios of MMA to AGU, graft lengths and thus graft densities were determined using a combination of quantitative \(^{13}\)C, quantitative HSQC and DOSY NMR analysis of grafts which had been cleaved off using different methods. The results showed that graft density was surprisingly low but molecular weight of grafted PMMA polymer was high. This is not apparent from any other methods of analysis of grafted CNCs.

**CELL 520**

**In situ visualization of structural changes to biomass during chemical reactions using neutron scattering**

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Biomass, a renewable carbon source, is converted to energy such as bioethanol by employing a chemical reaction such as acidic, basic or ionic liquid pretreatment followed by enzymatic hydrolysis. The goal of the chemical reaction is to improve accessibility and decrease hindrance to enzymatic breakdown and thereby increase overall efficiency. Understanding the structural changes to biomass components such as cellulose, hemicellulose and lignin in the nano- to meso-scale during these chemical reactions is critical for increasing biomass conversion efficiencies. Specifically, ex-situ studies showed the formation of lignin globules and the aggregation of cellulose fibers due to dilute acid pretreatment of biomass. However, no insights into the processes that drive these structural changes were obtained. For this purpose, a pressure reaction cell was developed and used to monitor morphological and structural changes as they occur by placing in a neutron beam and collecting time-resolved small-angle neutron scattering data. This study was first applied to study steam explosion pretreatment, SEP. Changes to cellulose morphology occurred mainly in the heating phase of pretreatment, whereas changes in lignin...
morphology occurred mainly in the holding and cooling phases. In particular, water is irreversibly expelled from cellulose macrofibrils as the elemental fibers coalesce during heating and lignin aggregates begin to appear and increase in number during the holding phase, which continues to grow into the cooling phase. And, this phase separation starts at ~140 °C during SEP. These results support previous MD simulations that suggest that lignin aggregation occurs during SEP as soon as lignin has phase separated from hemicellulose. This experiment demonstrates the unique information that in-situ SANS pretreatment studies can provide and the potential to extend these types of studies to other chemical reactions.

CELL 521

Recovery of high-purity levoglucosan and other anhydrosugars from pyrolysis oil

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Fast pyrolysis is a direct approach to the thermal conversion of biomass into pyrolysis oil, noncondensable gases, and biochar. Lignocellulosic biomass is rapidly decomposed during fast pyrolysis at approximately 500°C in the absence or presence of oxygen (auto-thermal pyrolysis). We have developed a fractionated pyrolysis oil recovery system allowing for the separation of products based on vapor pressures. This research focuses on the heavy ends pyrolysis oil. Heavy ends consists of phenolics derived from the lignin and sugars originating from the cellulose and hemicellulose. A liquid-liquid water extraction is utilized to separate the heavy ends pyrolysis oil into the water-insoluble phenolics and water-soluble sugars. The water-soluble portion contains the majority of sugars: mainly levoglucosan, an important anhydrosugar, as well as, cellobiose, cellobiosan, xylose, and galactose. Our team has shown that the water-soluble sugar fraction does not contain oligosaccharides with the most abundant sugar being levoglucosan followed by cellobiosan. Levoglucosan is chiral with potential to be utilized in various fermentation regimes, pharmaceuticals, and as a platform chemical for conversion to green solvents and other bio-based products. Any phenolic inhibitory compounds that may inadvertently be within the water-soluble matrix after the extraction can be successfully removed via an adsorption resin, Sepabeads SP207, which allows for crystallization. We have successfully separated crystallized levoglucosan from the other crystallized sugars and remaining water-soluble constituents using a cold solvent rinse. The mass balance of the mother liquor after the resin was 81.1 wt% db sugars, 10.1 wt% db non-sugar water-soluble constituents, and 12.4 wt% levoglucosan/cellobiosan crystals. Crystallized anhydrosugar levoglucosan was at ≤ 98% purity with cellobiosan accounting for ≤ 2%.
Probing the dehydration induced changes in the organization of cellulose microfibrils in primary cell walls using Sum-Frequency-Generation (SFG) vibrational spectroscopy

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To investigate the dehydration effect on the organization of cellulose microfibrils in primary cell walls, we used transmission mode sum-frequency-generation (SFG) vibrational spectroscopy to detect the mesoscale structure of cellulose microfibrils of the abaxial (outer) onion scale epidermis under the never-dried (hydrated with D2O) and the fully air-dried states. Significant changes in the cellulose organization were observed by SFG after dehydration of epidermal walls. In the detection of the hydrated state, epidermal walls exhibited a strong alkyl (CH) stretching peak centered at 2944 cm⁻¹ in SFG spectra, whereas this 2944 cm⁻¹ peak was diminished and a new broad peak at 2920 cm⁻¹ appeared in the fully air-dried state. Further studies on pectate lyase treated onion epidermis with reduced pectin content, and Calcium ions treated epidermis were analyzed by SFG spectroscopy and field-emission scanning electron microscopy (FESEM). Our results proved the collapse of cellulose layers after dehydration. Moreover, it was also confirmed that with the existence of pectin, the dehydration induced shrinkage disrupts or curves the microfibrils within or between each adjacent cellulose lamella.
completely change wetting characteristics and to guide an aqueous fluid by capillary forces inside polymer-defined paper channels. The capillary-driven fluid flow of an aqueous solution inside the channels is a function of the fiber source, paper sheet porosity and channel width, the latter being defined by the hydrophobic barriers. As such this flow can be reproducibly tailored over a wide range by simple to adjust, intrinsic paper properties (Figure). Further concepts that will be highlighted include the spatially definition of reaction/detection zones prepared on paper, which are useful to carry out cascade model reactions inside the channels, and the use of such functional microfluidic paper substrates as simple colorimetric sensor devices.

CELL 524

Combined mechanical and chemical modifications towards super-stretchable paper-based materials

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Paper-based packaging materials have sparked a growing interest due to their biodegradability, recyclability and renewability. One of the main factors limiting the use of paper-based packaging materials is their somewhat poor extensibility which in turn has detrimental effects for the final shaping properties of the material. However, this problem might be solved by combining facile chemical treatment of fibers and modification of fiber network structure. In this study, bio-based water dispersions were introduced onto cellulose fibers followed by in-plane compaction of paper handsheets. The mechanical properties of the resulting composites were investigated by using tensile tester, dynamic mechanical analysis (DMA) and 2D formability tester. For example, such treatment of a paper handsheet increased its ductile properties (up to 20% elongation at break) even with moderate polymer addition (up to 4 wt.% based on fiber dry mass). Moreover, despite induced deformations tensile strength index improved by 30% (up to 54 Nm/g). Finally, most promising samples were converted in press forming experiments with fixed blank. Main results and possible applications for the developed composite materials will be discussed.

CELL 525

Fiber fines: Properties and influence of cellulosic microparticles

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Fiber fines are generated during pulping (primary fines, mechanical fines) and refining (secondary fines) in the stock preparation process. Besides fibers and fiber-fiber bonds, these cellulosic microparticles are
a further component of the paper network. Fines, which are defined as the fraction of pulp that is able to pass through a mesh screen or a perforated plate having a hole diameter of 76 μm [1], are known to influence the properties of the final paper product [2]. To better understand the effect and properties of this material, fines have to be separated from the pulp and investigated as an independent material.

In the present study, fines are isolated from the pulp fraction by means of a laboratory pressure screen. To allow further processing, the solids content of the produced fines suspension has to be increased. Morphological properties of different types of fines and other cellulosic materials such as MFC and NFC are determined and compared to each other. Furthermore, handsheets are prepared from these materials and properties such as apparent density, contact angle, modulus of elasticity and strain are measured. In order to evaluate the influence of fines on the properties of paper, pulp handsheets having defined amounts of fines are formed and tested. The exploration of the properties of fiber fines contributes to a better understanding of how this material influences the final paper products and also helps in identifying other potential applications of this material.

CELL 526

Utilization of polymerized technical lignins in the development of surface sizing formulations for packaging papers

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Technical lignins, which are the byproducts of the pulping industry, have a high potential to be used as value added products. In principle, the complex structure of lignin is a good prerequisite for using it as an additive for different applications. In our work, we investigated the use of two types of technical lignins in surface sizing formulations for packaging papers with the target to better understand the influence of the physico-chemical properties of laccase polymerized and raw technical lignins on the development of paper strength and hydrophobicity. Prior to surface sizing the lignins are purified by ultrafiltration and precipitation respectively. The solubility of the lignosulfonate at neutral pH was achieved straight after the ultrafiltration process. The solubility of the precipitated kraft lignin at neutral pH was not ensured after the purification process and therefore an additional solubilization process was performed. Water solubilized precipitated kraft lignin and ultrafiltrated lignosulfonates were polymerized using laccase at neutral or slightly alkaline conditions. An increase in strength properties of lignin sized samples was observed which was in the same range or slightly better compared to starch sized samples. The substrates sized with the enzymatically modified technical lignins showed a significantly higher hydrophobicity compared to the raw lignin sized samples while the strength properties remained on the same good level. Ongoing work is focusing on a further improvement of the performance of technical lignins in surface sizing of packaging grades by optimization of the enzymatic polymerization process.

CELL 527

Layer-by-layer modification of cellulosic materials for green antibacterial materials

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The most common way to produce cellulosic materials with antibacterial properties is to incorporate an antibacterial agent into the materials that is designed to slowly leach and inhibit bacterial growth in the surrounding media. This method however is associated with both environmental problems, due to toxicity of antibacterial agents to water living organisms, and an increased risk of development of resistant bacteria. It is however possible to make non-leaching contact active antibacterial cellulosic materials using environmentally friendly methods. The charged surface of cellulose makes material made from cellulose easily modified by adsorbing polyelectrolytes according the layer-by-layer procedure. By adsorbing the polyelectrolytes in a way that the surface consists of a highly charged cationic polymer, such as polyvinyl amine, it is possible to produce materials with antibacterial functionality. The adsorption of polyelectrolytes on cellulosic materials is done completely in aqueous solutions at room temperature using non-toxic chemicals making it an environmentally benign procedure. The polyelectrolytes are irreversibly adsorbed on the surface limiting the spread of potentially harmful compounds. Bacteria are inactivated by a contact active mechanism where the bacteria strongly adhere to the surface of the cellulosic material. Cellulose is an excellent material for making environmentally friendly antibacterial materials due to the inherent properties of cellulose which are preserved. The described procedure has been used to modify a wide range of cellulosic materials ranging from nanocellulose barrier films to water filtration materials made from pulp fibers. This paper will cover an overview of the activities within this area and demonstrate some of the endless possibilities of using environmentally friendly contact-active antibacterial materials made from cellulose.

CELL 528

Purification of water using cellulose: A safe way to remove bacteria

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Access to safe drinking water is vital for survival. Untreated water from nature is often contaminated with fecal bacteria that can cause diarrheal diseases, which have high mortality rates when not treated. There are some methods utilized today for disinfecting drinking water but new method and approaches for portable onsite water purification techniques are desired to provide people in remote areas or in emergency situation with clean water. Most new technologies for onsite water purification is based on the release of biocides e.g. chlorine or silver nano-particles to kill the bacteria but this method has considerable drawbacks since the released compounds are often toxic to water living organisms and can potentially select for antibiotic resistant bacteria in nature. A more sustainable alternative is to use contact-active antibacterial cellulose that removes bacteria from water up on physical contact, without releasing any chemicals. The contact-active cellulose is created by functionalizing the cellulose fiber surface with cationic polyelectrolytes through physical multilayer adsorption, according to the layer-by-layer method. The cellulose fibers gains a positive net charge and can thereby attract and bind to the negatively charged bacteria. So far, over 99.9 % of bacteria in water can be removed using the functionalized cellulose with contact-active antibacterial properties. This is, to the author’s knowledge, the first attempt to purify water from bacteria using cellulose functionalized with cationic polyelectrolytes through multilayer adsorption.

CELL 529

Evaluation of Antibacterial functionalizations of CNF/PVAm multilayer modified cellulose fibre and surface studies on silica model surface

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The creation of contact-active surfaces has become an essential approach for creating antibacterial surfaces with promising bacterial reducibility and good environmental sustainability. Previous studies
have shown that the bacterial reduction of cellulose fibres treated with polyelectrolyte multilayers of polyvinylamine (PVAm) fibres can reach up to 99.99%. The multilayers were assembled by 1st layer of positively charged PVAm followed by negatively charged polyacrylic acid (PAA) and with PVAm as a final layer. In this study, to make a move step ahead, the petroleum based PAA middle layer was replaced by more sustainable wood based cellulose-nano fibre (CNF). So that a bleached chemical softwood fibre was modified by 3-layer PVAm/CNF/PVAm system, and its antibacterial activities were evaluated from bacteria removal and bacteria growth inhibition. Interestingly, the antibacterial efficacy of this system is similar and even better than the previous PAA/PVAm system that exceeded 99.99%. To find out the optimised CNF assembling condition, different PH and salt concentrations were applied. It can be observed that higher salt concentration and lower assembling PH yield better bacteria reduction, which is the result of higher surface charge based on higher adsorption amount of PVAm that probably due to the increasing of surface area and higher ionization. Since the surface of pulp fibre is very heterogeneous that is hard to characterize and visualize, the more homogeneous model surfaces were prepared by spin coating the dissolved pulp fibre on silica surface to simulate the fibre surface in this study. With the increase of ionic strength, more island and heterogeneous structures can be observed on CNF/PVAm modified model surfaces. With the help of scanning electron microscopy (SEM) and fluorescing microscopy, the adsorbed bacteria distribute align the island parts of the surfaces can be clearly visualized, degrees of bacteria deformation and cell damage can be also found under SEM. The surface roughness of the modified model surface was examined by Atomic Force Microscopy (AFM), and hardly the conclusion of correlation between the surface roughness and the number of adsorbed bacteria can be drawn, surface charge is likely the most dominant factor comes to the bacteria redcution.

**CELL 530**

**Film formation and performance of different nanocelluloses obtained from different cellulose sources after different preparation processes**

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Disintegration of cellulose into nanocellulose (NC) could improve processibility and product performance. Cast-film preparation and physiochemical properties have been investigated using different NCs prepared from different cellulose sources after different preparation processes in order to reveal the dependence of the film forming and performance on the NC’s chemical and physical structures. The NCs applied were prepared from tunicate (TNC), softwood (SWNC) or hardwood (HWNC) cellulose by conducting an identical homogenization treatment after either enzymatic hydrolysis or TEMPO-mediated oxidation. It has been found that the obtained NCs show a large diversity in terms of chemical composition, degree of polymerization (DP), crystallinity index (CI), fibrils size, aspect ratio, and chemical charge. These differences have significant impacts on the morphology, optical properties, mechanical property, thermal stability and hydrophilicity of the cast-films. For example, more microfibrillar aggregates are observed for woody NCs while TNC is dominant by individual fibrils. TNC is very pure (purity>99%) but both hemicellulose and lignin are present in SWNC and HWNC. TNC is in a sharp contrast to the woody NCs with higher DP, larger aspect ratio and higher CI with more pure β crystalline. These differences result in lower hydrophilicity, better mechanical properties and higher thermal stability of the obtained TNC cast-film. However, the woody films are more transparent. TEMPO-mediated oxidation introduces charged carboxyl groups making the cast-films much denser and smoother than the enzymatic hydrolyzed NC films. However, the oxidation deteriorates the thermal stability and hydrophobicity. Lignin correlates to low hydrophobicity and high UV-barrier property while hemicellulose is responsible for improved film flexibility but lower hydrophobicity and poorer thermal stability. Having more glucomannan than xylan, the SWNC films show higher thermal stability than HWNC ones. Moreover, the former have stronger mechanical strengths than the latter. Meanwhile, the relatively higher content of rigid lignin structures present in latter is another reason for the lower mechanical properties. These direct comparisons conducted in this study among different NCs and their cast-films will provide useful information and knowledge for the applications of tunicate and woody cellulose or NCs for various bio-based material preparations.
Cellulose nanofibrils in emulsions stabilized by an ionic surfactant and effect of electrolyte in phase transitions

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Cellulose nanofibrils (CNF) are shape-anisotropic nanoparticles extracted from plant and other resources, which offer great prospects as a natural stabilizer of colloidal dispersions and complex fluids for applications in food, pharma, and cosmetics. In this study, an ionic surfactant (sodium dodecyl sulfate, SDS) was used to produce oil-in-water emulsions that were further stabilized with CNF. The emulsions were prepared by mechanical blending of the oil and aqueous phases. The interfacial properties of SDS in both CNF dispersions and emulsions were investigated. The influence of CNF and SDS concentration on phase behavior and emulsion formulation and stability was elucidated. The ionic strength of the aqueous phase was used as formulation variable. The phase transition behavior of CNF-stabilized emulsion systems was controlled by molecular transfer in oil-in-water systems at low salinity, while oil-in-water systems with irregular droplets and bi-continuous morphologies were observed at medium and high salinities, respectively. These findings open a new possibility to develop environmental friendly emulsions that attain high stability by the addition of CNF in the aqueous phase and that respond to ionic strength as is expected for classical emulsion systems.

In situ biomineralization of hydroxyapatite on bacterial nanocellulose and use as bioink for 3D bioprinting scaffolds to engineer bone

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There is a great need of bone tissue, since for example, only in the US approximately 1.5 million bone grafts are performed annually. Even if bone naturally regenerates, there are causes where bone lacks regeneration due to large size of defects, collapse of surrounding tissue, or large strains in the repairing tissue. 3D bioprinting offers a solution for bone regeneration by allowing osteoconduction, osteoinduction and ultimately osteogenesis. In this work we induced the formation of hydroxyapatite like mineral by modifying bacterial nanocellulose and fibrillated nanocellulose in order to be used as components in bioinks to create bone by 3D bioprinting.

Deep Eutectic Solvent (DES) treatment in nanofibrillation of secondary cellulose raw materials

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More environmental friendly and inexpensive chemicals are desired in the production of nanocelluloses. Deep Eutectic Solvents (DES) are a new class of solvent, which has been investigated as a green media in biomass processing. These solvents are easy to synthesize, based on readily available bulk chemicals, and they have low toxicity and are mainly biodegradable, which make DES one of the most promising solvents for sustainable material production. The utilization of secondary raw materials, such as waste paper and board, in preparation of micro- and nanocellulose would further improve the sustainability of production, since those materials have a high cellulose content even though they may have shortened fiber lengths and decreased mechanical strength in the macro-scale. DES prepared by mixing choline chloride and urea was used as chemical pretreatment in a nanofibrillation of different secondary fiber sources using Masuko grinder without any other chemical treatments. The characteristics of the nanofibrils obtained from the DES pre-treated materials, such as waste board (B), fluting (F), and waste milk container board (MCB) were compared with the nanofibrils obtained directly from virgin bleached chemical birch pulp (BCP), NaOH swelled waste board (NaOH-B), and bleached chemical birch pulp (NaOH-BCP). In addition, the prepared nanocelluloses were used as strengthen additives in board. DES treated board pulps were nanofibrillated more easily than NaOH swollen pulps. The nanofibril suspensions obtained from the DES pretreatment had viscous gel-like appearances, with shear thinning behavior without changes in their initial crystalline structure. Strength properties in board increased highly with the addition of nanofibrillated waste boards, but the best results according to strength properties and dewaterability obtained with the addition of less fibrillated microfibrils. Consequently, DES chemical pretreatment with a disk grinder appears to be a promising route to obtain cellulose micro-and nanofibrils from waste board and paper that can be used as strengthening additives in board.

**CELL 534**

**Oil in water Pickering emulsions stabilized by cellulose nanocrystals-xyloglucan complexes**

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In this work, we take advantage of the interaction between cellulose and hemicelluloses to fabricate complexes with cellulose nanocrystals (CNC) and xyloglucan (XG). In previous works, we have described two regimes of adsorption as a function of XG concentration. Thus, at low XG/CNC ratio, this polymer adsorbs on CNC in a rather flat conformation. Differently, if the XG/CNC ratio increases, the XG adsorption results in the formation of loops and tails onto the CNC surface. Here we investigate the surface properties of CNC-XG complexes fabricated at low and high XG concentration in an attempt to get more insights into the role of xyloglucan conformation on the properties of the assembly. CNC-XG assemblies were fabricated by the complexation of cotton CNC and XG in dispersed media at two different XG ratios (at 0.05 and 0.25, wXG/wCNC). Oil-in-water Pickering emulsions were prepared by the mixture of aqueous solutions of CNC-XG complexes with hexadecane. Both CNC-XG complexes stabilized the hexadecane/water interface, promoting monodispersed oil-in-water droplets around 10 μm in diameter stable for several months. However, the CNC-XG assemblies fabricated at high XG/CNC ratio (0.25) resulted in higher emulsion volume compared to assemblies fabricated at low XG/CNC ratio (0.05), suggesting the participation of the XG at the interface stabilization. Emulsions were destabilized by the addition of a xyloglucan-specific endoglucanase, which supports the adsorption of CNC-XG complexes at the interface and the role of XG in surface stabilization, opening the road to enzymatically tunable emulsions.
Low XG concentration:

High XG concentration:

CELL 535

Water-based bentonite fluids modified by cellulose nanoparticles for minimizing fluid loss and formation damage

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Cellulose nanoparticles (CNPs), including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), were used as an environmentally friendly and high performance additive in water-based bentonite drilling fluids for minimizing fluid loss and formation damage. The effects of CNP dimension and concentration on the rheological and filtration properties of the fluids were investigated. With half of the bentonite in the fluid replaced by a small fraction of CNPs, the resultant fluids showed excellent shear thinning behavior and the fluids' viscosity, yield point, and gel strength increased with the concentrations of CNPs. The addition of CNPs did not produce a pronounced effect in loss of the fluids under low temperature and low pressure (LTLP) conditions. However, reduced fluid loss and formation damage were observed with use of CNPs under high temperature and high pressure (HTHP) conditions, demonstrating CNP’s potentials for HTHP well applications. Additionally, CNCs and CNFs functioned differently in the rheological and filtration properties of the fluids, attributed to their distinct morphology and surface functionality, which could be controlled to maximize the performance of the fluids.

CELL 536

Mechanical isolation of nanocellulose from paper industry waste by ball mining

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In recent years, the researches for sustainable, green and environmental friendly materials are increasing. Also seeks to reduce the generation of residues. The use of lignocellulosic biomass is a
possible alternative to reuse solid waste. This type of biomass is found worldwide, including agricultural, forest, municipal and industrial waste. The paper industry is considered one of the most polluting industries in the world. The majority paper industry waste is incinerated. However, these residues have large amount of cellulosic material, and it can be repurposed in the isolation of cellulose nanostructures. The objective of this work was the mechanical isolation of nanocellulose from primary waste of paper industry by the ball milling. Also, it aimed at comparing three milling times (4, 6 and 24 hours) and two pretreatment methods (mercerization with acid and with detergent). The waste was mercerized for removal of oils and greases, bleached for lignin removal and milled for isolation of cellulose nanostructures (CNS). The composition was analyzed by Fourier transform infrared spectroscopy (FTIR). The thermal stability was evaluated by thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) shows the morphologies of CNS and the sizes were measured by dynamic light scattering technique (DLS). The nanocellulose samples show higher purity than the virgin sample (paper waste), and lower thermal stability. SEM showed agglomerates formed due to drying the samples. The samples milled during 24 hours show lower particle sizes for both pretreatment methods. The smaller particles mercerized with acid have size between 28,75 nm e 1,59 µm, and size between 31,05 nm e 1,33 µm for the smaller particles mercerized with detergent. The sample was mercerized with acid shows more homogeneous as compared with mercerized samples with detergent. However, both exhibit wide variation in particle size, suggesting the presence of agglomerates. This work obtained successful to isolation nanostructure of cellulose in all evaluated parameters.

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Chemical isolation and characterization of cellulose nanofibers to produce bionanocomposite films onto chitosan matrix for seafood packaging

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Antimicrobial properties of chitosan films provide a great enhancement in self-life and safety of sea food products. However, chitosan films exhibit poor barrier against water vapor and poor mechanical performance which restrict its wide application in food packaging industry. Therefore, the purpose of this study was to isolate and characterize different cellulose nanofibers (CNFs) from agricultural post harvesting wastes and finally incorporate them onto chitosan matrix to improve both mechanical and barrier performance of bionanocomposite films. Cellulose isolated from cotton stalks was used to prepare four different CNFs by sulfuric acid hydrolysis, TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl) oxy radical]-mediated oxidation, and mechanical treatment followed by ultrasonication. Physical and chemical properties of the prepared CNFs such as morphological (FE-SEM, AFM), structural (FTIR), and thermal gravimetric analysis (TGA) were investigated. TEMPO-mediated oxidation produced brighter and higher yields (>90%) of CNFs compared to other methods. FE-SEM and AFM analysis clearly indicated that, TEMPO-mediated oxidation produced uniform nano-sized fibers with a very small diameter (3–15 nm width) and length (10–100 nm). This was the first time uniform and very small nanofibers were produced. Finally, aqueous suspension of chitosan, sorbitol and TEMPO-CNFS were cast at a room temperature of 23°C and 50% relative humidity. The surface morphology of the films was revealed by FE-SEM and AFM. The thermal properties and crystal structure of the films were evaluated by TGA and X-ray diffraction (XRD). Thus, incorporation of TEMPO-CNFS (5-25%, based on the total dry mixture) into the film resulted in enhanced mechanical properties due to the high aspect ratio and mechanical strength of TEMPO-CNFS and strong interaction between TEMPO-CNFS and chitosan matrix. This effective method makes it possible to produce TEMPO-CNFS/chitosan based biomaterials of high quality.