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Cosponsored by COLL and PMSE

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T. Budtova, F. Liebner, Organizers

N. Baccile, C. Freire, Presiding

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Cosponsored by ANYL

M. Gama, Organizer

D. O. Klemm, T. Rosenau, Presiding

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Bioenergy & Bio-Based Chemicals
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Division of Cellulose and Renewable Materials

Cellulose & Other Structural Biopolymers: Structure, Formation & Degradation: Anselme Payen Award Symposium in Honor of Junji Sugiyama

CELL 1

Structural heterogeneity and matrix polysaccharide interactions of cellulose in plant cell walls from multidimensional solid-state NMR

Pyae Phyo, Tou Wang, Mei Hong, meihong@mit.edu. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Cellulose microfibrils provide the structural scaffold of plant cell walls, but the molecular structure of cellulose in native plant cell walls has been difficult to determine because of the noncrystalline nature of plant cell walls and the significant interactions between cellulose and matrix polysaccharides. We have recently overcome this barrier by enriching entire plants with 13C and conducting two- and three-dimensional high-resolution 13C-13C correlation solid-state NMR experiments. This talk will summarize our key recent discoveries. 1) Cellulose microfibrils of both dicot and grass primary walls contain at least 7 different molecular conformations, as manifested by 7 sets of 13C chemical shifts for the interior crystalline chains and the surface chains. 2) These molecular conformations are located at different positions of the microfibrils, based on correlation signals between cellulose and matrix polysaccharides and between cellulose and water. 3) Quantitative 13C SSNMR spectra show that the primary-wall cellulose microfibrils contain at least 24 glucan chains. 4) The glucan chains on the surface of the microfibril have distinct exocyclic conformations from that of crystalline bacterial cellulose, as determined using 1H spin diffusion NMR experiments. This gives new molecular structural information about how cellulose microfibrils interact with matrix polysaccharides. 5) Finally, NMR correlation data show that specific types of pectin bind cellulose. Combining solid-state NMR data with viscoelastic and growth measurements, we show that the pectin-cellulose interaction affects wall expansion during plant growth and is thus important for function.

CELL 2

Cellulose - simple polymer, but not so simple biosynthesis

Shawn Mansfield, shawn.mansfield@ubc.ca. University of British Columbia, Vancouver, British Columbia, Canada

The plant cell wall is an intricate assembly of biopolymers that is often proportionally dominated by cellulose, which is particularly true of plant secondary cell walls. This abundant, linear, homopolymer confers vital structural support to the plant, and is synthesized at the plasma membrane by Cellulose Synthase proteins (CesA) that form unique complexes (Cellulose Synthase Complexes: CSCs). Although simple in structure, the quantity and quality (ultrastructure) of cellulose can be impacted by an increasing number of “associated proteins” necessary for normal cellulose deposition – many of which still have unknown biological mechanisms. In recent years, live cell imaging of fluorescently-tagged CSCs has provided important insights into the deposition in primary cell walls. However, complementary imaging of secondary cell wall-specific CesAs has largely been hampered by the inherent location of secondary cell wall deposition, occurring deep within the plant tissues. Using an inducible master transcription factor controlling tracheary element cell fate, VASCULAR-RELATED NIC-DOMAIN (VND7), we recently developed a means to visualize, with high resolution, the active deposition of secondary cell wall-specific cellulose. Moreover, we are now able to quantify and compare the inherent velocities, their individual trajectories, and their densities at the plasma membrane, in a spatial and temporal transition from primary to secondary cell wall formation. We believe that employing this technique to study cell wall biosynthetic dynamics represents a critical step in understanding the cell biology behind secondary cell wall cellulose deposition.

CELL 3

Revisit of microfibril structure diversity in higher plants

Yoshiharu Nishiyama1, yoshih@cermar.cnrs.fr, Tomoko Kunitabayashi2, Yu Ogawa1. (1) CERMAV, Grenoble, France (2) The University of Tokyo, Tokyo, Japan

Since the establishment of the two-phase system, by Junji Sugiyama, of native cellulose, cellulose of various origins has been classified in terms of the composition of the two phases, I and II, related to the type of synthase complexes. All higher plants celluloses are classified as I- or II- dominant, resulting from the 6-membered rosette-type cellulose synthase complex. Furthermore, most wood samples show very similar X-ray diffraction patterns and small angle scattering features suggesting that the microfibril shapes are the same. These diffraction patterns can be explained by a 18-chain cross section compatible with the current model of the synthase complex. However, there are several exceptions: cotton or some bast fibers such as ramie show much sharper diffraction patterns indicating larger fibril width. We further investigated nineteen wood species from wide phylogenetic spectrum, and found three wood specimens that show significantly sharper diffraction features, but to different extent. To date, there is limited accumulation of data or any other structural data on cellulose microfibrils. We expect that the different lateral crystallite sizes among species would be a good starting point to understand the mechanism leading to the distinct nano-structure of native cellulose.

CELL 4

Nematic structuring of transparent and multifunctional nanocellulose papers

Mengchen Zhao1, Farhan Ansari2, Miyuki Takeuchi3, Michiko Shinizu1, Tsuguyuki Saito1, asaito@mail.ecc.u-tokyo.ac.jp, Lars Berglund2, Akira Itagaki1. (1) Department of Biomaterial Sciences, The University of Tokyo, Tokyo, Japan (2) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (3) KTH Royal Institute of Technology, Stockholm, Sweden

The conceptually new and sustainable “transparent papers” of wood cellulose nanofibers (CNFs) are characterized by exceptionally high strength, thermal expansion as low as for glasses, and superior gas-barrier properties, high thermal conductivity and electrical resistivity. Their possible applications thus range from structural members of energy, electronic, and sensing devices to direct uses as display panels and packaging materials. Here, the nematic structuring of CNFs is proposed as a nanostuctural engineering tool for making full use of the potential of CNFs in transparent and multi-functional papers. We compare two types of macroscopically isotropic CNF papers with different nanofiber arrangements: one formed through vaporization condensation of nematic-ordered CNF dispersions with polymer domains, and one through vacuum filtration of randomly-oriented CNF dispersion. Accordingly, the nematic-ordered CNF papers with densely-packed nanofiber arrangement exhibit superior mechanical properties, optical transparency, gas-barrier properties, heat transfer properties and electrical resistivity, compared with the conventional randomly-oriented CNF papers. The strategy proposed here for CNF arrangement is also applicable in the structuring of other one dimensional nanomaterials, such as carbon nanotubes, protein nanofibrils, and silver nanowires, for exploiting their potentials in macroscopically isotropic film structures.

CELL 5

Accessibility of hydroxyl groups related to cellulose aggregation

Lennart Salmén, lennart.salmen@innventia.com. RISE/Bioeconomy, Stockholm, Sweden

The interaction between water and cellulose is of utmost importance in order to understand and control the properties of cellulosic materials. Although the topic has been studied extensively there is still no consensus regarding all aspects related to moisture interaction with different hydroxyl groups of the cellulose and how ultrastructural changes of the cellulose may affect these interactions. To a large extent this relates to the complex structure of the cellulose itself with only partly crystalline microfibrils surrounded by, more or less, unoriented molecules. The fact that these microfibrils may further aggregate into larger units of a broad range of sizes further complicates the structural interpretations. The crystalline parts of the cellulose are not accessible by moisture and it has also been advocated that the areas in-between microfibrils in the aggregates would also be inaccessible. Measurements of moisture mobility by FTIR and NMR indicate however that there are two different types of sorbed, bound water in the relative humidity, RH, range, one type exhibiting restricted motion and another type representing a more mobile bound water. Examining the behaviour of these types of water suggests that the less mobile water could be associated to surfaces in-between microfibrils while the more mobile water would be associated to the microfibril surfaces facing outwards from the aggregates, i.e. areas of easier access. In processing of cellulosic fibres, like pulp and drying, substantial changes in both aggregate size, porosity and water holding capacity takes place. These changes, associated with aggregation/de-aggregation of the microfibrils, will affect the moisture sorption ability and the accessibility of hydroxyls as well as the water holding capacity. These issues will be further delved upon.

CELL 6

Manufacturing high performance cellulose fibres from solution

Stephen J. Eichhorn, s.j.eichhorn@bristol.ac.uk, Chenchen Zhu, Anastasia Koutsomitopoulou, Kevin D. Potter. Bristol Composites Institute (AC CIS), University of Bristol, Bristol, United Kingdom

We have achieved a novel, one-step dissolution, and cost-effective route to produce high stiffness cellulose fibers, using low molecular weight microcrystalline cellulose that is usually used for low
Cellulose is one of the most abundant biopolymers on earth. It has been clarified that the algal-bacterial type cellulose is hydrolyzed preferentially by the cellulase. Furthermore, the radii of gyration of cellulose microfibrils is 80 °C, then maintained at 180°C for 60 min and finally the cell.

In the present study, the radius of gyration of cellulose and its fractions. Research in my lab addresses these unique requirements and seeks to develop these new technologies using catalysis for biorefining. This first of this dual-part talk will introduce research on catalytic reduction and deoxygenation reactions using metal boron materials. These materials demonstrate high chemoselectivity for deoxygenation of aliphatic moieties in technical lignin, which produces a viscous brown resinous material consisting of monomers and oligomers. The second portion will discuss utilization of this resin as a feedstock for stereolithography. The resulting material can be photopolymerized using commercial photoinitiators, and the presence of modified depolymerized lignin has a positive effect on the kinetics of polymerization and the thermal and mechanical properties of the resulting materials. Combining of catalytic deconstruction and judicious chemical modification affords a new material platform that allows for incorporation of technical lignin into bio-based soft materials.
the valorization of biomass, we have developed a hybrid (i.e., thermo-catalytic and biological) conversion platform to generate value-added products from lignin. This hybrid conversion platform consists of two sequential processes: a thermo-catalytic process that depolymerizes lignin into an aqueous-soluble lignin breakdown product and a biological process that converts and funnels compounds in the lignin breakdown product into a single bio-product, a tricaprylinol (TAG, a biodiesel precursor). To overcome well-known challenges to lignin conversion, lignin breakdown products will be generated via a “light-boost” depolymerization process and characterized and classified by a novel combination of gas chromatography-mass spectrometry and positive matrix factorization methods. Herein, we present the results of studies that elucidate the effect that biomass source, depolymerization catalyst, and biosensor conditions have on the depolymerization of lignin into an aqueous-soluble lignin breakdown product and the effect that different lignin breakdown product compositions have on its biological conversion with a bacterium, Rhodococcus opacus.

**CELL 13**

Anisotropic composite foams from lignocellulosic biomass: Mechanical and thermal properties

Nathalie Lavoine, nlatvoie@gmail.com, Varvara Apostolopoulou Kalkavou, Lennart Bergstrom, Stockholm University, Stockholm, Sweden.

The past two decades, focus has been directed towards lignocellulosic biomass valorization as a possible alternative of fossil resources. The production and development of nanocellulose-based materials is in particular promising for diverse applications, such as insulation, packaging, or electronic.

Most studies on nanocellulose use bleached wood pulp for producing cellulose nanofibers (CNF) by high-shear mechanical treatment. Unbleached wood pulp containing residual lignin, hemicelluloses and extractives is an attractive low-cost raw material to consider for the production of lignocellulose nanofibers (LCNF). The use of lignin can enhance the resistance of cellulose materials to moisture and bacteria; two challenges that limit the use of cellulose-based materials in many important applications. Here, we investigate the influence of residual and synthesized lignin on the structural, mechanical and thermal properties of anisotropic CNF- and LCNF-based foams. CNF and LCNF were produced from unbleached and bleached softwood pulps respectively, using a supermucilaginous grinder. Commercially available Kraft (KL-) and sulfinate (NaS-L) lignins were combined in different weight ratios with the CNF and LCNF suspensions for the production of anisotropic composite foams with a controlled lignin content by ice templating. The lightweight composite foams displayed a higher toughness and moisture resistance than neat CNF foams. The foams thermal conductivity at different relative humidity and temperatures will be presented and the potential of lignocellulose foams to be used as thermally insulating green materials will be discussed.

**CELL 14**

Nanocellulose/polymer composite microparticles prepared by emulsion-templated synthesis

Shuji Fujisawa1, fujisawas@flit.uh.hcmusc.edu, Eiji Togawa2, Katsushi Kuroda2, (1) The University of Tokyo, Tokyo, Japan; (2) Forestry and Forest Products Research Institute, Tsukuba, Japan.

We report on a facile method to prepare nanocellulose/polymer composite microparticles by templating an oil/emulsion stabilized by nanocellulose. Surface-carboxylated nanocellulose with a width of ~3 nm was prepared by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation of softwood bleached Kraft pulp and subsequent mechanical disintegration of the oxidized pulp in water. Nanocellulose-stabilized monomer/emulsion system was formed by sonication of the nanocellulose/water dispersion and monomer, and the average diameter of the monomer droplets was ~3 µm. By polymerizing the monomer encapsulated, polymer microparticles stabilized by the nanocellulose were successfully prepared. The microparticles kept the size and shape of the original monomer droplet, and had an average diameter of ~3µm. The microparticles showed good dispersibility in water, because the surfaces are densely covered with the TEMPO-oxidized nanocelluloses. The potential of the nanocellulose/polymer composite microparticles was about ~50 µm, which is as high as that of the original TEMPO-oxidized nanocellulose. Scanning electron microscopic images showed that the surfaces of the microparticles are homogeneously covered with the nanocellulose. This novel composite material could be extended to many applications, including food, pharmaceutical, and biomedical applications, due to the unique characters originating from their fine sizes. Therefore, this technique paves the way toward novel green nanocomposite production using a facile and scalable process.

**CELL 15**

Detection of human neutrophil elastase with fluorescent peptide sensors conjugated to TEMPO oxidized nanocellulose foams

Krystal R. Fontenot1, krystal.fontenot@jars.usda.gov, Vince Edwards2, (1) USDA-SCRC, New Orleans, Louisiana, United States; (2) Private Citizen, New Orleans, Louisiana, United States.

Nanocellulose foams are hydrophilic and lightweight biocompatible materials with a high porosity and specific surface area structure, which is easily modifiable via its reactive hydroxyl groups that facilitates grafting or functionalization of the surface. Such a material is ideal for biosensor dressing interface and therefore, we report the preparation, synthesis, and characterization and bioactivity of PEGylated peptide-tempo-oxidized nanocellulose foams made from nanofibrillated cellulose that was designed for elastase detection activity. The tempo-oxidized nanocellulose foams were prepared by pyrolySization of a freeze-dried nanocellulose suspension to yield a three-dimensional structure with a porosity of 99% and a specific surface area of 28 m2/g. The tempo-oxidized surface was PEGylated with a protected heterobifunctional polyethylene glycol linker, deprotected, and conjugated to a fluorescent tripeptide-substrate (succinyl-alanine-alanine-proline-valine-4-amino-7-methyl-4-coumarin) or tetratripeptide-substrate (succinyl-alanine-alanine-proline-valine-4-amino-7-methylcoumarin) that resulted in the biosensor. The degree of substitution, mass spectral analysis, and attenuated total reflectance infrared spectroscopy indicated that the peptide substrate was immobilized on to the surface of the tempo-oxidized nanocellulose foams. It afforded the biosensors ability to detect elastase as supported by its bioactivity assay. The polyethylene glycol linker provided an extended conformation and the biosensors swelling capacity maximizes the pore size that enhances interaction between the tripeptide or tetratripeptide substrate and elastase protein, which accounts for its lower sensitivity of 0.06 or 0.03 units/milliliter, respectively for human neutrophil elastase protein compared to other nanocellulose materials i.e. nanocellulose composites 0.125 – 0.25 units/milliliter and nanocellulose aerogel 0.125 units/milliliter. The physical properties of the PEGylated peptide-substrate Tempo-oxidized nanocellulose foams are suitable for interfacing with an intelligent protease sequestant wound dressing.

**CELL 16**

Bio-based intumescent flame retardant coating for nylon-cotton fabric based on synergistic combination of tannic acid and phytic acid

Zhiyu Xia1, zhiyu_xia@student.ume.edu, Shang Yu1, Wee Reidhe Kiratianvanit2, Jayant Kumar2, Ravi Moosuk2, Ramaswamy Nagapan1, (1) Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States; (2) Physics and Applied Physics, University of Massachusetts Lowell, Lowell, Massachusetts, United States; (3) US Army Natick Soldier RDEC, Natick, Massachusetts, United States.

Abstract: Nylon-cotton fabric (Nyco) is widely used in clothing due to the combination of good mechanical properties and comfort. However, Nyco presents a potential fire risk because the cotton fibers catch fire at relatively low temperatures (ignition point ~ 350 °C) while Nylon 66 fibers tend to melt and burn continuously, adhering to the fabric by the cotton. Currently very few flame retardant (FR) solutions are effective for Nyco. Bio-based compounds, such as tannic acid (TA) and phytic acid (PA) have been reported to exhibit beneficial FR characteristics. TA is an abundantly available bio-based polyphenol while PA is a naturally occurring poly-phosphoric acid. TA forms intumescent char upon exposure to fire while PA is a catalyst to char formation of cellulosic materials. Here we report a unique combination of tannic acid and phytic acid applied as semi-durable coating onto Nyco fabric that provides excellent fire resistance. TAPA-coated Nyco fabric demonstrates self-extinguishing behavior and reduced char length (less than 10 cm) in vertical flame tests. Detailed thermal characterization using thermogravimetric analysis (TGA), pyrolysis flow combustion calorimetry (PCFC) and limiting oxygen index (LOI) measurements will be reported. Preliminary results indicate that synergistic combination of TA and PA produces intumescent char which forms the basis for the excellent fire resistance. This research opens the possibility for utilizing abundantly available and non-toxic bio-based polyphenol and phosphorus compounds as intumescent char forming FR coating for textiles.

**Frontiers in Glycoscience, Bridging the Gap Between Carbohydrate & Polysaccharide Chemistry**

Lai-Xi Wang, wang518@uml.edu, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States.

Glycosylation is one of the most prevalent posttranslational modifications of proteins. Compelling data have demonstrated that glycosylation can profoundly affect a protein’s structure and functions, including folding, stability, antigenicity, immunogenicity, and other important biological activities. Nevertheless, a detailed understanding of the impact of glycosylation, as well as the related biomedical applications, is often hampered by the glycan heterogeneity and the difficulties to obtain homogenously glycosylated glycoproteins. This presentation highlights recent progresses in the development of new chemoenzymatic methods for protein glycosylation with a focus on the endoglycosidase-catalyzed glycan remodeling and glycoprotein synthesis. Examples to be discussed include: 1) chemoenzymatic site-selective glycosylation of polypeptides and glycoproteins such as human erythropoietin (EPO) with multiple glycosylation sites; 2) direct enzymatic glycosylation of proteins with N-glycosyltransferase (NGT) and novel fucosidases; and 3) site-specific glycan remodeling of therapeutic antibodies.

**CELL 17**

Recent advance in chemoenzymatic glycoprotein synthesis

Benjamin G. Davis, ben.davis@chem.ox.ac.uk, Univ of Oxford Chem Ranch Lab, Oxford, United Kingdom

Glycosylation is one of the most prevalent posttranslational modifications of proteins. Compelling data have demonstrated that glycosylation can profoundly affect a protein’s structure and functions, including folding, stability, antigenicity, immunogenicity, and other important biological activities. Nevertheless, a detailed understanding of the impact of glycosylation, as well as the related biomedical applications, is often hampered by the glycan heterogeneity and the difficulties to obtain homogenously glycosylated glycoproteins. This presentation highlights recent progresses in the development of new chemoenzymatic methods for protein glycosylation with a focus on the endoglycosidase-catalyzed glycan remodeling and glycoprotein synthesis. Examples to be discussed include: 1) chemoenzymatic site-selective glycosylation of polypeptides and glycoproteins such as human erythropoietin (EPO) with multiple glycosylation sites; 2) direct enzymatic glycosylation of proteins with N-glycosyltransferase (NGT) and novel fucosidases; and 3) site-specific glycan remodeling of therapeutic antibodies.

**CELL 18**

Sugars & proteins: Exploring and exploiting sugar chemical biology

Sugars and Post-Translational Modifications are critical biological markers that modulate the properties of Proteins. Our work studies the interplay of proteins, sugars and modifications. This lecture will cover emerging areas in our group in: (a) biomolecule construction with an emphasis on new bond-forming processes compatible with biology & (b) use of chemical probes & modulators of carbohydrate & protein processing events: (i) Synthetic Biology’s development at the start of this century may be compared with Synthetic Organic Chemistry’s expansion at the start of the last; after decades of isolation, identification, analysis and functional confirmation the future logical and free-ranging redesign of biomolecules offers tantalizing opportunities.
(ii) ‘Synthetic Biologics’ and their applications: drug delivery; selective protein degradation; nanomolar inhibitors of bacterial interactions; gene delivery vehicles; probes of in vivo function; non-invasive pre-symptomatic disease diagnosis; targeted high-intensity radioprobes; designed glycoconjugate vaccines. (iii) Chemical Probes and Modulators: Delineation of mechanisms of carbohydrate- and protein-processing systems and their ligands allows not only an understanding of their fundamental role in Biology and Immunology but also the use of molecules to modulate and manipulate such processes, with a strong associated potential for diagnosis, therapy and intervention in Medicine.

4

CELL 19

Analysis of glucose mediated glycoprotein folding events in the endoplasmic reticulum

Yukishige Ito, yukito@riken.jp, Synthetic Cellular Chemistry Laboratory, RIKEN, Wako, Japan

Structures of glycoproteins are characterized by their complexity and diversity. To clarify their functions, synthetic approaches are considered to be promising. Development of synthetic methodologies for efficient and facile preparation of oligosaccharides is a focal issue in carbohydrate chemistry. In light of their structural diversity, practical strategy to facilitate the synthesis of oligosaccharide is expected to be highly valuable. Glycoprotein glycans are known to play numerous biological roles, both intra- and inter-cellular, through their interaction with various proteins such as lectins, glycosidases, and glycosyltransferases. However, their precise analysis has been hindered by structural heterogeneity of glycoproteins. Under these circumstances, our effort has been directed to synthesis of glycoprotein glycans and related probes for analysis of their intracellular functions. In glycoprotein folding events in the ER, incorporation and detachment of glucose to high-mannose-type glycans on immature folded glycoproteins serve as key signals. To understand them, our efforts have been directed to analyze enzymes and chaperones in the ER, such as Calnexin/Calreticulin, UGGT (UDP-Glc:glycoprotein glucosyltransferase), glucosidase II, Sep15, and ERP29. Extensive use of structurally defined substrates including high-mannose-type glycan derivatives and glycoproteins, which are obtained by chemical or chemoenzymatic synthesis, will be featured.

CELL 20

O-GlcNAc glycosylation: From reductionism to systems biology

Linda C. Haieh-Wilson, lh@caltech.edu, Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States

The dynamic posttranslational modification of proteins by O-linked-β-N-acetylglucosamine (O-GlcNAc glycosylation) plays many important roles in physiology and disease. Remarkably, only a single enzyme catalyzes the modification, raising the question of how this enzyme (O-GlcNAc transferase or OGT) selects from among its diverse substrates to regulate specific cellular processes. Here we will describe a new systems-level approach for studying the functions, specificity, and regulation of O-GlcNAc glycosylation. Elucidation of these dynamic O-glycosylation networks provides insights into the key functions of this modification and may reveal novel approaches for therapeutic intervention.

CELL 21

Hyphenated IM-MS methods as high-resolution sequencing tools for carbohydrates

Sabine Flitsch, sabine.flitsch@gmail.com, Chemistry, The University of Manchester, Manchester, United Kingdom

The lack of robust, high-throughput and sensitive analytical strategies that can conclusively map the structure of glycans has significantly hampered progress in fundamental and applied aspects of glycoscience. Resolution of sugar epimers and anomeric glycan linkage within oligosaccharides remains a particular challenge. We have shown that after fragmentation, high-resolution stereochemical information can be obtained by ion mobility-mass spectrometry (IM-MS). In addition, ‘memory’ of anomeric configuration is retained following gas-phase glycosidic bond fragmentation during tandem mass spectrometry (MS2). These findings allow for integration of MS2 with ion mobility spectrometry (IM-MS2) and lead to a strategy to distinguish α- and β-linkages within natural underivatised carbohydrates. We have applied this fragment-based hyphenated MS technology to oligosaccharide standards and to de novo sequencing of purified plant metabolite glycoconjugates, showing that the anomeric signature is also observable in fragments derived from larger glycans.

CELL 22

Hybridization of mass spectrometry and laser spectroscopy: A new technology for glycobiology

Isabelle Compagnon1,2, isabelle.compagnon@univ-lyon.fr, (1) Institut Lumiere Matiere, University of Lyon, Villeurbanne, France (2) Institut Universitaire de France, Paris, France

Deciphering the sequence of carbohydrate is a major challenge in glycosciences today. Whereas spectroscopic approaches (NMR, Raman, ...) and Mass Spectrometry (MS) offer valuable information on carbohydrate structure, they also suffer from severe technical limitations: on one hand, spectroscopy provides direct and refined structural detail but requires a relatively large amount of thoroughly purified sample, on the other hand MS readily applies to complex samples in small amounts, but does not disambiguate all carbohydrate isomers. In this context, we have developed a unique hybrid Glycanalytical approach, which adds a spectroscopic dimension to MS analysis. Based on this technology, it is possible to measure simultaneously the MS spectrum and the spectroscopic fingerprint of a carbohydrate. This enables the disambiguation of all kinds of carbohydrate isomers (monosaccharide content, regiochemistry and stereochemistry of the glycosidic bond, and positional isomers of functional modifications) without the need for chemical modification, labeling, or time-consuming purification. While this new carbohydrate metric mitigates the lack of structural specificity of MS without the limitation of traditional spectroscopic analysis, the identification of a carbohydrate however still relies on the availability of reference standards. In order to enable true “de novo” analysis, we have established a top-down sequencing strategy based on the demonstration of a memory of the carbohydrate sequence within MS fragmentation products. [1, 2] The performance of de novo carbohydrate sequencing will be illustrated on various classes of carbohydrates.

CELL 23

Glycomics in health and disease

Anne Dell, dells@imperial.ac.uk, Life Sciences, Imperial College London, London, United Kingdom

In partnership with bioscience collaborators worldwide, my laboratory specialises in the development and exploitation of mass spectrometry in the field of glycochemistry with the aim of establishing the roles glycopolymers play in health and disease. Mass spectrometry, with its ultra-high sensitivity and ability to analyse complex mixtures of glycans, is the most powerful tool currently available for glycan structure analysis. Much of glycobiology research seeks to understand how sugar oligomers (glycans) on glycoproteins engage with glycan-binding proteins (GBP's also called lectins) to mediate adhesive and signalling events. Such recognition is central to cell communication including interactions between mammalian eggs and sperm, between pathogens, parasites and their hosts, between cells of the immune system, and between the microbiome and the GI tract. This talk will illustrate how mass spectrometry-based glycomics research is providing key insights into these biological processes.

CELL 24

Glycan spatial sequencing with regio-specific spectral documentation

Vernon N. Reinholt, vnr@unh.edu, University of New Hampshire, Durham, New Hampshire, United States

This study demonstrates that neutral gas activated carbohydrate ions can be dissociated in a state-wise, structurally dependent manner to yield regio-specific linkage fragments. Such ions can be captured, documented and shared, retaining all aspects of structure for sequence understanding. Extensive studies for over two decades have shown the fidelity of disassembly with a large cross selection of synthetic and natural carbohydrate samples. Identical results have also been observed with abbreviated steps in triple quadrupoles and exacting results in both linear and quadrupolar ion traps, supporting the concept that following activation, disassembly is an independent physiochemical process controlled only by its inherent structure. Moreover, three additional facts complement this approach as an effective sequence technology: 1.) a loss of native background ions with early MS steps, allows commensurate sample ion amplification; 2.) double and triple charging significantly extends mass range; and 3.) incrementing steps of disassembly occur at higher energies that must be shared with smaller oscillator number, a feature that provides greater structural detail in core areas of stability. This latter feature is predicted by the quasi-equilibrium theory, (IRRM). With support from these basic physicochemical facts, we turned our attention to challenging stereo-isomers, as known in the equatorial-axial pyran isomers, (the C4 Gal/Glc; GlcNAcN and the C2 Glc/Mann monomers). Synthetic regio-specific disaccharide samples that included these specific stereoisomers did produce differential spectra upon disassembly, completing a spatial regio-specific analysis. Since synthesis is revered as a proof of structure, so in a reverse sense, disassembled products allow an opportunity to document precursors in defining sequence. Equally important is the opportunity to challenge all products by spectral documentation. Such searchable files and documentation would greatly facilitate collaborative research, a fundamental component long missing in glycosylation studies.
Incorporation of cellulose nanofibers into pPADs: Stable storage of bio-related labile substances and function as a biochemical reaction field

Yoshikuni Teramoto1,2, teramoto@gifu-u.ac.jp, Rina Murase1, (1) Department of Applied Life Science, Gifu University, Gifu, Japan (2) Center for Highly Advanced Integration of Nano and Life Sciences (CHAIN), Gifu University, Gifu, Japan

Research on microfluidic paper-based analytical devices (pPADs) is remarkable in recent years from the viewpoints of analytical chemistry and biochemistry. On the other hand, we can contribute to components incorporated into pPADs from the standpoint of material science. We here propose that 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO-oxidized) cellulose nanofibers (TOCN) can be reasonably mounted as a module of pPADs by effective use of the following features of TOCN, namely:

-“oxygen barrier capability in a dry state” as “storage of unstable substances”
-“exchangeability of molecules if swollen in water” as “biochemical reaction site”
-“immobilization on papers” for “fixation of the sensing site”

The TOCN aqueous dispersion exhibiting thixotropy can be printed with an inkjet apparatus, thus simplifying the manufacturing process of pPADs. As nanofibers derived from cellulose, which is the main component of paper, are printed on paper, incineration ash does not remain and post-treatment is hygienic. In this presentation, we report several examples of bioassay systems on paper using TOCN. Our future plans include elucidating the mechanism of stable storage of unstable molecules and extending the variety of available bio-related substances and their reactions.

Grafting density design of surface-modified nanocellulose for polymer composites

Hiroto Soeta1, hiroto.soeta@gmail.com, Tsuguyuki Saito2, Lara Berglund3, Akira Isgo4, (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) The University of Tokyo, Tokyo, Japan (3) Department of Biomaterials Science, The University of Tokyo, Tokyo, Japan (4) Univ Tokyo, Tokyo, Japan

Grafting density of nanocellulose surfaces is an important parameter to control the mechanical and physical properties of nanocomposites. We are developing surface-modified cellulose films, which can be used for a variety of applications. Here, we report the effect of the grafting density of cellulose triacetate (CTA)/TOCNs or PEG for improving the dispersibility of TOCNs (PEG-TOCN) in polymer matrices. Various phenomena occur at the interface area, which governs bulk properties of the nanocomposites. Designing the structure and properties of the interface area is thus important for nanofiller-reinforced composites. However, it is difficult to minutely design the interface structure and properties without changing the dispersibility of nanofillers. We prepared TEMPO-oxidized cellulose nanofibers (TOCNs) which have good dispersibility in polymer matrices, and investigated the contributions of the grafting density on the nanofiller surface using two types of TOCNs, or neat TOCNs and poly(ethylene glycol)-grafted TOCNs (PEG-TOCNs). The PEG-TOCNs were prepared by amine-terminated PEG onto TOCN surfaces via ionic bonds. The grafting density was controlled by changing the molar ratio between the TOCN carboxy group and the PEG amine group. Cellulose triacetate (CTA)/TOCNs or CTA/PEG-TOCNs composite films were prepared to investigate the influence of the grafting density on the mechanical and physical properties. A spring’s modulus and tensile strength of CTA films were improved by the addition of TOCNs or PEG-TOCNs, and the reinforcing effect of TOCNs decreased with increasing the grafting density. The elongation at break and toughness of the nanocomposite films increased with increasing the grafting density. These results suggest that the soft PEG layers on the TOCN surfaces hindered stress transfer between TOCNs and CTA matrix and enhanced energy dissipation during deformation. Coefficients of thermal expansion of the CTA films decreased with the addition of TOCNs, and increased with increasing the grafting density. It is likely that the coefficients of thermal expansion of the nanocomposites resulted from both TOCN-induced dimensional stability and PEG-induced thermal expansion. In conclusion, the grafting density influences the mechanical and thermal properties of nanocomposites and should be controlled to exploit the favorable properties of the nanofillers.
colours might form the basis of an anti-counterfeiting feature that could be incorporated into currency and other security paper documents. Some attempts to scale up the slower thin-film forming process were envisaged. The use of silicone moulds from which indescent CNC planchettes could be readily detached. However, despite the occasional brilliance of the coloured, the attempts were unsuccessful for a number of reasons that will be discussed in broader detail. In an attempt to find other applications for the basic phenomenon, we have assembled a multidisciplinary team that includes two CNC-obssesed chemists and a biochemist, a graphic designer (and part-time improver), an architect and a textile designer. An unexpected result has been the development of a new kind of butterfly, pseudopapilionoides cellulosea, whose existence we predict will lead to increasing interest in sustainable biomimetic grant applications.

Pseudopapilionoides cellulosea (Left) As first observed circa 2001 in the Gray lab, McCull University, Toronto, Canada. (Right) As recently observed in the Shoosoy lab, the Hebrew University of Jerusalem, Israel.

CELL 31

Included? Not included! (Nano)Cellulose inclusion compounds

Andreas Maunert, Koon-Yang Lee, Eero Kontturi, Alexander Bismarck
alexander.bismarck@durvies.ac.at (1) Department of Forest Products Technology, Aalto University, Aalto, Finland (2) Department of Chemical Engineering, Imperial College London, London, United Kingdom (3) Department of Aeronautics, Imperial College London, London, United Kingdom (4) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (5) Faculty of Chemistry, Institute of Materials Chemistry and Research, University of Vienna, Vienna, Austria

Cellulose inclusion compounds were first described by H. Staudinger in the 1940s. They studied the uptake of organic solvents by ligno-cellulose fibres. They found that cotton or flax fibres can incorporate up to 8 wt-% of cyclohexane. As a consequence, cellulose modification reactions of these fibres were accelerated significantly. They proposed that the uptake of organic solvents was due to the formation of inclusion compounds between cellulose and the organic solvents. In recent years, cellulose nanofibers (CNF) or bacterial cellulose (BC), have generated huge interest for various applications, e.g. as reinforcement in composites or as membranes. Nanopapers are commonly produced from aqueous suspensions of cellulose nanofibers via a paper-making process to establish a fibrous network of cellulose nanofibers. Changing the dispersion medium for nanofibers to aqueous suspensions of a more hydrophilic organic dispersion medium prior to filtration affects arrangement and interfibrillar interactions of the nanofibril. This allows for a better control of nanopaper porosity and consequently mechanical performance. But can this be explained by the formation of cellulose-solvent inclusion compounds? We aimed to explore this by changing the dispersion medium from which bacterial cellulose nanofibers were prepared. We use various organic liquids with low surface tension and similar size. Nanopapers were prepared by a paper-making process via solvent exchange in order to tune the physico-chemical behavior of BC nanopapers. While the nanopapers had very different properties as compared to conventional nanopapers produced from aqueous suspensions we only found out that no solvent inclusion compounds from but that solvent adsorption occurs on the surface of the nanofibrils.

CELL 32

Turning “nano”dreams into “mega”nightmares: How the expectations of academic and industrial R&D players on nanocellulose could be frustrated by policies and regulations on nanotechnologies in Europe

Denilso Da Silva Perez, denilson.dasilvaperez@iblae.fr. InTechFibres, FGBA, Grenoble, France

According to the official definition by the European Commission, a nanomaterial is “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm” [1]. Because of the intrinsic nature of the cell wall organization of the fibers used for the production of nanocarbons and nanofibrillated cellulose, those materials will certainly be considered as nanomaterials. In this paper, an overview of the restrictions on nanotechnologies in Europe, in particular for the applications where cellulose nanocarbons and nanofibrillated cellulose could be used, will be presented and discussed. Technical considerations in terms of risks during manufacturing and processing, health issues for the consumers, but also measurements and characterization will be addressed. Some academic and industrial R&D centers are currently avoiding, as much as possible, the usage of the prefix “nano” which has been replaced by “micro”fibrillated cellulose. In summary, the idea of this contribution is to illustrate how a great euphoria on nanotechnology is being quickly replaced by a growing frustration when considering nanocellulose in different applications.

Wood-Based Materials for Energy & Water

CELL 33

Fluorescent sensing of water diffusion and its effects in CNC based composites

Sindhu Seetharamraju, sindhu.seetharamraju@gmail.com, Jeremiah W. Woodcock, Ryan Beans, Stephan Stranick, Jeffrey W. Gilman (1) NIST, Gaithersburg, Maryland, United States (2) MS 8541, NIST, Gaithersburg, Maryland, United States (3) MML, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Cellulose nanocrystals (CNCs) are widely used for the development of composites for various applications. The end properties of interest are impacted by the compatibility of CNCs with the organic polymer as well as the water transport properties of the composite. Inorder to enhance their commercial properties and restrict interfacial water uptake, modified CNCs are used. The localized water effects in these composites can be probed using fluorescence lifetime imaging (FLIM) and a water sensing fluorophore (aquafluor). Aquafluor is a fluorogenic dye that gets activated in the presence of water and UV irradiation. It is covalently attached to the epoxy in an epoxy-CNC composite. FLIM technique based on time-correlated single photon counting is used to characterize the local environment of CNCs for polymer dynamics in various CNC-epoxy composites in dry and saturated conditions. Further, CNCs tend to hold water inherently prior to the absorption from environment. Fluorescence intensity measurements are used to visualize the interfacial water with CNCs and calculate localized water diffusions after absorption. These results reflect the variations in interfacial water uptake characteristics and provide dynamic information in different regions of the sodium and phosphonate CNC-epoxy composites.

CELL 34

Strategies towards tough, stiff and strong poly(lactic acid) composites

Xiangtao Meng, mengxt@bmi.gov, Halil T. Tokinalt, Soydan Ozcan2. (1) Materials Science and Technology Division, Oak Ridge National Laboratory, Knoxville, Tennessee, United States (2) Mechanical, Aerospace, Biomedical Engineering, University of Tennessee, Knoxville, Tennessee, United States

Poly(lactic acid) (PLA) is a biobased and biodegradable polymer with relative high strength and stiffness, but low toughness. Previous studies aiming to develop modified PLA materials were fruitful towards tougher and more ductile PLA for durable applications. Yet, these strategies often involved problems such as complex synthesis and extra cost to PLA resin which are not industrially desirable. Moreover, strength and modulus were very often sacrificed as a result of the toughening approach. Here we report two strategies by our group towards (super)tough PLA with no or minimal decrease in strength and stiffness. We designed a tertiary composite system using all renewable components – PLA, nanocellulose (CN), and epoxidized soybean oil (ESO) – in order to afford materials with both strength and toughness. The thermal and mechanical properties of the composites were studied and compared with those of neat PLA and binary composites. The results showed that the combination of nanocellulose and ESO was able to significantly improve ductility of the material with only slight losses in strength and modulus. Moreover, we investigated the roles and interactions of nanocellulose and ESO in the composite system. Combined evidences from thermal, dynamic mechanical, Raman, and mice tests analyses suggested that the plasticization effect of ESO, may be the main cause of the ductile behavior at low CNF concentrations, while at high CNF levels, CNF percolation dominates in stress transfer. We will also share our study of PLA-organosilane hybrid materials towards supertough PLA. By simply mixing a low amount (0.5-1 wt %) of organoalkoxysilane with PLA, supertough PLA hybrids with over 12 fold elongation to break and 10-fold toughness were achieved. Through thermal, mechanical, electron microscopical study, and dynamic light scattering, we proved the in-situ formation of PLA-silane nanohybrid structure, which we believe have contributed the excellent mechanical property of the new materials. This approach may also be applied to other polymer and composite systems.

CELL 35

Cellulose nanocrystals grafted with Poly(glycidylmethacrylate) for their compatibilization in nanocomposites

Manon Le Gar3, manon.le-gars@lps2.grenoble-inp.fr; Marisol Jifs, Hanene Salmi4, Naceur Belgacem1, Philippe Roger1, Julien Bras1. (1) Univ. Grenoble Alpes - Grenoble INP - LGBP2, Grenoble, France (2) University Paris Sud, Orsay, France

 Nowadays,ядor food packaging is turning to high performance biomaterials. Among bio-based materials produced from biomass, cellulose, one of the most abundant natural polymers, is a semi crystalline polymer with a microfibrillar structure. Since the last decades, interest on based materials produced from biomass, cellulose, one of the most abundant natural polymers, is a semi crystalline polymer with a microfibrillar structure. Since the last decades, interest on cellulose materials has increased with its use as nanostructured materials, either in the form of cellulose nanocrystals (CNC) or in microcellulose micro/nanofibrils (CNF). Indeed such nanocellulose are very good reinforcing materials and could also help in barrier properties. One drawback is their compatibility with classic polymer matrices used in packaging. The aim of this work is to functionalize CNC for the design of new active packaging.

Firstly, CNC are modified with the esterification SolReaect process, in order to introduce reactive ethylene oxides at their surface. Chemical grafting is proved by direct methods (FTIR, NMR, Elemental Analysis). Secondly, these modified CNC are grafted from with Polyy(glycidyl methacrylate) (PGMA), in order to improve their compatibility in a poly(lactic acid) (PLA) matrix. Moreover, in order to understand the influence of the degree of polymerization (DP) of PGMA, two polymerizations with two different DP of PGMA have been carried out. Finally, polymerized CNC are characterized by FTIR, size exclusion chromatography, TEM and contact angle. Their
compatibility is studied after their incorporation in PLA films. Proofs of the different graftings and polymerizations have been highlighted and such biomaterials have been successfully designed for developing new active packaging.

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Modification of cellulose nanocrystals with semiconducting polymers

Allen Chang, Sandra Chen, Kenneth R. Carter, krcarter@polysci.umass.edu, Department of Polymer Science and Engineering, University of Massachusetts - Amherst, Amherst, Massachusetts, United States

Cellulose nanocrystals (CNCs) were grafted with semiconducting poly (2-ethylhexyl-9,9-dihexylfluorene) via Sonogashira cross-coupling chemistry to yield composite nanoparticles. CNCs were first surface functionalized with 4-bromobenzyl chloride to provide any halide anchors for Sonogashira cross-coupling. Using a graft-thru polymerization, the bromide functionalized CNCs (s-Br-CNCs) were reacted with 2-bromo-7-acylene-9,9-dihexylfluorene monomers using a (PPh3)2PdCl2 catalyst to yield grafted poly2-ethylhexyl-9,9-dihexylfluorene) CNC (g-PeF-CNC). The intermediate product, s-Br-CNC, was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) to validate the success of the esterification reaction and approximate the degree of substitution. The grafted product, g-PeF-CNC, was analyzed using XPS, showing the expected trends in C1s deconvolutions with addition of solely carbon based polymer. Grafted chains were cleaved via acid hydrolysis and further analyzed by Matrix Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry (MALDI-ToF MS), not only providing evidence of oligomer formation and quantifying the approximate degree of polymerization for the growing chains, but also allowing us to assign end groups and compare grafted chains to free solution polymerized PEF side product.

Scheme 1. General synthesis pathway starting from stock CNC to bromo-benzyl substituted CNC (s-Br-CNC) (1) after polymerization the g-PeF-CNC product (2).

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Intelligent paper: Printed electronics on advanced cellulose nanomaterials

Bernard Kippelen, bernard.kippelen@ece.gatech.edu, Georgia Tech, Atlanta, Georgia, United States

Smart packaging is a growing market in which innovations are enabled by the emerging field of printed electronics; yet, the surface roughness of conventional paper has proven to be a challenge. Here, we discuss how specialty papers based on advanced nanocellulose nanomaterials can provide a solution to directly print the thin organic semiconductor layers that form the basis of functional building blocks such as organic transistors, light-emitting diodes and power harvesting devices. In particular, we will report on top-gate organic field-effect transistors (OFETs) fabricated on specialty paper, coated with a buffer layer composed of a polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) blend. OFETs operate at low voltages and display average carrier mobility values of 0.2 cm²/Vs, defining the state-of-the-art. We will also present organic solar cells fabricated on cellulose nanocrystalline substrates that yield power conversion efficiencies of 4%.

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Nanocellulose based energy storage devices

Zhaoxi Wang1, Petter Tammela2, Maria Strömme2, Leif Nyholm2, Leif.Nyholm@kemi.uu.se, (1) Department of Chemistry - Ångström Laboratory, Uppsala University, Uppsala, Sweden (2) Department of Engineering Science, Uppsala University, Uppsala, Sweden

There is currently a strong need for the development of inexpensive, flexible, light-weight and environmentally friendly energy storage devices. This has led to the development of a range of new cellulose-based electrode materials, batteries and supercapacitors. In this presentation it will be demonstrated that flexible nanocellulose and polypyrrole composites, manufactured by chemical polymerization of pyrrole on a nanocellulose substrate, can be used as electrodes in water-based charge storage devices [1-3]. The latter paper-based devices exhibit both high charge storage capacities and excellent power capabilities due to the combination of the large surface area (up to 260 m²/g) of the nanocellulose and the thin (i.e. 50 nm) layer of polypyrrole on the nanocellulose fibres. The composite synthesis method and the electrochemical properties of the composites will be discussed, as well as the possibilities of using polypyrrole coated nanocellulose fibres in the manufacturing of free-standing, high active mass paper electrodes [4-8]. With the latter approach, devices with unprecedented cell area capacitances at high current densities during thousands of cycles in aqueous solutions can be readily realised. As the cellulose composites also can be used in lithium-ion batteries [9,10] they provide new exciting possibilities for the development of green and foldable devices for a range of novel applications, many of which are incompatible with conventional batteries and supercapacitors.
Small-angle neutron and x-ray scattering (SANS and SAXS) offer versatile tools for characterizing the structure of wood and other cellulose-based materials. The methods cover a spatial range roughly from 1 to 500 nm, thereby extending over multiple levels of wood's hierarchical structure. They are sensitive to the lateral dimensions and packing of cellulose microfibrils, as well as the presence of water in the nanoscale structure of wood. A major bottleneck for wider applicability of small-angle scattering in wood-related studies is the challenging data analysis, which is necessary to obtain quantitative results from the scattering data. As efficient x-ray and neutron sources are becoming increasingly available to non-specialist users, the development of a widely-applicable small-angle scattering data analysis method for wood and other plant cell wall materials is highly desired.

We used SANS and synchrotron-SAXS to characterize the nanoscale structure of Northern European wood species and developed an analytical model to interpret the data. The model is based on hexagonally packed cylinders and yields realistic numerical values for the microfibril diameter (2.6-2.9 nm) and their packing distance (3-4 nm in wet state). The capabilities of the method were demonstrated with never-dried and air-dried wood samples as well as in situ SAXS measurement during drying. The model produced good agreement between SANS and SAXS data and reflected well the moisture-dependent changes in wood nanostructure even on a limited scattering vector range and using fitting in batch mode. In particular, the packing distance of the microfibrils decreased from 3-4 nm to below 3 nm during drying in room air. The presentation will discuss the potential of small-angle scattering methods in structural studies of wood and other cellulose materials, highlighting the role of a proper analytical model that would enable high-throughput characterization of wood and cellulose nanostructure for various applications.

**CELL 42**

In situ measurement of cellulose biosynthesis using small angle X-ray scattering

Hirotsuka Tajima, Paavo A. Penttilä, Kyoko Yamamoto, Yoshiki Yaguchi, Junji Sugiyama, Tomoya Imai, timar1@ishir.kyoto-u.ac.jp. (1) Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto, Japan (2) Institute Laue-Langevin, Grenoble, France (3) Osaka Electro-Communications University, Neyagawa, Osaka, Japan (4) Nanjing Forestry University, Nanjing, China

Cellulose synthase is an interesting enzyme because its product is an assembly of many polymer molecules – microfibril. Then this enzyme has molecular assembly mechanisms in addition to glycogen/transferase activity to polymerize glucose residues. Our group has attempted to produce cellulose microfibril with crystallographic cellulose I polymorph in order to clarify the molecular assembly mechanism of cellulose synthase. However, cellulose II aggregation is the product of our in vitro cellulose synthase with bacterial enzyme. While several reports have recently demonstrated cellulose microfibril formation in vitro with plant cellulose synthase, in this study, we aimed to understand cellulose II aggregation process by in situ measurement of in vitro cellulose synthesis using time-resolved small angle X-ray scattering (SAXS).

Crude enzyme of cellulose synthase was extracted from Komagataeibacter xylinus ATCC35524 (formerly Acetobacter xylinus) by solubilizing membrane fraction with detergent, deoxy-β-d-maltoside or deoxy-β-d-maltoside. In vitro synthesis of cellulose with the obtained enzyme preparation was conducted in a liquid cell with quartz plate window (light path = 3 mm) for in situ SAXS measurement. The time-resolved SAXS measurement was made with a wavelength of 0.1 nm every 4 – 5 min at 28°C, at BL40B2 in Spring-8, Japan. Two-dimensional scattering pattern was azimuthally integrated to have 1-D scattering profile with absorbance correction. An increase of intensity was observed specifically for the reaction with c-di-GMP, the activator of bacterial cellulose synthesis. Given that the purified cellulose product showed a significant scattering in the corresponding q-range, the gradual increase of intensity is due to accumulation of cellulose molecules during the in vitro reaction. However, a scattering in a lower q-region slightly increased even in the absence of c-di-GMP. This increase was partly suppressed in the reaction with G1,2-D (glycerol, which has been reported to inhibit the protein aggregation by X-ray radiation damage. Then the increased scattering in this lower q could be partly derived from protein aggregates in addition to cellulose accumulation. Compiling the data, the increase of scattering intensity during the reaction of our in vitro system appears to be monotonic in a q-range measured in this study. It is interesting to analyze the temporal development of SAXS feature of other in vitro systems for comparison.

**CELL 43**

Characterization of electrospun nanofibers composed of water soluble xylans

Jiuliang Duan, Muzaffar Karasash, Mi-Jung Cho, Li-Yang Liu, Amanda M. Johnson, Scott Renneckar, scott.renneckar@ubc.ca. (1) Department of Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) College of Materials Science and Technology, Beijing Forestry University, Beijing, China

Isolated hetero-poly saccharides such as xylan have a complex structure that have different degrees of branching, substitutions, and molecular weight. The content is based on species, isolation method, and post-treatment such as bleaching. These features provided complexity with working with xylan impacting properties such as solubility and utilization. In this study, water-soluble xylan extracted from the cell wall of wheat straw was characterized and subsequently mixed with polyethylene oxide (PEO) and electrospun into nanofibers. Ratio of xylan to PEO, mixing procedure, total polymer solution concentration, and electrosprinning parameters such as voltage and distance were used to spin xylan nanofibers that contained broad-free morphology with average diameters between 167 nm to 634 nm, dependent upon solution concentration. Fourier transform infrared spectroscopy and differential scanning calorimetry were used to characterize the interactions of the blends of xylan and PEO and the glass transition temperature of PEO was impacted by the addition of xylan to the system. Overall the study provided a novel route for the production of nanofibers of xylan from aqueous systems.

**CELL 44**

Frequency filtered molecular dynamics trajectory compared with crystallographic temperature factor in highly crystalline chitin

Yu Ogawa, ayogwa@gmail.com, Yoshinari Nishiyama, Karim Mazeau, (1) CERMAV, Grenoble, France (2) CNRS, Grenoble Cedex 9, France (3) Cermav, CNRS, Grenoble, France (4) Department of Chemistry, University of Cambridge, Cambridge, United Kingdom

Molecular dynamics (MD) simulation is widely used to investigate structures and properties of materials at molecular and atomic levels. Since the Newton’s law governs the atomic motions, the trajectory is expected to be an approximation of the real world. However, thermal motions obey quantum physics, and thus thermal-kinetic properties are not reproduced in the MD. For example, the modelled molar heat capacity is simply 3R at any temperature, (is the number of atoms and R the gas constant), though it is true only for ideal gases and not for condensed matters at around room temperature. Thermal vibration obeys the Bose-Einstein (B-E) statistics and high frequency vibration modes such as OH stretching are not excited at room temperature. In classical MD simulation, there is no such control of phonon energy distribution, and thus, typically the high-energy OH and CH stretching vibration amplitudes are far overrepresented. In this study we showed that realistic vibrations at given temperatures can be estimated by frequency filtering according to the B-E distribution. The MD trajectory of chitin crystals was post-processed to analyze its thermal behaviour according to a frequency cut-off. The filtered thermal atomic displacements were in good agreement with that of X-ray crystallographic analysis.

**CELL 45**

Visualization of freeze-fixed distribution of monoglucosyl disaccharides in plants

Dan Aoki, Yasuyuki Matsushita, Kazuhiko Fukushima, kazug@agr.nagoya-u.ac.jp, Nagoya University, Nagoya, Japan

Lignification is an important differentiation process in plant cell walls in which lignin is deposited in the polysaccharide matrix. The regulating mechanism of lignin biosynthesis is still controversial. In this study, cryo-time-of-flight secondary ion mass spectrometry (cryo-TOF-SIMS) was used to investigate the tissue and cellular distribution of chemical compounds related to the lignification process. The major targets are monoglucosyl disaccharides, coniferyl (coniferyl) alcohol glucoside and syringyl (syringyl alcohol glucoside). Monoglucosyl disaccharides are the promising candidates of a lignin precursor but their actual distribution in living plants were unclear because of their water-solubility. The samples were quick-frozen and the freeze-fixed distributions of the target chemicals were visualized by cryo-TOF-SIMS analyses. Target chemicals were quantified by HPLC measurements. The localization stage of the cells was confirmed by microscopic observations using visible, polarized, and UV light. Cryo-TOF-SIMS images were obtained for the transverse and radial surface of freeze-fixed stem of Ginkgo biloba. G. biloba is an old gymnosperm having guaiacyl lignin. Coniferin distribution visualized at the transverse and radial surfaces of freeze-fixed stem of G. biloba suggested that coniferin was stored in the vacuoles, and showed good agreement with the assaignment timing of coniferin to lignin in differentiating xylem. Consequently, it is suggested that coniferin is stored in the trachidal cells of differentiating xylem and is a lignin precursor. Syringa vulgaris is an angiosperm. The lignin structure consists of guaiacyl and syringyl units. A series of measurements using cryo-TOF-SIMS/SEM, HPLC microscopy was conducted for the freeze-fixed stem of S. vulgaris. Syringin was detected in bark strongly and also distributed at the differentiating xylem region. As a conclusion, syringin in S. vulgaris should have several uses and one of them should be a lignin precursor.

**CELL 46**

Chromophores from hexenuronic acids (HexA) – identification of structures, formation mechanisms, and destruction by peroxide bleaching

Thomas Roseau, thomas.roseau@boku.ac.at, Anthe Potthast, Takashi Hosoya, Nele Zwirchmayr, Thomas Deitl, (2) Dept. of Chemistry, BOKU University Vienna, Vienna, Austria (3) Ecrion, Hanau, Germany

Hexenuronic acids (HexA) have been known for long as triggers for discoloration processes in gluconoxylan-containing cellulose pulps, but the chemical structure of the actual chromophoric compounds have remained elusive. HexA is formed under the conditions of pulping from 4-O-
methylglucuronic acid residues, and are removed in an 'A stage' along the bleaching sequences, which mainly comprises acidic washing treatments. The chemical structures of HexA-derived chromophoric compounds, which make up for 90% of the HexA-derived chromophores, have been clarified by means of isotopic labeling (\(^{13}C\)) in combination with NMR spectroscopy and mass spectrometry. The labeled HexA model units carried a \(^{13}C\) label at either of the six carbon atoms. Final structure confirmation was provided by X-ray structure analysis. The HexA-derived chromophores compounds are ladder-type, mixed quinoid-like oligomers of the bisfuraranos-[1,4]-benzoquinone and bisbenzofuranos-[1,4]-benzoquinone type. The same chromophoric compounds are generated independently of the starting material, which can be either HexA in pulp or also HexA model compounds. These results disprove the frequent assumption that HexA-derived or furfural-derived chromophores are linear furanoid polymers, and might have a direct bearing on structure elucidation studies of "humins", which are formed as dark-colored byproducts in depolymerization of pentoses and hexoses in different biorefinery scenarios. The HexA-derived chromophores were subject to conditions of peroxide bleaching. They are degraded relatively fast to one major product, 2,5-dihydroxy-[1,4]-benzoquinone (DHBQ), and a minor component, 2,5-dihydroxycyclohexophenone (DHA). These two compounds, which have already been identified as two of the three key chromophores (besides 5,8-dihydroxy-[1,4]-naphthoquinone, DHNO) in aged cellulosics, are potent chromophores themselves and are subsequently more slowly degraded to non-colored degradation products. The occurrence of DHBQ and DHA in the bleaching treatment of the HexA-derived chromophores establishes the link between HexA chemistry and the three general key chromophoric classes of residual chromophores found in aged cellulosic materials.

**CELL 47**

**Desorption behavior of guest molecule from cellulose I-EDA complex crystals: Molecular dynamics study**

Toshifumi Yui*, tyui@cc.miyazaki-u.ac.jp, Takuya Uto1, (1) Faculty of Engineering, University of Miyazaki, Miyazaki, Miyazaki, Japan (2) Graduate school of Science and Engineering, Kagoshima University, Kagoshima, Kagoshima, Japan

It has been known that cellulose I fibers swell on exposure to ethylene diamine (EDA) as the amine molecules penetrate into the cellulose crystals, which forms a cellulose-EDA crystalline complex. Following treatment of the complex with polar solvent leads it to, through desorption of the EDA molecules, re-arrangement of cellulose chains to form another crystalline allomorph called cellulose III. In the present study, the molecular dynamics (MD) calculations of the cellulose I-EDA complex models were carried out in solution state at either 300 K or 370 K for 200 ns. The three complex crystal models were built based on the X-ray crystallographic data. It was observed that the EDA molecules involved in the crystal surface were quickly desorbed from the surface, which was accompanied by penetration of water molecules. While an EDA molecule migrated through the EDA channel consisting of the cellulose chain sheets, the EDA molecule often changed its orientation and conformation (see Fig. 1). The EDA molecules belonging to the surface, or the first layers and to the second layers were only allowed to desorb from the complex crystals during the 200 ns simulation time. In order to observe migration and desorption of EDA molecules from the inner layers, the enhanced sampling techniques of MD were adopted to the complex models.

**Fig. 1 Migration of an EDA molecule between cellulose chains sheets.**

**CELL 48**

**Atomic level structure characterization of carbohydrate pre and post lignin treatment by dynamic nuclear polarization: Enhanced solid state NMR**

Hao Luo, luoha08905@gmail.com. UCSB, Goleta, California, United States

Lignocellulosic biomass is a promising sustainable feedstock for the production of biofuels, biomaterials, and biospecially chemicals. Unfortunately, the molecular level structure of biomass was poorly understood, due to its rigid and compact structure. The crystallinity of cellulose and its crosslinking with lignin renders it particularly resilient to biodegradation. In this study, lignin was removed effectively by using an abundant metal catalyst through catalytic depolymerization of lignin (CDL) process.

The remaining carbohydrates was then subjected to structure study as well as further catalytic conversion. Dynamic Nuclear Polarization (DNP) Enhanced Solid State NMR and XRD study on post CDL treated cellulose indicated that the CDL process was highly selective for the removal of lignin, while the structure of remaining carbohydrates remained intact. Comparison of post CDL treated cellulose. Catalytic conversion of post CDL treated carbohydrates with iron chloride gave higher yields of platform chemicals (furfural and levulinic acid), compared with raw biomass. Enzymatic hydrolysis comparison were performed using Celli™ Clett2, which indicated that cellulose is largely inaccessible in raw biomass, due to the crosslinking with lignin. However, the enzymatic hydrolysis yields on post CDL treated cellulose increased significantly.

**New Horizons in Sustainable Materials**

**CELL 49**

**Toward carbon fibers from single component Kraft lignin systems: An application of green chemistry with forest biomaterials**

Shradha V. Patil1, Shradha@vit.edu, Hasan Sadeghifar1, Sanghamitra Sen1, Dimitris Argyropoulos1,2, (1) Forest Biomaterials, NC State University, Durham, North Carolina, United States (2) Chemistry, North Carolina State University, Raleigh, North Carolina, United States

Carbon fibers represent a class of materials with enormous potential for many material and other engineering applications for our society. There are projections that by 2020 the actual demand for carbon fibers will be such that the traditional poly-acrylonitrile precursors used today will not be enough to address the projected demand. Consequently, it is imperative that new precursors based on the foundations of Green Chemistry need be developed. Technical lignins present us with formidable challenges but also with enormous opportunities and they are to be explored in detail during this presentation. In our earlier effort, we have embarked in discussing the importance of propargylation chemistry on lignin to synthesize lignin macromonomers for thermal polymerization via Claisen rearrangement. We have also discussed that molecular weight and glass transition temperatures of the thermally polymerized lignin improves significantly. The intricate polymer structure created within lignin as a result of the benzoxynan thermal polymerization chemistry (see Scheme 1) is offering a regular covalently linked framework from which, after carbonization, a carbon fiber material could be produced. As such, thermally polymerized propargylated softwood lignin emerges as a prospective material for the synthesis of bio-based Carbon Fiber precursor. Various reactivity considerations were addressed by a series of experiments where initially Acetone Soluble Kraft Lignin (ASKL) was propargylated, thus occupying readily accessible and highly reactive phenolic-OH’s, followed by methylation of the remaining phenolic OH’s to limit phenoxyl radical induced thermal polymerization. As anticipated, the installation of the propargyl groups in more reactive positions, more readily prone to Claisen rearrangement and thermal polymerization events, offered much better developed molecular weights able to offer Carbon Fibers.

**New Horizons in Sustainable Materials**
Clicking lignin towards functional renewable materials

Youssef Habibi, Youssef.Habibi@list.lu. Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette, Luxembourg

Lignin is after cellulose the second most abundant biopolymer in the biosphere, and the main polymer based on aromatic units. 50 million tons of lignin are generated every year mainly from wood pulp in the form of sulfonated lignin, but only 2% of this production is used as filler in plastics, as dispersants or for the synthesis of vanillin and DMSO; the remaining is used as energy source. The main limitation to its use as chemical building block is the high content of sulphur moieties, associated with the traditional extraction processes, which impede its reactivity. However, with the emergence sulphur free-lignin classes, there is a renewed interest in exploring the potential of this natural polymer, through its conversion by various chemical pathways, toward the production of chemical, additives, fillers, different classes of polymeric materials for a wide range of applications [1-3]. This presentation will provide our recent work in converting lignin into functional polymers. An emphasis will be giving to sustainable green chemistries we have developed recently by using click chemistry. Indeed, different synthetic strategies have been applied to introduce new chemical groups to produce lignin derivatives suitable for “thiolene” click polymers in order to produce new functional polymeric materials. These new materials exhibit interesting properties not only in term of thermal and mechanical properties but also in term of processability and healing, which open new horizons for this unexplored renewable feedstock.

Gelatin hydrogel actuators

Laura Hanzy. lhanzy@vt.edu, Justin R. Barone. (1) Biological Systems Engineering, Center for Soft Matter and Biological Physics, and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Biological Systems Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Soft actuators could be made into robots or sensors that are flexible and adaptable. Here, water-sensitive actuators are created using simple gelatin hydrogels. Gelatin hydrogels can be crosslinked to various degrees with glutaraldehyde. As gelatin crosslink density increases, gel stiffness increases and swelling in water decreases. Forming gelatin hydrogel bilayers with layers of differing crosslink density results in a gelatin soft film that bends when swollen in water and relaxes when dried. The extent of bilayer bending is dependent upon layer thickness and the difference between layer crosslink densities. The mechanical properties of the gelatin bilayers are quantified using rheology, swelling, and the extent of bending.

Interactions at biopolymer blend thin films

Katrin Niegelhell, katrin.niegelhell@student.tugraz.at, Michael Süssensbacher, Jürgen Sattekow, Kai Zhang, Harald Plank, Tamilselvan Mohan, Stefan Spirko, Stefan.Spirko@tugraz.at. (1) Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz (2) Institute for the Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria (3) University of Maribor, Maribor, Slovenia (4) Institute for Paper-, Pulp- and Fibre Technology, Graz University of Technology, Graz, Austria (5) Institute for Electron Microscopy and Nanoscopy, Graz University of Technology, Graz, Austria (6) Wood Technology and Wood Chemistry, Georg-August University Göttingen, Göttingen, Germany

In this contribution, we present the fabrication of various phase separated cellulose-based blend thin films. Mixtures of trimethylsilyl cellulose and poly-3-hydroxybutyrate or different lignocellulosic esters were dissolved in chloroform and films were formed via spin coating followed by regeneration of trimethylsilyl cellulose to cellulose. The resulting films were characterized by means of infrared spectroscopy, contact angle analysis and profilometry. Atomic force microscopy images reveal similar phase separation behavior for all types of blends. In this case, phase separation followed by enzymatic treatment was exploited to achieve positive and negative type patterned thin films displaying features from the nano to the micron size range.

Electron Microscopy and Nanoscopy, Graz University of Technology, Graz, Austria (6) Wood Technology and Wood Chemistry, Georg-August University Göttingen, Göttingen, Germany

Bacterial NanoCellulose: closer to the market

Miguel Gama, mgama@deib.unimo.it, Fernando Dourado. (1) Minho University, Braga, Portugal (2) Satisfabre, Braga, Portugal

This work aimed at the optimization of bacterial nanocellulose (BNC) production by static culture, using Gluconacetobacter xylinus BPR 2001. Several parameters were considered such as the composition, surface area and depth of the culture media and the duration of the fermentation. Response Surface Methodology - central composite design was used to evaluate the effect of nutrients on the BNC production yield. The maximum yield and BNC productivity were 7.5 ± 0.62 g/L and 0.035 g/L/h, respectively, after 9 days of static culture fermentation, at 30°C. BNC dry mass production increased with the surface area, and with the media volume (depth) and fermentation time. The results show that a high BNC production yield can be obtained by static culture of Gluconacetobacter xylinus BPR 2001 using a low-cost medium. These are thus promising conditions for the industrial scale BNC production, since as compared to agitated bioreactors, higher productivities may be reached, while avoiding costs and operational issues. This presentation will further review the main efforts towards the production of BNC at large scale. It will present an historical record of the main companies and current ones. Finally, it will show some techno-economical data on a novel BNC large-scale fermentation developed by the research team at the University of Minho. This technology has been licensed to a company Satisfabre, S.A. (Portugal), which is currently operating at pilot scale. Finally, an overview on the efforts of Satisfabre towards the commercialization of this biopolymer and its applications will be presented.

Highly porous and highly permeable bacterial cellulose nanopaper as reinforcement for polymers

Alba Santmarti, Maria Hery, Andreas Mautner, Anett Kondor, Alexander Bisemar, Koon-Yang Lee, koonyang.lee@imperial.ac.uk. (1) Aeronautics, Imperial College London, London, United Kingdom (2) Aeronautics, Imperial College London, London, United Kingdom (3) Department of Chemical Engineering, Imperial College London, London, United Kingdom (4) Department of Aeronautics, Imperial College London, London, United Kingdom (5) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (6) Surface Measurement Systems, London, United Kingdom

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 produced 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 acrylic epoxidised soybean oil (AESO). The mechanical properties and architecture of the composites varied depending on the porosity degree of the nanopapers.
Length distributions of nanofibrillated celluloses can be evaluated by rheological measurements of their dispersions. We have experimentally addressed this concept of glycan processing and followed the time microheterogeneity of N-glycans in a species-specific manner. The ER and Golgi cisternae is necessary to provide the high concentration of processing enzymes that can act only for a short time on secreted substrates. Antibodies have been developed as therapeutic agents for the treatment of cancer, infection, and inflammation. In addition to binding activity toward the target, IgG antibodies also modulate the effector functions through the interaction of the fine structures of Fc N-glycans and the Fc receptors on immune cells. It has been demonstrated that antibodies lacking core fucosylation show a large increase in affinity for FcγRIIA leading to an improved receptor-mediated effector function, antibody-mediated cellular cytotoxicity (ADCC). Terminal alpha-2,6-sialylation of Fc glycan was speculated to play a critical role for the anti-inflammatory activity of human intravenous immunoglobulin (IVIG). To identify the optimal glycan structures for individual antibodies with desired activity, we have developed an effective method using new glycosynthase mutants to efficiently transfer predefined N-glycans oxazolines to the Fc-deglycosylated intact IgGs to furnish a homogeneous glycoform. In this study, we found that the biantennary N-glycan structure with two terminal alpha-2,6-linked sialic acids is a common and optimized structure for the enhancement of antibody-dependent cell-mediated cytotoxicity, complement-dependent cytotoxicity (CDC), and anti-inflammatory activities.

**CELL 55**

Homogeneous N-glycoprotein containing a common glycan structure for the improvement of antibody-based therapeutics

**CELL 56**

Nanocellulose for nanotechnologies

**CELL 57**

Concepts of N-linked protein glycosylation

**CELL 58**

Regioselective derivatizations of E. coli chondroitin polysaccharide through tailored multi-step procedures

**CELL 59**

Systematic synthesis of glycosaminoglycan oligosaccharides

**CELL 60**

Frontiers in Glycoscience, Bridging the Gap Between Carbohydrate & Polysaccharide Chemistrys

**CELL 61**

Regioselective derivatizations of E. coli chondroitin polysaccharide through tailored multi-step procedures

**Emiliano Bedini**, ebedinij@unina.it. Department of Chemical Sciences, Università degli Studi di Napoli Federico II, Napoli, Italy

By comparison with monosaccharides, the development of reliable methods for well-defined structural modifications of polysaccharides falls far behind. This is due to several factors: i) the generally poor solubility of many polysaccharides in several solvents; ii) the difficulties in achieving (regioselective) derivatizations of the hydroxy position(s) in each subunit of the polymer chain; iii) the necessity to avoid harsh reaction conditions that might alter the polysaccharide structure by breaking glycosidic linkages and/or the decorations (sulfates, acetamides, acetics etc.); iv) the potential present on the polymer; iv) the difficulties encountered in elucidating in full detail the structural features of polysaccharides and derivatives thereof.

In this communication it is shown how these limitations were faced in the case of a chondroitin polysaccharide derived from fed-batch fermentation of *Escherichia coli* K4. Indeed, it was successfully regioselectively sulfated and/or fucosylated to give a number of (fucosylated) chondroitin (sulfate) derivatives with structure and properties often very close to animal-derived polysaccharides of high biomedical value (Figure 1). Special attention is devoted to the role – sometimes quite peculiar – played in such polysaccharide transformations by protecting groups usually employed in mono- and oligosaccharide synthesis.
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Propelling chemically modified glycosaminoglycans into the clinic

Glenn D. Prestwich1,2, gprestwich@pharm.utah.edu. (1) Medicinal Chemistry, University of Utah, Salt Lake City, Utah, United States (2) Symic Bio, Inc. Emeryville, California, United States

Glycosaminoglycans (GAGs) are ubiquitous, complex, and essential components of the extracellular matrix, and have been used therapeutically for years. The focus of this talk is chemically modified GAGs, several of which are in clinical development for regenerative and reparative medicine, including wound healing, adhesion prevention, cell therapy, reduction of inflammation, and mitigation of vascular disease. To fulfill the imperative of translational medicine imperative, laboratory-scale biomaterials developed in university settings have now reached veterinary and human patients. Several examples of this bench to business to bedside paradigm will be presented for companies at different stages.

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Protection-free direct anomeric activation for key glycosyl intermediates

Shin-Ichiro Shoda, shoda@poly.chetyohoku.ac.jp, Masato Noguchi, Gefeii Li, Tohoku University, Sendai, Japan

A novel method for the activation of anomeric position has been developed by using formamidinium reagents. Several important synthetic intermediates, sugar oxazolines, glycosyl azides, thio glycosides, and 1,6-anhydro sugars, were prepared directly from the corresponding unprotected sugar in good yields. The new method possesses the following merits.

- No need to protect the hydroxy groups
- The reaction can be carried out in aqueous media.
- Applicable to oligosaccharides
- Applicable to saccharides having a carboxylic acid, a sulfuric acid, and a phosphoric acid
- One-pot chemo-enzymatic glycosylation has become possible by using this method.

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Understanding and engineering the deacetylation pattern of chitin deacetylases

Antoni Planas, antoni.planas@iics.edu. Bioengineering Department, Institut Quimic de Sarrie, University Ramon Llull, Barcelona, Spain

Chitin processing, mainly in the form of depolymerization and de-N-acetylation reactions by chitin-modifying enzymes (chitinases and deacetylases), generates a series of derivatives including chitosan and chitosan-oligosaccharides (COS), which play remarkable roles in multiple fields. COS are particularly involved in molecular recognition events, including the modulation of cell signaling and morphogenesis, the immune response, and host-pathogen interactions. Chitosans are also attractive target materials for the development of biomaterials for drug delivery and tissue engineering applications. Most of the biological activities associated with COS seem to be largely dependent not only on the degree of polymerization but also on the acetylation pattern, which defines the charge density and the distribution of GlcNaC and GlcNH₂ moieties in chitosans and COS. Chitin de-N-acetylates (CDAs) catalyze the hydrolysis of the acetylom group in GlcNaC residues of chitin, chitosan, and COS. The deacetylation pattern exhibited by CDAs and related chitosan deacetylases (CE4) enzymes active on COS is diverse, some being specific for a single position, others showing multiple attack. A major challenge is to understand how CDAs specifically define the distribution of GlcNaC and GlcNH₂ moieties in the oligomeric chain. By means of structural and bioinformatic studies, we have proposed a subunit caging model, which proposes that substrate specificity is governed by a series of variable and flexible loops that shape the binding cleft of CE4 enzymes.

Based on structural and bioinformatics analyses, here we will report the characterization of CE4 enzymes active of chitoogiosaccharides and the engineering of loops by enzyme engineering approaches (rational and directed evolution) towards the production of pGCGS with defined and novel deacetylation patterns.

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Pectins - are they polysaccharides, proteoglycans, glycan domains of multi-glycan polymers, or all three? Evidence from studies of pectic homogalacturonan biosynthetic galacturonosyltransferases and mutants/transgenics thereof

Debra Mohonen1, dmohonen@ccrc.uga.edu, Melani A. Atmodjo1, Ajaya K. Biswal1, Li Tan1, Kristen Engle2, Robert A. Amos1. (1) Complex Carbohydrate Research Center, Department of Biochemistry and Molecular Biology, University of Georgia, Athens, Georgia, United States (2) Complex Carbohydrate Research Center, Plant Biology, University of Georgia, Athens, Georgia, United States

Each year more than 100 billion tons of carbon dioxide are fixed via photosynthesis into plant biomass, a renewable resource for production of chemicals, fuels, clothing, wood products, nanocomposites, food fiber, gelling/stabilizing agents and nutraceuticals/ pharmaceuticals. Plant cell walls are the bulk of plant biomass. Hundreds of millions of years of biotic and abiotic challenge have led plants to evolve complex cell walls that provide longevity spanning thousands of years and mechanical strength supporting 90 meter tall trees. These strikings structural and physical properties arise from the fine structure of individual wall polymers, the covalent and non-covalent interactions between them, and their architectural arrangement in each cell type. Among the three cell wall polysaccharides, cellulose, hemicellulose and pectin, pectin is the most complex. A detailed understanding of the structure of plant cell walls across species and cell types is essential for effective and innovative development of plant biomass in a bio-based economy.

The pectic polysaccharides, homogalacturonan (HG), rhamnogalacturonan I (RGI-) and rhamnogalacturonan II (RG-II), are defined as a family of glycans containing galacturonic acid linked at the 1- and 4- positions. Among these glycans, HG is the most abundant. HG is a partially methyl esterified and acetylated homopolymer of alpha-1,4-linked D-galacturonic acid synthesized by the GAUT gene family of proven and putative HG:alpha1,4-galacturonosyltransferases (HG:GaATs). In efforts to generate plant biomass 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, and improves plant agronomic performance. The results of studies aimed at identifying the specific wall polymer(s) affected in different GAUT transgenics/mutants, and studies to understand the mechanism(s) for improved wall recalcitrance and agronomic properties, lead us to propose that specific GAUT’s synthesize specific HG glycans that are incorporated into unique polysaccharides and proteoglycans with unique roles in the wall. An in depth understanding of the specific pectin structures, their mechanical, biological properties and their chemical, biological properties are critical to enable effective use of biomass for energy, bioprocess and food production in a sustainable bioeconomy.

Assembly & Colloidal Interactions of Cellulose Nanocrystals

CELL 65

Probing assembling and aggregation of cellulose nanocrystals at the nanoscale using small angle scattering

Yinglei Lü1, Daniela Stoecek2, Komelia Gordeyeava3, Christina Schütz2, Andreas b. Fall1,2, andreas.fall@giis.ee, Lennart Bergström1. (1) Risø Bioeconomy, RISø, research institutes of sweden, Stockholm, Sweden (2) Stockholm University, Stockholm, Sweden

Nanoscaled structural evolution of aqueous cellulose nanocrystalline (CNC) dispersions during drying can be studied with high-resolution small angle scattering techniques, using both x-rays and neutrons, i.e. SANS and SANS. Both static and dynamic measurements can be used to follow
the process. Here it will be shown that the change in the self-assembled helical arrangement of CNC can be followed as well as the formation and formation of CNC aggregates. We also studied the structural evolution during redispersion upon the addition of water to dried CNC films. It was found that counterion exchanged CNC freely redispersed into a nanoscale assembly, closely resembling the state before drying.

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Cellulose-based multifunctional photonic structures

Giulia Guidetti,1,2 gg389@cam.ac.uk, Andre Espinha,3 Bruno Frika-Petesic,1 Shiam Aibi,4 Maria C. Semano,5 Abu G. Dumanli,6 Alvano Blanco,3 Wadood Y. Hamad,7 Celie Lopez,3 Silvia Vignolini,1 (1) Chemistry, University of Cambridge, Cambridge, UK, United Kingdom (2) Instituto de Ciencia de Materiales de Madrid, Spain (3) Biomaterials Division, FPIInnovations, Vancouver, British Columbia, Canada (4) Hospital Nacional de Parapléjicos, Servicio de Salud de Castilla La Mancha, Toledo, Spain

The brightest colours in nature are not from pigmentation but they originate from structural coloration, the interaction of light with nanostructured materials. Such structural colorations are widespread in nature, where both animals and plants, e.g. butterflies and tulips, account for many spectacular examples. In the context of plants, the structural colour originates from the assembly of cellulose fibres in helicoidal multilayers at the nanoscale.

Cellulose nanocrystals, isolated from plants and dispersed in water, can spontaneously self-assemble into structures that mimic the architectural organization, which produces structural colours in nature. This property enables the fabrication of solid indescent films, via drying of the cellulose aqueous mixture.

Biomimetic with cellulose-based architectures enables the fabrication of novel photonic structures using low cost materials at ambient conditions. Cellulose nanocrystals films displaying both tunable structural colour and mechanical properties can be obtained via the use of zwitterionic surfactants, thus allowing a widespread use of cellulose-based materials as bio-compatible spray colour coatings. Cellulose nanocrystal films integration with shape memory polymer lead to the fabrication of thermo-responsive biocompatible sensors, suitable for clinical applications.

In this talk the fabrication route of complex bio-mimetic cellulose-based photonic composites will be presented, their optical and mechanical properties will be analyzed and compared with the ones of the single components.

CELL 67

Bimodal cellulose nanocrystal blends for bioinspired damage tolerant photonic films

Bharath Natarajan1, bharath.nikke@gmail.com, Ajay Kishnamurthy2, Caglar D. Emingolgu3, Xin Qin4,5,6, Amanda Forsey,7,8,9, Douglas Far1, Johan Fostere,8, Christophe Wedere,1 Jan Orbruge,5, Sinan Keter1, Jeffrey W. Gilman2. (1) University of Fribourg, Adolphe Merkis Institut, Fribourg, Switzerland (2) American University, Washington, District of Columbia, United States (3) Physics, Georgetown University, Gaithersburg, Maryland, United States (4) MSL, Georgetown University/NIST, Gaithersburg, Maryland, United States (5) MS 8541, NIST, Gaithersburg, Maryland, United States (6) Virginia Tech, Blacksburg, Virginia, United States (7) National Institute of Standards and Technology, Gaithersburg, Maryland, United States (8) Northwestern University, Evanston, Illinois, United States

The twisted plywood or helicoidal structure is a commonly observed microstructural motif in biological composites that enables superior toughness via extrinsic toughening routes such as crack twisting, deflection, and arrest, as well as by the filtering of shear wave energies. These mechanisms have motivated numerous efforts to mimic helicoidal structures through top-down assembly or 3D printing. However, attempts to emulate strong and tough natural composites using wood cellulose nanocrystals (CNCs) fall short in mechanical performance due to the low shear transferability of CNC interfaces in their helicoidal ensembles. This shortcoming is ascribed to the small CNC-CNC overlap lengths that minimize the cumulative interaction strengths. In this presentation, we will demonstrate a simple green strategy to fabricate superior helicoidal CNC films with properties that rival those of the best natural materials. Assembling the wood CNCs (w-CNCs) with a minority fraction of large aspect ratio tuneable derived CNCs (h-CNCs), we report remarkable tunable enhancements in modulus, strength, ductility, and toughness. These mechanical properties (E = 20.2 GPa ± 0.9 GPa, ρ = 138 MPa ± 4.3 MPa and toughness = 1.09 MJ/m² ± 0.01 MJ/m²), which are the best reported for photonic CNC films thus far, rival those of gold-standard natural composites such as cortical bone, nacre, ivory and stomatopod clubs. Using scanning electron microscope-based fractography and multiscale simulations, we explain the observed enhancements to be due to increased effective overlap lengths (i.e., enhanced CNC-CNC interfaces) and the activation of additional toughening mechanisms such as bridging by the long CNCs. The effectiveness of this strategy and role of parameters such as long-CNC modulus and aspect ratio are evaluated by preparing a second set of bimodal mixtures using cellulose nanofibrils that are of lower modulus and crystallinity as compared to CNCs. All blended films with long-CNC contents greater than 5% by mass also display UV reflective behavior. We identify these films as excellent starting materials or scaffolds for biomimetic nanocomposite fabrication. As is, these damage tolerant optically active materials hold potential for application as protective coatings in the automobile, aerospace, electronics and infrastructure industries.

CELL 68

Controlling the diffraction of light by cellulose nanocrystal assemblies using electric or magnetic fields

Bruno Frika-Petesic1,2 bbf284@cam.ac.uk, Giulia Guidetti1, Gen Kamita3, Hantsoa Radoavision4, Bruno R. Jean5, Laurent Heur6, Silvia Vignolini1. (1) University of Cambridge, Cambridge, United Kingdom (2) CERMAV-CNRS, Grenoble Cedex 9, France

Cellulose nanocrystals (CNCs) are bio-sourced chiral nanorods that can form colloidal suspensions either in water or apolar solvents and spontaneously self-assemble above a critical concentration into a cholesteric liquid crystalline phase. Here, we utilize the orientational coupling of individual CNCs with external electric or magnetic fields in order to control the self-assembly over larger length scales. CNC cholesteric order is locally characterized by a helicoidal arrangement of the rods, with a characteristic periodicity usually in the range of few microns, allowing for light diffraction and iridescence when observed in transmission. First, we demonstrate that AC electric fields can dynamically tune both the alignment and the pitch of a cholesteric suspension of CNCs in apolar solvent (Figure a). Secondly, in order to improve the orientation on the macroscopic scale, we introduce the concept of fast or slow electric field annealing, whereby the cholesteric is reversibly unwound, to either randomize or uniformize the overall light diffracted by the cholesteric suspension. A key advantage of CNCs over molecular liquid crystals is their ability to retain their cholesteric order in the solid-state e.g. by slow drying. The produced films present much smaller, sub-micron periodicity, allowing for strong reflection of circularly left-polarized light. While the non-fading chiral photonic properties and bio-sourced origin of these films are relevant for cosmetics, food, security or aesthetics, their polymodal cholesteric structure on the macroscopic scale impedes our control over the resulting photonic properties. Taking advantage of the weak diamagnetic anisotropy of cellulose nanocrystals, we show that commercial magnets can improve the macroscopic orientation of the cholesteric phase in a slowly drying suspension. This technique improves the cholesteric uniformity and provides additional control over the tilt of the cholesteric domains, creating films with an unprecedented photonic response (Figure b).

Cellulose nanocrystals (CNCs) can form films and deposits with tunable optical properties. Inducing and light-diffacting properties can be reversibly obtained by depositing CNCs on a substrate and could be used in inkjet printing. The characteristics of the particle deposition process together with the self-assembly in the drying suspension has a direct effect on the optical properties of the obtained films. The particle deposition onto a substrate is directly affected by the
flow dynamics inside sessile droplets and usually yields a ring-shaped deposition pattern commonly referred to as the coffee-ring effect. In our work, we set out to measure and to understand the drying kinetics and the effect of the flow dynamics on the way the CNCs deposit. In this presentation I will discuss the insights we have gained as well as different approaches to manipulate and understand the internal flow dynamics leading the specific deposition patterns. We have been able to use the knowledge gained to obtain indescent films with a homogenous deposit without any coffee-ring effect.

CELL 70

Development of nanoparticle alignment regimes in drying cellulose nanocrystal droplet suspensions for additive manufacturing

Cailean Pritchard1, capritch@vt.edu, Fernando Navarro-Arzate2, Maren Roman3, Michael Bortner4. (1) Chemical Engineering, Virginia Polytechnic Institute and State University, Lexington, Virginia, United States (2) Department of Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (3) University of Guadalajara, Zapopan, Mexico

Microparticle formation of the cholesteric CNC suspension within a microdroplet. Upon evaporation, this helicoidal assembly of the CNCs deposit in a confined geometry, offering significant advantages over the conventional planar geometry. The pitch evolution allows for conversion to the solid state to produce buckled microparticles (Fig. C). By using a sustainable reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D printing. In order to control the quality of alignment during the 3D printing process, the printing pressure and the viscoelastic properties of the material have to be well characterized. After printing, the resulting part and its mechanical properties are determined in order to create composites with well-defined properties. By understanding the effect of the concentration of reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D objects with improved printability and mechanical properties were obtained. Our findings pave the way towards the fabrication of high-performance materials with renewable resources using a cost-effective additive manufacturing technique.

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Hierarchical self-assembly of cellulose in a confined geometry

Richard Parker, mmp53@cam.ac.uk, Bruno Fika-Petesic, Giulia Guidetti, Gen Kamita, Tianheng Zhao, Silvia Vignolini. University of Cambridge, Cambridge, United Kingdom

Microparticle formation of the cholesteric CNC suspension within a microdroplet. Upon evaporation, this helicoidal assembly of the CNCs deposit in a confined geometry, offering significant advantages over the conventional planar geometry. The pitch evolution allows for conversion to the solid state to produce buckled microparticles (Fig. C). By using a sustainable reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D printing. In order to control the quality of alignment during the 3D printing process, the printing pressure and the viscoelastic properties of the material have to be well characterized. After printing, the resulting part and its mechanical properties are determined in order to create composites with well-defined properties. By understanding the effect of the concentration of reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D objects with improved printability and mechanical properties were obtained. Our findings pave the way towards the fabrication of high-performance materials with renewable resources using a cost-effective additive manufacturing technique.

CELL 72

Rheology and application of cellulose nanocrystal inks for direct ink writing

Michael Hausmann1,2, michael.hausmann@empa.ch, Gilberto de Freitas Siqueira1,4, Rafael Libanori5, Dimitri Kokkinis4, Patrick Rühle3, Tanja Zimmermann1, André R. Studart1. (1) ETH Zurich, Zurich, Switzerland (2) Empa, Dübendorf, Switzerland (3) Applied Wood Materials, Empa, Dübendorf, Switzerland (4) Complex Materials, ETHZ, Zurich, Switzerland

Cellulose nanocrystal (CNC) is a bio-based and renewable material extracted from wood and algae or produced by bacteria. The alignment of CNCs is crucial for direction specific enhanced mechanical properties in composite applications. We utilize direct ink writing (DIW) to assemble complex cellulose-based geometries with controlled orientation and spatial distribution of nanocrystals within the printed structure. Using polarized imaging rheology we correlate the dynamic flow behavior of CNC-based inks with the quality of nanocrystal alignment occurring during 3D printing. In order to control the quality of alignment during the 3D printing process, the printing pressure and the viscoelastic properties of the material have to be well characterized. After printing, the resulting part and its mechanical properties are determined in order to create composites with well-defined properties. By understanding the effect of the concentration of reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D objects with improved printability and mechanical properties were obtained. Our findings pave the way towards the fabrication of high-performance materials with renewable resources using a cost-effective additive manufacturing technique.

CELL 73

Polydopamine assisted Cu NPs deposition on biomass substrates for flexible, wearable and self-cleaning electronics

Xiaohui Wang, fiewangh@scut.edu.cn, Yang Yang, Quanbo Huang. South China University of Technology, Guangzhou, China

Recent years have witnessed the booming development of flexible electronics. To date, it is still a great challenge to fabricate high conductive paper based electrodes with both low cost and high stability. Here we propose a novel, facile and versatile approach to fabricate the highly flexible and conductive papers, textiles and fibers by electroless deposition (ELD) of the copper nanoparticles with the assistance of polydopamine as the adhesion layer. Polydopamine plays the key role which not only assisted the electroless deposition of copper nanoparticles on the paper, but also enhanced the adhesion strength between metal nanoparticles and substrates. The obtained Cu NPs coated papers were highly conductive with a significant low resistance of 0.1 Ω sq-1 with ELD time for only 10 min and their mechanical stability performed very well. Notably, these conductive papers and textiles has the excellent hydrophobic and photothermal conversion properties which could be used as wearable and self-cleaning electronics. In a word, this low-costed method could be easily scaled up to large-scale fabrication of conductive papers and opened up new opportunities for flexible and wearable electronics.
Industrial textile dyeing technology is water intensive and produces large quantity of wastewater charged with contaminants. Particularly for cotton dyeing, it is highly desirable to reduce the use of salt and alkali that are indispensable to increase the utilization of reactive dye. We report a sustainable dyeing technology with nanocellulosic (NC) fibers that will decrease the amount of salt and alkali used in cotton dyeing by an order of magnitude. NC hydrogel produced by high-pressure homogenization is mixed with reactive dye molecules and dye auxiliaries, and the coloration of textile is completed by printing of NC dye mixture onto cotton fabric followed by thermal curing. NC-based dyeing exhibits comparable dyeing and colorfastness properties to conventional exhaust dyeing with the reduction of the use of salt and alkali by a factor of 10, which leads to the decrease in its effluent emission by a factor of 6 by a gate-to-gate life-cycle assessment. The large surface area (430 m$^2$/g) of NC fibers and their strong affinity to cotton fibers enable the described sustainable dyeing technology, which presents a potential of NC hydrogel as a versatile coating and a finishing material in textile applications.

CELL 75

Paper fines as renewable source for supercapacitor electrode materials

Mathias A. Hobisch$^{1,2}$,* mathias.hobisch@student.hbugas.at, Etelene Mourad$^{3}$, Wolfgang Fischer$^{4}$, Armin Zankel$^{5}$, Stefan Freunberger$^{6,}$, Renate Eichhorn$^{7}$, Wolfgang Bauer$^{8}$, Stefan Spirk$^{9,10}$, (1) Institute for the Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria (2) Institute for Paper, Pulp and Fiber Technology, TU Graz, Graz, Austria (3) Institute for Materials Chemistry & Research, University of Vienna, Vienna, Austria (4) Institute for Chemistry and Technology of Materials, TU Graz, Graz, Austria (5) Institute of Electron Microscopy and Nanoanalysis, TU Graz, Graz, Austria

In this contribution, we explore the use of fines for advanced energy applications. Fines are a major side stream in fiber manufacturing industries. Here, we present a strategy how to make use of fines as electrode materials with applications in supercapacitors. Different activation procedures for fines to obtain highly porous activated carbons are tested with KOH being the most effective one, allowing for manufacturing materials with specific surface area as high as 1570 m$^2$/g. A further increase of the SSA (up to 2200 m$^2$/g) is realized by incorporation of cellulose nanocrystals into the fines, thereby creating a hierarchical structure. The electrode materials are implemented in symmetric supercapacitors using organic electrolytes (TEABF4 in acetonitrile). The capacitance of the materials is up to 164 F/g, depending on the CNC content and the Ragone plot demonstrates that the performance of the fines based carbonaceous materials is significantly better than those reported in literature.

CELL 76

Structural design of cellulose paper composites for green chemistry and electronics

Hirotaka Koga, hikoga@eco.sanken.osaka-u.ac.jp, ISIR, Osaka University, Ibaraki, Osaka, Japan

Wood-derived cellulose is the most abundant and renewable bioresources. Among many cellulolic materials, paper is the most common one. Since the invention of paper approximately 2000 years ago, it has been traditionally used on a daily basis for various purposes such as writing, printing, wiping, and packaging applications. The recent trend toward green and sustainable technology has led to a growing emphasis on the development of new functionalized paper materials to extend their use in advanced applications.

Here we show functional innovation of cellulose paper by material and structural design, i.e., composting of metal or carbon nanomaterials, chemical modification, control of porous structures from micro to nanoscale, and their combination. The as-designed paper composites are successfully applied as transparent conductive paper, paper antenna, paper memory, and paper supercapacitor for electronic applications. These paper composites provided high flexibility and biodegradability as well as excellent device performances. Recyclable and renewable catalytic paper reactors are also developed for continuous-flow and highly-efficient chemical manufacturing. This “renovation of paper” strategy opens new doors for the development of advanced functional paper materials to realize green chemistry and electronics.

Schematic illustration of "renovation of paper" for green chemistry and electronics

CELL 77

Conductive wood membrane electrode for energy recovery from wastewater treatment

Zhiyong Ren$^{1}$, zhiyong.ren@colorado.edu, Zhe Huang$^{1}$, Amy Gong$^{2}$, Liangbing Hu$^{1}$, (1) Civil and Environmental Engineering, University of Colorado Boulder, Boulder, Colorado, United States (2) Materials Science and Engineering, University of Maryland College Park, Hyattsville, Maryland, United States (3) Department of Materials Science and Engineering, University of Maryland College Park, College Park, Maryland, United States

Microbial electrochemical technology (MET) shows great potential to recover renewable energy from wastewater. However, it has been insufficient to be a stand-alone treatment process because of its poor energy efficiency. In this study, a new wood-based membrane anode microbial fuel cell (MFC) was presented to improve the removal efficiencies of chemical oxygen demand (95-97%), total nitrogen (85-91%), and total phosphorus (89-93%) from wastewater compared with a traditional carbon cloth anode. The effluent quality from wood-anode MFC was in compliance with the wastewater effluent discharge standards. Similar power outputs (248-285 mW/m$^2$) were obtained from MFCs equipped with different anodes, and no significant fouling was observed on the membrane anode. Surface characterization showed that the new wood anode had long and well-aligned channels, which had high surface area to allow cell acclimation without blocking water flow. The new wood filtration anode enables MFCs to become a stand-alone technology for energy efficient wastewater treatment.

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Functional lignocellulosic materials for water purification applications

Eléonore Cabane$^{1,2}$, cabaneec@ethz.ch, Marta Videgli del Bianco$^{1,2}$, Selin Vita$^{1,2}$, (1) Wood Materials Science, ETH Zürich, Zürich, ZH, Switzerland (2) Applied Wood Materials, EMPA, Dübendorf, ZH, Switzerland

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 (CO$_2$ storing material). Recently, we observed a renewed interest in the utilization of wood for diverse applications, due to the following reasons: an increased utilization of the resource wood may help to solve pressing concerns regarding environmental issues; recent developments led to novel micro-porous wood-based materials that can be used either to improve wood intrinsic properties or to develop novel and advanced lignocellulosic-based materials. We will present our approaches to the design of functional lignocellulosic materials with unusual properties, focusing on targeted applications as membranes for wastewater purification and oil-water separation. In these fields of utilization, we identified main advantages for wood in comparison to other materials: being optimized by nature for long-distance water transport and mechanical stability in the tree, wood is a highly ordered porous material with excellent mechanical performance and robustness in the wet state, which facilitates substantial throughput and large-scale possibilities. We show that wood cross-sections may be used to develop hydrophilic and underwater superhydrophobic materials suitable for oil/water separation (see Figure 1a) [2]. We also report on the design of wood filters for water purification, in particular for heavy metal remediation (based on affinity interactions, see Figure 1b) and removal of particles and bacteria (based on size exclusion).

 modification of transparent wood for photonics functions

Lars Berglund$^{1,2}$, blilund@kth.se, Yuanrui Li$^{1}$, Qi Liang Fu$^{1}$, Sergej Popov$^{2}$, Ilya Sychugov$^{1}$, Min Yan$^{1}$, (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Materials and Nano Physics, KTH Royal Inst of Technology, Kista, Sweden

Transparent wood can be prepared by removal of lignin and filling of wood porosity by a polymer of suitable refractive index. The resulting material is bio-based, of comparably low cost and has interesting properties by itself, such as anisotropy, high optical transmittance, haze, excellent mechanical properties, low thermal conductivity etc. In addition, the optical function of the material can be enhanced by addition of molecular scale organic dyes, nanoscale quantum dots or other
additives extending the range of properties. Preparation strategies for transparent wood materials will be discussed. Challenges include controlling optical properties, avoiding defects, facilitating processing etc. This becomes ever more difficult as additives are included.

Considerations with respect to selection of material components, nano-structural control and the effect of wood structure on optical properties will be discussed. The possibilities to predict thickness effects on optical properties are probed. Theoretical considerations need to be based on a physical reality corresponding to the structure of the wood scaffold, as well as potential defects arising from the preparation method.

The mechanical properties of transparent wood are to a large extent controlled by the wood scaffold. It is characterized by anisotropy of moduli and strengths. Toughness is also important, since alternative materials such as glass tend to be brittle. As wood is modified by a polymer, the toughness properties are improved, and this will be analyzed.

In the context of applications, the possibility to utilize cold luminescence is demonstrated. Also, lasing effects are demonstrated using a combination of organic dyes and the wave-guiding effect from the wood cells.

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Energy storage and energy generation based on the materials and structures derived from wood

Hongli Zhu, h.zhu@neu.edu, Alolika Mukhopadhyay, Lei Yang. Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States

The electrical energy storage becomes necessary as there is an ever-increasing need to rapidly provide for the enormous amount of energy mainly in hybrid vehicles and portable consumer electronic devices. Currently, electrochemical energy storage primarily depends on metal-based components; however, they suffer from the high cost of material synthesis, shortage of metal-rich materials, and high toxicity. In order to find a cheaper and more sustainable alternative, carbonized wood derived materials can be used as electrodes. In this system, it was cleared that Imidazolium carboxylate worked as good solvent and condition. In this system, it was cleared that Imidazolium carboxylate worked as good solvent and condition. In this system, it was cleared that Imidazolium carboxylate worked as good solvent and condition.

In addition, we utilized the well-carbonized wood channels as a substrate to support the in-situ vertical growth of metal molybdenum disulfide (MoS2) as a catalyst for hydrogen evolution. Moreover, the MoS2 nanosheets grown on carbonized wood display notable electrical conductivity and increases the electrolyte and hydrogen transport by a physical reality corresponding to the structure of the wood scaffold, as well as potential defects arising from the preparation method. The unique porous structure of the wood-derived substrate with well-aligned channels provides high surface area and facilitates high mobility of ions and electrons in the carbonized cell walls.

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Additionally, we used the well-carbonized wood channels as substrates and support the in-situ growth of metal molybdenum disulfide (MoS2) as a catalyst for hydrogen evolution. Moreover, the MoS2 nanosheets grown on carbonized wood display notable electrical conductivity and increases the electrolyte and hydrogen transport by a physical reality corresponding to the structure of the wood scaffold, as well as potential defects arising from the preparation method.

Additives extending the range of properties. Preparation strategies for transparent wood materials will be discussed. Challenges include controlling optical properties, avoiding defects, facilitating processing etc. This becomes ever more difficult as additives are included.

Considerations with respect to selection of material components, nano-structural control and the effect of wood structure on optical properties will be discussed. The possibilities to predict thickness effects on optical properties are probed. Theoretical considerations need to be based on a physical reality corresponding to the structure of the wood scaffold, as well as potential defects arising from the preparation method.

The mechanical properties of transparent wood are to a large extent controlled by the wood scaffold. It is characterized by anisotropy of moduli and strengths. Toughness is also important, since alternative materials such as glass tend to be brittle. As wood is modified by a polymer, the toughness properties are improved, and this will be analyzed.

In the context of applications, the possibility to utilize cold luminescence is demonstrated. Also, lasing effects are demonstrated using a combination of organic dyes and the wave-guiding effect from the wood cells.

CELL 81

Modification of cellulose with methyl ester through transesterification reaction in imidazolium carboxylates

Samuel Budi Wardhana B. Kusuma, samuelbud@stu.kanazawa-u.ac.jp, Shuhei Nomura, Makoto Yamaguchi, Daisuke Hirose, Yoshiro Yamasaki, Kazuaki Ninomiya, Kenji Takahashi. Institute of Science and Engineering, Kanazawa University, Kanazawa, Japan

Modification of cellulose has been intensively studied to produce bio-based plastic from the viewpoint of green chemistry. Ionic liquids were known as good solvents for cellulose, and enable to easily modify cellulose in homogeneous condition. Recently, we have reported acylation of cellulose with imidazolium acetate and isopropanoylacetate, which is one of vinyl esters, efficiently providing desired cellulose esters showing high degree of substitution in homogeneous and neutral condition. In this system, it was clarified that imidazolium carboxylate worked as good solvent and catalyst for the acylation reaction of cellulose. However, commercially available vinyl esters are very limited and also difficult to prepare. In contrast, abundant variety of commercially available methyl esters are known, but they show low reactivity in transesterification with alcohols. In order to the low reactivity, strong base or metal catalysts were generally used for acylation of methyl ester. In this study, we investigated modification of cellulose using methyl esters as abundant acid donors in imidazolium carboxylates. As a result of optimization about the counter anion of ionic liquids and reaction temperature, the desired cellulose esters could be obtained.

CELL 82

CO2 adsorbent material based on cellulose nanofibers derived from agricultural wastes

Fabiola Valdebenito1, Gustavo Ciudad2, Gary Chinga-Carrasco1, Youssuf Habbib1, Youssuf Habbib@ilstu.it. (1) Departamento de Ingeniería Química, Universidad de la Frontera, Temuco, Chile (2) Centro de Desarrollo de Estudios y Bioenergía, SEEG, Universidad de la Frontera, Temuco, Chile (3) RISE PF, Trondheim, Norway (4) Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette, Luxembourg

Under of the burgeoning trend of using renewable feedstock for the development of chemicals and materials as viable alternative to oil-derived counterparts, agricultural wastes are attracting a tremendous interest. In this context, cellulose nanofibers (CNFs) were produced from corn husks and oat hulls and deeply characterized. To further develop more sophisticated materials from these feedstocks, CNF-based composites with tunable CO2 adsorption capacity were produced through a simple and straightforward chemical modification. The produced films were thermally stable and when subjected to 99.9% CO2 flow at 25°C these modified films based on CNFs extracted from the three feedstocks show a great adsorption of CO2. This presentation will summarize our findings.

CELL 83

Cellulose-cycloexdextrin co-polymer for removal of microcystin on water remediation

Diego Gómez Malodnado1,2, ares_dgm@hotmail.com, Maíra N. Hornus3,4, Beatrice Vaga3,5, Ilari Filippini1,2, Matthias Willig1,2, ares_dgm@hotmail.com, Maíra N. Hornus3,4, Beatrice Vaga3,5, Ilari Filippini1,2, Matthias Willig1,2, ares_dgm@hotmail.com, Maíra N. Hornus3,4, Beatrice Vaga3,5, Ilari Filippini1,2, Matthias Willig1,2, ares_dgm@hotmail.com, Maíra N. Hornus3,4, Beatrice Vaga3,5, Ilari Filippini1,2, Matthias Willig1,2. (1) School of Fisheries, Agriculture, Aquaculture, and Aquatic Science, Auburn University, Auburn, Alabama, United States (4) Department of Crop, Soil and Environmental Sciences, Auburn University, Auburn, Alabama, United States (5) School of Fisheries, Agriculture, Aquaculture, and Aquatic Science, Auburn University, Auburn, Alabama, United States

Microcystin-LR has been reported as one of the main cyanotoxins related to a liver cancer and its abundance in water is constantly monitored. The World Health Organization (WHO) stipulates that the maximum concentration in water should be 1 μg/L, but the Environmental Protection Agency reported studies where the measurements in national lakes have concentrations between the limit and 1 μg/L with a mean concentration of 3.0 μg/L. The traditional ways of treatment are chlorination, filtration and ozonating, but this could not always be effective, especially in blooming seasons. Therefore, a need exists to develop feasible methods to remove the toxin from drinking water. Furthermore, the state of Alabama has over 11 million hectares of forest, making it one of the most forest rich states in the country, and valued more than $15.7 billion per year. So, to support the State’s economy, the pulp and paper industry plays a key role and is constantly seeking new avenues to grow. The use of cellulose base products as materials for water treatment, can also generate valuable-added products that are green with the environment, and whose production, use and recycling can reactivate part of the local economy.

In this project, we used a cellulose based material modified with cyclic polysaccharide (cyclodextrin) under different conditions and the produced material was used for the recovery of microcystin. The characterization of the modified substrate was performed with FT-IR and SEM, while the recovery uptake of (microcystin) was assessed by QCM-D, spectroscopic measurements, and chromatographic techniques. All in all, we present a sustainable method for water remediation which may pave the way for the new forest-based products.

CELL 84

Application of ATR FT-IR spectroscopy in monitoring the cellulose crystallinity of developmental cotton fibers

Yongliang Liu1, yongli_liu@yahoo.com, Hee Jin Kim1. (1) Cotton Fiber Bioscience Research, USDA, ARS, CRRC, New Orleans, Louisiana, United States (2) Cotton Structure & Quality Research, USDA, ARS, CRRC, New Orleans, Louisiana, United States

The knowledge of cellulose crystallinity in developmental cotton fibers is of value to cotton breeders and growers for cotton enhancement. Here, we applied the previously proposed simple algorithms to analyze the attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra of developmental cotton fibers at various growth stages and further to compare the cellulose crystallinity of developmental cotton fibers between the varieties. Merit of IR crystallinity determination includes the direct and non-destructive fiber measurement, uses small amounts of fiber (as little as 0.5 mg), and is rapid (less than two min. for one sample).

CELL 85

Enhancing in situ hydrogen peroxide generation of greige cotton nonwoven wound dressings via ascorbate stabilized copper micro- and nano-particles

Nicolette T. Prevost1, nicolette.prevost@ars.usda.gov, Vincent Edwards1, Brian D. Condon1, Dome Yogar1. (1) SRRC, USDA-ARS, New Orleans, Louisiana, United States (2) Surgery, Virginia Commonwealth University, Richmond, Virginia, United States

Understanding how wound dressings may be designed to address critical unsolved issues in wound repair and treatment influences the development of dressings and new concepts of promoting healing. The vast majority of commercial dressing materials focus on the physical absorbent wound, e.g., absorbing the physical level of moisture, and removing excess exudate. Cotton in its many forms remains the most widely used material that forms the basis of wound dressings. Greige cotton (unbleached cotton) is an intact plant fiber with the cuticle and primary cell wall near the outer surface of the cotton fiber containing pectin, pectinases and trace metals, which are associated with hydrogen peroxide (H2O2) generation during cotton fiber development. When greige cotton is hydrolyzed into cellulose, some nonwoven material, the components of the cotton fiber cuticle are retained. We have recently determined that greige cotton can generate low levels of H2O2 (5–50 micromolar) examining both brown and white cotton varieties with brown cotton producing more in part due to natural polyphenols/antioxidants present. Low level hydrogen peroxide generation in the range of 5–50µM has been characterized as inducing accelerated wound healing associated with enhanced...
cell signaling and proliferation. This study is a continuation to develop formulations to enhance the peroxide production, controlling release of hydrogen peroxide in white cotton varieites comparable to those observed in untreated brown cotton, and at a level commensurate with enhanced fibroblast proliferation. Here we assess hydrogen peroxide levels produced in a variety of treated nonwoven analogs to retain sustained hydrogen peroxide production in a therapeutic range associated with enhanced cell proliferation.

CELL 86

Design, preparation and activity of intelligent cellulose-based protease sensor & modulating/fibroblast promoting (PROTOS-FIBRO) dressings

Vince Edwards¹, vincent.edwards@ars.usda.gov, Krystal R. Fontenot², Nicolette T. Prevost², Dome Yager³, Fatik Wolfgang Lieber⁴, Brian D. Condor⁵ (1) Dept of Chemistry, Boku University Vienna, Tulln an der Donau, Austria (2) SRRC, USDA-ARS, New Orleans, Louisiana, United States (3) USDA ARS SRRC, Opelousas, Louisiana, United States (4) USDA-ARS, New Orleans, Louisiana, United States (5) Dept. Reconstructive & Plastic Surgery, Virginia Commonwealth University Medical College of Virginia, Richmond, Virginia, United States (6) SRRC, USDA-ARS, New Orleans, Louisiana, United States

Chronic wounds are a major clinical problem with an estimated 40 million people suffering from them worldwide, and one of the most costly healthcare problems today. ‘Intelligent’ dressings may be defined as materials that respond to specific changes in the wound environment i.e. exudate volume, and harmful protease levels by altering structure or properties to bring about a useful result i.e. most wound healing conditions or normal protease levels respectively. Considerable promise in the application of nanocellulosic hydrogels, aerogels, and nanocomposites as dressings has been demonstrated due to favorable properties that promote optimal moisture conditions. However, there have been few reports of multifunctional dressings designed to remedy the pathology of a chronic wound. Here we present a series of modified nanocellulosic- and cellulosic materials designed to remove harmful proteases from a chronic wound while detecting protease levels, and generating therapeutic levels of hydrogen peroxide that enhance cell proliferation. These materials which originate from cellulose fibers are defined as protein modulation/sensor/fibroblast proliferative (PROTOS-FIBRO) dressings, i.e. Greek root for: ‘first protease-smart fibers’/fibroblast promoting’ dressing. The sensor portion is a fluorescent peptide-cellulose conjugate that is interchangeable on the surface of different semi-occlusive dressing motifs and sensitive to protease levels found in chronic wounds. The protease modulation portion is based on the degree of surface zeta potential required on the material surface to remove excess wound protease levels. While the fibroblast proliferative portion of the dressing generates low-level therapeutic doses of hydrogen peroxide based on low levels of nanocrystalline copper and ascorbate embedded in the dressing.

CELL 87

Production of cellulose nanoparticles by the use of combined chemical and mechanical processing

Inese Sable, sable.inese@gmail.com, Linda Rozenberga, Laura Andze, Velta Fridrihsone. Cellulose department, Latvian State Institute of Wood Chemistry, Riga, Latvia

Cellulose is one of the most abundant and promising natural carbohydrate polymers in the world. In order to obtain new materials with unique properties reducing the size of cellulose has been put to the forefront in the last decades. Furthermore many efforts have been made to produce nanocellulose in easier, cheaper and sustainable way. Ammonium persulphate (APS) has been proposed as a hydrolyzing agent to obtain cellulose nanocrystals instead of commonly used sulfuric acid. Since then many other authors published their researches of using hydrolysis of cellulose by high concentration solutions of above mentioned agent for extracting nanocrystals from different source of cellulose, however insignificant attention has been paid for studies of obtaining nanofibrillated cellulose, combining chemical processing with diluted solutions of APS and continues mechanical treatment. New approach for nanofibrillated cellulose production has been proposed in our studies. It includes combined chemical and mechanical treatment of the cellulose fiber. Diluted APS solutions were used for initial destruction of cellulose with continuous mechanical treatment in high shear mixer. The effect of APS hydrolysis parameters on cellulose structure and chemical properties, as well as the effect of mechanical treatment parameters on formation of nanofibrillated cellulose was studied.

The significant structural and chemical changes of fibers were detected during chemical treatment depending on APS and cellulose ratio. It was observed that with increasing APS to cellulose ratio (from 1:1 to 1:10) the reaction yield, fiber length and degree of polymerization decreased. The effect of mechanical treatment depended on the treatment time, as well as on the chemical pretreatment results. To conclude it is possible to obtain nanofibrillated cellulose, combining APS pretreatment with mechanical disintegration of the cellulose fiber.

CELL 88

Nano-emulsions and nano-lattices stabilized by hydrophobically functionalized cellulose nanocrystals

Yefei Zhang⁶, yefiez@uchicago.edu, Vahed Karimkhani⁵, Brian T. Makowski⁵, Gamini Sanni⁵-6, Shannon Williams⁵, Brian D. Condon⁵ (1) Dept of Chemistry, Boku University Vienna, Tulln an der Donau, Austria (2) SRRC, USDA-ARS, New Orleans, Louisiana, United States (3) USDA ARS SRRC, Opelousas, Louisiana, United States (4) USDA-ARS, New Orleans, Louisiana, United States (5) Dept. Reconstructive & Plastic Surgery, Virginia Commonwealth University Medical College of Virginia, Richmond, Virginia, United States (6) SRRC, USDA-ARS, New Orleans, Louisiana, United States

Carboxylic acid cellulose nanocrystals (CNC-COOHs) that have been covalently functionalized (via peptide coupling chemistry) with a range of different hydrophobic groups have been investigated as nanoparticle surfactants to stabilize styrene-in-water nanoemulsions. It is shown that the size and stability of these nanocrystals depend on both the amount of surface carboxylic acid groups as well as the amount and type of hydrophobic alkyl groups on the CNC surface. Two different biosources for the CNCs, microcrystalline cellulose (MCC) and Miscanthus x Giganteus (MxG), were investigated to see the effect that the CNC aspect ratio has on these nanocapsules. Stable oil-in-water (o/w) Pickering emulsions with particle diameters of only a few hundred nanometers can be accessed using these hydrophobically functionalized CNCs, and the resulting emulsion can be further polymerized to access nanometer sized lattices. The hydrophobic/hydrophilic balance of the functionalized CNCs was found to be critical to lower the interfacial tension between oil and water, allowed access to stable emulsions with droplet diameters < 1 mm. The ability to stabilized nano-sized emulsions and lattices extends the potential of CNCs as green surfactants for numerous technological applications, such as food, cosmetics, drug delivery systems and coatings.

CELL 89

Tannin micro- and nanocapsules for storage and controlled delivery of hydrophobic molecules

Eliasaf D. Battagzaka¹, Heiko Lange¹, heiko.lange@uniroma2.it, Luc Zongo¹, Pasquale Mossesso¹, Claudia Crestini¹ (1) Department of Chemical Sciences and Technologies, University of Rome “Tor Vergata”, Rome, Italy (2) Department of Ecological and Biological Sciences, University of Tuscia, Viterbo, Italy

Nanostuctures of natural polymers have received steadily growing interest as a result of their peculiar properties and applications superior to their bulk counterparts. These nanostuctures can be generated in aqueous medium, avoiding thus the use of eventually environmentally non-benign organic solvents. Along these lines, we achieved the encapsulation of active small molecules into micro- and nanoscaled capsules made out of tannins using sonochemistry. The ultrasound technique proved to be an essential tool in this production of nano- and micro-sized capsules, since it offers simplified ways to achieve reactions and size-determining conditions that would otherwise require extreme conditions or the use of toxic reagents. Starting from oil in water emulsions containing tannins and actives, we present thus a rapid, simple, and robust method of one step assembly of tannins and their suitable coordination complexes into metal-free as well as iron-re-enforced nano- and microparticles, TNCs, TMCs, Fe-TNCs and Fe-TMCs, respectively, exploiting the propensity of tannins to associate and to form metal ions. Under fully optimized conditions, the formation of TMCs, respectively, exploiting the propensity of tannins to associate and to form metal ions. Under fully optimized conditions, the formation of TNMCs and Fe-TNMCs using various tannin species is possible; assembly is generally driven mainly by physical interactions, with only marginal chemical modification during sonication (quantitative ¹H NMR, gel permeation chromatography).

Studies regarding effective loading and release capacities under various conditions show increased stability of Fe-TNMCs with respect to TNMCs as an additional effect of the complexation of the metal ions by the various phenolic OH groups in addition to the stacking interactions occurring in the TNMCs. Fe-TNMCs showed also reduced shell thickness and thus increased encapsulation efficiency and slower release kinetics when compared to corresponding TNMCs.
Fluid flow in paper-derived silica-polymer hybrids

Nicolette Herzog1, nicolette@cellulose.tu-darmstadt.de, Markus Galie1, Tobias Meckel1, Markus A. Biseläder1, Annette Andrieu-Brunsend1, (1) Technical University Darmstadt, Darmstadt, Germany

Fluid flow modulations in porous materials and especially in paper is highly relevant for many applications from delivery, lab-on-chip devices to sensors and membranes. Microporous paper-based devices, as introduced by Whitesides in 2007, are low-cost, disposable and thus sustainable. But the role of the fiber nanoporosity on transport is often neglected and it is hard to control and maintain during the preparation process.

The presented study provides deeper insights into the role of the fiber surface and nanoporosity on the capillary fluid flow by comparing water uptake of dense and mesoporous silica coated cotton linters paper. This fluid stop is observed macroscopically as well as microscopically following fluid flow into the paper fiber structure by resolution fluorescence microscopy. Specifically, we are able to stop fluid flow by adjusting fiber density and the mesoporosity of the silica fiber coating while using all hydrophilic materials. Secondly, our study introduces a method to functionalize silica-coated paper of different fiber mesoporosity in a way that capillary fluid flow can be gated on and off by external redox stimuli. To this end we functionalize hybrid silica-paper sheets with redox-responsive polymers allowing reversible, dynamic gating of fluid flow, demonstrating the potential of length scale specific, dynamic, and external transport control. This behavior has been extended to other fibers like eucalyptus allowing to derive systematic understanding into the cross correlation of fiber mesoporosity and wetting on fluid transport in paper.

with CS content for the BC while 2% of CS halved filtration time for CNF suspensions. Addition of more than 2% CS in the CNF nanopaper, however, increased filtration time exponentially. The zeta potential measurement of the suspensions revealed the stability of the BC suspension was not influenced by CS whereas the addition of CS in CNF suspensions facilitated flocculation. For both BC and CNF nanopapers, the addition of CS lead to an incremental decrease in porosity. The tensile modulus and strength of BC nanopapers increased with CS content reaching up to 21.4 GPa and 249 MPa respectively. This was also the case for CNF nanopapers up to 2% CS. Further addition of the cationic additive degraded significantly the nanopaper strength which was accompanied by a decrease in strain at break. This was hypothesised to be due to an overlapping effect of CS with the (~23%) hemi-cellulose in our CNF nanopapers. The mechanisms leading to the increase in mechanical properties of the nanopapers with the addition of CS will also be discussed in the presentation.

Cellulose nanofibers production using deep eutectic solvents and twin screw extrusion

Hugo Spieser1,2, Fleur Roi3, Fanny Bardot1, Valerie Meyer1, Julien Bras1, Julien.Bras@grenoble-inp.fr, (1) Univ. Grenoble Alpes - Grenoble INP - LGPI, Grenoble, France (2) CTP, Grenoble, France

Firstly introduced in 1980’s, the field of cellulose nanofibers has seen a recent enthusiasm boom in the past ten years. The applications for cellulose nanofibers are numerous, for instance active food packaging, cosmetics, wound healing or tissue engineering. Cellulose nanofibers are produced by mechanical disintegration of the cellulose-based raw materials. Different steps can be divided in the process of CNF: Pretreatments are classically used to enhance the further extraction of the raw material by the principal mechanical treatment. In 2015, Sirviö et al introduced the use of deep eutectic solvents as a new pretreatment for the production of cellulose nanofibers. Deep eutectic solvents (DESs) are components formed by mixing a hydrogen bond donor and a hydrogen bond acceptor, being associated with each other by hydrogen bond interactions. Same year, the use of twin-screw extrusion (TSE) was introduced by Ho et al. (2015) as a new pretreatment, and it is reported to get results as it enables the processing of high solid contents materials.

The aim of this project was to develop a new process of cellulose nanofibers production using combination of deep eutectic solvents pretreatments and TSE. The project relied on using a deep eutectic solvent formed by mixing choline chloride (ChCl) and urea to work as a pretreatment of cellulose fibers. Different ratios of ChCl and urea were performed and the CNF produced were characterized following a recent quality index strategy using microscopy tools, fibre morphology, turbidity and nanofiber characterization. It was proved that the DES pretreatment was beneficial to obtain MFCl after 7 passes and that an optimum ratio (1:2) is obtained regarding energy consumption.

The role of residual lignin in lignin containing cellulose nanofibers (L-CNF)

Maria C. Iglesias1,5, mcil0006@txgemail.auburn.edu, Roland Gleisner1, Junyong Zhu5, Laurencie Tetard5, Karin Stana-Kleinschel5, Charles E. Fraser5, Maria Soledad Perares5,6, (1) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States, (2) USDA Forest Service, Madison, Wisconsin, United States, (3) NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States, (4) Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States, (5) Laboratory of Characterization and Processing of Polymers, University of Marbór, Marbór, Slovenia, (6) Forest Products Development Center, Auburn University, Auburn, Alabama, United States

Over the years, the use of cellulose nanofibers (CNF) as an additive to improve materials properties has been increased widely, due to a successful combination among the characteristics conferred by the nanoscale and the intrinsic properties of the cellulose. Nowadays, the main source for CNF is bleached cellulose pulp. These CNFs are characterized by the subfractionation of lignin and hemicelluloses by chemical treatments. The removal of those cell wall components has proven to improve the visco-elastic properties of the fibers. However, the presence of residual lignin in raw materials from the production of CNF might hold several benefits; some of the proved advantages are the reduction of dewatering time and oxygen permeability of films. Additionally, using unbleached cellulose pulp to produce lignin-containing cellulose nanofibers (L-CNF) is possible to obtain higher production yields while reducing costs, due to the lower energy consumption during the manufacture process.

The main objective of this project is to understand how lignin content can affect the properties of the CNFs, aiming on the modification of these properties for the final applications as L-CNF are incorporated in the materials. The difference of interactions among CNF films and water as well as the viscoelastic properties were studied using Atomic Force Microscopy (AFM), Quartz Crystal Microbalance with Dissipation (QCM-D), TA thermo-meter instrument, and Surface Contact Angle (SCA). Also, the surface chemistry and stability of the CNFs were evaluated with Z-potential, and the morphology of the samples was analyzed using AFM, and Scanning Electron Microscopy (SEM).

Morphological, chemical, thermal and mechanical effects of cellulose nanocrystals ratios on silk fibroin/cellulose nanocrystals electrospun mats

Simon Sanchez Diaz1,4, ss10197@auburn.edu, Thomas J. Elder4, Adriana Restrepo Osorio5, Oladiran Fasina5, Maria Soledad Perares6,1, (1) Forestry, Auburn University, Auburn, Alabama, United States, (2) USDA Forest Service, Pineville, Louisiana, United States, (3) Forest Products Development Center, Auburn University, Auburn, Alabama, United States, (4) New material research group, Universidad Pontificia Bolivariana, Medellín, Colombia, (5) School of Textile Engineering, Universidad Pontificia Bolivariana, Medellin, Colombia, (6) Professor and Head
Silk fibroin (SF) is a natural, renewable and broadly available material that is biodegradable, biocompatible, and in its regenerated form can be processed into aerogels, films, fibers or non-wovens through techniques like electrospinning. Electrospun materials exhibit high porosities and surface areas, and increased surface energy and thermal properties, such that electrospun SF may be an attractive alternative for the manufacture of high value-added products for biomechanics, food packaging, textiles, or tissue-engineering. These potential opportunities notwithstanding the poor degradation control in human body, rigidity and brittleness of silk fibroin limits its applications. To improve the mechanical properties of electrospun SF, special attention has been focused in cellulose nanocrystals (CNC), as a reinforcing material because their mechanical properties, aspect ratio, interfacial adhesion, renewability, biocompatibility, biodegradability. Also, the use of CNC as reinforcement may represent a new source of income for the forest products industry, which is mainly focused in the production of commodity products.

In the current work, SF aqueous solution was blended with CNC in different ratios and then electrospun in order to demonstrate the capacity of CNC as a reinforcing material for SF. The morphology, crystallinity, mechanical and thermal properties of the different SF/CNC electrospun blends were tested, analyzed and compared to and commercial biopolymers to find the target applications.

**CELL 95**

Synthesis and characterization of novel crystalline hydroxyapatite derived from eggshell for biomedical applications

*Esperidiana Moura*, eamoura@upen.br, Aline Lodis*, Pedro Reis†, Renate Welzen† (1) Center of Chemical and Environmental Technology, Nuclear and Energy Research Institute, Sao Paulo, Brazil; (2) Materials Engineering Department, Federal University of Paraiba, Joao Pessoa, Brazil

Hydroxyapatite (HAP) a crystal-chemical analog of the bone tissue mineral component has been intensively studied in recent years as a potential bone substitute in orthopedic and dentistry because of its biocompatibility, biodegradability, bioactivity, and osteoconductive properties. Hydroxyapatite in a nanocrystalline state with uniform size and morphology has many applications in different fields of medicine ranging from targeted drug delivery to designed load-bearing implants. This work presents the synthesis and characterization of nanocrystalline hydroxyapatite derived from hen’s eggshell waste for biomedical applications. Firstly, bio-hydroxyapatite was synthesized by the wet precipitation method in which white hen’s eggshell waste was used. The white hen’s eggshells were washed, dried and reduced to powder with particle size ≤ 30 μm. Then, the eggshell powder was subjected to a heating cycle at 800 °C for 3 hours to obtain calcium oxide. Calcium oxide was converted to bio-hydroxyapatite by the addition of a solution of distilled water and phosphoric acid under magnetic stirring at 100 °C, until a viscous slurry was formed, which was oven dried at 110 °C for 24 hours. The dried material was disintegrated and calcined at 900 °C for 2 hours to obtain the hydroxyapatite phase. The bio-hydroxyapatite was irradiated with a high intensity ultrasonic (20 kHz, and 450W/cm²) in order to obtain nanocrystalline hydroxyapatite. These synthesized nanocrystalline hydroxyapatites have been characterized by XRD, FE-SEM, FTIR, and TG analyzes.

**CELL 96**

Synthesis and characterization of nanocellulose obtained from pineapple peel wastes

*Jose Vega-Baudrit*, jvegab@gmail.com, Melissa Camacho³, Yendry Regina Corrales Urena³, Mary Lorett³, Galia Moreno³ (1) University of the Republic (UdelaR), Montevideo, Uruguay; (2) National University of Costa Rica, Heredia, Costa Rica; (3) National Laboratory of Nanotechnology, San Jose, Costa Rica

Pineapple peel biomass was used as raw material for nanocellulose extraction. The raw material is a residue from the Costa Rican fruit industry. The nanocellulose was obtained by a two-step hydrolysis process. Firstly, the cellulose was hydrolyzed with HCl to obtain microcrystalline cellulose. In the second step, the hydrolysis was carried out using H2SO4 to obtain smaller soluble cellulose used in previous process, retain part of the fiber organization and are extremely soluble nanofiber structure and requiring energy and chemicals. Recently, the microfibrillated cellulose (MFC), as a reinforcing material because their mechanical properties, enhancement in hydrogel mechanical properties, increased stability to degradation, and the potential to create nanoscale anisotropy via the addition of CNCs to PEOGMA networks. By simply increasing the CNC loading, these readily tunable hydrogels show increased cell adhesion without any significant increases in protein adsorption or inflammatory response in vivo. Furthermore, we also evaluate the in vivo biodistribution of CNCs, both in solution and within these hydrogel networks in order to gain a better understanding of their biodegradation and clearance.

**CELL 97**

Evaluating the biological response and biodistribution of cellulose nanocrystal nanocomposite hydrogels

*Kevin J. De France*1, k.j.defrance@gmail.com, Maryam Badvi2, Jonathan Derogin1, Emily D. Cranston1, Todd Hoare1 (1) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (2) J. Hodgins Eng, McMaster University, Hamilton, Ontario, Canada

Hydrogels have garnered increasing research attention recently due to their high swellability, potential for chemical functionalization, and overall biodegradability, and overall biodegradability, promising show for a wide range of potential drug delivery and tissue engineering applications. However, these biomaterials have largely as of yet not been translated to a clinical setting, due in part to a need for more thorough toxicity, and biodistribution evaluations. Here, we investigate the in vitro and in vivo behaviour of injectable hydrogel crosslinked poly (oligoethylene glycol methacrylate) (PEOGMA) hydrogels with incorporated cellulose nanocrystals (CNCs). We have previously shown significant

**CELL 98**

Continuous composite fiber based on TEMPO-oxidized cellulose nanofibril/chitosan obtained by interfacial polyelectrolyte complexation

*Rafael Grande*, rafaelgrandee@gmail.com, Elaine Trovatti2, Antonio J. Carvalho2,1 (1) SMM, USP, Sao Carlos, Brazil; (2) Materials Engineering, Universidade de Sao Paulo, Sao Carlos - SP, Brazil

Living organisms are formed from simple molecules in bottom-up way, leading to high optimized structures. In fact, bio-produced fibers, such as spider and worm silk, cotton and wool has been an inspiration for many researches encouraging the development of man-made fibers. These natural fibers are formed by hierarchical structures with basic structures are linear macromolecule, nanofibers and the microscopy fiber. Man-made fibers such as Rayon, Viscose and Lyocell® are examples of commercial fibers in which cellulose fibers was used to produce a solution were cellulose is regenerated. In this process the non-fiber structure is destroyed losing of the non-fiber structure and requiring energy and chemicals. Recently, the microfibrillated cellulose (MFC), which is in fact nanofibers of cellulose with 10-40 nm in diameter and thousands of nanometers in length emerged as a new green material. These nanofibers, in opposition to the soluble cellulose used in previous process, retain part of the fiber organization and are extremely尺寸的。Here, a composite fiber was produced by the association of nanoscale fibers (TNF), with macromolecules of chitosan in a liquid-liquid interface. The process for fiber drawing involves the continuous pulling of the aqueous media incorporating each polymer at their interface. Our choice of using the nanofibrillated form of cellulose prepared in the presence of 2,2,6,6-tetramethylpiperidin-1-yl-oxo (TEMPO) was based on the fact that it provided negative charges associated with the carboxylic groups at nanofiber surface. NFCs with a negatively charged surface could then be associated with macromolecules carrying positive charges (polyelectrolyte), in our case chitosan, giving rise to fibers by interfacial complexation in a process (IPC). Indeed, initial tests with this method, generated continuous fibers of virtually any length. The morphology of the wet and dry fibers, assessed by optical (fig 1a) and electron microscopy (fig 1b), showing that the cellulose were aligned along the fiber direction. This result was supported by high mechanical properties of the dry fibers (fig 1c).

**CELL 99**

Tunable surface energy wood-biopolymer macrofibers

*Tiina Nypo*, tiina.nypo@gmail.com, Shinn Assaad2, Günter Knedinger2, Herbert Sista2, Johannes Konnert1 (1) Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Tullin, Sweden; (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland; (3) Institute of Wood Technology and Renewable Materials, Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences, Vienna, Vienna, Austria

Manufacturing of regenerated fibers is vital for clothing, medical textiles and composites. For manufacturing regenerated cellulose fibers the traditional options have been spinning derivatized
cellulose xanthate dissolved in sodium hydroxide or cellulose directly dissolved into N-methylmorpholine N-oxide. Ionic liquids have been recently added to the group of direct solvents for cellulose prominent for fiber spinning process. We contribute to development of fibers spun from ionic liquids by preparing fibers from dopants of cellulose, xylan, lignin and their blends. We demonstrate tunable surface chemistry of the fibers via adjustable composition and apply Wilhelmy plate technique to define fiber surface free energy, its dispersion and polar contribution and acid-base character.

CELL 100

Residual wood polymers facilitate compounding of microfibrillated cellulose with poly(lactic-acid) for 3D printer filaments

Armin Winter, armin.winter@boku.ac.at, Wood Technology, Vienna, Austria

The distinct hydrophobicity of MFC prevents efficient drying without loss in specific surface area, necessitating storage and processing in wet condition. This greatly hinders compounding with important technical polymers immiscible with water. Differently from cellulose, the chemistry of the major wood polymers lignin and hemicellulose is much more diverse in terms of functional groups. Specifically, the aromatic moieties present in lignin and acetyl groups in hemicellulose provide distinctly less polar surface-chemical functionality compared to hydroxyl groups which dominate the surface chemical character of cellulose. It is shown that considerable advantages in the production of MFC-filled poly(lactic-acid) filaments for 3D printing can be obtained through the use of MFC containing residual lignin and hemicellulose due to their advantageous surface-chemical characteristics. Specifically, considerably reduced agglomerations of MFC in the filaments in combination with improved printability and improved toughness of printed objects are achieved.

CELL 101

Protein/polysaccharides biocomposite characterization via confocal microscopy

David E. Verrill1, blackbelt23av@comcast.net, Abneris Morales1, Stephen Brown1, Sean M. O'Malley2, David Salas-de la Cruz1. (1) Chemistry, Rutgers University, Medford, New Jersey, United States (2) Physics, Rutgers University, Camden, New Jersey, United States

As interest in understanding the structural and physicochemical properties of natural-based biocomposites is increasing in the scientific community, new characterization methods command development. Biomaterials are presently characterized by many instruments such as FT-IR, TGA, AFM, SEM, DSC, DTA, and X-ray Diffraction. While these instruments have led to our understanding of compositional, thermal, structural, and mechanical properties of biomaterials, the answer to the main question regarding understanding the relationship between structure and morphology is still unclear. Herein, a new characterization method using Confocal Microscopy is presented to study the morphology of a biocomposite material of silk and cellulose. Taking advantage of the silk amino acid sequence, this method utilizes an ELISA maker to study and map the location of the protein within the matrix. This renders a 3D representation of how the silk is interacting with the cellulose, revealing the influence of beta-sheet compositions and cellulose crystallinity, into the physicochemical properties. This characterization tool, in combination with X-ray Diffraction and AFM, could enhance understanding into how the protein chains are intercalated with the polysaccharide chains, and will allow us to map the location of how the proteins interact with the polysaccharides at the molecular level.

CELL 102

Different strategies for the preparation of nanocellulose composites with three-dimensional structure

Arantxu Santamaria-Echart, Leire Urbina, Altor Arbeloiz, Aloxia Retegi, Maria Angeles Concura, Arantxa Eceiza, arantxa.eceiza@ehu.eus, Materials Technologies Group, University of Basque Country, Donostia-San Sebastian, Spain

Cellulose, one of the most abundant natural polymer on Earth, is a source of renewable nanomaterials. In the last years, nanostructured celluloses have been attracting attention due to their exceptional properties such as nano dimension, high strength and stiffness, abundance and renewability, biocompatibility, biodegradability and low cost. Typically, nanocelluloses can be isolated from lignocellulosic resources by a top down disintegration strategy using various chemical, mechanical or chemo-mechanical processes in order to remove pectin, hemicellulose and lignin. Depending on the isolation method, cellulose nanofibers (NFC) formed by crystalline and amorphous domains and cellulose nanocrystals (CNC) formed by the crystalline fraction can be obtained. In addition to lignocellulosic biomass, bacteria can also synthesize cellulose with the same structure at the molecular level, but building up via bottom-up synthetic routes a gelatious pellicle with a continuous three-dimensional (3D) network of assembled microfibrils in the form of hierarchically structured ribbons. Nanocelluloses have received huge attention in a wide variety of applications. They can be used in several forms as an independent functional material or as a reinforcement unit in composite materials. The aim of this work has been to investigate different strategies for the preparation of nanocellulose composites with 3D network structures. Electrospinning from aqueous dispersion of polymer reinforced with cellulose nanocrystals and impregnation of bacterial cellulose with a water soluble polymer were used. The final properties of the 3D network materials were characterized by several techniques.

CELL 103

Valorization of hemicellulose hydrolyzates into eco-friendly surfactants

Wei Liu, wliu0@vt.edu, Maren Roman, Department of Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States

Biorefining refers to the process of converting renewable raw materials into biobased chemicals and fuels. First generation biorefineries, focusing only on ethanol or related biofuel production, have limited opportunities for profitability. To achieve commercial viability, biorefineries will have to integrate the production of low value fuel with that of high-value chemicals. Various pretreatment technologies that prepare biomass for further downstream processing within a biorefinery have been developed. However, most commercially viable pretreatment technologies suffer from significant cross-contamination. To enable profitable next-generation biorefineries, pretreatment must evolve into fractionation processes that fully separate lignocellulosic biopolymers in the yield and purity needed for the parallel production of both fuels and chemicals. Numerous uses and conversion processes exist for the cellulose fraction and the lignin fraction is receiving increasing attention. This study focuses on valorizing the hemicellulose fraction. Hemicellulose hydrolyzates will be a complex mixture of sugars and impurities. Here we will present our current efforts to analyze sugar mixtures and valorize hemicellulose hydrolyzates into high-value eco-friendly surfactants.

CELL 104

New foamed materials from hemicelluloses

Linda Hardelin, hardelin@chalmers.se, Anna Strim, Anette Larsson, CHALMERS UNIVERSITY OF TECHNOLOGY, GÖTEBORG, Sweden

Foam materials constitute a large production volume in our society and are today mainly made from fossil fuel based raw materials. This is considered unsustainable, since such raw materials are non-renewable, non-biodegradable and will have a net release of greenhouse gases if the products are burnt after usage. In paper producing pulp mills most of the hemicellulose is separated and burnt for production of heat and electricity. Using hemicellulose for material applications could be favourable economically as well as being environmentally friendly, but at this point in time the applications are few. Foams have properties such as low density, good absorption properties and good insulation properties, which make them interesting in a wide range of applications. In this study we have functionalized the hemicellulose. The products were purified via dialysis and then freeze dried. Several analytical techniques such as NMR, FTIR-ATR, carbohydrate analysis, and compression test were used to characterize the products.

CELL 105

Food packaging made from chitosan and hemicellulose

Amanda M. Johnson1, amanda.marie.j@gmail.com, Daniele Camacho2, HyoonLung Jeon1, Scott Rennecker3. (1) University of British Columbia, Vancouver, British Columbia, Canada (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada

Packaging conveniently protects and contains the products we consume every day. Worldwide, consumption of flexible packaging has reached 15 megatons per year. There is growing consumer interest in preserving the environment, but in order for sustainable consumption to become a reality, greener packaging is required. Green packaging can be made from biopolymers, which are derived from biomass and processable using environmentally benign procedures. Using more biopolymer packaging would result in fewer petroleum-based plastics being sent to the landfill. Xylan is a biopolymer comprising up to 30% of lignocellulosic biomass. Chitosan is produced by fungi, and is the most abundant polymer in belowground ecosystems. Forests produce billions of tonnes of xylan and chitosan every year, making these potentially available at a low cost. The objective of the research was to assess xylan and chitosan packaging films as an alternative to petroleum-sourced packaging. For this work, smooth, transparent and semi-flexible films were developed. Tensile strength of the polysaccharide-based films was compared with that of paper packaging and plastic (polyethylene) packaging. Xylan-chitosan packaging was four times stiffer than paper packaging. Water vapour permeability and thermal stability of the films were also determined. A sensory evaluation of xylan-chitosan versus paper packaging was conducted by trained panellists. The polysaccharide-based bags were appreciated for transparency and flexibility over the conventional paper bags. Overall, this study explored the use of carbohydrate polymers for food packaging applications.
Clicking hemicelluloses and nanocellulose toward functional fully bio-based materials

Laura Puchol1, Jeremy Cornwall1, Denilton Da Silva Pereira2, Yousef Habibi2
Yousef.Habibi@list.lu, (1) Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette, Luxembourg (2) FCBA, Grenoble, France

Over the past years, due to the increasing scarcity of oil-based resources, the interest in renewable and naturally occurring compounds for their use as raw materials for chemistry has considerably grown. In particular, lignocellulosic materials have received increased attention and are considered as one of the most promising renewable resources to replace fossil counterpart for the synthesis of various polymeric materials. Indeed, their low cost, renewability, and large availability are favorable factors for more sustainable chemicals and materials productions. Among these interesting sources of raw materials, hemicelluloses represents 15% to 35% of plants and wood and is used in a wide range of industrial applications, such as hydrogel, cosmetics and drug carriers. Indeed, hemicelluloses carry abundantly hydroxyl functions allowing numerous chemical modifications and various conversions of this bio-polymer into value-added materials have been investigated. Nevertheless, hemicelluloses are an underexploited source of bio-based building blocks due to difficult extraction from the cell wall, and to their hydrophilic nature inducing phase separation and poor mechanical properties when blended with hydrophobic polymers. The present work reports the elaboration of hemicelluloses-based polymeric materials reinforced by surface-modified nanofibrillated-or nanocrystalline-celluloses through thioc- maleimide click polymerization. In-depth characterization as well the properties of these fully bio-based materials will be discussed during this presentation.

From low-molecular weight hemicelluloses to new biopolymers

Laura Puchol1, laura.puchol@list.lu, Denilton Da Silva Pereira2, Yousef Habibi2
(1) Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette, Luxembourg (2) FCBA, Grenoble, France

During the past recent years, the interest in the chemistry of sustainable and renewable resources used for the production of polymeric materials gained considerable interest. Indeed, up to now the majority of the raw materials are used as chemical compounds for the production of polymeric materials stem mainly from fossil resources. However, facing the depletion of fossil resources as well as their increasing prices and the growing concern of their impact on the environment and on the human health, it is of urgent need to find a viable and renewable alternative. In this context, renewable building blocks derived from biomass such as plant oils, polysaccharides, lignin or human health, it is of urgent need to find a viable and renewable alternative. In this context, renewable building blocks derived from biomass such as plant oils, polysaccharides, lignin or renewable and naturally occurring compounds for their use as raw materials for chemistry has considerably grown. In particular, lignocellulosic materials have received increased attention and are considered as one of the most promising renewable resources to replace fossil counterpart for the synthesis of various polymeric materials. Indeed, their low cost, renewability, and large availability are favorable factors for more sustainable chemicals and materials productions. Among these interesting sources of raw materials, hemicelluloses represents 15% to 35% of plants and wood and is used in a wide range of industrial applications, such as hydrogel, cosmetics and drug carriers. Indeed, hemicelluloses carry abundantly hydroxyl functions allowing numerous chemical modifications and various conversions of this bio-polymer into value-added materials have been investigated. Nevertheless, hemicelluloses are an underexploited source of bio-based building blocks due to difficult extraction from the cell wall, and to their hydrophilic nature inducing phase separation and poor mechanical properties when blended with hydrophobic polymers. The present work reports the elaboration of hemicelluloses-based polymeric materials reinforced by surface-modified nanofibrillated-or nanocrystalline-celluloses through thioc- maleimide click polymerization. In-depth characterization as well the properties of these fully bio-based materials will be discussed during this presentation.

Synthesis and mechanical characterization of high pressure laminates modified with Kraft lignin

Maria Eugenia Taverna1, Verónica V. Nicolai2, Diana Estenoz1, destenoz@santafe-conicet.gov.ar, (1) INTEC-CONICET, Santa Fe, Santa Fe, Argentina (2) GPo – Dpto. Ing. Quimica, Universidad Tecnológica Nacional, San Francisco. Córdoba, Argentina

Phenol-formaldehyde resins (PF) are thermosetting polymers used as adhesives for plywood and other structural wood products including high pressure laminates (HPLs). HPLs are composite materials comprised of a paper-based decorative surface and a substrate impregnated with PF resin. PF adhesives are synthesized using two reagents made from petrochemicals: phenol and formaldehyde. The substitution of such substances by natural products including lignin, tannin, and furfural among others has been increased in the last 20 years due to environmental and economic benefits [1]. Lignin is an inexpensive, abundant and non-toxic-by-product from pulp production, used as replacement of PF, due to its similar structure to PF resins. In this work, the industrial synthesis and characterization of three resol-type phenol-formaldehyde resins modified with 10, 20 and 30 wt% of Kraft lignin from hardwood were studied. The Kraft lignin was activated by hydroxylation in all cases. The resols characterization involved industrial measurements of free formaldehyde, viscosity, total solids and density. The resins were used for the industrial impregnation of Kraft-type paper and the production of laboratory laminates. The mechanical and thermal properties of the laminates were measured. Mechanical measurements included tensile, flexural, impact and interlaminar tests. Thermogravimetric and dynamic mechanical analysis were used for the thermal characterization. In addition, the aging of materials in water was studied. No significant differences in mechanical and thermal properties between traditional and modified materials were found with replacement up to 20 wt% of phenol. Modified laminates exhibited better water resistance due to the lignin presence in the formulation. This study suggests that resols modified with 20 wt% of Kraft lignin could be used for the production of HPLs, while resols modified with 30 wt% of lignin for postformable laminates. Industrial tests were carried out at Centro S.A, San Francisco, Córdoba.

Search for production of high quality lignin from technical lignins by enzymatic catalysis

Joona Mikkilä1, Joona.mikkila@helsinki.ﬁ, Jaana Kuuskari1, Mia R. Mikkilä2, Jussi Konti1, Paula Nousiainen1, Jussi Spila, Kristinha Hilden1, (1) Department of Chemistry, University of Helsinki, Helsinki, Finland (2) Department of Food and Environmental Sciences, University of Helsinki, Helsinki, Finland

Lignin is the primary biological resource for aromatic chemicals and more than 50 million tons of different technical lignins are produced annually as side products of pulp and paper industry. However, it is still a challenge to develop valuable and economically feasible applications for lignin to produce valuable products in biorefineries. A prominent method for bioengineering is to apply biotechnological approaches. In the case of biotransformation, the limiting factors are slow transformation rates and the mainly composed of white rot fungi are naturally occurring lignin degraders and therefore we have studied the ability of several different fungal species to incubate with technical lignins. We examined how the culturing conditions with the presence or absence of different dietary elements and nutrients affect the expression of specific enzymes and modification of the lignin’s chemical structure. The changes in the chemical structures were analyzed by Pyr- GC, 1H NMR, GPC and elemental analysis. The results can be utilized for the development of more efficient, controlled and faster methods to modify low value technical lignins into high value bio-based products.

Design of a new, accurate laccase activity assay method based on “lignin-like” compounds

Valentina Perna, valper@ikt.dtu.dk, Jane Agger, Jesper Holck, Anne S. Meyer, Center for BioProcess Engineering, Technical University of Denmark, Lyngby, Denmark

Laccase (benzenediol: oxygen oxidoreductases; EC 1.10.3.2; AA1) is a blue multi-copper oxidoreductase enzyme produced in nature by different species of organisms, i.e. fungi, plant and bacteria. Laccases are able to catalyze the oxidation of phenolic compounds using oxygen as final electron acceptor. Due to this capability laccases are currently receiving high attention because of its potential role in lignin degradation. Enzymatic laccase activity has traditionally been determined spectrophotometrically by monitoring the oxidation of artificial chemical compounds such as syringaldazine and 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), also known as ABTS. However, these artificial structures can poorly be related to lignin and such assays provide little information about the true laccase oxidative mechanism. We have developed a highly sensitive, accurate methodology based on UPLC-MS to assess laccase activity on more “lignin-like” compounds. In contrast to spectrophotometric assays, this method also provides information about product formation and time-dependent reaction development. We provide proof-of-concept for methodology to study the ability of different laccases to oxidize different hydroxycinnamic acids (sinapic acid, ferulic acid and p-coumaric acid) and a dimers lignin model compound, determination of kinetic parameters and product profile evaluation. The results show that laccases exhibit highest activity on substrates containing methylated phenolic moieties, and that the product profile during the initial part of the reaction consists of a limited number of dimeric species derived from the substrate. The method is independent of laccase protein purity and can therefore also be used to assess activity of unpurified laccases.
Ceramic membranes for lignin valorization

Stefan Schoenher1, Daniel Humpert1, Mehrdad Ebrahimi1, Peter Geigle1, Stephan Dehmarter1, Steffen Schuetz1, Frank Ehlen1, Peter M. Czemak1,2, czemakpetri@biomat.uni-freiburg.de, (1) IBPT, University of Applied Sciences Gießen, Gießen, Germany (2) BIOPSY, Fraunhofer Institute IMAS, Gießen, Germany (3) Chair of Forest Biomaterials, Faculty of Wood and Biomass, Department of Chemistry, Technical University Darmstadt, Darmstadt, Germany

Despite decades of research aiming at utilizing lignin in bio-based materials, lignin remains mainly used as biofuel in pulp mills. However, the more controlled molecular design of lignin made recently possible by organosolv pulping, opens new opportunities to tailor lignin attributes towards specific process streams and applications. In this context, we are investigating the possibility to template the organization of organosolv lignin into highly structured composite materials. Additionally, we propose that lignin processing and structuration can be facilitated by templating with cholesteric and lyotropic celluloses’ mesophases. In this presentation, we will present the proof of concept for the design of organosolv lignin/cellulose composites to be illustrated on systems comprising organosolv lignin and various cellulose components.

Functionalized lignin as building block for biobased polyurethane foams

Mareike Zieglofski1, zieglofski@cellulose.tu-darmstadt.de, Simon Trosien2, Markus A. Biesalski3, (1) Technical University Darmstadt, Darmstadt, Germany (2) TU Darmstadt, Darmstadt, Germany (3) Department of Chemistry, Technische Universität Darmstadt, Darmstadt, Germany

Polyurethane foams are an important class of polymers, which are synthesized by a polyaddition reaction between isocyanates and polyols to form a urethane linkage. Depending on the chemical structure of used building blocks, their mechanical properties reach from rather rigid to soft and flexible materials. Due to these unique and modular properties, PU foams have a wide range of applications, progressing from furniture-coatings to filter material, automotive seating and thermal insulation. Currently, both the isocynate-component and the polyols are mostly derived from fossil resources. Owing to sustainability issues in the preparation, there is a growing interest to replace such petroleum-based polyols by polyols from renewable feedstocks.

Lignin, a biofuel in pulp mills. However, the more controlled molecular design of lignin made recently possible by organosolv pulping, opens new opportunities to tailor lignin attributes towards specific process streams and applications. In this context, we are investigating the possibility to template the organization of organosolv lignin into highly structured composite materials. Additionally, we propose that lignin processing and structuration can be facilitated by templating with cholesteric and lyotropic celluloses’ mesophases. In this presentation, we will present the proof of concept for the design of organosolv lignin/cellulose composites to be illustrated on systems comprising organosolv lignin and various cellulose components.

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dependent increases in intensity in the EPR signal allowing a direct quantitative monitoring of the radical formation and thus providing for laccase enzyme kinetics assessment on lignin. The experimental data verified that the laccases acted upon the insoluble lignin substrates in the suspensions and that a direct radical formation action of fungal laccases occurs on lignin without addition of mediators. EPR methodology provides a new type of enzyme assay of laccase on lignin and it will be discussed how such type of assay provides more insight into the interaction between laccases, lignins and mediators.

CELL 118

Lignin based polyurethane foam: Relationship between chemical structure, molecular weight, and foam properties

Li-Yang Liu, liyang.liu@alumni.ubc.ca, Lun Ji, Saurabh C. Patankar, Mi-Jung Cho, Scott Renneckar, Wood Science, University of British Columbia, Vancouver, British Columbia, Canada

Lignin, containing a high amount of hydroxyl groups (OH), is an excellent aromatic polyal polyelectrolyte to make polyurethane (PU) foams. However, increasing amount of lignin is known to have negative impacts on final properties of PU foam due to non-uniform characteristics of lignin. The structure of lignin would change dependent on their species, isolation and modification methods. In this study, softwood Kraft lignin (SKL), hydroxypropyl SKL, organosolv lignin from pine bark and oak bark were made to study the relationship between structure and foam properties. Lignin’s structure was thoroughly characterized by quantitative $^{1}$H, $^{13}$C nuclear magnetic resonance. Their molecular weight and thermal properties were also analyzed by gel permeation chromatography, thermal gravimetric analysis, and differential scanning calorimetry. After the viscosity analysis, the lignin-polyol mixture with different ratios were reacted with polyisocyanate, polyurethane disocyanate to obtain PU foam. The maximum amount of lignin in the PU foam was 25% by weight that had properties that resembled the neat PU foam. Comparing with molecular weight and thermal properties, lignin’s structure had more directly impacts on properties of PU foam. For example, a lower ratio of aliphatic OH/aromatic OH led to a higher density and Young’s modulus of the PU foam.

CELL 119

Applicability of laccase mediator systems of recombinant laccase catalyzed oxidation of lignin at low pH

Jussi Kontro1, jussi.kontro@helsinki.fi, Paula Nuutinen2, Mika Kähkönen2, Ulla Hyvärä2, Jooni Mikkilä3, Mika R. Mäkelä3, Kristina Hilden2, Jussi Sippila1 (1) Chemistry, University of Helsinki, Helsinki, Finland (2) Food and Environmental Sciences, University of Helsinki, Helsinki, Finland

Oxidative enzymes, peroxidases and laccases, are the key catalysts in lignin biodegradation. Unlike peroxidases, laccases can only oxidize the phenolic components of lignin on their own, however, their activity can be expanded using mediators. Mediators are low molecular weight compounds capable of extending the oxidation range of laccase to non-phenolic compounds by providing new oxidation mechanisms. The lignin-degrading white rot fungus Ophiostoma novo-ulmi produces several laccases with technically interesting properties such as thermostability, thermal activation and extremely low pH optima. Heterologous expression of the nol. rivulosa laccases in Pichia pastoris enables the detailed study of their properties and the evaluation of their potential as oxidative biocatalysts for conversion of wood lignin, lignin-like compounds, and soil-borne xenobiotics. The enzymatic properties of the recombinant laccases demonstrated low pH optima of pH 3-4. The oxidase efficiency of these recombinant enzymes in various laccase mediator systems (LMS) using different lignin model compounds and analyzing the products using HPLC. The results showed that LMS can be used to selectively oxidize different types of non-phenolic substrates. We further compared these results with the performance of LMS-oxidation on biorefinery sourced poplar lignin.

CELL 120

Mediator supported lignin enzymatic degradation for aromatic production

Lionel Longe1, lionel.longe@monash.edu, Gil Garnier1, Kei Saito2 (1) Monash, Clayton, Victoria, Australia (2) Monash University, Malvern East, Victoria, Australia

Lignin depolymerisation is critical for the implementation of biorefineries and to promote the creation of new biobased materials. The high recalcitrance of lignin to degradation is usually overcome by processes operating under extreme conditions of pH, temperature or pressure. Here, we present a green and nature-inspired methodology for the efficient and selective degradation of lignin. Enzymatic depolymerisation allows aqueous toxic free reaction under normal condition of temperature and pressure. We report how lignin can be degraded using a series of complementary enzymes: lignin peroxidase, manganese peroxidase, laccase, and a white rot fungus secretome from Grammothele fulgida. Five mediators — tert-butyli-di-methyl phenol, tri-tert-butyliphenol, ABTS, viologen acid, HBT — involved in laccase mediated systems, were tested to enhance depolymerisation by selectively favouring cleavage-specific bond in the lignin structure. Degradation by single enzyme systems could degrade lignin by reducing the molecular weight by up to 70% in 24h and at room temperature. Further degradation was obtained with laccase mediated systems (LMS). tert-butyli-di-methyl phenol (TBDMP), a new mediator, proved as efficient as the well-known ABTS mediator for LMS. However, TBDMP target different bonds (4-0, 5-5) in the lignin structure than ABTS or VA do, suggesting possible synergistic effect of simultaneous or sequential treatment of lignin by different LMS. Three different types of technical lignin, namely organosolv grass lignin, kraft hardwood lignin and alkaI hardwood lignin, of different chemical structure were studied to compare the action of ligninolytic enzymes and provide insight on the degradation mechanism. Analyses of the recovered products by 2D NMR was used to understand the oxidation reaction on the different bonds of lignin and the degradation mechanism. Variation of the $\beta$-O-4, $\beta$-S and $\beta$-C was monitored as well as the preferential oxidation of S or G over H.

CELL 121

Application of lignins in phenol formaldehyde adhesive

Hasan Jameei1, Xiao Jiang2, xjiang11@ncsu.edu, Fengta Zhang2, Jing Du1, Hou-min Chang1 (1) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States (2) Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing, China

Lignin has great potential for substituting phenol in the phenol formaldehyde adhesive. Three different lignins were used to synthesize lignin-phenol-formaldehyde resin, namely a commercial pine Kraft lignin, a hardwood (sweet gum) and a non-wood (wheat straw) residual lignin isolated from a biofinery process involving autohydrolysis and enzymatic hydrolysis (AER). These lignin sources were chosen based on their differences in structure, functionality and molecular weight. Lignins were characterized including chemical composition, molecular weight and reactive sites. The effect of phenolation was also investigated, since phenolation can increase the lignin reactivity and also decrease the molecular weight. Phenolization is an economically viable method for lignin modification since the excess phenol used during phenolization can be used to develop crosslinks during the curing process for adhesives. The lignin-phenol-formaldehyde resins were applied on the yellow poplar plywood and evaluated in terms of shear strength. The results indicated that up to 25% phenol could be replace by pine kraft lignin without significantly sacrificing the adhesive strength. Phenolizing the pine kraft lignin enabled an increase in the substitution to approximately 45%. Lignin-phenol-formaldehyde resin prepared using AER from both sweet gum and wheat straw exhibited comparable adhesive performance as phenol formaldehyde resin at substitutions levels up to 35%. However, phenolization did not improve the performance of AER based adhesives. This research has demonstrated that lignin can be used to substitute for phenol in PF adhesives and the degree of substitution that can be achieved depends on the lignin source and reactivity.

CELL 122

Carbonization of electrospun and wet spun lignin based fibers

Tripp Hinkle1, jah0095@tigersmail.auburn.edu, Christopher Upp1, cwu001@tigersmail.auburn.edu, Archana Bansode1, as0062@tigersmail.auburn.edu, Hyungseok Nam1, Bari Filipponi1, Sushil Antha1, Mana Auad1 (1) Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) Center for Polymers and Advanced Composites, Auburn University, Auburn, Alabama, United States (3) Biosystems Engineering, Auburn University, Auburn, Alabama, United States

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 a large fraction being burned as low-valued fuel, lignin represents a significant valued fuel, lignin represents a significant
Cellulose-based carbon fiber reinforced polymers: Intensifying interfacial adhesion

Laszlo Szabo1, lasz.szabodi@gmail.com, Sari Imanishi1, Rina Hoshrno, Naohiro Kawashima1, Daisuke Hirose, Takayuki Tsukeg8, Keri Takahashi1. (1) Institute of Science and Engineering, Kanazawa University, Kanazawa, Japan (3) Innovative Composite Center, Kanazawa Institute of Technology, Kanazawa, Japan

Carbon fiber reinforced polymers (CFRPs) are the paragon of advanced green materials that help reducing CO₂ emissions in several transportation applications owing to their lightweighting effects. Nevertheless, in these high-performance composites, thermosetting epoxy resins are mostly applied that are inherently not green. Introduction and successful implementation of cellulose-based thermoplastic polymers would undoubtedly bring a breakthrough in this field providing a renewable, biocompatible feedstock for this industrial segment.

In order to reach high strength for the cellulose-based composite, the carbon fiber surface needs to be modified to improve interfacial adhesion that is a crucial factor to efficiently transfer the physical stress from the matrix to the fiber. Our research aimed at covalently binding cellulose propionate, a promising candidate for the matrix, to the carbon fiber surface to increase interfacial shear strength between the fiber and the polymer matrix. In doing so, we have successfully bound cellulose propionate to the carbon fiber surface by grafting small molecule first with appropriate functional group to take part in the following click reaction or nucleophilic replacement involving the corresponding cellulose propionate derivative (Figure 1). The covalent modification lead to an increase in interfacial shear strength and allowed us to have a deeper insight into the interfacial behavior of these kind of composites.
azodicarbonamide (ADC), dicyandiamide (DCD), 5-hydroxymethylfurfural (HMF), and hydroxypropyl (HP) cellulose. Based on TGA, ADC and DCD appear to be the best candidates for enhancing aerosol injections to increase yields of high-molecular weight compounds. The onset of decomposition for ADC and DCD is 200 and 250, respectively. Cellulose begins to lose mass under TGA between approximately 300-350, and each of the derivative TGA curves for ADC and DCD have local maxima within this temperature range. Future work will investigate the experimental pyrolysis of cellulose/hemicellulose/additives mixture with TGA and through analysis of collected products with spectrosopic and chromatographic methods.

CELL 128
High performance cyanate esters and poly(benzoxazine) from fast pyrolysis of lignocellulosic biomass

Mehul Barde,1,2* mb00083@aub.edu, Charles W. Edmunds3*, Nicole Labelle2, Maria Auzaitis1,2, (1) Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States (3) Center for Polymers and Advanced Composites, Auburn University, Auburn, Alabama, United States

Fast pyrolysis of pine wood was carried out in an Auger reactor at 500°C. The bio-oil was fractionated into organic and aqueous phases. Cyanate ester resin was synthesized from the organic phase of bio-oil by reacting with cyanogen bromide in presence of triethylamine at -10°C. Fourier transform infrared spectroscopy (FTIR) confirmed the synthesis of cyanate ester functionality and its further conversion into triazole rings during crosslinking. Bio-oil-based cyanate ester resin was heated in aluminum mold in inert atmosphere to produce crosslinked polymers. Differential scanning calorimetry (DSC) of the crosslinked polymer showed high glass transition temperature, 172°C and was comparable to traditional petroleum-derived poly(cyanate) esters. Dynamic mechanical analysis (DMA) was performed for comparing thermo-mechanical performance of bio-oil-based and petroleum-based resins. Organic phase of bio-oil was also reacted with paraformaldehyde and a polyetheramine to yield bio-oil-based benzoxazine monomer. Benzoxazine was crosslinked similarly to produce poly(benzoxazine) thermoset that displayed glass transition temperature as 120°C. Morphology of cured polymers was observed through scanning electron microscopy and the solvent resistance was assessed by Soxhlet extraction. The high oil derived cyanate ester and benzoxazine polymers provided high performance thermosetting materials aimed at high-end applications including aerospace and electronics.

CELL 129
Synthesis of unsaturated monomers from carbonyl compounds in pyrolytic bio-oil

Mehul Barde1,2*, mb00083@aub.edu, Katrina Avery1,* jna00100@aub.edu, Charles W. Edmunds3*, Nicole Labelle2, Maria Auzaitis1,2, (1) Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States (3) Center for Polymers and Advanced Composites, Auburn University, Auburn, Alabama, United States

The goal of this research is to convert carbonyl compounds found in fast pyrolysis bio-oil into unsaturated monomers for polymer synthesis. Bio-oil is a liquid product obtained through the pyrolysis of biomass. In our research, carbonyl containing compounds, aldehydes, and ketones were derived from the pyrolysis of corn stover. These compounds were extracted from the bio-oil by column chromatography. The carbonyl compounds were converted into alkylated esters and ketones through AlCl3 catalyzed oxidation. Then, through Wittig reaction, aldehydes and ketones were converted into olefins. Two different Wittig approaches were performed. Firstly, a water-mediated Wittig reaction was carried out using a stabilized ylide, which yielded an terminal olefin from aldehydes present in the bio-oil. Secondly, Wittig methylenation reaction of aldehydes and ketones with an unstabilized ylide produced terminal olefins. Finally, the unsaturated products were polymerized by AIBN initiator at elevated temperature to build polymers.

CELL 130
Effective adsorption and recovery of furfural and 5-hydroxy-3-methylfurfural by cross-linked polyethyleneimines

Qiang Yang, qiang.yang@wmich.edu. Chemical and Paper Engineering, Western Michigan University, Kalamazoo, Michigan, United States

Cellulosic ethanol can be produced from lignocellulosics through the fermentation of hemicellulose and pentose sugars. The lignocellulosics are inherently recalcitrant to enzymatic attacks, which necessitates a chemical pretreatment to disrupt the structure and create more reactivity for cellulose to cellulosic enzymes. However, the hemicellulose and pentose sugars can be respectively degraded to 5-hydroxy-3-methylfurfural (HMF) and furfural, which can inhibit cell replication and thus decrease the ethanol production. Therefore, it is very important to recover furfural and HMF. On the other hand, furfural and HMF are valuable chemicals, and therefore could provide value if easily separated. This study demonstrated the effective adsorption and recovery of furfural and HMF by cross-linked polyethyleneimine (CPEI). The results showed that the adsorption was very dependent on the furfural or HMF concentration, CPEI dosage, and pH. The CPEI showed the exclusive adsorption of furfural and HMF without the adsorption of the fermentable sugars (glucose and xylose). The presence of organic acids such as formic, acetic, and levulinic acids could interfere with the adsorption of furfural and HMF. The adsorbed furfural and HMF can be recovered through acid treatment and reprocessing as valuable chemicals, and the spent CPEI can be readily separated and regenerated with base treatment for reuse.

CELL 131
Analysis of the influence of lignocellulosic characteristics on thermal behavior using pyrolysis gas chromatography/mass spectrometry

Sarah Hodges1,2, sarah.hodges@uiuc.edu, Gerd Mortha3, Capucine Dubrulle4, Eduardo Santillán-Jiménez1, (1) Center for Applied Energy Research, University Of Kentucky, Lexington, Kentucky, United States (2) Chemistry , University of Kentucky, Lexington, Kentucky, United States (3) IMAPP-Pagas, University of Grenoble-Alpes, Grenoble, France (4) Atomic Energy and Alternative Energies Comission , Grenoble, France

In the production of biofuels, biomass undergoes various chemical treatments and synthesis processes. When producing biofuels from lignocellulose, the feedstock must undergo the thermochemical conversion process of torrefaction. As an element of the torrefaction process, the Biochip team at the LP2G laboratory at the University of Grenoble, France, in collaboration with the Biofuels and Environmental Catalyst group at the University of Kentucky Center for Applied Energy Research (UK CAER) began a joint project to analyze the thermal effects of the modification of carbohydrates in biomass. These modifications to cellulose occur throughout the various chemical treatments to the biomass feedstock, affecting properties such as degree of polymerization, crystallinity, and content of functional groups. The thermal behavior of treated cellulose was primarily analyzed utilizing pyrolysis gas chromatography- mass spectrometry (Py-GCMS). The crystallinity was observed through scanning electron microscopy (SEM), in addition to various chemical properties of cellulose being measured through standard chemical analysis methods. Cellulose samples mainly underwent chemical treatments at the LP2G laboratory, while analysis was mainly completed at UK CAER.

CELL 132
High value carotenoids from biorefinery waste streams

Makua Vin-Najiofo1, makua.vin@aub.edu, Jian Shi2, LaiLutendu Das3, (1) Biosystems Engineering, University of Kentucky, Lexington, Kentucky, United States (2) Biosystems Engineering, University of Kentucky, Lexington, Kentucky, United States

Antioxidants are a class of substances that suppress oxidation and protect the cell from damage caused by free radicals. Antioxidant compounds, such as carotenoids, have wide applications towards food, cosmetic, pharmaceutical and agricultural industry and the fast-growing demand for natural carotenoids is fostering a multimillion-dollar market. Producing carotenoid from the waste stream of renewable lignocellulosic biomass by naturally occurring microbes offers an environmentally friendly and sustainable solution to this biochemical challenge. In this study, we explored the feasibility of using the undervalued biorefinery waste streams to produce high-value carotenoids such as β-carotene and astaxanthin. First, we prepared and characterized two liquid streams from dilute sulfuric acid and alkali pretreatment of corn stover. Cullation conditions (temperature, N-source and dilution ratio) were then optimized for microbial growth and heterotrophic carotenoid production using Blasckia trispora and Xanthophyllomyces dendrorhous. Based on the elemental data, a preliminary cost analysis was conducted using Excel dashsheet to understand the carotenoid production cost using the proposed technology. Production and purification of β-carotene is a complex process, i.e. it can only create extra revenue for the biofuels industry but also help to mitigate the adverse environmental impact.

CELL 133
Oxypyrolysis of lignocellulosic agro-industrial residues: New approaches and tools towards process optimization

João A. Pinto1, Miguel A. Pêto2, Isabel C. Ferreira3, Naceur Belgacem4, Aílio E. Rodrigues4, Filomena Barreiro2,1*, barreiro@ipb.pt. (1) Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Bragança, Portugal (2) LSRE-CLM, Polytechnic Institute of Bragança, Bragança, Portugal (3) CIMO, Polytechnic Institute of Bragança, Bragança, Portugal (4) Laboratoire de Génie des Procédés Papetiers, Domaine Universitaire, St. Martin d’Hères, France (5) LSRC, University of Porto, Porto, Portugal

Nowadays a great interest is devoted to the production and use of bio-based products. The main scope of the oxypyrolysis process is to obtain polyols, in the form of viscous liquids, which can be used as co-monomers to produce polyurethanes and polystyres. The efficiency of an oxypyrolysis process depends on several variables (e.g., lignocellulosic composition, the crystalline organization, hydroxyl content etc.) and processing conditions (catalyst content (% w/w), the AS/O (AS/α, β units) ratio, which may limit reagent’s access to biomass and cannot be generalized to all substrates. Therefore, owing to biomass variability, selection of the appropriate conditions for oxypyrolysis and their optimization is an important issue. In the present work the oxypyrolysis of different biomass substracts was performed and related with the properties of the produced polyols (homopolymer content (HOMO, % (w/w)) and the AS/O (α, β units)), which can only create extra revenue for the biocells industry but also help to mitigate the adverse environmental impact.

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Single crystals of biosynthesized and biodegradable Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHx)

Changhao Liu, chiuliu@udel.edu, Isada Noata,2 David C. Martin,1 Bruce Chase,1 John F. Rabolt1
(1) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States
(2) Danimer Scientific, Bainbridge, Georgia, United States

Single crystals of biosynthesized biodegradable Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHx)

Bio-based materials draw much attention due to their renewable nature and comparable properties with their petro-derived counterparts. As one of those emerging bio-derived materials, biodegradable Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBHx) biosynthesized through bacteria fermentation has favorable physical properties tunable through different amount HHx content incorporated. PHBHx exists as amorphous materials in microorganism cells. Upon extraction, this material crystallize due to the iso tactic nature of the β carbon along the backbone. To investigate the crystallization behavior, single crystals of PHBHx with varying HHx content have been prepared at varied crystallization conditions. All the crystals adopt the alpha phase of homopolymer PHB. However, crystal morphology and texture structure varies significantly, which are summarized below:

1. For PHBHx(3.9mol%), the crystal has a 2-D like spindle shape, characterized by hundreds nanometer long, 50 nm wide, and 5 nm thick. Growth rate along the α-axis of the unit cell is ~70 times faster than that along the β-axis at high degree of supercooling, whereas this rate ratio decreases to 16 at low degree of supercooling (as shown in image). This anisotropic growth habit is believed arising from the difference of molecular interaction between the the β-axis which involve H-bonding interaction and the α-axis which has only van der waals’ interaction.

2. For PHBHx(13mol%), the crystal has a 3-D like spindle shape, with hundreds nanometer long, 50 nm wide, but 70 nm thick. Anisotropic growth behavior also exist but with an inverse manner than that of PHBHx (3.9mol%). In this case, larger supercooling, smaller aspect ratio whereas smaller supercooling, higher aspect ratio (as shown in image). Additionally, the crystals are extremely size uniform. Preliminary results show an ordered packing of these crystals (as shown in image). A novel structure formed by single crystals connecting with each other was also observed (as shown in image).

Effect of hot water pretreatment in simple pulping utilizing a laboratory scale microwave reactor

Uula T. Hyvakko1, uula.hyvakko@helsinki.fi, Paula Nousiainen1, paula.nousiainen@helsinki.fi, Petri Kiveläinen1,4, Jussi Sipila2,4, (1) Chemistry, University of Helsinki, Helsinki, Finland (2) University of Helsinki, Helsinki, Finland (3) Organic chemistry, University of Helsinki, Helsinki, Finland (4) Luomonenkokeskus (LuKe), Helsinki, Finland

Pretreatments play a pivotal role in valorizing biomass in order to break down its recalcitrant composite structure that protects the plant from the environment. The objective of this is to collect value-added fractions such as cellulose, hemicellulose and lignin rich fractions for further processing to e.g. biofuels or other valuable materials or chemicals. Currently, Kraft process is by far the most dominant process for valorizing many woody species, such as pine, birch and spruce. Cellulose of Jerusalem, Rehovot, Israel (2) RISE Bioscience and Materials – Chemistry, Materials and Surfaces, RISE Research Institutes of Sweden, Stockholm, Sweden (3) Silberman Institute of Life Sciences, The Center for Nanotechnology and Nanomedicine, The Hebrew University of Jerusalem, Jerusalem, Israel (4) Department of Chemistry, McGill University, Montreal, Quebec, Canada

A series of four cellulose nanocrystal (CNC) suspensions were prepared from bleached softwood Kraft pulp using different conditions of sulfuric acid hydrolysis. The CNCs were identical in size (95 nm in length × 5 nm in width) but had different surface charges that increased with increasing harshness of the hydrolysis conditions. Consequently, it was possible to isolate the effects of surface charge on the self-assembly and rheology of the CNC suspensions across a range of surface charges from 0.27 % to 0.86 %. The four suspensions (free of added electrolyte) all underwent chiral nematic phase separation but the concentration at the emergence of the chiral nematic phase shifted to higher values with increasing surface charge. Similarly, suspension viscosity was also influenced by surface charge, with suspensions of lower surface charge CNCs more viscous and tending to gel at lower concentrations. The properties of the suspensions were interpreted in terms of the effective diameter of the particles, which decreased with increasing surface charge, but also by the formation of end-to-end aggregates at relatively low concentrations in the suspension of lowest surface charge CNCs. The results suggest a threshold surface charge density (~0.3 μC/cm²) above which effective volume considerations are dominant across the concentration range relevant to liquid crystalline phase formation. Above this threshold value, phase separation occurs at the same effective volume fraction of CNCs (~10 vol%), with a corresponding increase in critical concentration due to the decrease in effective diameter that occurs with increasing surface charge. Below this threshold value, the formation of end-to-end aggregates hastens gelation and interferes with ordered phase formation.

Function of the Golgi apparatus in differentiating xylem in Chamaecyparis obtusa

Keeji Takabe, kjtakabe@kaist.ac.kr. Graduate School of Agriculture, Kyoto University, Kyoto, Kyoto, Japan

The Golgi apparatus is known to be involved in synthesis and transport of pectins and hemicelluloses. PATag staining results show that the Golgi apparatus in the differentiating xylem, indicating the Golgi apparatus involved in the synthesis of hemicelluloses. Although this method stained polysaccharides selectively, it is difficult to distinguish one hemi cellulose from another one. Antibody raised against targeting hemicellulose is a powerful tool to label the hemicel lulose selectively. Glucomannan and xylan are main hemicelluloses in softwood. We applied the immuno labeling to investigate how these hemicelluloses are synthesized in the Golgi apparatus and transported towards the developing cell walls in softwood.

Materials and methods

Differentiating xylem of Chamaecyparis obtusa compression wood was excised into very small pieces with a razor blade, and fixed by high-pressure freezing. Then the specimens were freeze substituted in acetone containing 4% osmium tetroxide and 8% 2,2-dimethylpropylene for 5 days at 80 degree Celsius, washed with acetone and embedded in epoxy resin. Ultrathin sections were cut and immunolabeled with LM11 for xylan, BGM C6 for glucoman nan, and LM5 for galactan independently or in combination.

Results and discussion

In case of immunolabeling of glucoman nan, more than sixty percent of the Golgi apparatus was labeled during secondary wall formation stages, suggesting glucoman nan continuously synthesized in the Golgi apparatus and transported towards secondary cell wall. In case of immunolabeling of xylan, more than forty percent of the Golgi apparatus was labeled, suggesting xylan synthesized and transported in the same manner of glucoman nan. In case of immunolabeling of galactan, more than seventy percent of the Golgi apparatus was labeled in one cell formation stage, suggesting galactan synthesized in the Golgi apparatus transported towards cell wall mainly in outer S2 formation stages. In case of double immunolabeling of glucoman nan and xylan, many Golgi apparatus showed double labeling. However, each Golgi vesicle was labeled independently with LM11 or BGM C6, namely, one Golgi vesicle was labeled with LM11, and another vesicle was labeled with BGM C6.Above results indicated that two or more hemicelluloses are simultaneously synthesized in the Golgi apparatus and each hemicellulose is independently packed in the Golgi vesicle.

Laccase/TEMPO oxidation in the production of hemicellulose hydro- and aerogels

Kirsti Parikka, Ida Nikkilä, Maija Tenkanen, maija.tenkanen@helsinki.fi. University of Helsinki, Helsinki, Finland

Refining of forestry and agriculture side streams possess high potentials for novel bio-based materials. Hemicelluloses are group of polysaccharides covering up to one third of lignocellulosic residues. Polysaccharides as renewable, non-toxic and biodegradable materials are highly valuable resources for modern advanced materials that have the potential to replace synthetic
plastics. The functionality of native polysaccharides can be improved by enzymatic and chemical modifications. New hemimellitose-based hydrogels and aerogels were prepared by hemimellitose crosslinking induced by laccase - TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) catalyzed oxidation. Laccase enzyme can regenerate TEMPO, which selectively converts primary hydroxyl groups of carbohydrates to aldehydes in acidic conditions. The degree of oxidation was ca. 10 % of the total carbohydrates of the polysaccharides. No formation of carboxylic acids was detected. The oxidized polysaccharides formed true hydrogels as shown by the storage and viscous moduli. Two freezing methods for the hydrogels, conventional freezing and ice crystal templating, were studied prior lyophilization to aerogels. The determined compressive moduli of the ice crystal templated arabinoxylan and glucomannan aerogels were high, ca. 1200 kPa and 600 kPa, respectively. Ice crystal templated arabinoxylan aerogels did not dissolve in water during the 24 h experiment. Scanning electron microscopy revealed different structural features. The arabinoxylan aerogel consisted of long and narrow pores with a length of a few hundreds μm and width of 50-100 μm, which had formed in the direction of the ice crystals’ formation, whereas glucomannan aerogel formed round pores with a diameter of ca. 50-100 μm. This type of novel products have potential in various applications, including the food, food packaging, and pharmaceutical fields.

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Electric and magnetic properties of cellulose nanocrystals in suspension revealed by field-induced birefringence

Bruno Fkra-Potesic1, Boldor@cam.ac.uk, Junji Sugiyama2, Bruno R. Jean1, Satoshi Kimura3, Henri D. Chanzy4, Laurent Heux4, (1) CERMÁV-CNRS, Grenoble Cedex 9, France (2) Research Institute for Sustainable Humanosphere, University of Kyoto, Kyoto, Japan (3) Department of Biomaterials Science, Graduate School of Agricultural and Life Sciences, University of Tokyo, Tokyo, Japan (4) Department of Physics, University of Konstanz, Konstanz, Germany

Cellulose nanocrystals (CNCs), isolated e.g. by sulfuric acid hydrolysis from cellulosic fibers, form coheribly stable suspensions of cellulose in their native crystalline form (cellulose I). While the application of electric or magnetic field was known to induce an alignment of the CNCs respectively parallel or perpendicular to their longer axis, the precise mechanism of this orientation coupling remained poorly documented.

In this invited talk, we report with two recent experiments how we addressed qualitatively and quantitatively the origin of electric and magnetic alignment of individual CNCs, exploiting the static and dynamic alignment of dilute suspensions under external fields, and monitoring their orientation from the induced birefringence.

Electric field alignment was performed on surfactant-stabilized cotton-source CNCs in apolar solvent. While static field alignment with increasing field strength allowed to measure the Kerr constant, constant for both static and induced electric alignment, the alignment measured in dynamic field reversal configuration allowed for discriminating the two contributions, with a dominant permanent dipole as high as 4000 Debye. Such giant dipole in native CNCs could be explained by the build-up of the polarity in the parallel chain conformation of Cellulose I.

Diamagnetic properties of cellulose I were experimentally investigated from the magnetic alignment of dilute aqueous CNC suspension. Micron-long tunicate cellulose crystals were aligned using strong magnetic source (up to 17.5 T) to reach nearly 90% alignment. The induced birefringence was then analyzed using three orientation-coupling scenarios (two uniaxial models and one biaxial), while both intrinsic and shape birefringence of CNCs in water were accounted for. Finally, a thorough statistical analysis of the CNC shape distribution allowed for an estimation using strong magnetic source (up to 17.5 T) to reach nearly 90% alignment. The induced birefringence of CNCs in water were accounted for. Finally, a thorough statistical analysis of the CNC shape distribution allowed for an estimation of both permanent and induced magnetic moment of cellulose I, slightly higher than the one we deduced from Pascal adiabatic law.

CELL 140

Putting a charge into polysaccharides

Brittany L. Nichols1, Yifan Dong2, Kevin J. Edgar2, kjedgar@vt.edu. (1) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (3) Mail Code 0232, Virginia Tech, Blacksburg, Virginia, United States

Charged polysaccharides are important in nature, comprising important primary and secondary cell wall components of all plants, up to 40% by weight of kelp, and comprising nearly all of the complex glycosaminoglycans that are so vital to human health, to cite only a few examples. Charged derivatives of polysaccharides are commercially important as well. Carboxymethyl cellulose (CMC) is the highest volume commercial cellulose ether, useful in cleaning products, obtaining creams, and many other applications. Hydroxypropyl methylcellulose acetate succinate (HPMCAS) is one of the most useful polymers for creation of amorphous solid dispersions, which help to enhance aqueous solubility, and thus bioavailability, of otherwise poorly soluble drugs. Synthesis of charged polysaccharides is challenging, especially in cases where the charges that can already have substrates of like charge is disfavored, in some cases limiting the amount of charge that can be attained. We will discuss here some of our recent work on applying new chemistries, and some more mature ones, to selective synthesis of charged polysaccharides. In all cases that we already describe we will see very good cromoselectivity, and in many cases the synthetic design enables us to achieve strong regioselectivity as well. The products are very interesting materials for application in drug delivery, tissue engineering, consumer products, and in many other potential applications.

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Magnetic field induced alignment of cellulose nanocrystals in polyvinyl alcohol suspensions

Masahisa Wada. wadam@kais.kyoto-u.ac.jp, Hiroki Mori, Ryosuke Kusumi, Fumiko Kimura, Tsubohisa Kimura. Kyoto University, Kyoto, Japan

Suspensions of cellulose nanocrystals (CNCs) produced by the sulfic acid hydrolysis of three different origins, i.e., cotton, tunicate, and a green alga Cladophora, were mixed with aqueous polyvinyl alcohol (PVA) solution. The CNCs/PVA suspensions were poured into polypropylene petri dishes and allowed to dry at 35°C under horizontal magnetic field ranging from 1 t to 8 T. The CNC/PVA films were subjected to X-ray diffraction analyses. From the recorded images, the orientation of the CNCs in the films was evaluated. The orientation patterns were different depending on the origin of the cellulose; tunicate and Cladophora showed uniaxial orientation, while cotton showed rather nematic orientation. The orientation degrees of tunicate and Cladophora were higher than the previously reported results for those prepared without PVA. This is probably because the PVA molecules anisotropically aggregated on the CNC surface enhancing the magnetic anisotropy of CNCs.

CELL 142

Tissue-specific cellulose microfibril assembly patterns in plant cell walls: A study with sum frequency generation microscopy

Seong H. Kim. seungkim@engr.psu.edu. Chemical Engineering, Pennsylvania State University, University park, Pennsylvania, United States

Cellulose microfibrils (CMFs) in plant cell walls play critical roles which vary depending not only the growth stage of cells, but also the tissue type, thus, it is critical to obtain spatially-resolved cellulose-specific spectroscopic information of CMFs in plant cell walls for better understanding of how CMFs are synthesized and deposited in plant cell walls under various independent and exogenous stimuli or conditions. Such information would provide more detailed structural information that could not be obtained from chemical composition analysis averaged over large area. In this talk, we will demonstrate that sum frequency generation (SFG) vibrational spectroscopy can be used to selectively detect CMFs in native plant cell walls as well as protein-free lignocellulosic biomass. The SFG scattering intensities can be used to nondestructively analyze polymeric structure of cellulose in the nanoscale, preferential packing of CMFs and changes in interfibrillar distances in the mesoscale (between nano and micro). This technique is now combined with optical microscopy, which allows full spectral imaging of CMFs with SFG with a special resolution of about 5 microns. This newly-developed SFG microscopy is used to investigate CMF deposition patterns or amounts in different types of cell tissues – for example, interfascicular fiber, xylem, phloem, cortex, and epidermis of Arabidopsis inflorescence stems or primary and secondary cell regions of Microtus tanairi. Also, utilizing the scattering principle, SFG is demonstrated to be able to distinguish the hydrogen groups inside CMFs versus those at the surface of CMFs, which opens up a new opportunity to spectroscopically study CMF-matrix polymer interactions in plant cell walls. Examples of these studies will be discussed in this talk.

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Outstanding toughness of cherry bark achieved by a unique cell wall structure

Kayoko Kobayashi1, kOka55kobayashi@gmail.com, Yoko Ura1, Satoshi Kimura1, Junji Sugiyama2. (1) Kyoto University, Uji, Kyoto, Japan (2) The University of Tokyo, Tokyo, Japan (3) Nare National Research Institute for Cultural Properties, Nara, Japan

Cellulose, a main component of cell walls, generally makes materials hard and brittle. Development of novel materials utilizing cellulose has been the trend for the last decades, with progress in the manufacturing technology of nanocellulose or cellulose nanofiber. One of the challenges for the cellulose-based materials is adding toughness; generally, strength and toughness are conflicting properties. In nature, however, an ultra-tough cellulose material is found: cherry bark. Surprisingly, it elongates by more than twice of its initial length, and behaves as a plastic film during stretching. This amazing mechanical property is achieved by a well-designed cell wall structure: cellulose fibers are folded like helical springs, covered by multiple flexible layers of lipid polymers. The helical cellulose microfibrils were extended rapidly when necking occurred. The extended helices had higher strength than the initial slow helices in the elongated direction. Therefore, the material did not fracture until the necking expanded to the whole material. The covering layers of suberin had also important roles, as both reinforcement of
Glucose to fructose isomerization over natural MgO catalysts

Konstantinos Triantafyllidis1,2, nikanta@chem.auth.gr, Asimina Marianou1,2, Chrysoula Michailod, Stamatis Karakoulis3, Eleoni Iopoulou3, Angelos Lapra1,1 (1) Aristotle University of Thessaloniki, Thessaloniki, Greece (2) CPERI, CERTH, Thessaloniki, Greece

Lignocellulosic biomass has attracted increased interest as an appealing alternative for the production of bio-fuels and bio-chemicals. Among these chemicals, fructose is a very important aldox which is not only required for a wide variety of commercial products, but also as a starting material for the synthesis of bio-based chemicals such as hydroxymethylfurfural, levulinic acid, lactic acid etc. Fructose can be synthesized from glucose via isomerization, a reaction which is currently performed enzymatically at industrial level entailing the limitations of enzymatic processes. Chemically the reaction can be performed either under basic or acidic conditions (mainly Lewis acidity). The most common homogeneous catalytic systems employed are based on alkali and alkaline earth hydroxides. Regarding heterogeneous catalysts, Sn, Beta, alkali-doped zeolites, hydroaluminas and Lewis acid oxides have been proposed. Nonetheless, the effectiveness of MgO was recently demonstrated by our group. When the reaction was conducted in aqueous solution, at mild reaction conditions (90 °C, 45 min), MgO resulted in high fructose selectivity of 75.8% and glucose conversion of 44.1%

In this framework, glucose isomerization to fructose over MgO catalysts (synthetic or natural produced from magnesite via calcination), with different morphology and properties was investigated further in the present study, with the aim of clarifying the correlation between their physicochemical characteristics (i.e. crystal size, surface area, basicity) and catalytic performance. According to the experimental results, the catalytic activity of MgOss depends significantly on the basicity which is affected by catalyst morphology (i.e. surface area, crystal size) and composition (i.e. CeO2 and SiO2 impurities of the natural MgO catalysts). Increased total/weak basicity was correlated with high fructose selectivity, contrary to increased strong basicity (due to CaO) that affected negatively the selectivity.

Catalytic transfer hydrogenolysis of aromatic ethers promoted by the bimetallic Pd Ni system

Emilia Paeo1, Rosario Pietropaolo1, Francesco Maurello1, francesco.maurello@unir.it, Rafael Luque1, (1) Department of Civil, Energy, Environmental and Materials Engineering (DICEAM), Mediterranean University of Reggio Calabria, Reggio di Calabria, Italy (2) Universidad de Cordoba, Cordoba, Spain

In order to develop selective catalytic processes for the production of aromatics from lignin, a complete understanding of the molecular aspects of the basic chemistry and reactivity of aromatic ethers is crucial. Diphenyl ether (DPE), Phenethyl phenyl ether (PPE) and Benzyl phenyl ether (BPE) are the simplest model molecules of 4-O, 5-, β-O-4 and α-O-4 lignin linkages.

In this context, a bimetallic Pd-Ni catalyst (with a nominal palladium loading of 3 wt%) has been prepared by the co-precipitation technique with the aim to test its catalytic activity in the cleavage of the C-O bond of DPE, PPE and BPE under catalytic transfer hydrogenolysis (CTH) conditions using 2-propanol as H-donor. CTH reactions have gained increasing attention as an efficient alternative to the direct use of molecular hydrogen. For comparison, a monometallic Ni catalyst was prepared with the similar procedure as above and tested under the same reaction conditions. The physico-chemical characterization of all investigated catalysts was performed through H2-TPR, TEM, XRD and XPS analysis.

Using Pt-Ni as catalyst and 2-propanol as H-source, under batch conditions, an appreciable DPE (0.1 M) conversion was achieved after 90 min at a temperature as low as 180 °C. The conversion of DPE increases by rising the reaction temperature and it is fully converted at 240 °C. On the other hand, the metallic Ni catalyst was found to be less active. At the same time, a lower bond dissociation energy (β-O-4 = 289 kJ/mol and α-O-4 = 218 kJ/mol) with respect to the C-O bond of DPE.
processes due to their simplicity of preparation, unique physicochemical properties, are biodegradable and recyclable, and, they are often of natural origin [2]. However, an understanding of the mechanisms underlying the solubilisation of biomass components that would enable a rational selection of DES and process conditions for specific applications is still needed [4]. In this communication, we will show the latest developments on the solubilisation of polysaccharides in several Natural Deep Eutectic Solvents (NADES) and their aqueous solutions, and the effect of NADES composition, concentration and temperature. The confirmation of DES potential will be further confirmed by some examples of their application in integrated and sustainable strategies for biomass fractionation and valorisation.

CELL 150

Catalytic C-O bond cleavage in non-derivatized alcohols

Joseph S. Samec, joseph.samec@su.se. Dept Chemistry, BMC, Uppsala University, Uppsala, Sweden

Alcohols are easily accessible organic compounds and the OH group constitutes the most abundant functional group in biomass. These substrates are used in organic synthesis as nucleophiles. When alcohols are used as electrophiles, the OH group needs to be transformed to a better leaving group. This transformation requires additional reagents, purifications and reactor time in industry. If the OH group could be substituted by a non-charged nucleophile, the only by-product would be water. In addition, efficient methodologies to substitute the OH group are essential if we want to transform into a bio-based economy in the future. A further challenge is to conserve the chirality of the easily accessible stereogenic alcohols in the substitution reaction. Our group has developed several methodologies to substitute the OH group in non-derivatized alcohols. We have developed a novel Pd[BBPhos]Phos complex that can substitute the OH group of non-derivatized enantiomeric allylic alcohols by O-, N-, and C-centered nucleophiles where the products can be isolated in excellent yields and enantioselectivities. Using a sugar-based phosphate ligand on the palladium, we have also been able to perform enantioselective substitution of racemic allylic alcohols. We have also developed a phosphoric acid-catalyzed intramolecular substitution of enantiomeric alcohols where the chirality is transferred from the starting secondary alcohols to the product. Not only allylic alcohols are reactive but also benzyl, propargylic, and alkyl alcohols are transformed to 5- and 6-membered heterocycles by O-, N-, and S-centered nucleophiles in excellent yields and enantioselectivities. Chirality transfers in tertiary alcohols have never been reported by a direct substitution of the OH-group. We have developed a Fe-catalyzed cyclization reaction to directly substitute the OH group in both secondary and tertiary alcohols in which the heterocyclic compounds are generated in high yields and enantiospecificities. During the talk both synthetic applications towards natural products as well as detailed mechanistic studies that reveal the activation mode of the OH group by different catalysts will be presented.

CELL 151

Benign-by-design methodologies for a more sustainable future: from nanomaterials to heterogeneous (photo)catalysis and biomass conversion

Rafael Luque, raf@uco.es. Universidad de Cordoba, Cordoba, Spain

The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years. Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials, designer nanomaterials for (photo)catalytic applications and catalytic strategies for biomass/waste conversion into useful materials, chemicals and fuels have been recently developed in our group in recent years. These topics have extensively covered the preparation and design of (nano)materials and their utilisation in heterogeneous (photo)catalysed processes, flow chemistry as well as in biomass and waste valorisation practices.

In this lecture, we aim to provide an overview of recent efforts from our group in leading the future of global scientists from chemical engineers to (bio)chemists, environmentalists and materials scientists in benign-by-design methodologies and processes for a more sustainable future chemical industry.

Frontiers in Glycoscience, Bridging the Gap Between Carbohydrate & Polysaccharide Chemistries

CELL 152

End-functionalization of polysaccharide in cellulose chemistry

Hiroshi Kamitakahara, hkimat@kais.kyoto-u.ac.jp. Ryo Suhan, Mao Yamagami, Haruko Kawanami, Ryoko Okanishi, Kentaro Mikita, Tomoyuki Asahi, Aota Yoshinaga, Yoshimasa Tanaka, Yoshuyuki Takano. (1) Graduate School of Agriculture, Kyoto University, Kyoto, Japan (2) Graduate School of Biomedical Sciences, Nagasaki University, Nagasaki, Japan

Synthesis of polysaccharides with blocky functionalization patterns is challenging because of the difficulty of blocky substitution along the linear polysaccharide backbone. From the viewpoint of material chemistry, our research has focused on the structure-property-function relationships of oligomeric (up to degree of polymerization (DP) = 6) and polymeric (DP from approx. 10 to 30) methylcellulose with blocky functionalization patterns. My talk will include the key reactions such as end-functionalization of methylcellulose derivatives and glycosylation of polymeric methylcellulose as a glycosyl acceptor. We will also discuss influence of molecular structure of diblock methylcellulose-derivatives on thermoresponsive supramolecular hydrogels consisting of them.

CELL 153

Multivalent glycopolyptide-based micelles and polymersomes

Sebastien Lecommandoux, lecommandoux@enscap.fr. LCPO-ENSCP2, University of Bordeaux, Pessac, France

Polymersomes (polymer vesicles) are among the most attractive systems for drug delivery applications. We report here an overview on the self-assembly in water of amphiphilic block copolymers into polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules. We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles and their development in nanomedicine. These copolymers that mimic the structure and some function of glycoproteins on virus represent an example of the effectiveness of a biomimetic strategy in implementing materials design. We especially evidenced the particular benefit of nanoparticles and their multivalency toward the interaction with biological receptors.

CELL 154

Microbial polysaccharides in pathogens

Laura L. Kiessling, kiessling@mit.edu. Dept of Chemistry, Massachusetts Institute of Technology, CAMBRIDGE, Massachusetts, United States

The glycans on microbes can be critical for microbial viability, microbial colonization of hosts, and pathogen-host cell recognition responses. Understanding microbial polysaccharide structure and function could therefore yield many benefits, including new antimicrobial therapies. The cell surface carbohydrate coat of Mycobacterium tuberculosis and related pathogens is composed of glycan building blocks absent from humans. The galactan, a polymer of repeating galactofuranose residues, is emblematic, as galactofuranose is not present in any mammals. To understand the roles of the galactan and related essential microbial polysaccharides, we are elucidating the molecular mechanisms that control polysaccharide localization, length, and patterning in the bacteria that cause diphtheria and tuberculosis. Our recent investigations focused on elucidating the mechanisms underlying glycan biosynthesis in microbes will be described. We expect that an increased understanding of the pathways and function of these non-human glycans will lead to advances in combating and controlling infectious disease.

CELL 155

Automated glycan assembly as basis for material science

Peter H. Seeberger, peter.seeberger@mpikg.mpg.de. Dept of Biomolecular Systems, Max Planck Inst of Colloid Interfaces, Berlin, Germany

Pure glycans are key to establishing structure-function-relationships for this class of biopolymers. Automated glycan assembly (AGA) allows now for the rapid assembly of polysaccharides using a commercial synthesizer. Access to diverse glycans including those with co-linkages and as long as 50-mer enables materials science investigations. These synthetic polysaccharides can be combined much like “molecular LEGO” to create even larger oligosaccharide assemblies to assess fundamental structural role of carbohydrate structure in folding and material science applications. The synthetic work is combined with molecular modelling calculations and physical methods to characterize carbohydrate structure.

CELL 156

Streamlining complex carbohydrate synthesis through enzymatic procedures

G Boons, giboons@ccrc.uga.edu. Complex Carbohydrate Research Centre, University of Georgia, Athens, Georgia, United States

Progress in glycoscience requires the development of procedures that can easily provide large libraries of symmetrical and asymmetrical N-glycans for glycan-array development, as analytical standards and for cell surface glyco-engineering. We have developed a methodology for the preparation of large libraries of such N-glycans employing a readily available symmetrical biantennary glycan isolated from egg yolk. Innovative enzymatic transformations have been used to desymmetrise this glycan. Furthermore, recombinant N-acetylgalactosaminyltransferases (MAGAT’s) have been employed to convert a bi-antennary glycan into tri- and tettra-antennary structures. In the latter transformations, chemically modified UDP-GlcNAc donors have been used to temporarily prevent an arm from enzymatic modification. Key to developing these new technologies is the recent progress in recombinant expression of mammalian glycosyltransferases.

CELL 157

Phase 2 clinical results of a carbohydrate (GloboH) based cancer vaccine
Tumor-associated carbohydrate antigens (TACAs) are overexpressed in many epithelial tumors. Globo H, a hexasaccharide TACA (Fucα1→2Ga1β1→3GalNAcβ1→3Ga1α1→4Ga1β1→4Glcβ1) was originally isolated from the human breast cancer cell line MCF-7, and later found on a variety of epithelial cell tumors such as breast cancer, etc. The marked difference in expression of Globo H between cancer cells and normal tissues makes it a promising target for cancer immunotherapy. In two phase I studies, vaccination with Globo H-KLHI and QS21 adjuvant was safe and induced anti-Globo H antibodies. We conducted a multi-national randomized phase II clinical trial to evaluate the efficacy of Globo H vaccine (OBI-822/OBI-821) in patients with metastatic breast cancers (MBC).

Three hundred and forty nine metastatic breast cancer patients with a maximum of two events of disease progression who responded to or became stable after at least one anticancer regimen were randomly assigned in a 2:1 ratio to receive OBI-822/OBI-821 or placebo. All patients also received a low dose of cyclophosphamide. The primary endpoint was investigator-assessed progression-free survival (PFS). Secondary end points included safety, overall survival, correlations of clinical outcome with peripheral immune response and Globo H expression in tumors.

The study did not meet its primary end point based on the designed protocol. The median PFS was 7.6 months (95% CI 6.5,10.9) with OBI-822/OBI-821 (N=224) and 9.2 months (95% CI 7.3, 11.3) with placebo (N=124); HR=0.96 (95% CI:0.74,1.25); P=0.7734. However, the patients immunized with the vaccine and whose sera had anti-Globo H-specific IgG or IgG tetramers equal or greater than 1:160 (53% and 50%, respectively) had a longer median PFS (11.1 months [95% CI:9.3, 17.6]) compared to those whose sera had anti-Globo H antibodies equal or greater than 1:160 (5.5 months [95% CI:3.7, 5.6]); HR=0.52, P<0.0001, or placebo-treated patients (7.6 months [95% CI: 6.5, 10.9]);HR=0.71, P=0.0295. The most common adverse events reported for OBI-822/OBI-821 treated patients were grade 1 or 2 infections (36.7%) and pyrexia (20.1%) compared to the placebo group (8.9% and 6.5%, respectively).

In conclusion, the vaccine-treated patients who had a humoral immune response to the Globo H antigen correlated highly with improved PFS when compared to those who did not have a humoral immune response or those who received placebo. Work is in progress to design a phase III trial.

CELL 18

Influenza vaccine and ADCC

Che Ma,
cma@gate.sinica.edu.tw, Chi-Huey Wong, Academia Sinica, Taipei, Taiwan

We have studied the effect of glycosylation on influenza virus major membrane glycoprotein hemagglutinin (HA) with regards to its role in receptor binding and immune response, and developed a new strategy for molecular vaccine design. Monoglycosylated HA is found to be a dominant determinant of HA-NA interactions and of immune response, and is responsible for the marked difference in elicited immune response to HA-based influenza vaccines for different influenza virus subtypes.

Formation of flexible hybrid materials with embedded hierarchically structured components

Biakie L. Tardy, bliase.tardy@saito.fu, Bruno D. Mattos, Luz Garcia Greca, Konrad Klockars, Maryam Borge, Orlando Rojas, Biopsystems and Biosystems, Aalto University, Espoo, Finland

The engineering of hierarchical architectures from crystalline cellulose is of interest for a wide scope of applications. Indeed, finely tuned optical and mechanical properties can be achieved from nanocellulose films. To this end, we present a generalization of a cross-over from soft to hard materials occurring from liquid state to the dry state require careful evaluation. This is essential to the formation of materials exploiting the unique combination of properties offered by crystalline cellulose fibers such as high thermal and chemical resistance, robust mechanical properties, and tuneable porosities of cellulose fibers and optical properties (transmission and reflection). We report the formation of microstructured flexible yet robust films formed by embedding hierarchically structured cellulose nanocrystals components within complex topographies. The embedded architecture results in films with conformable and flexible properties while bearing the opto-mechanical properties as well as the chemical and thermal resistances unique to cellulose nanocrystals. The 3D morphology of the membranes are obtained by scanning electron microscopy and its opto-mechanical properties can easily be tuned through this simple fabrication process. The fiber network properties were evaluated by scanning electron microscopy, several optical microscopy techniques (polarized microscopy, bright field etc.) and by ultraviolet-visible spectroscopy. We evaluate the effect of the substrate on these optical properties and tie them to the mechanical properties of the hybrid materials that was assessed by 3-points-bending measurements. The framework developed herein for the 3D microstructuring of cellulose is expected to have implications across all disciplines involving the use of crystalline cellulose because it allows micrometer precision in the fabrication of mechanically robust cellulose materials while bearing a high degree of versatility in properties and structure. Furthermore the
developments brought by this study are expected to be impactful in the formation of flexible and functional coatings from nanocelluloses.

**CELL 163**

Novel multilayered nanostructured drug delivery systems obtained by layer-by-layer assembly of cellulose nanocrystals

Marta Maia2, Carla Vilela1, Ricardo J. Pinto1, Bruno Valente1, Tiago Carvalho1. Carmen Freire2. cfreire2011@gmail.com. (1) University of Aveiro, Aveiro Institute of Materials, Aveiro, Portugal (2) University of Aveiro, Aveiro, Portugal

Nanostructured functional materials typically display tailored architectures and superior properties, and therefore, have emerged as an alternative in many fields. One way to obtain these nanomaterials is by using the layer-by-layer assembly methodology (1,2). For example, multilayered polymeric nanocapsules show controlled release properties and allow the increase of the efficacy, specificity, tolerance and therapeutic index of different drugs. Biopolymers have gained increasing importance in this area due to their availability, biocompatibility and specific properties and functionalities (3). In this communication, we will describe the layer-by-layer assembly of different biopolymeric substrates, including cellulose nanocrystals, for the design of innovative multilayered nanostructured capsules for controlled drug delivery.

**CELL 164**

Kinetic of polymers and nanoparticles adsorption on cellulose nanocrystal surfaces

Zahraa Jaafar1, Cyprien Mauroy2, Ana Vilàres1, Alexandre Broesse1, Jacqueline Vigouroux1, Hadige Beury1, Clément Levard1, Jérome Rose1, Marc Lahaye1. Bernard Cathala1. bernard.cathala@nantes.inra.fr. (1) BIA, INRA, Nantes, France (2) CEREGE, Aix-en-Provence, France

The surface properties of cellulose nanocrystals are key elements in many applications and they can be modified or tuned either by chemical modifications or physical adsorption. In the latter case, the final properties of the cellulose nanocrystals are driven by the adsorption behaviour of the adsorbing species. In an ideal thermodynamic approach, adsorption is expected to be associate with description process to reach thermodynamic equilibrium. However, in many cases in practice, description process, if any, occurs at far larger time scale than adsorption suggesting irreversible adsorption. As a consequence the process is not thermodynamically but kinetically controlled. In this paper, we investigated the kinetics of adsorption processes of polyelectrolytes, neutral polysaccharides (hemicelluloses) and cationic nanoparticles on cellulose nanocrystals model surfaces. The adsorption kinetic was monitored by quartz-crystal microbalance with dissipation (QCM-D). The adsorption of polymers and nanoparticles under flow at different concentrations did not result in the same surface concentration, which evidenced the kinetically-controlled process. In an attempt to describe the binding process, adsorption data were fitted to a kinetic model comprising the contribution of adsorption onto uncovered CNC and the contribution of adsorption on saturated surface. Kinetic studies evidenced the presence of different adsorption regimes according to the polymers or particles structures. Energy dissipation changes during the adsorption process were also examined by QCM-D for the different polymers and nanoparticles as a function of chemical structures and adsorption regimes. Finally the morphologies and the adsorption kinetic were monitored by quartz crystal microbalance with dissipation (QCM-D). 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Cellulose nanocrystals are rod-like and highly crystalline nanoparticles obtained after acid hydrolysis of cellulose fibre. In addition to their low density, high aspect ratio, high specific surface, and chemically reactive surface, this material is well known for its high stiffness and Young's modulus. Thanks to these particular properties, cellulose nanocrystals can be used as very good reinforcing agent in nanocomposites within a wide variety of applications. Coating is one of the promising applications for nanocellulose composites mainly for barrier applications but also for rigid layer deposition. Precise methods exist for determination of film mechanical properties. Among them, we count tensile test, dynamic mechanical thermal analysis or three points bending flexural tests. However, these methods are only feasible with thick free-standing films. It has been proved that coating processes modifies CNC organization in nanocomposites. To perfectly understand the effect of cellulose nanocrystals embedded in a polyvinyl alcohol matrix as a coating layer, a strain-induced elastic buckling instability method has been studied and adapted. The principle of this method is to measure how a rigid material (the tested film) surface wrinkles when it is compressed on a soft substrate (PDMS). This recent method implemented by Stafford (Stafford et al. 2004) has been tested with thin film of nanocellulose composites or (Cranson et al. 2011) in the case of layer by layer method with ultrathin films corresponding to thicknesses of 35 to 75 nm. However, the adaptation of this method to bar coating systems with micrometrics layers is new and uncertain. In this study it is question to understand the buckling model limits and adaptation for simulate the mechanical properties of a paper coating layer. The second objectives are to study the influence of coating process, paper drying and amount of cellulose nanocrystals on these mechanical properties. First results are promising and clear influence of process parameters can be seen with using this new methodology.

Bacterial cellulose (BC) is a natural and environment-friendly polymeric material produced by different microorganisms. It is understood and composed by fibrils, made up of (1-4) 

Hierarchical alignment of chitin fiber as a novel non-woven separator for metal-based batteries

Chitin nanofiber transparent paper: A renewable material platform for green electronics and energy devices

Chitin – 'the cellulose of the sea' – is a structural polysaccharide that is a major constituent of the exo-lentiform case of marine crustaceans and is the 2nd most abundant biopolymer on earth only after cellulose. Ever since its discovery in the early 19th century, chitin has been considered a promising material due to its atypical yet compelling combination of mechanical and physicochemical properties, such as high elastic modulus (150 GPa), biodegradability, and excellent biocompatibility. Despite the promising traits, however, it is only quite recent that scientific interest on chitin has thrived and the utilization of chitin for engineering applications has revived considerably. In this presentation, I will introduce some of my research endeavors to create structural/functional materials (e.g., transparent nanopaper) using chitin nanofibers (ChNF) as the basic building-blocks. I will also describe proof-of-concept examples of electronics and energy devices constructed using the ChNF paper platform.
Form factor-free, flexible paper power sources

Sang-Young Lee, sty1232@unist.ac.kr. Department of Energy Engineering, UNIST, Ulsan, Korea (the Republic of)

Forbidding smart ubiquitous era, which will involve widespread use of electric vehicles, stationary energy storage systems, and flexible/wearable electronics, is in relentless pursuit of advanced rechargeable power sources. Here, we demonstrate a new class of form-factor-free, flexible power sources based on cellulose nanofibers (CNFs) as an environmentally-friendly multifunctional 1D building block. Our first approach is focused on development of CNF-based flexible all-paper lithium-ion batteries. In addition, a large amount of dehydrogenation polymer (DHP) of coniferyl alcohol was formed inside the film in the presence of xylan. The CNFs presented herein hold a great deal of promise as a reliable and versatile 1D building block to open a new route toward high-performance/flexible power sources.

Optimum utilization ways of cellulose toward high-power, environmentally friendly, and renewable energy storage devices

Haipeng Yu, yuhapeng2000@aliyun.com. Northeast Forestry University, Harbin, China

Cellulose is the most abundant, renewable and biodegradable natural biopolymer on earth. The properties of cellulose such as low cost, high dimensional/thermal/chemical stability, excellent mechanical strength and flexibility, can meet some key requirements for various applications, and energy storage utilization is also included. Here, three kinds of optimum utilization ways of cellulose toward high-power, environmentally friendly, and renewable energy storage devices are reported. (i) The dissolved cellulose molecules can be used to construct a flexible and conductive cellulose/PEDOT:PSS/MWNT composite. The composite films fabricated using the present approach exhibited desirable mechanical and electrochemical properties and showed great promise for use in electrodes. (ii) A renewable and biodegradable cellulose membrane with controllable mesoporous structure is produced via a simple phase-inversion method. The cellulose membrane has a high porosity above 70%, an excellent tensile strength of ~40 MPa, a high electrolyte wetting state, and an outstanding thermal stability >275 ºC, which are all crucial for ideal polymer electrolyte separator uses in all-solid-state supercapacitors and Li-type batteries. (iii) A renewable and biodegradable all-nanofiber asymmetric supercapacitor was constructed based on a wood-based, cellulose nano-fiber-derived hierarchical porous carbon (HPC) anode, a mesoporous cellulose nanofiber membrane separator and a HPC/NiCoO cathode. The all-nanofiber supercapacitor possesses highly continuous and conductive pathways for fast electron transport, and provides hierarchical pores (macro-, meso- and micro-pores) not only benefit the electrolyte penetration but also accelerating the ion transport but also provide abundant active sites for charge storage.

Solar-driven simultaneous steam production and electricity generation from seawater

Jun Zhou, jun.zhou@mail.hust.edu.cn. Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, Hubei, China

Worldwide, governments have programs of renewable energy strategies to deal with the possible future exhaustion of fossil fuels. The ocean provides a vast source of clean and renewable energy, and contains sufficient amount of seawater for extracting freshwater to address the human demand. Solar-driven interfacial water evaporation has attracted increasing interests in pursuing highly efficient solar desalination. Here we present a new concept hybrid energy utilization technology, using solar energy for desalination and extracting electricity from the evaporation induced salinity gradient. By employing a hybrid system based on a piece of carbon nanotube modified cellulose paper and a commercial Nafion membrane, we achieved a maximum solar thermal efficiency up to 75% and derived extra electricity power of ~1 W m−2 under one sun illumination. In addition, a large-scaled hybrid prototype was built to demonstrate the practicability of this design under natural sunlight. The performance can be further promoted by improving the solar absorber, ion selective membrane and system structure. These results provide a novel avenue for blue energy utilization, demonstrating the potential for solar desalination and electricity generation under natural sunlight simultaneously.
Enzymes degrading cellulose: From molecular mechanisms to traffic simulator

Kiyohiko Igarashi, aquarius@mail.ecc.u-tokyo.ac.jp, Department of Biomaterial Sciences, The University of Tokyo, Graduate School of Agricultural and Life Sciences, Tokyo, Japan

Cellulose is a major component of plant cell wall and the most abundant biomass on earth. Efficient degradation of cellulose makes it possible to produce fuels and chemicals from plant resources for the achievement of Bioeconomy, although biochemical conversion of cellulose by cellulases is quite slow and the reaction becomes a bottleneck of the process. Cellulolytic enzymes (CBHIs) are types of cellulases hydrolyzing crystalline cellulose to soluble oligosaccharides, and one of the key enzymes in the cellulose biorefinery. CBHIs share a common two-domain structure, cellulose-binding domain and catalytic domain, and these domains cooperatively function for the effective hydrolysis of crystalline cellulose. Since the reaction is carried out at the surface of insoluble substrate, it is not straightforward to analyze the reaction at a solid/liquid interface. We recently reported the real-time visualization of crystalline cellulose degradation by individual cellulase molecules using a high-speed atomic force microscopy, having sub-second time resolution and nanometer space resolution. Cellulase-degrading ascomycete Trichoderma reesei cellulolytic enzymes I (TcCel7A) were observed to slide unidirectionally along the crystalline cellulose surface, but at some point the movement of individual molecules was halted, leading to the appearance of traffic jams of enzyme molecules. From the comparison with GH family 6 cellulolytic enzymes (TcCel6A), the basalidiozyme Phanerochaete chrysosporium cellulolytic enzymes (PcCellC and PcCellD) and chinatinases, we discuss possible molecular mechanisms of these processive enzymes and the natural degradation of crystalline cellulose. We will also introduce application of traffic simulator to the analysis of molecular behavior of cellulases to connect mesoscopic gap between biochemical and single molecule analysis.

Highly strong nanofibers constructed from cellulose solution based on formation of nanofibers

Lina Zhang, zhanglin@wuht.edu.cn, Ang Lu, Jie Cai, Chunyu Chang, Kunkun Zhu, Dongdong Ye. Wuhan University, Wuhan Hubi, China

Faced with a threat to the environment and consuming resources caused by petroleum based non-biodegradable plastics, it makes a growing urgency to develop the next generation materials according to the principles of green chemistry and eco-efficiency. Herein, a series of highly strong materials including fibers, films and hydrogels were constructed from cellulose solution in alkali/urea aqueous system at the low temperature, in which the extended semi-stiff chains of cellulose aggregated in parallel manner under mild coagulating environment to form dense nanofibers. Thus, the cellulose fibers, films and hydrogels containing nanofibers with mean diameter of about 30 nm were fabricated, displaying an orientation microstructure and excellent properties. As the first example of nano-structured fibers, the cellulose multifilaments exhibited high orientation degree with Herman's parameter of 0.9 and excellent mechanical properties with a tensile strength of 3.5 CN/dtex. Furthermore, cellulose hydrogels exhibited the rapidly responsive birefringence behaviors with highly stable colors under mechano-deformation, and the high mechanical strength and elasticity with loading-unloading cycles of 1000 times.

Natural nanofiber films welding via ionic liquids

Guillermo Reyes1, guillermoreyes@udec.cl, Orlando J. Rojas2, Maryam Borgher3. (1) Ingeniería en Materiales, Universidad del Bio-Bio, Concepción, Región del Bio Bio, Chile (2) Departament of Chemical Technology, Aalto University, Espoo, Helsinki, Finland

Introduction

Cellulose based nanomaterials synthesis, demands sustainable processes, this means low energy consumption, without secondary products production or total recyclability of these, allowing the production of high mechanical performance fibers and films used extensively as textiles, support and degradable matrices in biomedical applications. The welding of natural nanofibers, the cellulose multifilaments exhibited high orientation degree with Herman's parameter of 0.9 and excellent mechanical properties with a tensile strength of 3.5 CN/dtex. Furthermore, cellulose hydrogels exhibited the rapidly responsive birefringence behaviors with highly stable colors under mechano-deformation, and the high mechanical strength and elasticity with loading-unloading cycles of 1000 times.

Density functional study of cross-coupling of lignin with trinac and ferulates

Thomas J. Elder1, thselden@fs.fed.us, Laura Berntsa2, Gregg Beckmann3, Michael F. Crowley4. (1) NREL, Golden, Colorado, United States (2) National Renewable Energy Lab, Lakewood, Colorado, United States (3) National Renewable Energy Laboratory, Golden, Colorado, United States (4) USDA Forest Service, Firewise, Louisiana, United States

While lignin is traditionally defined as a polymer of the cinnamyl alcohols, it has also been found to exhibit extensive plasticity through the incorporation of other units into the macromolecule. Such

average toughness of welded samples increase about 27% with respect to CNF untreated film. X-ray diffraction patterns showed individual

yarns are quenched without losing the fiber nature and complete removal of the ionic Liquid.
cross-linking may be the result of natural mutations, induced genetic manipulation or inherent to the lignin itself. The current work addresses the latter point through an examination of lignin-tricin and lignin-ferulate cross-linking. The flavonoid tricin has been found to generally occur in the lignin of monocots, where it is proposed to function as a nucleation site for lignin. Ferulate esters with polysaccharides can further react through homocoupling or cross-coupling with monolignols, and may also act as nucleation sites for the subsequent polymerization steps. By the application of quantum mechanically based density functional theory calculations, the current work is concerned with determining the thermodynamics of the coupling reactions between tricin, the methoxy-ferulate ester and cinnamyl alcohols. Furthermore, bond dissociation energies of the products, with implications for overcoming recalcitrance in biofinery settings, are presented.

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**Novel structural model for softwood kraft lignins**

**Claudia Crestini**, crestinijunioroma2.it, Heiko Lange1, Marco Sette2, Dimitris Argyropoulos2. (1) North Carolina State Univ, Raleigh, North Carolina, United States (2) Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, Rome, Italy

Two constitutional structural schemes are proposed attempting to unify and rationalize a series of focused NMR and chromatographic determinations aimed at providing an integrated picture for the structure of softwood kraft lignin. The complexity of native softwood lignin when coupled with the complexity of the kraft pulping process is known to lead to a rather heterogeneous material that has eluded us to date. The present work embarks at applying state of the art quantitative 1D and 2D NMR methods on carefully isolated softwood kraft lignin samples and fractions. The accumulated data, when coupled with size exclusion chromatography, mass spectrometric analyses and literature accounts that pertain to the chemistry of kraft pulping, provides the following picture for the softwood kraft lignin: softwood kraft lignin is composed of two distinct fractions that can be separated by anhydrous acetone. The acetone insoluble fraction (example shown as structure A) is a somewhat branched polymeric material that still contains a variety of native wood lignin bonding patterns, albeit in significantly reduced abundance shown as structure A) is a somewhat branched polymeric material that still contains a variety of native wood lignin bonding patterns, albeit in significantly reduced abundance, as well as new structures induced during the process. The acetone soluble fraction (example shown as structures B) is a significantly more branched and less polymeric material with an abundance of chemical structures that may be created when aromatic phenols react under kraft pulping conditions.

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**The chemical character of lignin: Interactions with solvents**

**Loukas Petridis**, petridis@ornl.gov, Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Understanding the interaction of water and other solvents with biomass components is critical to rationalizing how different thermochemical pretreatments work. Here, we differentiate between pure water and water-tetrahydrofuran (THF) co-solvents in terms of their interaction with lignin. In pure water, which is a “poor” solvent for lignin, lignin adopts collapsed conformations and aggregates on the surface of cellulose. The amphiphilic character on lignin monomers, with both hydrophobic phenolic rings and hydrophilic hydroxyl moieties, makes low molecular weight lignin polymers to adopt less spherical conformations in water than high molecular weight counterparts. In addition, water is shown by neutron scattering and dielectric spectroscopy to enhance the dynamics of lignin. In contrast, THF-water co-solvent, lignin adopts open coil conformations and become soluble, facilitating its removal during pretreatment. Overall, the results describe mechanisms related to biopolymer-solvent interactions that account for the recalcitrance of lignocellulosic biomass to enzymatic deconstruction.

**CELL 187**

**Green gasoline and road diesel from black liquor in three steps**

**Joseph S. Samec, joseph.samec@su.se**, Organic chemistry, Stockholm university, Stockholm, Sweden

Pulping generates immense amounts of lignin worldwide that is often burnt to the heating value in best cases. An important note is that the operation that burns the lignin, the recovery boiler, is half of the cost of a pulp mill and thereby already the rate-limiting step in the process. Therefore, taking out for example the lignin from the black liquor enables an increase in pulp production. Therefore, several mills (Domtar, USA; Sunils; Finland; Domjoji, Sweden) have developed lignin separation steps to their pulp mills in order to increase the pulp production which is the main focus of a current pulp mill. Up to 30% of the lignin can be separated from most pulp mills without any other modifications. However, with modifications to the pulp mill, e.g. a larger solid fuel fired boiler 70% of the lignin can be removed from the process. The separated lignin from a sulfite pulp mill has high value applications. However, lignin that is obtained from the kraft process does not at the moment.

Given that precipitated kraft lignin is a product that is generated at the moment and its production should increase in the future, it would be worthwhile to develop high value products. While native lignins consist of relatively weak carbon-oxygen bonds that are susceptible for catalytic reactions exemplified in the lignin first approach to generate well defined monomeric aromatic species, technical lignins from the kraft process are not. Therefore lignin from the kraft process, do not show the same reactivity as, for example, lignin model compounds or organosolv lignin.

Taking all this into account, a series of stakeholders including: a pulp mill; a lignin precipitation technology company; a start-up; academic groups; and an oil refinery have developed a three step process to convert black liquor to green diesel and gasoline. It was found that a key to make the lignin compatible in an oil refinery unit was to transform the amphiphilic polymer to a more lipophilic species that was soluble in refinery carrier liquids. Given that the process should be commercially viable, a simple and cost efficient chemical reaction without: (1) high pressure operations; (2) expensive transition based catalysts, 3) and reagents such as reducing agents; has been developed. By this operation, current hydroprocessing units can convert lignin to either high octane gasoline or road diesel. A technical presentation with cost estimation will be presented during the talk.

**Frontiers in Glycoscience, Bridging the Gap Between Carbohydrate & Polyasacharide Chemistries**

**CELL 188**

**Dissolution of cellulose in NaOH/zinc nitrate at low temperature**

**Ang Lyu**, ang-lu@163.com, Sen Wang1, Lina Zhang1. (1) Wuhan University, Wuhan Hubei, China (2) Department of Chemistry, Wuhan University, Wuhan, Hubei, China

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 w%, 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.
Highly selective polysaccharide modification

Brittany L. Nichols2, Yiyan Dong2, Laura I. Mosquera-Giraldo1, Lynne Taylor1, Kevin J. Edgar1,2, kjenigar@vt.edu. (1) Purdue University, West Lafayette, Indiana, United States (2) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Polysaccharides constitute an enormous, renewable, benign, diverse set of resources for society. However, to date they have been poorly exploited, with only cellulose commonly used to prepare useful derivatives of commerce, and only a few polysaccharides being harvested and purified from nature for use as materials or as raw materials for synthesis. One important reason for this neglect has been the low reactivity of polysaccharide functional groups, due to poor solubility of the polymer, restricted approach angles, and low mobility. This low reactivity necessitates harsh conditions for modification, which of course are poorly conducive to selectivity.

We will discuss advances by our laboratory to develop new approaches to selectively functionalized polysaccharides. These approaches are chemoo- and often regioselective, and provide valuable functionality that may greatly enhance the value and utility of the polysaccharide. They are flexible with regard to polysaccharide substrate, and frequently with regard to which functional group can be appended. They greatly extend the range of functional, high-performance materials that are accessible in an efficient manner from natural, sustainable polysaccharides, thereby expanding the potential of these diverse and ecofriendly materials.

Alternative chemical modification of polysaccharides by using organo-soluble intermediates

Thomas J. Heinzé. thomas.heinze@uni-jena.de. Friedrich Schiller University of Jena, Jena, Germany

To make polysaccharide chemistry more attractive for organic chemists and to design novel structural- and functional materials, reactions with activated and organo-soluble polysaccharides are interesting alternative paths compared to reactions at the hydroxy groups. Besides cellulose tosylates, polysaccharide phenylcarbonates (PPC) 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 be easily controlled and even a complete or regioselective functionalization is possible. The PPCs dissolve in common organic solvents and can be efficiently converted with a broad variety of functional group can be appended. They greatly extend the range of functional, high-performance polymers for biofunctionalization.

Amphiphilic polysaccharide Schiff base delivery vehicles for controlled release of biologically active compounds

Brittany L. Nichols2, brittan@vt.edu, Kevin J. Edgar1, (1) Sustainable Biomaterials, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States

Aqueous solubility and controllable release are essential for bioactive compounds. In the case of oral drug delivery, the poor aqueous solubility of a drug leads to low bioavailability. Thus, higher drug dose is required to achieve a therapeutic effect in systemic circulation which can increase undesired side effects. The aqueous solubility and release rate of a bioactive molecule can be improved by conjugation to a solubile carrier molecule, to form a pre-active delivery system. Polysaccharides have great potential as carriers since they are biodegradable, nontoxic, and sustainable. We have utilized an efficient, economical synthetic route to provide amphiphilic polysaccharides and their crystallized supermolecular structures provide readily applicable platforms for functional materials. For this purpose, chemical modifications demonstrate great tools for the functionalization, which leads to specific materials requiring particular further material formation. Herein, novel functional materials derived from cellulose and nanocellulose with smart and stimuli-responsive properties will be presented. These materials could be further transformed into diverse shapes ranging from particles to membranes. Different than monosaccharides, the chemical modifications for the introduction of stimuli-responsive functional groups along polysaccharide backbone are generally limited, so that the choice of appropriate modification strategy maintaining the polymeric nature and crystalline structure of nanocellulose is critical. Otherwise, the contents, distribution of these functional groups in particular within the polymeric backbones of polysaccharides and the surface density of functional groups on the nanocellulose are the major parameters affecting the performance of materials.
of CNCs with quantum dots. I will also briefly describe how differences in the surface charge of CNCs translate to differences in effective particle size, which impact properties like self-assembly and rheology.

**CELL 197**

**Grafting well-defined CO2-responsive polymers to cellulose nanocrystals via nitroxide-mediated polymerization: Effect of graft density and molecular weight on dispersion behaviour**

Joe Glasing1, Jean Bouchard1, Pascal Champagne4, Philip G. Jessop1, Michael F. Cunningham5, Michael.Cunningham@chee.queensu.ca. (1) Chemical Engineering, Queen’s University, Kingston, Ontario, Canada (2) Dept Chem Eng, Queens Univ, Kingston, Ontario, Canada (3) Dept of Chemistry, Queen’s University, Kingston, Ontario, Canada (4) Civil Engineering/Chemical Engineering, Queens University, Kingston, Ontario, Canada (5) PPInnovations, Pointe-Claire, Ontario, Canada

CO2-responsive cellulose nanocrystals (CNC) were prepared by grafting preformed poly(N,N-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(N-3-(dimethylamino) propyl methacrylamide) (PDMAPAM) to CNC. Two different tertiary amine polymers were selected to investigate how differences in their pK\textsubscript{a} and T\textsubscript{g} affected the final properties of the graft-modified CNC. Hydroxyl groups on the CNC surface were functionalized with glycidyl methacrylate (GMA) prior to grafting. Living polymers of different molecular weights, showing low dispersity, high livingness and end group fidelity were grown via nitroxide-mediated living radical polymerization and then grafted to the surface of GMA modified CNC. The effect of the polymer molecular weight on the graft density was investigated in detail and was shown to have a direct influence on the dispersion behaviour and CO2-responsiveness of the grafted CNC particles, as demonstrated by zeta potential measurements in water and phase shifting experiments between oil and water. We have found that the surface properties of the final graft products could be tailored effectively and reversibly using only N\textsubscript{2}, slight heat (40 °C) and CO2 as external triggers, allowing the nanocrystals to convert from a highly hydrophilic to a completely hydrophobic state and vice versa. The surface charge and (re)dispersion behaviour could be tailored based on the pK\textsubscript{a}, graft density and graft length. The results suggested that a particular pK\textsubscript{a}, minimum graft density and graft length are required to effectively switch the CNC from a hydrophilic to a fully hydrophobic state.

**CELL 198**

**Pickering emulsions stabilized by esterified cellulose nanocrystals: application to the elaboration of polymer latexes and colloidosomes**

Gilles Sèbe1, gilles.sebe@ubordeaux.fr, Arthur Wemer1, Valérie Héroguez2, Zhen Zhang1. (1) LCPC, University of Bordeaux, Pessac, France (2) LCPC, CNRS, Pessac, France

Cellulose nanocrystals (CNCs) are rod-like colloidal particles, which are increasingly considered for the stabilization of oil-in-water (o/w) or inverse water-in-oil (w/o) Pickering emulsions, with potential applications in cosmetics, biotechnology or material science. In these systems, the stabilization is imparted by the particles, which irreversibly adsorb at the oil/water interface and form a rigid structure around the droplets. This typically requires an optimum balance between the solid-liquid and liquid-liquid interfacial tensions, which can be achieved by controlling the hydrophile/hydrophobic balance at particles surface by chemical modification. In this context, esterified CNCs with tailored wetting properties were prepared and used to stabilize o/w and w/o Pickering emulsions, later applied for the design of polymer latexes or colloidosomes. The polymerization of monomer-in-water emulsions was conducted in the presence of a thermosensitive initiator, leading the production of latexes composed of the mixture of microbeads and nanobeads, which could be easily separated by filtration/centrifugation. The nanobeads formation was partly attributed to the extrusion of monomer through the many holes resulting from the incomplete coverage of the emulsion droplets by the cellulose nanoparticles. In another approach, inverse w/o Pickering emulsions containing silica precursors were also prepared. The stabilized droplets were subsequently locked by cross-linking the precursors at the w/o interface, leading to an intricate network of polylsioxane within the cellulosic shell. In optimized conditions, the colloidosomes obtained displayed a robust and compact shell, which ensured a long-term encapsulation of rhodamine B or biological molecules such as fluorescent deoxyribonucleic acid (DNA).
incorporating cellulose nanocrystals into the core of polymer latex particles through polymer grafting

Stephanie A. Kedzior1, kedziosa@mcmaster.ca, Michael Kiriazou2, Elina Ninivaras2, Marc A. Dubé3, Carole Fraschini4, Richard M. Berry1, Emily D. Cranston1. (1) CelluForce, N-D-D-life-Perrot, Quebec, Canada (2) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (3) Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, Canada (4) FPInnovations, Pointe-Clair, Quebec, Canada

This work explores the incorporation of cellulose nanocrystals (CNCs) into the core of synthetic latexes by modifying the surface chemistry of CNCs with grafted polymers. CNCs are stiff anisotropic nanoparticles derived from renewable resources such as wood pulp and cotton and have the potential to be used as reinforcing agents in nanocomposites. However, challenges due to incompatibility between cellulose and hydrophobic polymers, and processing difficulties such as aggregation and low thermal stability, have limited the performance of CNC nanocomposites produced to date. In this work, we have used surface-initiated atom transfer radical polymerization to graft hydrophilic poly(3lyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA) from CNCs to overcome the issue of incompatibility. The polymer-grafted CNCs were used in the miniemulsion polymerization of methyl methacrylate whereby modified CNCs were added to the monomer phase. Polymer-grafted CNCs with short graft lengths (degree of polymerization = 50) were incorporated inside the core of the latex particles, producing a PMMA-CNC nanocomposite latex in situ. The effect of grafted polymer type, length and loading on the latex size, surface charge, and morphology was investigated. Transmission electron microscopy indicated that grafted polymer type did not have a significant effect on CNC incorporation and that CNCs with long polymer grafts (degree of polymerization = 200) may be too large/aggregated to be integrated into the latex core. This work provides a novel method for incorporating CNCs into nanocomposite latexes and is anticipated to extend the use of CNCs in applications such as adhesives, coatings, and other synthetic latex-based products.

Sustainable Production & Processing of Agricultural Crops: The Food, Energy, Water Nexus

Changmou Xu1, cxu13@unl.edu, Xiaoping Xie1, Jiang Lu2, Maurice R. Marshall1. (1) Food Science and Technology, University of Nebraska-Lincoln, Lincoln, Nebraska, United States (2) Center for Viticulture and Enology, Shanghai Jiao Tong University, Shanghai, China (3) Food Science and Human Nutrition, University of Florida, Gainesville, Florida, United States

Grape is one of the most valued conventional fruits in the world with more than 75 million tonnes produced yearly, according to the FAOSTAT (2014). Considering approximately 75% of the whole grape production is utilized into winemaking, and 25% of the original grape weight is pomace (skin, seeds and stalks), there is around 14 million tonnes of winery pomace produced every year globally. Large amounts of pomace are produced during a short period of harvesting, and discarded in land field may be detrimental to the environment, such as surface and ground water pollution, food odor, Res and pests attraction that may spread diseases and oxygen depletion in soil and ground waters by tannins and other compounds. In order to reach a sustainable and environment-friendly winemaking process, there is a need of a waste reduction strategy. Considering a significant amount of bioactivity compounds (polyphenols, dietary fibre, and oil) retained in the winery pomace, the potential use of grape by-products can be a promising alternative, not only motivated by environmental issues, but also by the possibility of enhancing food quality and developing high added-value ingredients and products. Furthermore, the increasing consumer demand for the use of natural over synthetic compounds for a clean label food, and the increased attention to sustainable of agricultural practices, are also driving forward the applications for grape pomace. Therefore, this presentation will address the factors during the value-added and sustainable product processing of by-products from grapes, and the potential applications or product development of grape pomace, such as in functional food, food processing, cosmetics, pharmaceuticals, and supplements.

Advances in immobilized enzyme systems to mine value-added products from agricultural waste streams

Julie M. Gordon1, gordon@comell.edu. Food Science, Cornell University, Ithaca, New York, United States

Enzymes enable high specificity in production of value-added agricultural products, but are limited by challenges in stability and recovery. Immobilization onto solid supports can improve recovery, with material factors such as size regime, magnetism, and surface chemistry playing a role in improving retained activity. This presentation describes recent advances in enzyme immobilization onto solid supports towards the goal of upcycling agricultural waste to value-added products. We have improved the temperature, pH, and solvent stability of lipase B from Candida Antarctica by its immobilization onto polymer particles. After two hours exposure to 50% acetonitrile, there was no measurable loss of enzyme from the microparticles, while the commercially available immobilized lipase lost 99.8% protein under the same conditions, suggesting robust design for use in solvent applications. Immobilized lipase particles were able to retain 60% activity in production of generally derived sugar ester surfactants at 50°C in deep eutectic solvents (a greener solvent system). In other work, we have demonstrated that the activity per gram of beta galactosidase (lactase) approaches that of free enzyme when immobilized onto magnetic particles of 20 nm, while it loses nearly 90% of activity per gram when immobilized onto either particles of 200 nm or magnetic surfaces. This work highlights that for some enzymes, bioconjugation chemistry has less influence than the nature of the solid support to which it is attached. Improving our understanding of immobilized enzyme systems can promote increased realization of waste streams (ie: upcycling) toward more sustainable food and bioprocessing applications.

Value-added applications of peanut processing plant waste

Lisa L. Dehn1, lisa.dean@ars.usda.gov, Brian J. Hessl2. (1) Market Quality and Handling Research, USDA, ARS, Raleigh, North Carolina, United States (2) Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, North Carolina, United States

Over 3 million tons of peanuts are produced in the USA each year generating almost 1 million tons of waste in the form of hulls and skins. For the most part, there are few markets for this materials. Increased regulatory focus on wastewater discharge standards from agricultural sources has created a need for new wastewater treatment methods. Waste biomass adsorbents, such as peanut hulls, have many benefits for agricultural use: they are plentiful, cheap, geographically convenient to agricultural sites, and can be modified for pollutant specificity through facile methods. Peanut hulls are presented here in for the treatment of wastewater originating from swine farms. In addition, the hulls are high in lignin which can be reduced and the fermentable sugars converted to bioethanol. Small amounts of peanut skins are used as low grade animal feed, but the use is limited by the high levels of anti-nutritional compounds present such as small molecules containing phenolic moieties. These phenolic compounds can be extracted and recovered to produce food ingredients with functional properties. Applications such as these can reduce the amount of peanut plant processing waste that goes to landfills and increase the value of the peanut crop.

Structural evaluation during conversion stages of lignin feedstocks to carbonaceous products

David P. Harper1, dharper@utk.edu. The University of Tennessee, Knoxville, Tennessee, United States

Lignin is an abundant polymer found mostly in woody plants that is a waste stream of pulp and biofuel production. Hardwood, softwood, and herbaceous plant lignin exists in nature with several structure variants making. The heterogeneous nature of lignin feedstocks makes elucidation of the relationship between processing and the resulting material structure difficult to predict. In this work, we investigate the relationship with lignin structure and carbon processing to the resulting development of nanocrystalline domains within an amorphous carbon matrix. We examine the role of each unit operation: pulping process, pyrolysis conditions, and reducing temperature. The impact of each of these unit operations on the resulting carbon composition and morphology was elucidated by a combination of elemental analysis and x-ray scattering. High temperature reduction of the carbons resulted in the formation of larger crystalline domains, but a lower overall crystallinity. Reducing temperature strongly correlates with charge capacities in assembled Li-ion half-cells. The electrochemical behavior of half-cell using lignin-based electrodes shows promise in providing competitive performance compared to traditional graphite electrodes, at a fraction of the cost.

Catalytic upgrading of bio-oils derived from agricultural crop residue: A study of application and mechanism

Najia Hao1, nhao@vols.utk.edu, Arthur J. Ragauskas1,2, Yang He1, Sinis Laursen1. (1) Chemical and Biological Engineering, University of Tennessee, Knoxville, Tennessee, United States (2) Joint Institute for Biological Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Sugarcane has been placed in the center of the food-energy-water nexus owing to its suitability as a feedstock for biofuel production. Sugarcane bagasse, once a “worthless” residue, now is attracting research efforts to maximize its utilization in the bioeconomy, rather than simply burn to generate power. We have been investigating the pyrolysis of the sugarcane bagasse to produce bio-oils as a potential fuel precursor. The bio-oils have very challenging properties as a fuel precursor, including high oxygen content, high acidity, and high viscosity. In this study, we upgrade the bio-oils derived from sugarcane bagasse in supercritical alcohol using transition metal catalysts. H+, O2, HSO4 NMR, GC-MS are exploited to provide a deep insight of the structures in the bio-oils. The mechanism and reaction pathways of the catalytic upgrading will also be discussed.
Comparison of biodiesel crude glycerol pretreatments of bamboo for efficient enzymatic hydrolysis

Li Ji, bjfu090524116@163.com, Jiang Jianxin. Beijing Forestry University, Beijing, China

Moso bamboo was pretreated with different resources of industrially crude glycerol at 150/160 °C for 3h. The effects of pretreatment processes and conditions on the degradation of lignin, contact angle and glucose yield of pretreated bamboo, and surface tension of enzymatic hydrolysate were compared. The highest glucose yield of 95% was obtained from bamboo pretreated by base biodiesel glycerol with pressure filtering (BBGP), in which major glycerol was removed by pressure filtering and a few of fatty acid soap still exist in the pretreated sample. It was confirmed that the addition of potassium oleate could decrease the surface tension and stabilize the enzyme activity in the enzymatic hydrolysis of bamboo pretreated by base biodiesel glycerol with water washing (BBSW). BBGP, pressure filtering after BBG pretreatment, could be a promising process of bamboo pretreatment for fermentable sugars production from pretreated bamboo with a few of fatty acid soap acting as a surfactant to decrease non-specific adsorption of cellulase to lignin.

Cellulose & Other Structural Biopolymers: Structure, Formation & Degradation: Anselme Payen Award Symposium in Honor of Junji Sugiyama

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The state of cellulose in cold alkali solutions

Tomas Larsson, tomas.larsson@it.se. RISE Bioeconomy, Stockholm, Sweden

During dissolution of cellulose rich fibers in cold alkali solvent, questions arise regarding the state of the cellulose in the spin dope. The state of the cellulose in the spin dope is dependent on several factors, the targeted cellulose concentration being one. As two extremes, the solute can be a molecularly dispersed or form a sol gel. Due to nature of the cold alkali system it is difficult to take measures representative of the state of the cellulose in the solution. This presentation describes an indirect approach attempting to draw conclusions about the state of cellulose in solution by studying the Kirkwood cell in cellulose after coagulation. After dissolution (complete or incomplete) the spin dope was coagulated in different non-solvents, and subjected to a sequence of non-solvent exchanges combined with drying. After each step GI/MAID

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Nanoporous cellulosics: Previously unknown forms, as the best primary feedstocks for energy, chemical and agricultural feed production

Rajai H. Atalla1,2, phatalla@eiuwic.edu, Rowan Atalla1. (1) Cellulose Sciences International, Madison, Wisconsin, United States (2) Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin, United States

A process has been developed for transforming lignocellulotics into previously unknown Nanoporous forms. The process is carried out at ambient temperature and pressure by a method that uses only water, ethanol, sodium hydroxide and carbon dioxide. Thus, both capital and operating costs are far less than those of traditional high-temperature and high-pressure biomass pretreatment processes. The treatment solution has NaOH dissolved in a cosolvent wherein ethanol is the major component. The key to success is removal of the NaOH prior to exposure to water to avoid mercerization. It is accompanied by extraction of biologically active antioxidants and secondary metabolites. The lignocellulosics products are easily converted to monosaccharides that can be used as feedstocks for biosynthetic processes, for fermentation to fuels or for other organic and inorganic synthetic processes. The process can also convert low-value agricultural residues into nutritious feeds for ruminant livestock. The effectiveness of the transformation is reflected by reduction of the enzyme dosages necessary for hydrolysis to monosaccharides by an order of magnitude. When applied to agricultural residues the process increases their digestibility by an order of magnitude. We have developed applications of Raman spectroscopy where such alterations can be detected and quantified. As reported previously, crystallinity change can be monitored by 380-Raman and 93-Raman methods. Similarly, “degree of lateral order” can be evaluated by the extent of band intensity increase at 1380 cm⁻¹ upon OH-to-OO exchange. However, detection of conformational change in cellulose is more challenging. Nevertheless, in the spectrum of cellulose, a band around 900 cm⁻¹ was found to be most appropriate for accomplishing this task. Based on these capabilities, some examples will be discussed where Raman spectroscopy was used to obtain information on alterations of wood-cellulose ultrastructure.

Lignin: From Fundamentals to New Materials & Applications

Eweldyn A. Capanaena31,2, ewellyncapanema@gmail.com, Mikhail Balashkin2. (1) Chemistry, Univ. of Natural Resources and Life Sciences, BOKU, Vienna, Austria (2) Biorefining and Energy, RISE Bioeconomy, Stockholm, Sweden (3) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States

Understanding three-dimensional structure of lignin is of primary importance not only for lignin fundamentals but also for evaluation of its reactivity and valorization of lignin-based products. Traditionally, lignin has been considered as a 3-dimensional cross-linked polymer. In strict contrast, it was claimed recently that Milled Wood Lignin (MWL), a model of native lignin, is linear. In spite of dramatic differences between these theories, the discussion on the topic is very limited. This paper reviews different methods for evaluation of the amount of different lignin branching points, such as etherified 5-ethoxyethyl-4,5-O- and other lignin units. The analytical methods include permanganate oxidation after CuO pretreatment (CuO-P), 31P NMR analysis of the products of "Dervatization Followed by Reductive Cleavage" (DFRC-31P NMR), lignin thioacidolysis followed by 31P NMR (TA-31P NMR) and various quantitative 13C and HSQC NMR approaches. The pros and cons of these methods in the analysis of softwood, hardwood and grass lignins are revealed and the obtained results are discussed in the light of the current general knowledge on lignin structure.

13C NMR analysis of NaBH₄ reduced lignin is apparently the most accurate method for the analysis of branching lignin units (etherified 5-5 and 4-5-O-S as a sum) in softwood native lignins. However, it works for isolated lignin preparations only while the other methods (CuO-P, DFRC-31P NMR and TA-31P NMR) can be applied to biomass lignin in situ. Unfortunately, NMR-based methods are not suited for the analysis of 5-S- and 4-5-O- moieties in hardwood and grass lignins as condensed G-units are overlapped with S-units in 13P and 13C NMR spectra. Therefore, only CuO-P method is applicable so far for lignins of the 5G and 5H types.

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Investigating individual wood cell wall layers with X-ray micro and nano beams

Martin Mueller, martin.mueller@giks.de. Heinmolt-Zentrum Geesthacht, Geesthacht, Germany

In the mid-1990s, with the arrival of third generation synchrotron radiation sources, it became possible to observe highly brilliant X-rays down to spot sizes of a few microns and still provide a sufficient X-ray flux to obtain diffraction patterns from weakly scattering materials within a few seconds. This makes it possible to investigate thin specimens such as cellulose microfibril orientation and crystal size within single cellulose fibers and single wood cell walls directly. The X-ray diffraction of poplar tension wood fibers is largely dominated by the highly oriented gelatinous (G) layer. By investigating single tension wood cells fiber diffraction diagrams with an unprecedented (for native samples) resolution of 0.11 nm are measured. Lines of diffuse scattering in the fiber diffraction pattern are probably arising from defects (possibly stacking faults) in the crystalline microfibrils. Moreover, a direct comparison of crystal parameters and sizes in the G and the S2 layer is possible.

Many experiments on wood profit from the high spatial resolution of micro diffraction. The nanostructure of the soft wood cell wall exhibits characteristic layers (G and S2, 30-400 nm thick), introducing another structural parameter, the microfibril (hexag) angle (MFA). With a 'coarse' resolution of 2 μm, only the thinnest secondary layer S2 significantly contributes to the scattering signal. Looking at cross sections, the helical arrangement of cellulose microfibrils is directly imaged. Extended high-resolution scans over annual rings reveal details of the seasonal variation of the MFA and its connection to mechanical and acoustic properties of different wood species. The micro diffraction analysis of developing xylotissue provides an elegant and direct access to the sub-micron thick S1 layer properties even with a beam larger than the cell wall layers.

Nowadays, with X-ray nano beams a spatial resolution of 100-200 nm is achieved so that the nanostructure of thin cell layers can be investigated. Recent examples of such results will be shown. Indications for a local breakdown of the ideal cellulose fiber texture in the cell wall are found. The homogeneity of the MFA inside a cell wall layer and the size of possible helicoidal transition layers are estimated.
process efficiency, it is now increasingly becoming available in isolated form. Lignin represents an important potential source of renewable aromatic chemicals. A magnitude to realizing this, however, is a lack of understanding of the Kraft lignin structure. Here, we report the most detailed description of the Kraft lignin structure to date, based on NMR analyses of the prototypical Kraft lignin and 8 other novel synthetic Kraft lignins obtained from cell wall-derived dimeric and polymeric lignin models. Analysis of the 2D HSQC spectra of Indulin AT and a set of polarity-separated fractions allowed for approximately 40-50% of the aromatic groups to be quantified, as part of native or Kraft-generated linkages. Interestingly, linkage abundance varied greatly as a function of MW, providing better understanding of the chemistry that occurs during Kraft pulping and offering opportunities for MW-specific valorization processes. The synthetic Kraft materials allowed a new, minor component to be isolated, which proved highly diagnostic and led to the discovery of a new condensation pathway involving homovanillic as key intermediate. Notably, this new linkage could be identified in a range of different Kraft lignins, suggesting that the newly discovered pathway is involved in most, if not all, Kraft lignins. Finally, NMR analysis of synthetic Kraft samples generated from \(1^3C\)-labelled beta-O-4 models (at the beta and gamma position), indicated that the labelled carbons are each found in \(\geq 80\) new chemical environments after Kraft reaction, explaining why the fate of the beta-O-4 units had so far been elusive. The novel structural insights and the newly discovered intermediate and condensation mechanism can guide future valorization efforts of this important renewable resource.

**CELL 216**

**Ligninomics: Nanoscience, structure determination and MW-based fractionation using SEC, MS, STEM, TD-pyr-GCMS and thermal carbon analysis**

**Alena Kubatova**, alena.kubatova@unl.edu, Anastasia Andrianova, Shelly Lu, Sarah Reagen, Adeline E. Scollon. 2D NMR spectra in iron and copper samples, and \(13C\) NMR spectroscopy, and gel permeation chromatography (GPC). The ultrastructure of untreated and pretreated corn stover from these different combinatorial pretreatments was also analyzed by scanning electron microscopy (SEM). The results showed that combinatorial pretreatment of corn stover decreased the G/I and H-lignin, reduced the lignin's aromatic monomers, thus facilitating lignin processability into polyhydroxyalkanates (PHA). The combinatorial pretreatments led to less aliphatic hydroxy groups, more phenolic hydroxy groups, more carbonyl and aromatic or aromatic aliphatic carbonate, which limited the pretreatment of native corn stover lignin, resulting in more breakage of the linkage network, and thus facilitating the lignin bioconversion to PHA. The absence of lignin droplets that are often produced after liquid hot water and dilute acid pretreatments is due to the high acid concentration and/or organosolv pretreatment in Step 2 that solidified these particles into liquid streams. Lignin isolated from combinatorial pretreatments reduced the molecular weight of lignin and increased the polydispersity index (PDI) value. A lower molecular weight and higher polydispersity index (PDI) also facilitates lignin utilization by lignin-degradable microbes.

**CELL 219**

**Study of a new chemical derivatization method on lignin hydroxyl groups for size exclusion chromatography analysis**

Esakkiammal Sudha Esakkimuthu, Sudha.Esakkimuthu@pg2.grenoble-inp.fr, Marie-Christine Brochier-Salmon, Nathalie Marlin, Gerard Mortha. 1. Univ. Grenoble Alpes, LGP2, F-38000, Grenoble, France (2) CNRS, LGP2, F-38000, Agfeps, LGP2, F-38000, Grenoble, France

Lignin is the most abundant aromatic biopolymer in earth. In order to enhance the value of lignin for bioenergy applications it is very important to provide detailed structural information. In particular, lignin functional groups quantification and molar mass distribution (MMD) by size exclusion chromatography (SEC) are more prominent studies for lignin structural characterization. However, the MMD analysis of lignin is more complex than other polymers due to its irregular, partially branched structure, leading to low solubility and partial aggregation in most chromatographic solvents. Because of this, SEC gives quantitatively insufficient and unreliable results, which limits the exploitation of lignins in new applications. Therefore, chemical modifications have to be performed on lignin hydroxy functional groups to improve dissolution in the conventional chromatography solvents used for lignin (DMF, DMAc, DMSO). Acetylation is the most widely used method for lignin hydroxy groups modification prior to SEC analysis. Its main drawbacks is incomplete reaction and aggregates formation in the presence of long chains. Here, we propose a new derivatization technique called Fluorobenzylation, which is simple and more efficient. Then, it can efficiently remove alkyl and phenylglyoxylic groups of lignin in corresponding fluor-derivatives. This decreases lignin polarity, facilitates dissolution and characterization by SEC. For the SEC analysis, mono-disperse polystyrene samples were used as calibration standards in THF, but lignin structural conformation (cross-linked) differs from polystyrene (linear polymer) and the obtained MW (weight average molar mass) were not fully reliable. To overcome this difficulty and calculate the molar mass of the universal calibration method was tested on the fluor-derivatives by combining SEC, DRI and viscometric detection. Contrary to former applications of this method to lignin, not very successful, it is here fully justified by the fast and easy separation of new derivatization group, reducing agglomeration, and increased molar mass which enhances the viscometric signal. Meanwhile, fluoro-derivatives were also analyzed by “F-NMR spectroscopy for the quantification of lignin phenolic and primary aliphatic hydroxy groups.”

**CELL 220**

**Structural analysis of lignin isolated from a novel bioferment process and identification of condensed structures using 2D NMR**

Lucas Lagerquist, lagerqutj@abo.fi, Patrik Eklund. Laboratory of Organic Chemistry, Abo Akademi University, Abo, Finland

Different combinatorial pretreatments with a low holding temperature were investigated in an effort to synergistically improve the carbohydrate output and lignin processability from corn stover. Combinatorial pretreatment used two-step pretreatments whereby acid/hot water pretreatment step was followed by alkali and/or organosolv pretreatment step. Lignins were recovered through precipitation of pretreatment effluents. Ball-milled cellulolytic enzyme lignin of stover was also isolated and characterized. This pretreatment reduced the carbohydrate output and lignin processability from corn stover. Lignin was recovered through precipitation of pretreatment effluents. Ball-milled cellulolytic enzyme lignin of stover was also isolated and characterized. This pretreatment reduced the carbohydrate output and lignin processability from corn stover.
In this work we have analyzed and characterized lignin (BLN lignin) from a novel pressurized hot water extractions process. The process, developed by ChiBioOxy, is based on thermal hemicelluloses from wood chips with hot water at oxygen-deprived conditions. After the separation of the hemicelluloses the lignin is removed by mild alkali pulping of the remaining fibers, also at oxygen-deprived conditions. This leaves both of the carbohydrate fractions as well as the lignin in both high yield and purity and as such it is of importance to determine the structure and properties of the lignin fraction for possible future utilization. The process is currently being up-scaled to a facility being able to process up to 100 k ton biomass annually.

The studied lignin was compared to a milled wood lignin (MML), from the same wood chips, to determine the structural changes the process induced. The lignin was analyzed with the 13C NMR, 13C DEPT experiments, 29P NMR, 2D HSQC, FTIR, size exclusion chromatography, elemental analysis, pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), methoxy group determination and carbohydrate determination after methanolysis. It was concluded that the lignin is fragmented and re-condensed during the process. We identified multiple structural anomalies caused to the lignin by the process by using 2D NMR and DEPT experiments. Some of the peaks originated from condensed structures in S-units and have often been mischaracterized. The findings strengthen the hypothesis of 2/6-condensation of hardwoods and seem to be a common trait in weakly acidic pretreated lignins.

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Do lignin-carbohydrates complexes (LCC) survive to acid chloride delignification?

Denilson Da Silva Perez1, denilson.dasilvaperes@email.ucsb.edu, Maria Gonzalez Martinez2,4, Capacine Dupont1,5, Xuandong Xing3,4, Christoph Flock3,4, Mario Landin-Jiménez2,5, Claudia Crespi2,5, (1) InTech Fibres, FCBA, Grenoble, France (2) University of Tor Vergata, Rome, Italy (3) IUTEN/DIT/BXL/PIB, CEA, Grenoble, France (4) INPT / UPS / LGC, Université de Toulouse / CNRS, Toulouse, France (5) Department of Environmental Engineering and Water Technology, d IHE Delft Institute for Water Education, Delft, Netherlands

Chlorite delignification has been used since the 50’s as a mandatory step for any studies on extraction, isolation or purification of polysaccharides from lignocellulosic raw materials. This chemical treatment is considered as the most selective to remove lignin yielding a mixture of hemicelluloses and celluloses, although it known that some hemicelluloses removal also takes place in the end of the process. Although there are no doubts about the existence of the so-called lignin-carbohydrates, the literature about the fate of LCC upon chlorite delignification is very rare. No clear mechanisms have been proposed to explain if and how those structure are degraded during the chlorite delignification. In recent studies, we have attempted to evaluate the contribution of the different biomass component to the kinetics mechanisms of thermal conversion, in particular torrefaction. This has been done by fractioning and purifying the main chemical components (extractives, lignin, hemicelluloses and cellulose) of five very different biomasses (pine, beechwood, aspen, lucerne and miscanthus). Hemicelluloses fractions were obtained from these biomasses after extractives removal, extensive chlorite delignification, DMSO extraction, dialysis and lyophilization. The sugars analyses of these hemicelluloses reveal that their composition is strongly dependent on the raw materials. The hemicelluloses fraction were torrefied using a non-isothermal TGA device coupled to a GC/MS between 200 and 300°C, at 3°C/min for heating rate, under helium (50mL/min). Volatiles samples were collected every 10°C for the whole temperature range. Volatiles were collected for 100°C and stored in vials kept at 200°C while waiting for analysis. Twenty-five different volatiles species produced in torrefaction were quantified. Traces of lignin moieties (phenol, guaiacol and syringol) were very surprisingly found as volatile compounds for all raw materials, suggesting that some components of LCC may have not been degraded during the acid chlorite treatment. In order to clarify this hypothesis, different attempts of isolating residual LCC structures present in hemicelluloses were carried out and compared to the LCC extracted directly from the biomasses. The resulting material was characterized by 31P NMR and analytical pyrolysis coupled with GC/MS. The ensemble of the results seems to confirm that some partially degraded LCC structures may survive the acid chlorite delignification.

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Carbohydrate stabilization with formaldehyde prevents degradation and facilitates sugar recovery during biomass depolymerization

Jeremy Luterbacher, ja268@cornell.edu. Institute of Chemical Sciences and Engineering, EPFL, Lausanne, Switzerland

Biomass-derived carbohydrates are important platform molecules for the production of renewable fuels and chemicals. Their production requires the depolymerization of cellulose and hemicellulose, the main polysaccharides in lignocellulosic biomass, to glucose and xylose, respectively. However, in insensitive systems such as pure water or aqueous dilute acid mixtures, carbohydrate monomer degradation rates exceed hemicellulose and especially cellulose depolymerization rates at most easily accessible temperature, leading to low simple sugar yields. Because of this kinetic problem, cellulose is often depolymerized in the presence of expensive enzymes, concentrated mineral acids or even ionic liquids. All of these systems are used because they feature high rates of polysaccharide sublimation compared to sublimation and enabling its recovery at higher yields. Here, we demonstrate an alternative strategy that involves the reversibility stabilization of xylose and glucose by acetal formation with formaldehyde. In solvent-water systems at low water concentrations (<20%) and dilute acid environments, the diols present on glucose and xylose readily react with formaldehyde to form acetals preventing their dehydration to furfural. Once the resulting protected sugars are treated in high water environments (>50% H2O), the acetals hydrolyze quantitatively releasing formaldehyde and simple sugars. When performing an extensive pretreatment of beech in the presence of formaldehyde, over 90% of xylan could be converted to diformylxylose. In comparison, the same pretreatment without formaldehyde lead to almost full xylose degradation into furfural with only 16% xylose recovery. Similarly, depolymerization of cellulose led to over 70% yields of glucose and a final concentration of ~5 wt%, whereas the same reaction in the absence of formaldehyde led to yields below 30%. Therefore, this stabilization strategy prevents degradation of carbohydrates at high yields and concentrations.

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Ru-Ni quasi-allyls with H radical transfer catalyzed aqueous-phase guaiacol hydrogenolysis at low H2 pressures

Chen Zhao, czhao@chem.ecnu.edu.cn. School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, Shanghai, China

Aqueous phase hydrogenolysis of renewable biomass at low H2 pressures is an attractive route to selectively produce renewable fuels and valuable chemicals. Here, we showed that the dispersive Ru and Ni nanoparticles (NPs) on HZSM-5 with an optimum H radical transfer catalyzed a rapid rate (152 mmol g−1 h−1) in hydrogenolysis of C=O bonds in lignin-derived guaiacol at 240 °C and 2 bar H2 pressure in water. The co-impregnated individual Ru and Ni nanoparticles (NPs) on HZSM-5 were highly dispersed and did not present an alloy structure, but the individual Ru and Ni NPs were in a close proximity. The guaiacol hydrogenolysis rates were proportional to the amounts of the adjacent RuO2 and NiO NPs on the calcined samples, suggesting the closely contacted Ru and Ni NPs on HZSM-5 are the active sites. In the water phase at low H2 pressures, Ru dissociated the hydrogen molecules to H radicals (H·), and then such radicals were transferred to adjacent N atoms for activating the capability of inert Ni centers. The adjustment of the H transfer length between Ru and Ni NPs led to shorter H transfer lengths, which resulted in activities as high as 118 mmol g−1 h−1. The transferring and anchoring of H radicals on the Ni islands was considered to be achieved by the Si-OH groups and their defects on HZSM-5, as demonstrated by temperature programmed desorption of hydrogen coupled with mass spectrometry (TPDH2-MS) experiment. To further shorten the H transfer length over uniformly formed Ru and Ni nanoparticles, the isolated Ni islands were removed through the incorporation of a Ru precursor that initially occupied the Brönsted acid sites on HZSM-5. By fully activating the two metals in the aqueous phase via an H transfer mechanism at low H2 pressures, the rational design of binmetallic quasi-allys catalysts provides a promising approach for achieving substantially high rates in selective hydrogenolysis steps.

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Highly efficient molecular transformation using ordered alloys as catalysts

Shinya Furukawa, furukawa@cat.hokudai.ac.jp. Institute for Catalysis, Hokkaido University, Sapporo, Hokkaido, Japan

Ordered alloys, also known as intemmetallic compounds, work as highly efficient heterogeneous catalysts for various catalytic reactions such as selective hydrogenation and oxidation, where the corresponding homogeneous catalysts show very low catalytic activities and selectivities. The formation of ordered alloy phase drastically modifies the electronic and geometric factors of the materials, which enhances the desired reaction pathways and/or inhibits the undesired side reactions. In addition to the conventional ligand and ensemble effects on alloying, we discovered a novel effect, which we coined "steric effect". This effect appears only on bimetalic surfaces with highly ordered atomic arrangement such as Rh/Sb(202), Rh(110), and Rh(110) planes, where the sophisticated steric restriction is imposed to surface reaction and reactant adsorption. This effect allows various challenging molecular transformation such as stereoselective isomerization of alkenes, regioselective hydrogenation of dienes, and chemoselective hydrogenation of nitroarenes.
Exploiting support effects and composition in Cu based bimetallic catalysts for sustainable chemical conversion

Phillip Christopher, christopher@engr.ucr.edu, Department Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States

Supported bimetallic nanoparticles have been identified as an important class of materials demonstrated tunable reactivity for a variety of industrial catalytic properties. The design of bimetallic surface structures with controlled geometries and compositions via density functional theory calculations has proven successful for catalyst optimization. However, the actual structure and composition of exposed catalytic surfaces on synthesized structures under reaction conditions is a complex function of interactions between the two metals, the metals and reactive environments and the metals and support. While reaction environment induced reconfiguration of bimetallic particles has been thoroughly explored, relatively little is known about how specific metal-support interactions can be used to tune and control exposed surface structures.

In this talk I will describe recent work from my group where we have identified how metal-support interactions can be used to control the surface composition of bimetallic Cu-N structures, and how segregation within the particles influences reactivity, selectivity and stability of the catalysts under harsh biomass-derived compound hydrolygolysis conditions. We propose a mechanism where we envision the support acting cooperatively with the bimetallic structure to control the exposure of desired catalytic surfaces. We will further describe how Cu addition to supported Cu catalysts enables the conversion of biomass-derived species to higher alcohols, such as pentanal, in high yields.

Perovskite catalysts for oxidative coupling of methane

Yujin Sim, Jihoon Yoo, Dahye Kwon, Ji Chul Jung, jchung@mu.ac.kr, Department of Chemical Engineering, Myongji University, Youngin, Korea (the Republic of)

Advances in the production technology for shale gas, which is mainly comprised of methane gas, have triggered intensive studies on catalytic processes for converting methane into various valuable chemicals and fuels. In particular, oxidative coupling of methane (OCM) to C2 hydrocarbons is attracting significant interest because C2 hydrocarbons such as ethane and ethylene are the most widely used chemicals in the world. However, the chemical stability of methane and the thermodynamically favorable formation of carbon monoxide and carbon dioxide from methane lead to difficulties in selective conversion of methane into C2 hydrocarbons. Therefore, despite continuous efforts of many researchers to develop an efficient and selective catalyst, any economically viable OCM process has not been commercialized yet. Although Na/WO/Mn/SiO4 is regarded as the best catalyst for OCM by most researchers, the nature and properties of the active sites are not yet fully understood owing to its complex composition and structure. In this presentation, we'll describe our insights into the nature of active sites with simpler compositions and structures is needed to develop a commercially viable OCM process. To address these issues, we conduct OCM over various perovskite catalysts, which are well-known not only as efficient photocatalysts but also as materials with outstanding catalytic activities in various methane conversion reactions. Accordingly, we attempt to identify and discuss the important factors that determine the catalytic performance in OCM. We hope that this study will contribute to the systematic design of high performance catalysts for OCM.

Halide perovskite nanostructures for energy harvesting and optoelectronics

Leitan Dou, dour10@purdue.edu, Chemical Engineering, Purdue University, West Lafayette, Indiana, United States

Semiconductor nanostructures are considered as a good perform for studying their interesting physical properties and potential applications in renewable energy harvesting and optoelectronic devices. Recently, there is a renaissance of halide perovskites as a promising class of semiconductor materials for a variety of optoelectronics and optoelectronics. This talk will focus on the new strategies for the syntheses of 1D and 2D halide perovskite nanostructures and fabrication of novel functional heterostructures and optoelectronic devices.

Firstly, we present new synthetic methodology of halide perovskite nanowires with desired size, composition, and properties. Such synthetic approach includes colloidal, solution-phase, and vapor-phase growth. Sub-micrometer single crystal nanowires from solution-phase growth were demonstrated as efficient optical medium for high-performance and robust laser application. Due to the relatively weak bonding in halide perovskites, ions are highly dynamic inside the crystal lattice. Anion exchange was demonstrated in these 1D materials with high PLQE throughout the exchange reaction. Based on this, we demonstrate perovskite nanowire heterojunctions with high spatial resolution. The solid-solid anion exchange dynamics can be resolved in CsPbI₂-xBrx/CsPbI₂-xClx hetero-junction nanowires through a non-destructive optical method. Secondly, we will discuss our new discoveries on the synthesis of atomically thin two-dimensional halide perovskites. These new 2D structure exhibits high PLQE and tunable optical properties for optoelectronics and photonics application. Thirdly, we demonstrate phase transition solar cells based on halide perovskites that can change color under different external stimuli. Overall, halide perovskites nanomaterials offer promising opportunities for exploring fundamental research and enable efficient renewable energy harvesting.

Techno-economic and life cycle optimization of multiple waste-to-energy and resources pathways

Huying Yang, Xiaoran Wang, xwang@uic.edu, Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore

Energy, water, food and waste systems analyses at a nexus level is key to move towards a more sustainable development pathway. In this paper, we apply techno-economic and life cycle optimization to emphasize multiple waste-to-energy and waste-to-resources pathways, aiming to develop waste treatment and recovery capacities with the minimal economic and environmental cost. A wide variety of waste categories are incorporated including wastewater (WW), municipal solid waste (MSW), agriculture waste and industrial chemical wastes, as the sources of combustion through incineration, gasification or pyrolysis for combined heat and power generation, or biological treatment such as anaerobic digestion (AD) and aerobic treatment, or chemical reactions to transit to value-added products. The application demonstrates how simulation and optimization models can provide new insights in the design of sustainable value chains, with particular emphasis on whole-system analysis and integration.

We will also present the collaborative work with Prof Ning Yan’s group on a suite of life cycle analysis (LCA) studies aiming to compare several novel waste-shell fractionation processes with the traditional process. The work demonstrates significant environmental and economic benefits of the waste-shell utilization methodology developed in Yan’s lab. For example, CO2 is used as a raw material, either with concentrated urea that is recycled multiple times to reduce the total energy consumption and carbon footprint, or hydrothermal-OC process without using any eco-unfriendly reactant to yield chitin with comparable quality and a shorter production cycle. For 100 kg shell waste process, the traditional operation consumes 797 kWh and carbon footprint reaches 283 kg (CO2-eq), while the novel process can significantly decrease the operation energy consumption and carbon footprint by 62% and 90% respectively. Besides, ten LCA impact categories based on CML method were investigated, all of which shows that the hydrothermal-CO2 process has much less environmental impacts than the traditional and urea-OC2 processes.

Shell biorefinery: Dream or reality?

Ning Yan, ningyan@nus.edu.sg, Faculty of Engineering, Natl University of Singapore, Singapore

An estimated 6–8 million tons of shell waste from crustaceans are produced annually. These shells have low monetary value; for instance, dried shrimp shell powders are sold at merely US$100–120 per ton, the price of which is comparable with agricultural lignocellulosic biomass waste. Valorization of these biomass waste can be done ecologically and economic benefits. However, there is no satisfactory solution to utilize them at present. A vast majority of the shells are directly disposed of or landfill without utilization, posing environmental issues. By harnessing the wisdom accumulated in woody biomass utilization, the concept of the shell biorefinery was the exploration of efficient, low-cost fractionation methods and the development of innovative transformations for chitin and other components in the shell. In this talk, we will present recent developments from our group along this line. In particular, we will present the potentials of converting chitin into N-containing chemicals (Scheme 1). Several strategies, including dehydration, liquefaction, hydrogenolysis and hydrothermal treatment, will be detailed in detail, which demonstrated that chitin is indeed an attractive starting material for the manufacturing of certain value added chemicals. [3-9]

Biobased Water Purification System Approaches

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Dynamics and kinetics of marine exoskeleton-based heavy metal biosorption and desorption

Carolina Londorno Zulugaita, clondon@ncsu.edu, Hasan Jamee5, Lucian A. Lucia, Ronald Gonzalez, (1) Departments of Forest Biometrics and Chemistry, North Carolina State University, Raleigh, North Carolina, United States (2) Department of Forest Biometrics, North Carolina State University , Raleigh, North Carolina, United States

Heavy metals are extensively found within the natural environment contributing significantly to potable water pollution. Heavy metals are found in potable water because of industrial and agricultural activities, fossil-fuels combustion, volcanic activity, or mineral erosion. Although specific heavy metals are essential for human, animal, and plant metabolic needs, only small amounts are needed and exceeding these amounts can be toxic. As a result, the development of new water remediation technologies, especially for heavy metal removal from water, has been progressively increased. Currently, the use of metal ion removal, adsorption is one of the most reliable, robust, and hence prevalent. The technical feasibility and cost effectiveness of this process is highly related to the materials used. Crustacean shells, a waste material, is used due to its advantageous properties as a heavy metal biosorbent. However, heavy metals biosorption may change the mechanical properties of the waste material, leading to a reduced use in different products. This work presents a comprehensive study on metal ion biosorption/desorption from crustacean shells. In order to achieve this, a large number of crustacean shells was collected and analyzed for their metal content. Then, the material was subjected to a series of desorption experiments using different methods. The results show that the material is highly efficient for heavy metal biosorption/desorption, and it can be used in various products. The study demonstrates the potential of this waste material for the production of new products and the environmental sustainability of the process.
Although water covers 71% of the Earth’s surface, only 2.5% is known to be freshwater, of which a minimal percentage is available and suitable for consumption. The increasing demand from industry and the consequent generation of wastewater urge for purification techniques to guarantee the quality of the water. One of these techniques include the removal of toxic heavy metals, which are extremely harmful to both public health and aquatic life. Therefore, it is of utmost importance to control the concentration of these chemicals in water streams. To remove heavy metal ions from aqueous streams, techniques such as precipitation, adsorption, oxidation, etc., have been widely used. The process of adsorption possesses several advantages, where chitosan shows promising results. Chitosan is a naturally occurring biopolymer that can be obtained from chitin, which in turn can be valorised from crustacean shells. Chemical modification of chitosan, in terms of the introduction of amine and hydroxyl groups, is known to enhance the adsorption capacity of certain heavy metals from aqueous streams. Preliminary research proves that simple modifications result in a highly efficient removal of platinum and palladium. Furthermore, the sustainability of chitosan lies both in its origin and its application.

A need for improved economical and greener approaches to remove and recover dyes and heavy metals from wastewater streams exists due to increasing resource scarcity. Chitosan is has been used as an adsorbent for these compounds, but suffers from some properties that can be disadvantageous to its effectiveness; it is difficult to effectively disperse in aprotic solvents. The materials may find use in applications for extraction of heavy metal ions prior to papermaking by filtration.

Chitosan derivatives for metal removal from wastewater

Stein Minckev1, stein.mincke@ugent.be, Tsegaye Grima1, Ivar Verheye1, Gijis Du Laing1, Christian V. Stevens1, Civil Engineering/Chemical Engineering, Queen's University, Kingston, Ontario, Canada

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Polymer-grafted chitosan for applications in dye and heavy metal removal and recovery from water

Omar Garcia-Valdèo2, Evan Madi3, Bryan Tsai4, Michael Cunningham3, Pascale Champagne1, champagne@civil.queensu.ca. (1) Civil Engineering/Chemical Engineering, Queen's University, Kingston, Ontario, Canada (2) Chemical Engineering, Queen's University, Kingston, Ontario, Canada

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Biosorbent films based on nanocellulose and lysozyme nanofibers for efficient removal of mercury (II) from natural waters

Nuno H. Silva1,2, Paula Figueira3,2, Carla Vilela3,2, Ricardo J. Pinto3,2, Isabel Marnocho1, Maria E. Pereira1, Carmen Freire1, crefre2011@gmail.com. (1) ITQB/UNL, Oeiras, Portugal (2) Central Laboratory of Analytical, University of Aveiro, Aveiro, Portugal (3) CICECO & Chemistry Department, University of Aveiro, Aveiro, Portugal (4) CESAM & Chemistry Department, University of Aveiro, Aveiro, Portugal

During the last century, industrial activity has led to seriously levels of environmental pollutants worldwide. For example, trace metals are produced daily without an adequate treatment, turning water pollution one of the inherent consequences which leads to a long-term negative impact on nearby bodies of water and a foremost risk for illness and diseases [1,2,3]. Therefore, the efficient removal of pollutants from water and wastewaters constitutes nowadays one of the most important environmental issues, and consequently, the development of efficient methodologies and materials for the decontamination of waters a central topic. In this communication, we will present the preparation and characterization of entirely bio-based nanofibrous adsorbent films, based on nanofibrillated cellulose and lysozyme nanofibers, for the efficient removal of Hg(II) from natural waters.

Modified cellulose ethers aerogels for the removal of organic pollutants from wastewater

Denise Petri, dsp@usp.br. University of Sao Paulo, Sao Paulo, Brazil

Bisphenol A (BPA), catechol, ethynyl estradiol (EE) are some of pollutants found in wastewater and aquatic environment. These compounds are sometimes present at trace levels (ng/L), making their analysis difficult. One strategy is the pre-concentration of pollutants in bioadsorbents, post-release in a good solvent and determination by conventional analytical methods. In the present work, hydroxypropyl methylcellulose (HPMC) aerogels were modified by the chemical attachment of β-cyclodextrin (CD) or inclusion of magnetic nanoparticles (MNP) and carbamoyl methylcellulose (CMC) aerogels were modified by inclusion of MNP/charcoal particles. Briefly, hydrogels of HPMC or CMC, and citric acid, as crosslinker, were freeze-dried in order to remove the water, and heated at 165 °C for 7 minutes for crosslinking. In the case of HPMC-CD, CD was added in the polymer solution prior to crosslinking. The amount of CD chemically attached to the HPMC chains was determined by phenolphthalein assay and confirmed by DSC. The inclusion of MNP or MNP/charcoal in the HPMC or CMC aerogels was determined by ICP-OES. The results were characterized by TG/DTA and X-ray absorption analyses. The equilibrium constant for the inclusion of biaphenol A (BPA) in the CD was determined by means of H-13C-NMR spectroscopy. The retention capacity of BPA by HPMC-CD aerogels amounted to 90 ± 3 mg/g. The adsorption capacity of EE by HPMC was 76 ± 3 mg/g, twice of that presented by HPMC-MNP-CMC. The aerogels were removed 70% of catechol from aqueous solution. These findings clearly indicate that cellulose based aerogels are potential adsorbents for pre-concentration of organic pollutants. Experiments to evaluate the selectivity of aerogels for the mixture of BPA, EE and catechol in aqueous media are under progress.

Hydrophobization by polymer adsorption to bacterial cellulose structures

Panagiota Spiliopoulou1, panagiota.spiliopoulous@aalto.fi, Aapo Lokki2, Eero Konttun1, (1) Bioproducts and Biosystems, Aalto University, Helsinki, Finland (2) Aalto University, Helsinki, Finland

The inducement of water repellent properties on bacterial cellulose structures via hydrophobic polymer adsorption from aprotic solvents was tried. Bacterial cellulose hydrogels were freeze-dried into aerogels, solvent-exchanged and subsequently immersed in polymer solutions of polyethylene oxide followed by extensive washing. Freeze-drying and determination of the porous structure mass uptake followed, while nitrogen adsorption provided information on the subsequent structural decrease and porosity determination. The bacterial cellulose surface were observed by SEM, and pycnometry measurements revealed the adsorption effect on the skeletal density. Finally, the modified structures exhibited decreased vapor sorption ability and increased oil/water sorption selectivity. The materials may find use in applications for extraction and collection of oil from water.

Biosorbent films based on nanocellulose and lysozyme nanofibers for efficient removal of mercury (II) from natural waters

Nuno H. Silva1,2, Paula Figueira3,2, Carla Vilela3,2, Ricardo J. Pinto3,2, Isabel Marnocho1, Maria E. Pereira1, Carmen Freire1, crefre2011@gmail.com. (1) ITQB/UNL, Oeiras, Portugal (2) Central Laboratory of Analytical, University of Aveiro, Aveiro, Portugal (3) CICECO & Chemistry Department, University of Aveiro, Aveiro, Portugal (4) CESAM & Chemistry Department, University of Aveiro, Aveiro, Portugal

During the last century, industrial activity has led to seriously levels of environmental pollutants worldwide. For example, trace metals are produced daily without an adequate treatment, turning water pollution one of the inherent consequences which leads to a long-term negative impact on nearby bodies of water and a foremost risk for illness and diseases [1,2,3]. Therefore, the efficient removal of pollutants from water and wastewaters constitutes nowadays one of the most important environmental issues, and consequently, the development of efficient methodologies and materials for the decontamination of waters a central topic. In this communication, we will present the preparation and characterization of entirely bio-based nanofibrous adsorbent films, based on nanofibrillated cellulose and lysozyme nanofibers, for the efficient removal of Hg(II) from natural waters.

Nanopaper filtration membranes from seawater suspensions of TEMPO-CNF

Andreas Mautner1,3, andreas.mautner@univie.ac.at, Koon-Yang Lee2, Alexander Biemarck1,3, (1) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (2) Department of Aeronautics, Imperial College London, London, London, United Kingdom (3) Department of Chemical Engineering, Imperial College London, London, United Kingdom

Membrane operations are important tools to tackle water contamination enabling supply of potable water for a growing number of people living on this planet. Conventional membranes for this task are usually produced from synthetic polymers, derived from fossil resources, or ceramics requiring significant amounts of energy, chemicals and solvents during their production. Therefore, utilization of membranes based on a renewable resource, such as nanocellulose papers, constitutes a true alternative. Cellulose papers have a long tradition as filter and membrane material dating back to ancient times. Unfortunately, conventional filter papers, produced from cellulose microfibers, exhibit certain limitations when pollutants in the nanometer range are to be removed. Recently, the utility of nanocellulose papers, so-called nanopapers, was demonstrated as tight aqueous UF membranes, capable of removal of viruses and contaminants larger than 5 nm. Key for an efficient preparation process was the fouling of TEMPO-CNF with divalent Mg2+ or trivalent Al3+ ions prior to papermaking by filtration.

In an effort to prepare these membranes on a more ecological friendly base than dissolving the TEMPO-CNF systems, Aalto University, Helsinki, Finland (2) Aalto University, Helsinki, Finland

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The inducement of water repellent properties on bacterial cellulose structures via hydrophobic polymer adsorption from aprotic solvents was tried. Bacterial cellulose hydrogels were freez
Nanocellulose for use in enhanced oil recovery: Transportation of nanocellulose dispersions through porous media
Ellinor Heggeset1, ellinor.heggeset@risoe.dk, Reidun Cecille Aadland2, Carter Jordan Daia3, Kristin Syverud1, Ole Torseter4, Steven Bryant5, (1) RISE PFI, TRONDHEIM, Norway (2) Department of Geosciences and Petroleum, Norwegian University of Science and Technology, TRONDHEIM, Norway (3) Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada

Nanocellulose serve as a potential new water additive for enhanced oil recovery (EOR) applications. Several advantages gives nanocellulose promising potential for EOR, e.g. excellent viscosifying and shear thinning properties, hydrophobic particles, excellent possibilities for chemical modification and particle character instead of dissolved polymers. Additionally, the material is biodegradable, non-toxic and obtained from an environmental-friendly resource. Also, the nanocellulose particles are different from traditional nanoparticles, such as silica, since they are rod-shaped instead of spherical. This adds a new element of complexity to their flow behavior.

The most likely mechanisms for EOR from injection of nanocellulose dispersions are increased viscosity, decreased interfacial tension and wettability alteration. However, the retention characteristics are the main concern initially and are investigated in this study.

The objective of this study was to identify the main retention mechanism affecting the transport of cellulose nanocrystals (CNC) through porous media. The experiments consisted of single phase flow through unconsolidated sandpacks and consolidated core plugs. Two floods were performed for each experiment – a tracer flood and a nanoflood. An ultraviolet (UV)-visible (VIS) spectrometer was used to measure the CNC concentration, and pressure data gave information about permeability alterations. For the sandpacks the effects of varying the salinity, grain size, particle size and velocity were examined. From these experiments it is clear that CNC suspended in aqueous phase, have the ability to flow through porous media. As a general trend, it was observed that larger particles or aggregates resulted in higher retention and permeability impairment. By increasing the salinity, particles started to aggregate more, which resulted in blocking and log-jamming. Thus, salinity was found to be the most important parameter affecting transport.

The core plugs had a permeability that was over three times smaller than the smallest grain size tested in the sandpacks. From these experiments there seem to be inaccessible pore volume present in the rock, meaning that some pores are too small for the nanocellulose particles to transport through. Thus, this resulted in different transport behavior where nanocellulose fluid breaks through earlier than the tracercurve.

Sustainable Production & Processing of Agricultural Crops: The Food, Energy, Water Nexus
CELL 238

Sustainable production of foods with berry polyphenols
Bradley W. Bolling, bwbolling@uwisc.edu. University of Wisconsin-Madison, Madison, Wisconsin, United States

Polyphenols are an important class of fruit phytochemicals. Increased polyphenol consumption is associated with the reduced risk of chronic disease, but polyphenol-rich foods are under-consumed. Berries are rich dietary sources polyphenols. The aronia berry has received attention as an emerging specialty crop, but a number of opportunities and challenges are pertinent to its sustainability. The genetic diversity of the crop is unknown, and benchmark quality and yield standards have not been developed. A large bank of aronia genotypes are accessible for improving quality, yield, and disease resistance in this crop. As with other crops, aronia berry polyphenol content varies by genotype and harvest date. Thus, certain polyphenol profiles could be targeted for particular food or ingredient applications. Only a small amount of fresh aronia berry is expected to be marketable, thus a significant portion of the crop requires preservation. Common berry products include juices, wines, concentrates, ingredients, and dietary supplements. Berry polyphenols are inherently unstable during processing and preservation. A greater understanding of the mechanisms of degradation is needed to maximize polyphenol consumption in processed products and storage conditions. New products are needed to target consumers and increase berry consumption. The polyphenol content and sugar profile of aronia berry present challenges toward consumer acceptance. Processing and horticultural strategies could overcome these issues. Berry consumption is expected to improve health, and emerging evidence suggests aronia may inhibit chronic inflammation and cardiovascular disease risk, among others. However, these health benefits are largely unproven. Identifying the contributions of specific polyphenols/bioactives, the inter-individual variabilty in polyphenol metabolism, can help guide selection of genotypes, processing conditions, and doses necessary to improve health. Therefore, while a number of challenges exist, a sustained research effort coordinating expertise in selection of genotypes, processing conditions, and doses necessary to improve health. The polyphenols/bioactives, the inter

How the commercialization of novel peppermint varieties is contributing to sustainable production of peppermint oil
Mark Morris1, mmmorris@wildflavors.com, Deven Holmgren2, Jie Liu3, Jacob G. Zeevaart4, Michelle Budnik4, (1) Corporate Sustainability, ADM, Decatur, Illinois, United States (2) WFSI, R&D Plant Sciences, ADM, Eugene, Oregon, United States (3) WFSI R&D, ADM, Erlanger, Kentucky, United States

In the USA, peppermint acreage varies between 60,000 and 100,000 acres depending on market conditions. Along with spearmint and arvensis mint, it is used to flavor chewing gum, toothpaste, confections, and health care products with a retail value exceeding $40B. Peppermint is affected by several challenges to its commercial sustainability including plant diseases, pests, water, and fertilizer usage resulting in cost increases that make U.S. peppermint oil less globally competitive.

The long-term sustainability of peppermint is an important objective at ADM. A.M. Todd, the mint
brand at ADM, has an ongoing agricultural program to increase peppermint oil’s economic and environmental sustainability including the development of non-GMO novel varieties that are higher yielding, resistant to key pests and diseases, and use less water and fertilizer.

An important achievement has been the identification of peppermint varieties that are highly resistant to aggressive strains of Verticillium wilt (Verticillium dahliae) and mint rust (Puccinia menthae). This important milestone has made peppermint more competitive by increasing oil yields and allowing for a longer peppermint plantation life span.

In addition to the significant cost reduction advantages these varieties and complementary agricultural practices have had, they have also provided beneficial environmental benefits. Over the past five years, ADM peppermint varieties have saved 33,623 million gallons of water, 6,332 tons of fertilizer, and 597,558 gallons of fuel. This reduction in fuel usage has allowed us to prevent the emission of 6,156 metric tons of CO₂, which is the equivalent of 466 homes’ electricity use for a year or 667 cars driven for a year.

The ADM Plant Science program has improved the economic sustainability of peppermint oil production and achieved significant environmental benefits while reducing the overall cost of producing a pound of peppermint oil.

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**CELL 243**

Microalgae cultivation for wastewater treatment and bioenergy production

Amit Bhatnagar, dr.amit10@gmail.com, Ehsan Daneshvar. Department of Environmental and Biological Sciences, University of Eastern Finland, Kuopio, Finland

In this study, a fresh water microalgae, Chlorella vulgaris, was cultivated in diluted pulp wastewater (PWW) with lake water (LW) and aquaculture wastewater (AWW). A higher microalgae growth rate with 80% PWW-20% AWW and 60% PWW-40% AWW ratios was found. The best mixture of PWW and AWW (PWW+AWW) was selected as microalgae culture medium. The influence of macro- and micro-nutrients to algal medium was examined on algae growth. The lowest (0.380 g/L) and highest (1.31 g/L) dry alga weight was observed in the medium without adding nitrate and micronutrients, respectively. Nitrate, ammonia, total phosphorus, chemical oxygen demand, total nitrogen, and total organic carbon removal efficiencies by microalgae were studied in PWW+AWW. Biochemical compositions viz., protein, carbohydrate and lipid percentage of harvested microalgae from real wastewater and BBM solution were analyzed and compared. Finally, lipid profile analysis was determined. C16 and C18 are the major fatty acid methyl esters (FAMEs) in C. vulgaris cultivated in BBM and PWW+AWW. These results suggest that C. vulgaris is a capable candidate for PWW and AWW treatment and bioenergy production.

**CELL 244**

Value-added bio-based food products

Madhav P. Yadav, madhav.yadav@ars.usda.gov. ERRC, ARS, USDA, Wyndmoor, Pennsylvania, United States

The alkali soluble arabinofuranosans (Hemicellulose B) and insoluble fibrous cellulose rich fractions from various low value agricultural residues (corn stover, wheat straw, etc.), agricultural processing by-products (corn fiber, wheat bran, rice fiber, sorghum bran, sugar cane bagasse, etc.) and energy crops (switchgrass and miscanthus) were isolated by alkaline treatment, characterized and their functionalities were studied. The soluble arabinoxylans and the insoluble cellulose rich fractions are referred to as Bio Fiber Gums (BFGs) and Cellulosic Arabinoylan Fibers (CAF's), respectively. The BFGs appear to have useful properties as emulsifiers, antioxidants, dietary fibers and other food ingredients. Like corn fiber gum (CFG), these polysaccharides are unique in their ability to make low viscosity solutions, even at high concentrations. CAFs prepared from the residues remaining after BFG isolation, were also characterized and their water holding capacity, rheological behavior and ORAC values were determined. The new insoluble fibers from multiple sources are expected to have unique applications as non-caloric food bulking agents and may be useful in replacing fat with healthy fiber and water without changing taste. The new insoluble fibers may also improve mouth feel of foods such as bakery products, dairy products, meats, dressings, macaroni and cheese etc.

Understanding the functional properties of new BFGs and CAF's will be beneficial for their commercialization and for identifying new applications in food industries.

**CELL 245**

Investigation of sugar beets as a feedstock for sustainable alternative jet fuel in south Florida

Christina Dorado1, christina.dorado1@gmail.com, Randall G. Cameron1, Kevin Cooper2. (1) Agricultural Research Service, United States Department of Agriculture, Fort Pierce, Florida, United States (2) Advanced Technology, Indian River State College, Fort Pierce, Florida, United States

Sugar beets have been grown primarily in the Midwest for the production of table sugar and have recently gained interest for planting and harvesting in other areas of the United States such as Florida based on their potential use as cattle feed, as a feedstock for ethanol production and as a cover crop to improve the quality of water via soil nutrient accumulation. Sugar beets grown in southern Florida and Minnesota were subjected to steam explosion using a continuous steam explosion pilot scale system located at the United States Horticultural Research Laboratory in Fort Pierce, Florida. Analysis of soluble and insoluble sugars as well as peclin from raw and steam exploded sugar beet were completed. Fermentations of raw and steam exploded sugar beets, with and without enzymes, were conducted. There was no significant difference in ethanol production from the fermentation of steam exploded sugar beets with and without enzymes indicating that addition of enzymes are not necessary for optimization of fermentation. Pilot scale fermentations of the steam exploded sugar beet gave 6.7-9.7 percent ethanol by volume. Investigations into using already established methods and infrastructure for the citrus processing industry for processing sugar beets were conducted and industrial scale processing of sugar beets at a local citrus processing plant was completed. This work is part of the Farm to Fly initiative which is aimed at creating a commercial scale south Florida sustainable alternative jet fuel and bio-products industry.

**Cellulose & Other Structural Biopolymers: Structure, Formation & Degradation: Anselme Payen Award Symposium in Honor of Junji Sugiyama**

**CELL 246**

Junji Sugiyama and CERMAV: A long lasting impact

Henri D. Chany, henri.chany@cermav.cnrs.fr. CERMAV-CNRS, Grenoble, France

In the early 90s, Junji Sugiyama joined our group at CERMAV for 18 months as a JSPS post-doc, followed by several short visiting scientist periods. This presentation will bring into perspective the advances resulting from his stay with us and the long lasting influence this collaboration had on our laboratory.

**CELL 247**

Allomorphic transition in native cellulose promoted by ultrasounds

Karim Mazeau, karim.mazeau@cermav.cnrs.fr, Pan Chen, Yu Ogawa, Laurent Heux, Sonia Molina Boisseau, Jean-Luc Pauth, Yoshitharu Nishiyama. CERMAV, Grenoble, France

Native cellulose is generally a mixture of two crystal phases, la and lb. It is well known that processes, such as hydrothermal treatment, influence the relative proportion of these two phases. We have recently shown that sonication has a similar effect: sonicated celluloses are indeed enriched in lb. Besides, they show a linked morphology and their crystallinity is decreased. We have studied the process of kinking the crystals of native cellulose, initially pure in la and pure in lb, by their hydrophobic surface by molecular dynamics simulation. A three-point bending causes a local amorphization of the structure at the kinking point while the two linear segments on both side remain highly organized but undergo locally and punctually longitudinal sliding of the hydrogen-bonded sheets. The magnitude of the sliding is 0.5 nm, which corresponds to the length of a glucose residue and thus to a local allomorphic transition. Even though la and lb share the same stress relaxation mechanism, lb accumulates such transitions with increasing kinking angle whereas in lb these transitions are only translatory. We have established a common mechanism leading to both kinking and allomorphic transition.

**CELL 248**

Ultrastructural characterization of cellulosics by solid state NMR: has everything been done?

Laurent Heux, heuxl@cermav.cnrs.fr. CERMAV-CNRS, Grenoble Cedex09, France

The ultrastructure of cellulose, that arose from a combination of biosynthesis and crystallization constraints offers to the scientific community a wide panel of significantly different allomorphic
forms. As a matter of fact, cellulotics are able to undergo several transformations of both academic and industrial importance, sometimes desired and sometimes annoying. After the seminal works obtained almost simultaneously by electron diffraction and 13C CP-MAS solid state NMR, the presence of two distinct allomorphs, most of the crystallographic studies have been elucidated by combining X-ray and neutron diffraction experiments, allowing a much more precise depiction of the hydrogen bond network. 13C CP-MAS solid state NMR can also bring interesting information on the conformation of the different cellulotic allomorphs, that does not require a periodic organization of the structure, allowing the investigation of poorly organized systems. In this context, we will systematic 2D INADEQUATE NMR experiments of fully 13C enriched bacterial cellulose samples in order to bring further information on the organization of the hydrogen bonding network of different cellulotic allomorphs. We will discuss the correlations between chemical shifts and hydrogen bond strengths and see how it can bring new insights in the ultrastructure of cellulose polymorphs. Additionally, the NMR experiments brought interesting information on the conformation of the chains at the surface of the cellulose nanocrystals or in disorganized areas. Last but not least, the experiments have been extended to more complex natural systems like modified cellulose or plant cell walls, bringing informations on different polysaccharides whose signals usually overlapped.

**CELL 249**

Mutation analysis to explore potential functional differences among plant CESA isoforms

*Candace H. Haiger*1, candace_haiger@ncsu.edu, Jason N. Burns2, (1) Deps. of Crop & Soil Sciences and Plant & Microbial Biology, North Carolina State University, Raleigh, North Carolina, United States (2) Crop & Soil Sciences, North Carolina State University, Raleigh, North Carolina, United States

The CESA gene family in seed plants is characterized by six major clades of isoforms, including three typically required for primary wall cellulose synthesis (by reference to Arabidopsis thaliana, AtCESA1,3,6 or 6-like isoforms) and three typically required for secondary wall cellulose synthesis (AtCESA4,7,8). In some species, there is more than one CESA isoform within one or more clades: for example, 15 CESAs exist in a diploid cotton species (Gossypium raimondii). The CESAs of the moss Physcomitrella patens exist in two other distinct clades as compared to the seed plants, each one reflecting specialized functions in this descendant of early-evolved land plants. We know little about any potential biochemical differences between the plant CESA isoforms. The existence of distinct clades could merely represent accidentally-evolved position requirements within the multicellular cellulose synthesis complex as a result of random mutations within separate protein lineages. Previously, we analyzed the effects of several analogous mutations in PopCESAs and AtCESA1 protein regions that may impact substrate access and coordination in the active site, as inferred from a bacterial cellulose synthase with a solved structure. Complementation of the respective mutants showed more severe impacts for sequence changes in this region for AtCESA1 protein regions that may impact substrate access and coordination in the active site, as determined from the very large arcing of the diffraction spots. Studies of single fibers give a different result, indicating that the large arcs are somehow caused by the study of many fibers in the bundle rather than by variation within a single fiber at any given point along the fiber axis. These fiber data can also be mathematically converted to powder data for analysis by Rietveld software. The Rietveld method of crystal structure study requires a set of input starting coordinates that are used to calculate the diffraction intensities for comparison with powder X-ray data. Coordinates for cellulose I and II have been provided by Nishiyama, Langan, Sugiyama, (biosynthesis data). Because of limited powder data, it is important to us to contribute cell dimensions, crystal size, preferred orientation, and relative amounts of crystalline and amorphous phases, analyses that are inherent in Rietveld software. Current results from studies of synchronised X-ray powder and fiber data, as well as analysis of some electron fiber diffraction data will be presented. At this writing, the results indicate that the cellulose microfibrils are not in different alignments with the fiber length, contrary to conventional understanding. Instead they vary in different locations along the fiber length on a length scale similar to that of convolutions.

**CELL 250**

All-atom structural model of plant cellulose synthase and cellulose synthase complex

*Abhishek Singh*1, Yaroslava G. Yingling1, yara_yingling@ncsu.edu, (1) North Carolina State Univ, Raleigh, North Carolina, United States (2) Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States

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 these proteins required for cellulose cell wall synthesis 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 CESA into cellulose synthase complex (CSC). We used a combination of de-novo, ab-initio, partial homology modeling and molecular dynamics simulations to predict an all-atom 3D structural model of cotton CESA protein structure. Using our 3D model we were able to design new experiments and shed light on the specific roles of various conserved regions of plant CESA, such as regions unique to plant CESA and Zn-finger. Moreover, we predicted how CESA 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 preferentially contains a trimers of CESA producing 18 cellulose chains per CSC and allows for exploration and testing of the structure-function relationship of CESAs.

**CELL 251**

Diffraction studies of cotton fibers

*Alfred D. French,* alフレンチ@ars.usda.gov, Southern Regional Research Center, U.S. Department of Agriculture, Metairie, Louisiana, United States

Diffraction patterns of cotton fiber bundles indicate unusually large microfibril angle values (determined from the very large arcing of the diffraction spots). Studies of single fibers give a different result, indicating that the large arcs are somehow caused by the study of many fibers in the bundle rather than by variation within a single fiber at any given point along the fiber axis. These fiber data can also be mathematically converted to powder data for analysis by Rietveld software. The Rietveld method of crystal structure study requires a set of input starting coordinates that are used to calculate the diffraction intensities for comparison with powder X-ray data. Coordinates for cellulose I and II have been provided by Nishiyama, Langan, Sugiyama, (biosynthesis data). Because of limited powder data, it is important to us to contribute cell dimensions, crystal size, preferred orientation, and relative amounts of crystalline and amorphous phases, analyses that are inherent in Rietveld software. Current results from studies of synchronised X-ray powder and fiber data, as well as analysis of some electron fiber diffraction data will be presented. At this writing, the results indicate that the cellulose microfibrils are not in different alignments with the fiber length, contrary to conventional understanding. Instead they vary in different locations along the fiber length on a length scale similar to that of convolutions.

**CELL 252**

An electron crystallographer of cellulose microfibrils - revisit and hereafter

*Junji Sugiyama,* sugiyama@nish.kyoto-u.ac.jp, Research Institute for Sustainable Humanityo, Kyoto University, Uji, Kyoto, Japan

It was more than 35 years ago, 13C stable isotope (solid state NMR) brought a new concept on solid state structure of cellulose that the native cellulose was a mixture of two distinct crystalline moieties. The concept, which is now universally accepted, had been debated until crystallographic evidence was presented in New Orleans ACS meeting in 1991. In this memorial city in my history, I would like to revisit the works done in collaboration with many friends and students until now. While stable isotope 13C of cellulose are expected to reveal human records and/or global climatic issues in the past, the 18-chain microfibril model proposed by biologists is now debated for a consensus that anticipates another breakthrough idea of cellulose structure. Variety and flexible thinking are worthwhile!

**Lignin:** From Fundamentals to New Materials & Applications

*Anna-Stina Jäskeläinen,* anna-stina.jaaselainen@ytt.f6, Tiina Liitä, Taaja Tamminen, VTT Technical Research Centre of Finland Ltd, FI-02044 VTT, Finland

Lignin is nature’s most abundant aromatic polymer and it has high potentials as feedstock for material applications. However, lignin is inherently heterogeneous since lignin is a composition of molecules that differ in molar mass, monomeric unit composition, number of functional groups, amount and composition of bound carbohydrates as well as branching. Improving lignin homogeneity is essential to improve its performance in material applications. In this presentation, we present that aqueous solvent fractionation procedure is powerful tool to produce lignin fractionations with more homogeneous structure and composition. In this process, lignin is first dissolved in aqueous organic solvent (e.g. acetone, ethanol) followed by selective precipitation of lignin fractions by increasing water concentration of the solution. The produced lignin fractions differed both in chemical composition and in structure. The precipitated lignin fractions were practically free from impurities (carbohydrates or ash) which enriched both in the insoluble and highly soluble fractions. The most soluble fraction had the lowest molar mass and it possessed more phenolic and carboxylic acid moieties than other lignin fractions. The performance of the produced lignin fractions as reinforcing fillers or antioxidants in composite materials and as phenol-replacing component in phenol formaldehyde resin is discussed.

**CELL 254**

Zambesi biorefinery: A novel lignin source with unique properties

*Anna L. Jongerius*1, Annelie.jongerius@avantium.com, Jan C. Van der Wael*2, G Van Klink*3, Ed Depuy*1 (1) Avantium Chemicals, Amsterdam, Netherlands (2) Avantium Technologies, North Holland, Netherlands

Many chemical building blocks can be produced from biomass, nowadays mainly from 1st generation based carbohydrates [1] but in the longer term, brand-owners want to have the option to choose between 1st and 2nd generation feedstocks. The use of non-edible lignocellulosic feedstocks is an equally attractive source to produce chemical intermediates and an important part of the solution addressing these global issues (Paris targets). Avantium’s strategic objective is to deliver it’s 2nd generation Zambesi technology the best in class 2G
“pure” glucose technology for (bio-)chemical & bioenergy applications for a sustainable future; in parallel delivering value generation from the implementation of this technology. With the production of 2nd generation glucose also a large amounts of a novel class of lignin will be available and all products streams should be marketed at their highest value [2].

In this presentation particular attention will be given to the Zambezi technology for the production pure 2nd generation glucose, a mixed sugars stream and a pure lignin stream that are produced during this process. The Zambezi process is based on the concentrated HCl Bergius process and the lignins produced are of the concentrated acid (Wisslätter) type. Valorization of these lignins is not trivial as most available research on lignin conversion is performed on lignins originating from kraft or organosolv processes [3]. Key physical and chemical properties of Zambezi lignin will be discussed, and the implications of these characteristics for the definition of the best economically viable processing and valorization routes will be given.

Aquam has achieved a range of technological improvements on the concentrated mineral acid based process to make the process technocompetitive. A consortium consisting of AkzoNobel, RWE, Chemport Europe and Staatsbosbeheer has been established to bring this technology to commercial scale. As a first step a demonstration plant is being built in Delfzijl, the Netherlands to be operational mid-2018. The subsequent flagship plant producing around 50.000 tons lignin/annum will be operational at the beginning of next decade underlining the importance to develop now tailor-made applications for this novel and interesting class of lignin.

CELL 255

Lignin acidolysis during thermomechanical wood refining

Mohammad Tasoqi1, mtasoqi@vt.edu, Charles E. Frazier1, (1) Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (2) Dept of Sustainable Biomaterials, Virginia Tech University, Blacksburg, Virginia, United States

Refining energy is a critical production variable for the thermomechanical processing of wood into composites such as medium density fiberboard. This work represents an industry/university cooperation to understand how refining energy (i.e. the gap between refiner plates) impacts the chemical and physical properties of Douglas fir (Pseudotsuga menziesii) fiber. Besides effects on specific surface area, and porosity, refining energy was correlated to an increase in the free phenol and biogenic formaldehyde content of the fiber. This is consistent with classic lignin acidolysis reactions, and oftentimes such reactions result in lignin repolymerization and additional crosslinking. However in this case, refining resulted in a reduced lignin glass transition temperature, suggesting that lignin benzyl cations were diverted from repolymerization and crosslinking reactions. The diversion of benzyl cations from repolymerization and crosslinking has implications for biorefinery technologies. However we discuss how lignin repolymerization might be promoted in the manufacture of wood-based composites, in direct opposition to biorefinery strategies for lignin removal.

CELL 256

Role of dispersion and polar interactions in the adsorption of cellulases onto lignin

Maren Romari1, maren.roman@vt.edu, Feng Jiang1, Chen Qian1, Alan Esker1, (1) Virginia Tech, Blacksburg, Virginia, United States (2) Department of Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (3) Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States (4) ExxonMobil, Baytown, Texas, United States

Residual lignin in pretreated biomass hinders its enzymatic hydrolysis. Nonionic surfactants are known to have beneficial effects on the enzymatic hydrolysis of lignocellulosic biomass but their mechanisms of action at the molecular level are incompletely understood. This study investigates the effect of a nonionic surfactant, Tween 80, on the adsorption of cellulases onto model lignin substrates. Lignin substrates were prepared by spin coating of flat substrates with three different types of lignin: organosolv lignin, kraft lignin, and milled wood lignin. Tween 80 and cellulase adsorption onto the lignin substrates was analyzed with a quartz crystal microbalance with dissipation monitoring. Supporting experiments of Tween 80 and cellulase adsorption onto self-assembled monolayers with lignin-related functional groups provided critical insights into the role of polar and dispersive functional groups in lignin on cellulase adsorption and the effect of Tween 80 on the process.

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Fractionation of sugar cane bagasse lignin using hydrotropic process

Pedro E. Fardim1,2, pfarlim@abo.fi, (1) Abo Akademi University, Turku, Finland (2) Chemical Engineering, KU Leuven, Leuven, Belgium

Sugarcane bagasse is abundant agro-industrial waste that can be potentially utilized as a source of valuable compounds and biopolymers. In the present study, sugarcane bagasse from Brazil was fractionated employing an environmentally friendly hydrotropic process. Several treatments were carried out at 150 and 170 °C and dwell times of 60 and 120 min using sodium 20% hydrotropic solutions as well as the solutions acidified with formic acid. The major produced fraction was cellulose pulp obtained with the yield of 44-67% (bagasse based) and the cellulose content of 60-65%. Lignins dissolved during the treatments were isolated from the spent solutions by dilution with water and filtration. The yields of the lignins were 11.8–14.7% (bagasse based) and their purity ranged from 88 to 94%. Generally, the purity of both fractions and the yield of lignin were higher at more severe process conditions. However, the more severe conditions resulted in lower average molar masses of the lignins and lower intrinsic viscosity values of the cellulose fractions. The composition of the spent solutions also varied with the treatment conditions, and, besides the lignins, they contained different amounts of dissolved hemicelluloses, sugar monomers, furfural and acetic and formic acids. The results of the present study showed that the hydrotropic process could be successfully applied for the valorization of sugarcane bagasse by its fractionation into lignin, cellulose and other products.

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Influence of fractionation and phenolization of LignoBoost – Kraft-lignin on formation and properties of lignin-hydrogels

Anton Hoffmann, Anton.Hoffmann@forst.tu-dresden.de, Martina Bremer, Uwe Fischer, Johanna P. Nong, Steffen Fischer, TU Dresden, Dresden, Germany

Technical lignin from Kraft pulping process of softwood was used for the formation of lignin-hydrogels by crosslinking with poly-(ethylene glycol) diglycidyl ether (PEG-DGE) in alkaline water. Crosslinking reaction mainly takes place at phenolic hydroxy groups. Products with different molecular weight contributions and thereby different contents of phenolic hydroxy groups results by fractionation of lignin in various acetone/water mixtures. As another method for increasing phenolic hydroxy groups phenolization of lignin at alkalphatic side chains was carried out. Phenol and catechol were used as phenolization agents. Changes in structure were analyzed by 1H-NMR, SEC, IR and thermal analysis like TGA/DSC and pyrolysis GC/MS. The molecular weight of the fractions increases with increasing acetone concentration. Molecular weight distribution influences the glass transition temperature Tg, the Klason-lignin content as well as the content of functional groups. Thus, also the phenolization reaction is affected. Crosslinking was investigated for all modified lignin products. Lignins with low molecular weight don’t form hydrogels. The swelling capacities depends on molecular weight and amount of cross linker. Hydrogels of phenolated lignins show lower swelling capacity at comparable amounts of cross linker. But, the necessary amount of cross linker for formation of hydrogels is slightly lower than for unmodified lignin. The lignins were investigated for adsorption and complexation of environmentally critical ions like copper(II), lead(II) or arsenate for water purification and enrichment of rare-earth elements. Phenolization affects the adsorption capacity of rare ions.

Phenolization affects the adsorption capacity of rare ions.
Functional Structures from Wood-Based Materials

CELL 259

Characterization of the quality of pulp fines and their effect on paper properties

Melanie Mayr, René Eckhart, Andreas Thaller, Wolfgang Bauer, Wolfgang.bauer@biganz.at Institute of Paper, Pulp and Fibre Technology, Graz University of Technology, Graz, Austria

It is widely accepted that pulp fines (particles passing a 200 mesh screen, i.e. a 76 µm hole diameter; SCAN-CM 66:05) largely affect pulp properties, sheet consolidation and the final paper properties. Especially fines produced during refining of pulp—so-called secondary fines—showing more fibrillar character compared to primary fines already produced in the pulp processing have a positive effect on strength properties of paper. Although this is common knowledge within the pulp and paper physics community, it is still largely unclear how and to what extent the character of these pulp fines influences pulp and paper properties. As microfibrillated cellulosics (MFC), having similar properties as pulp fines, are starting to be applied in the paper industry these questions are becoming relevant also for this type of cellulosic materials.

In this study we apply established and novel methods for pulp fines characterization such as fines content, water retention value (WRV) of the given materials and an image analysis based method to characterize the structure of pulp fines. A suitable experimental setup to isolate the technological impact of pulp fines on paper properties is presented. Using this approach we are able to selectively evaluate the effect of aforementioned characteristics of pulp fines on paper properties. The results clearly show that categorization in primary and secondary fines is insufficient when it comes to the technological impact and that only an in-depth analysis of the fines present in a given pulp allows to understand the full picture regarding their effect on paper properties.

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Wood-based cellulosic fibers: Current challenges and further developments from an industrial perspective

Markus Pichler, m.pichler@lenzing.com, Clemens Bisjak, Christian Spenger, Josef Innelfohinger, Global R&D, Lenzing AG, Lenzing, Austria

Regenerated cellulose fibers from pulp were the first man-made fibers and already produced at the end of the 19th century. With the rise of synthetic fibers in the middle of the 20th century they lost importance and market share. Nowadays, going in hand with the global megatrends, there is a resurgence in regenerated cellulose fibers, both in the academic and the industrial field. This growth is supported by the beneficial attributes of cellulose as a raw material, resulting in unique fiber properties, and a growing demand for sustainable products.

For the fiber producing industry, a transfer from laboratory and small scale to industrial scale, fulfilling economic and ecologic criteria, is essential. In a holistic view, the raw material and the production process finally define the fiber as a truly sustainable product. Lenzing AG, as the world leading manufacturer of wood-based cellulosic fibers, follows the strategy to continuously improve its production processes and products regarding quality, functionality and environmental impact. In addition, also new processes and products are investigated and developed.

This paper presents the most recent innovations by Lenzing AG, namely Refibra™, a fiber produced from recycled cotton and wood, and Tencel® Luxe, a lyocell filament, opening new perspectives with respect to quality, performance and sustainability.

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Effect of particle dispersion on mechanical properties of filaments made of cellulose nanofibrils

Karl Haakansson, k.haakansson@ri.se. Nanocellulose, RISE Bioeconomy, Stockholm, Sweden

Products made of filaments as a building block are all around us, from clothes to car parts. Finding a filament made from a sustainable resource by a sustainable process is however difficult. Therefore, interest in filaments made from cellulose nanofibrils has recently increased with a vision of producing a truly sustainable and biodegradable filament. Still, optimization of the mechanical properties and identification of the optimal process for a demonstration application are open challenges to tackle. Here, the influence of the homogeneity of the starting material on the mechanical properties is determined, it is shown that in order to keep the nano-scale properties in a macro-scale material, the dispersion is crucial. This result is not surprising, however, it highlights the difficulty of obtaining a good dispersion in a fibrillar system. Furthermore, the influence of online drawing on the fibril alignment and mechanical properties is investigated. When the property space is spanned and understood, it is possible to design a suitable process, with respect to volume, energy consumption, etc. to meet the desired filament properties.

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Developing Pd-based nanomagnets in the lignocellulose matrix for natural fiber welding applications

David P. Durkin1,2, durkin@usna.edu, Jennifer R. Moore1, Kenneth J. Livi1, Paul C. Trulove2, Haten Eliboldev5, (1) Johns Hopkins University, Annapolis, Maryland, United States (2) United States Naval Academy, Annapolis, Maryland, United States

In previous work, we optimized catalytic Pd-based nanoparticles in lignocellulose, and demonstrated how to post-process them via Natural Fiber Welding (NFW) into free-standing structures to catalytically remove nitrates from drinking water. In the current study, we present a novel Pd bimetal system that exhibits distinctly different magnetic or nanoparticle properties depending on the composition of the nanoparticle. Using a variety of spectroscopic and magnetic measurement techniques, we explore how nanoparticle composition and structure relate to each system’s observed magnetic properties, and how some show nanomagnetic behavior at low temperature. We then discuss how these sustainably-supported nanoparticle systems may be post-processed via NFW into advanced functional materials for magnetic sensing and/or catalytic applications.

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Interfacial interactions in lignin/carbon nanotubes precursors of carbon fibers

Marie-Pierre G. Laborie1,2, marie-pierre.laborie@biomat.unibas.ch, Jan Badorek1,2, Gopa Sivasankaranpillai1,2, Michael Walter1 (1) University of Freiburg, Chair of Forest Biomaterials, Faculty of Environment and Natural Resources, Freiburg, Germany (2) Freiburg Biomaterials Research Center (FRM), Freiburg, Germany (3) Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), Freiburg, Germany

For lignin to be more effectively used as precursor of carbon fibers, cohesive and stable precursor fibers must be produced. One potential strategy to improve the stability of lignin-based precursor fibers is to incorporate carbon nanotubes (CNT) in their formulation. However, the success of this strategy hinges upon the ability to tailor interfacial interactions between lignin and CNT. In this study, we investigate the interfacial interactions between lignin and CNT as a function of their molecular attributes. The impact of lignin functional groups and CNT degree of oxidation on interfacial adhesion is experimentally and computationally assessed in pairs of systematically varied lignin and CNT components. Both experimental results and theoretical predictions are concordant to establish the nature of interfacial interactions in lignin/CNT pairs and provide guidance on the tuning of the components’ molecular attributes for producing cohesive and stable lignin/CNT precursor fibers.

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Characterization of composite fibers from wood-based polymers: Investigation as a carbon fiber precursor

Daisuke Sawada1, d.sawada.u.bm@gmail.com, Nilda Zahra1, Mikaela Trogen1, Herbert Siesta1, Nolene Byrne1, Michael Hummel1, (1) Department of Bioproducts and biosystems, Aalto University, Espoo, Finland (2) Deakin University, Geelong, Victoria, Australia

There has been a demand for low cost carbon fiber precursors from many high-volume segments such as the automotive or sports industries. Wood-based polymers are recently gaining attention because they have a potential to be a carbon fiber precursor. However, wood-based polymers requires pre-processes to be utilized as a carbon fiber precursor. This superbase-neutral IL solvent maintains the high degree of polymerization of cellulose during the dissolution and spinning process and allows for a pronounced longitudinal polymer orientation during the spinning process. Therefore, cellulose fibers from this IL exhibit excellent mechanical properties. Secondly, the IL can dissolve not only cellulose but also lignin, hemicellulose and even other biopolymers. Thus, cellulose-based composite fibers are available from the IL by dry-jet wet spinning.

In this study, we report the structures in these composite fibers. The fiber-pore structures of composite fibers were elucidated using small angle X-ray scattering and wide angle X-ray fiber diffraction (XRD). The orientation of the components were parameterized from 2D XRD and polarized micro Raman spectroscopy. In addition, micro Raman spectroscopy, bulk elemental analysis, and X-ray photoelectron spectroscopy were applied to resolve the skin-core structure present in a single composite fiber. Finally, the correlation between such structures and final carbon fiber products was discussed.
Valueoration of Renewable Resources & Residuals into New Materials & Multiphase Systems

CELL 265

Lignin and nanocelluloses in food and other emulsions

Siqi Huan, Long Bai, Blaise L. Tardy, Maniko Ago, Janika Lehtonen, Orlando J. Rojas, ojmjasncsu.edu. Bioproducts and Biosystems, Aalto University, Espoo, Finland

We discuss lignin and nanocelluloses (cellulose nanofibrs, CNF and cellulose nanocrystals, CNC as well as bacterial celluloses) as materials that are readily available, renewable, and sustainable. They represent interesting opportunities, especially in the field of emulsion formulation. The case of food emulsions is most relevant. Many options for deployment of lignin and cellulose nanomaterials can be anticipated if used in the design of multiphase systems. Such consideration comes from lignin surface activity and the ability of nanocelluloses to network and self-assemble in aqueous dispersions and at interfaces. The combination with surfactants and surface functionalization expands further the possibilities, for example, in converting emulsions into high order, solid structures and stimuli-responsive and active materials. Lignin and nanocellulose-based emulsions should be factored in order to advance the knowledge in the field. Our recent developments and those reported in the literature, summarized in this talk, provide many promises in these directions.

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Applications of molten salt hydrates in fractionation, conversion, and valorization of lignocellulosic biomass

Xuejun Pan, xpan@wisc.edu. Biological Systems Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States

Molten salt hydrates (not molten salts) are aqueous solutions of inorganic salts at extraordinarily high concentrations. Molten salt hydrates have many unique properties such as high boiling point, low vapor pressure, and liquid status at moderate temperature. Similar to ionic liquids, some molten salt hydrates are able to swell and dissolve cellulose and biomass, but they have much lower cost, viscosity, and toxicity than ionic liquids. Therefore, molten salt hydrate can be used as solvent and reaction medium for biomass conversion and valorization. This presentation reports our recent research activities on using molten salt hydrates for fractionation, conversion, and valorization of lignocellulosic biomass, including cellulose dissolution and hydrolysis, biomass saccharification and fractionation, glucose isomerization, sugars/biomass to furan derivatives, and lignin valorization.

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Cellulose nanofibers from potato (Iotomoea batatas) and bamboo tacuara argentinio (Guadua angustifolia)

Nancy Garcia, nancylv@gmail.com, Norma D’Accorso, Alain Dufresne, Fleur Rol. (2) Centro de Investigaciones en Hidratos de Carbono (CIHIDECAR), Universidad de Buenos Aires, Buenos Aires, Argentina (3) Facultad de Ciencias Exactas y Naturales, Departamento de Química Orgánica, Universidad de Buenos Aires, Buenos Aires, Argentina (4) Grenoble INP-Pagora, Grenoble Institute of Technology, Grenoble, France

In this work, the production of cellulose nanofibers (NFC) extracted from INTA sweet potato (Ipomoea batatas) and Bamboo Tacuara Argentino (Guadua angustifolia) is presented using a novel chemical and mechanical treatment with high pressure homogenization (HPH). Such a procedure produces NFC with interesting crystal arrangements. It should be noted that the cellulose obtained from the Batata peel (considered and currently used as waste without added value). Bamboo cellulose is obtained from a variety considered as a pest in the coastal area of the north of the province of Buenos Aires, Argentina. The results will be presented by infrared spectroscopy where it can be seen that most of the hemicellulose and lignin were extracted from the original material. Cellulose nanofibers were also characterized by electron microscopy (SEM), X-ray diffraction (XDR) and their thermal stability was evaluated by thermogravimetric (TGA) analysis. The ultimate objective of these NFCs is to evaluate the reinforcing effect in matrices such as low molecular weight polylactic acid (PLA), previously synthesized in our laboratory.

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Depolymerized lignin & acrylate-based renewable photopolymers

Kalavathy Rajan, krajain@utk.edu, Jeffrey K. Mann, Yagya N. Regmi, David P. Harper, Nicole Labetb, Stephen C. Chmely. (1) Biosystems Engineering & Soil Science, The University of Tennessee, Knoxville, Tennessee, United States (2) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States

Depolymerized lignin (DPL), obtained as a product of catalytic transfer hydrogenolysis of organosolv lignin, was used in this study to generate lignin & methyl methacrylate (MMA) based photopolymers. Initially, the functional groups (OH) of DPL were modified to append a methacrylate moiety and then bulk polymerized with methyl methacrylate (90% w/w) in the presence of UV-Vis-activated (365 to 405 nm) radical initiator, BAPO (bisacylphosphine oxide). Kinetic studies using real-time FTIR showed that the photo-polymerization rate of DPL-MMA resin (0.009 s^-1) was twice as fast as the control (0.004 s^-1). Thermogravimetric analysis showed that the DPL-MMA copolymer had a single prominent decomposition domain near 400 °C, which was superior to PMMA (poly-methyl methacrylate). Dynamic mechanical analysis showed that the Tg of DPL-MMA copolymer increased by 10 °C, whereas the viscous modulus (G”) decreased by 1 fold in magnitude when compared to PMMA. Therefore, crosslinking with bi-functional DPLs reduced the linear polymer’s flexibilities, as well as increased the material stiffness. Finally, we also used lignin model compounds, namely 4-ethyl guaiacol and apocynol, to elucidate the changes in photopolymer properties brought upon by the variable nature of DPLs.
Sustainable Production & Processing of Agricultural Crops: The Food, Energy, Water Nexus

CELL 269

What method to measure natural fiber size distribution in polymer composite? Advantages and limitations of 2D scanner, automated analysis and microtomography

Erika Di Giuseppe1, Romain Castellani1, Simon Dobosz2,3, Jerome Malvesti1, François Berzin1,2, Johnny Beaugrand1,2, Christine Delislet1, Bruno Vergnes1, Seif Hamd4, Tatiana Budtova1, Tatiana.Budtova@mines-paristech.fr (1) CEMEF/Mines ParisTech, Sophia Antipolis, France (2) university of Reims, Reims, France (3) INRA, Reims, France (4) university of Bordeaux, Bordeaux, France

The mechanical properties of natural fiber reinforced composites depend on many factors, fiber dimensions being one of the most important. During compounding, fibers’ bundles and elementary fibers are breaking, and quantification of the fragments length, width and aspect ratio is therefore crucial to predict and understand the mechanical properties of a composite.

The lack of an international standard for the measurement of the biomass morphology opened the way to the development and the utilization of several different methods. In this work we investigated the advantages and the limitations of three techniques that are commonly employed to measure lignocellulosic fragments’ dimensions, i.e. high resolution 2D scanner, automated dynamic fiber analyzer, and X-ray microtomography. Two types of fibers of different morphology and composition, hemp and miscanthus, are chosen. Composites are prepared by using a laboratory-scale co-rotating twin-screw extruder, at two feed rates and constant screw speed. We show that the analysis of the morphology of lignocellulosic fragments is still complex and does not allow an objective estimation of the sizes. Each method has its own advantages and disadvantages. Overall, the three methods are complementary and the use of each depends on the goal of the work.

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Carbon fibers from nanofibrillated lignocellulose for supercapacitors

Ling Wang1, Ling.wang@aalto.fi, Maryam Borgheli1, Panu Lahtinen2, Anastasios Papageorgiou4, Merr Luneste1, Marko Ager1, Orlando Rojas1, (1) Aalto University, Espoo, Finland (2) VTT, ESPPO, Finland (4) Turku Centre for Biotechnology, Turku, Finland

There is increasing global demand for carbon fibers, with 10% annual rate up to 89,000 tons in 20101. The rising interest to replace petroleum-based precursors (such as polycrylonitrile and mesoporous pitch2) with renewable and sustainable alternatives has motivated our efforts for developing bio-based alternatives. Therefore, we applied lignocellulose for developing carbon fibers from wet-spin natural fibers. The high content of lignin in the precursor was counted as an advantage to achieve carbon fibers with high yield. Lignocellulose-derived carbon fibers (LCCF) showed much higher mechanical properties, conductivity and carbon yield compared to the nanocellulose-derived carbon fibers. The LCCF provided potential applications for supercapacitors. Figure 1 illustrates the LED light circuit successfully built with 1 cm long of LCCF.

Figure 1. LED circuit built with 1 cm of LCCF.

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Modification of the celluloseic surfaces through adsorption of reactive polysaccharides

Arthur Bouchut1, Asja Pettigano2, Celine Moreau1, Bernard Cathala1, Michel Lecocq1, Michel Petit-Conil2, Julien Bernard3, Aurelia Cherif2, Ettienne Fleury1, ettienne.fleury@insa-lyon.fr (1) BIA, INRA, Nantes, France (2) IMP, INSA de Lyon, Villeurbanne, France (3) Institut technologique FCBA, GRENOBLE, France

Cellulose represents a promising alternative regarding the development of innovative materials due to its ubiquitous presence in biomass, its hierarchical structure and the possibility to be modified through numerous chemical reactions (1). However, despite a large panel of processes described in literature (2), there is still a need for developing new approaches conjugating sustainability and economical improvement. Herein we describe the rational use of modified polysaccharides chains to build an intermediate organic layer (physically) interacting with cellulose substrates and capable to undergo chemical reactions to modify cellulose surface properties (Fig. 1).

In this study, allyl, acrylate and alkyne functionalized xylogan and carboxymethyl cellulose were prepared in mild and non-degrading aqueous medium (3). Their affinity to celluloseic surfaces was investigated via gravimetric method and QCM analysis on cellulose paper and cellulose microfibers respectively. The latter results were correlated with those obtained with chemical titration analysis of the modified surfaces (4). A mapping of the deposition was also performed by confocal Raman spectroscopy. Finally, the reactivity of these new derivatives was evaluated through their capacity to copolymerize in water with acrylic acid and acrylamide monomers leading to new bio-hybrid hydrogels. This approach opens the way for designing a platform of new celluloseic materials.

Figure 1: Surface functionalization of celluloseic substrates through adsorption/polymerization process

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Microalgae: A new resource for processing bio-based polymer materials

Nicolas Le Moigne1, nicolas.le-moigne@mines-paristech.fr, Florian Deltue1, Jean-François Sass3, Guilhem Arcischat1, (1) IMT Mines Alès, Alès, France (2) CEA Cadarache, Saint-Paul-lès-Durance, France (3) Institut de chimie séparative de Marcoule (ICSM), Bagnols sur Cèze , France

The research on microalgae currently shows a strong worldwide development. Although existing productions and commercial applications mainly concern the food industry and the pharma-nutraceuticals and cosmetic, the capacity of microalgae to efficiently use solar energy and CO2 to produce lipids, proteins and carbohydrates as well as unique products like antioxidants, fatty acids, peptides, steroids... make them promising sources of energy, intermediate chemicals and materials. The present research work aims to prepare bio-based polymer materials from microalgae. Two main processing strategies are investigated: (i) the dissolution of microalgae to prepare biopolymer based solutions and (ii) the direct plasticization of microalgae to prepare biopolymer blends. To this aim, a screening on various freshwater and seawater microalgae exhibiting different biochemical composition and cellular structures, was conducted. Furthermore, growing conditions of microalgae were controlled so as to investigate the possibility to enrich cells in biopolymers of interest (especially starch). The dissolution of microalgae was achieved in ionic liquids (ILs) with controlled hydrophilic/hydrophobic balance, due to their high ability to solvate organic compounds and their environmental compatibility compared to chemical extraction methods involving organic solvents. The plasticization of microalgae was achieved by twin screw extrusion with glycerol as a plasticizer, and biopolymer blends composed of plasticized microalgae with fractions of Poly(butylene succinate) (PBS) were prepared. First microalgae based objects were produced in the form of gels, foams and bulk materials (See Figure). This set of results opens interesting perspectives about the use of microalgae for producing bio-based polymer materials.
Due to the shortage of petroleum reserves, the importance of developing lignocellulosic biomass for the production of fuels and chemicals that offer economic, environmental, and strategic advantages has been increasingly emphasized. Hemicelluloses, as the non-cellulose polysaccharides in plant cell wall, represent an immense renewable resource of biopolymers. The renewability, modification potential, biodegradability and nontoxicity of hemicelluloses contribute to the rapidly growing interest in hemicellulose. The hemicellulose used herein was isolated from poplar with 10% sodium hydroxide. Two processes were used to produce hemicellulose-based hydrogels. In one process, the hemicellulose was modified with a carboxymethylation reaction, in which isolated hemicellulose was activated with aqueous sodium hydroxide and reacted with sodium chloroacetate yielding the carboxymethylated hemicellulose derivative. Hemicellulose-based hydrogels were produced from carboxymethyl hemicellulose (degree of substitution (DS) range 0.04–0.68) crosslinked with N,N'-methylenebisacrylamide (MBA). As reference, hydrogel produced from unmodified hemicellulose has a 15 g/g water absorbency. The effect of DS on hydrogels absorbency ability will be discussed. In a second process, hemicellulose-based hydrogels were produced by a free radical graft polymerization with acrylic acid (AA) and acrylamide (AM) and using MBA as crosslinking agent. The effect of the ratios of hemicellulose, AA and AM on hydrogels absorbency ability will be discussed. In specific, hydrogel produced with a ratio of 1:1:1 of hemicellulose: AA: AM was shown to have up to a 290 g/g water absorbency. The findings here are important steps in developing suitable hydrogels from hemicellulose for absorbency applications.

Application of subcritical water to the sustainable production of agricultural crops and processing by-products

Jerry W. King, kingiw100@hotmail.com, Luke Howard, Keerthi Srinivas, (1) Univ of Arkansas, Fayetteville, Arkansas, United States (2) CFS, Fayetteville, Arkansas, United States (3) Washington State University, Tricities, Richland, Washington, United States

Pressurized water above its boiling point, i.e., subcritical water, is an environmental benign “green” solvent amenable to producing extracts and hydrolyzates from agricultural feedstocks for food and energy utilization. We summarize in this presentation of over 20 years of research in the application of this medium as applied to lipid- and polysaccharide-containing substrates using temperatures in the range of 100–300 °C. Using temperatures from 100–180 °C, extracts have been produced from a number of materials such as fruit/berry pomaces, herbal botanicals, and essential oils in less than 20 minute extraction times. Increase of the water temperature to between 200–350 °C results in an increase in the non-polar solvent characteristics of subcritical water assuring increasing miscibility of the components in switchgrass and corn stover (polysaccharides) as well as increasing levels of triglycerides from seed oils such as soybean and coconut oils. In these latter cases, the high temperature water medium under appropriate requisite temperatures is acting as both an extraction-reaction medium particularly for the depolymerization of polyphenols- and cellulose or hemicellulose-containing matrices, or hydrolysis to fatty acids in the case lipid containing moieties. Several methods for separating the extraction-reaction products from the aqueous medium will be cited including drying, precipitation, and membrane-based concentration. Efficient use of water in these processes will be discussed with respect to processing optimization and required thermal input. Finally, cost of manufacturing (COM) criteria will be cited to justify the use of subcritical water for the above processes.

Synthesis and characterization of hemicellulose-based hydrogels

Joel Pawlik1, joewawick@ncsu.edu, Wenhui Geng1, 2, Richard A. Venditti3, (1) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States (2) Forest Biomaterials Dept, North Carolina State University, Raleigh, North Carolina, United States

In the field of biopolymers, academic and industrial research has focused on the development of sustainable composites or nanocomposites based on aromatic and/or aliphatic polyesters filled with nanoparticles (montmorillonite, layered double hydroxide, mica) or with renewable resources such as cellulose, soy stalk, starch and lignin for various applications such as food packaging or composites for flims. Thus, different ways are investigated to lead to nanostructured polymers with unprecedented properties. Very recently, one innovative pathway is the introduction of ionic liquids (ILs) within polymer matrix. In fact, these organic salts have unique physical-chemical properties such as their incompressibility, their low vapour pressure, their excellent thermal and chemical stability and their endless number of cation/anion combinations which make them suitable ideal additives for advanced biopolymers. For these reasons, the combination of the excellent intrinsic properties of phosphonium ionic liquids to biodegradable aliphatic and/or aromatic polymers such as poly(ε-caprolactone) (PLA), poly(butylene adipate-co-terephthalate) (PBAT) have been studied. The influence of the chemical nature of phosphonium ionic liquids (chloride, bis(triflimide), bis(triflimide)phosphate, carbonate) has been investigated as new compatibilizing agents of polymer blends blends composed of PBAT / PLA and PBAT / PLA / lignin, as surfactant agents of layered silicates or as structuring agents of the PBAT matrix.

Towards added value biomaterials: Hemicellulose isolation and its application as thermoreversible network

Wissam Farhata, wfarhath2@gmail.com, Richard A. Venditti2, Ali Ayoub2, Mohamed Taha2, Nathalie Mignard2, Frederic Becquart1, (1) IMP@LUM Ingénierie des Matériaux Polymères, Saint-Etienne cedex 2, France (2) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States (3) Forest Biomaterials Dept, North Carolina State University, Raleigh, North Carolina, United States

The increased use of renewable materials is considered as one of the key issue of the sustainable development. It has been estimated by the National Research Council in the USA that 25% of the produced organic chemicals should originate from renewable materials in 2020. Hemicelluloses (HC) are one of the most common polysaccharides next to cellulose and chitin, representing about 20-35% of lignocellulosic biomass, and have not yet found broad industrial applications as does cellulose.

Hemicellulose is a hetero-polysaccharide and a green substitute for petroleum based polyols and is a non-food-based substitute for starch polyls. Therefore, extraction of hemicellulose would have great potential to supply raw materials for the new bio-economy. To expand its applications to the field of self-healing materials, printable polymer networks, as well as drug-delivery systems, the properties should be functionalized by introducing reactive groups on its backbone. Responsively bonding polymers have become a vital class of materials in the preceding period. Such materials have outstanding mechanical properties in the crosslinked and excellent processability in the decrosslinked state.

In this work, we will present an efficient technology to isolate hemicellulose from the biomass and a common strategy employed for dynamic covalent bonding is Diels-Alder (DA) chemistry. By incorporating a suitable pair of diene and dienophile, the [4+2] cycloaddition can be induced at ambient temperature (DA reaction) in the absence of a catalyst. The cyclo-reversion can be triggered at elevated temperatures (re-DA (rDA) reaction) as depicted in the Figure below. The hemicellulose was modified with furan ring followed by crosslink step through the reaction with bismaleimide. The properties of the obtained thermoreversible network will be presented.

Scheme of hemicellulose network that debonds at elevated temperatures via cycloreversion and can be crosslinked again via the corresponding DA reaction at lower temperatures.

Plant Heteropolysaccharides: Interactions within Lignocelluloses, New Modifications & Future Applications

Gunnar Henriksson1, ghenrikis@kth.se, Jennie Berglund2, Jakob Wahlo2, Martin Lawoko2, Selma Aminzadeh1, Mikael E. Lindström1, Francisco Vilaplana1, (1) Glycoscience, KTH Royal Institute of Technology, Stockholm, Sweden (2) Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

Hemicellulose occurs with few exceptions together with other cell wall polysaccharides, which structure and polysaccharide composition differs between species and cell wall location. Common such polysaccharides include xylans, glucomannans, β (1→4) glucans, mixed glucans, galactanes, and monosaccharide composition differs between species and cell wall location. Common such polysaccharides include xylans, glucomannans, β (1→4) glucans, mixed glucans, galactanes, and polysaccharides taking into account their molecular and conformational features, which in turn affect their association with cellulose and lignin and their function in the cell wall. We suggest that hemicelluloses are polysaccharides with a backbone chain that can adapt the same conformation as the cellulose I type structure, i.e., a flat 2-fold helical screw, whereas pectins cannot. This structural division might also reflect a functional difference, where hemicelluloses with their possibility to line up, or “co-crystallize”, with cellulose chains might be designed for a very close
contact with cellulose – maybe as a part of a ‘composite’ material forming flexible bridges between cellulose fibrils, whereas pectins are also located more in regions with lower cellulose content, such as middle lamella, – maybe more act as a filling substance. However, within both groups there are differences between different polysaccharides; for instance, the organization of hydrophilic and hydrophobic groups and side chains around the glycosidic linkage give different flexibility of the main chain and ability to adapt to other structures than the “cellulose-type” 2 fold screw, which have been studied by molecular dynamics simulations and NMR studies. Furthermore, different pectins have structural and flexibility differences in their main chains. Also, side chains/groups can affect main chain conformation.

Another way to divide non-cellulose wood polysaccharides are for neutral respectively negatively charged polysaccharides. The role of the charges might differ in the pectin galactururonan they form complexing by ‘gelling’ complexes with calcium ions, and in xylan they might play a role in affecting lignin structure and form covalent bonds to lignin, and maybe also disperse cellulose.

Bamboo, a fast-growing grass, has higher strength-to-weight ratios than steel and concrete. Here we have experimentally and numerically studied mechanical and fracture properties of bamboo at multiple scales from atomistic scale to the culm scale. The unique properties of bamboo come from the natural composite structure of fibers that comprises mainly cellulose nanofibers in a matrix of interwoven hemicellulose and lignin called lignin carbohydrate complex (LCC). We have utilized atomistic simulations to investigate the mechanical properties and mechanisms of the interactions of these materials in the structure of bamboo fibers. It is shown that a control hemicellulose model has better thermodynamic and mechanical properties than lignin while lignin exhibits greater tendency to adhere to cellulose nanofibrid. Therefore, the role of hemicellulose found to be enhancing the mechanical properties while lignin provides the strength of bamboo fibers. We have studied the effects of water on thermodynamics of bamboo at multiple scales. Elastic modulus of lignin, calculated by molecular dynamics simulations, increases initially with increasing moisture content, and then decreases. In contrast, elastic modulus of hemicellulose decreases constantly with MC. Below 10% MC, water molecules tend to break hydrogen bonds between polymer chains and form new hydrogen bond bridges between the polymer chains, while above 10% MC, water molecules aggregate together and create nano-droplets inside the materials. During the process of bridging, the fractional free volume of lignin decreases. The free volume reduction along with formation of hydrogen bond bridges causes a growth in elastic modulus of lignin. Water molecules that aggregate because of the hydrogen bond creation, however, causes the aggregation of voids in the system and diminution of elastic properties.

The lignocellulosic biomass valorization, for biofuel production, is industrially performed under acid condition, mainly at high acid concentration. The aim of this treatment is the production of monomeric sugars that can be transformed into biofuel for the glucose and syrups for the xylose. Another pathway could be the alkaline extract formed under acid condition that structural conformation of residual hemicellulose was greatly differed among the different oxides and temperatures. A significant effect could be observed on the molecular weight distribution, measured by size exclusion chromatography, of lignin for both oxidants, ozone being the most efficient. Both oxidants were very effective in reducing the furfural and HMF content in the autohydrolysate. It was checked that these oxidation treatments did not have any significant impact on the carbohydrate content (monomers and oligomers measured by HPAEC-PAD) in the autohydrolysates: the ozone treatment did not have any significant effect which can be explained by the fact that ozone is much more reactive with lignin and other unsaturated compounds. However, oxidative stages did not affect the sugar content of the hydrolysate provided that the temperature was below a certain limit. This work is an original contribution to the removal or modification of some of the contaminants present in hemicelluloses containing hydrolysates. More particularly the reduction in molecular size of insoluble and soluble lignin is expected to reduce sticky deposit problems. These post treatments should facilitate further processing.

During the cellulose derivatization process, hemicellulose is known as the main reason for the deterioration of final product quality and processability problems such as poor filterability, increased viscosity, and discoloration. Therefore, dissolving pulp with high cellulose purity and reactivity is required for the production of cellulose derivatives. Typically less than 1.5% of residual hemicellulose is required for cellulose acetate grade to avoid the haze and color formation. However, the detailed mechanism on how hemicellulose affects this deteriorating issue is not fully understood and it is only known by practical experience.

To understand the chemical and structural characteristics of residual hemicellulose, we have extracted hemicelluloses in dissolving pulps by two-stage alkaline extraction. It was found that refining treatment and cold-temperature extraction enhanced hemicellulose extraction. Compared to the hemicelluloses from untreated dissolving pulps at a room temperature, hemicellulose extraction yield was improved up to four times. Also, their effects on the carbohydrate composition and molecular weight of extracted hemicellulose were studied. Glycosidic linkage analysis revealed that the chemical conformation of residual hemicellulose was greatly altered among the different dissolving pulps. Some of the extracted xylan retained their branched structure, while others showed almost complete linear structure. Commercial xylan products were also analyzed as a
Structural colour from a heliodial cellulose fibres architecture in the cell wall of *Margaritaria nobilis*

**Lisa M. Steiner**, 1 Lims88@cam.ac.uk, **Yu Ogawa**, 1 Marta Busse-Wicher, 1 Paul Dupree, 1 Silvia Vignolini, 2 (1) Department of Chemistry, University of Cambridge, Cambridge, United Kingdom (2) Department of Biochemistry, University of Cambridge, Cambridge, United Kingdom

Structural colour is caused by the architecture of materials at the nanoscale, interfering with visible light, and giving rise to some of the most spectacular colourations in nature. A beautiful example is the fruit of *Margaritaria nobilis*, where the arrangement of cellulose fibres in the plant cell wall of the endocarp gives the fruit a brilliant blue appearance. In an approximation, the cellulose fibres lie parallel in layers, and the layers are stacked up with a small rotation angle, thus building up a heliodial architecture, which selectively reflects left-handed circularly polarized light, mainly in the blue region.

In order to unravel how nature makes up this fascinating architecture, it is key to understand the main building blocks of this specific plant cell wall. We therefore isolated the cellulose fibres and characterised their morphology via electron and atomic force microscopy. Crystallinity of the cellulose fibres was assessed by NMR and XRD measurements and was found to be higher than wood cellulose. Small angle X-ray scattering experiments were carried out on the native endocarp to estimate the fibre dimensions and spacings. Additionally to cellulose, another major component is xylan, a type of hemicellulose. Via enzyme digestions, gel electrophoresis and mass spectrometry, it was established that the xylan in the *Margaritaria nobilis* endocarp has a very regular acetylation pattern, an acetyl group is attached on every other xylose unit. Other decorations are sparse, no arabinose decoration is found, and only a small amount of glucuronic acid, which seems to be attached in clusters. Furthermore, computational modelling is in progress to understand the influence of xylan on the heliodial arrangement of the cellulose fibres. We hope to better understand how nature produces such intricate nanostructures and to get inspiration for synthesising novel optical materials.

*Margaritaria nobilis* fruits, the average diameter is 1 cm.

**Lignin: From Fundamentals to New Materials & Applications**

**CELL 284**

Fabrication of lignin nanoparticles for developing natural broad-spectrum sunscreens

**Yong Qian**, qiangyong86@163.com, Jingyu Wang, Dongjie Yang, Xingping Ouyang, Xueping Qiu. School of Chemistry and Chemical Engineering, South China University of technology, Guangzhou, China

Lignin is the second most abundant and unique aromatic natural polymer in plants. It exhibits good UV-absorbing, antioxidant and biocompatibility due to its functional groups such as phenolic, ketone and other chromophores, thus making it an excellent candidate for the development of nature-inspired sunscreens. Experiments showed that a small amount of lignin could significantly enhance the UV-blocking performance of commercial sunscreens. The synergistic effect between lignin and chemical sunscreen was first observed. This effect was found to be even more obvious after UV irradiation. One of the main obstacles for developing lignin-based sunscreens is the dark color imparted by lignin. We demonstrated two effective methods to reduce the color. First method involves the modification of lignin through acetylation, followed by self-assembly in selective solvents to prepare uniform lignin colloidal spheres. An alternative way to whiten lignin is by exposing it to UV radiation in solvents producing peroxide. After radiation, the color could be reduced by 65%. Both whitening methods sacrifice the phenolic hydroxyl groups of lignin, which are not only responsible for scavenging free radicals, but also helpful for blocking UV radiation. In order to preserve the phenolic hydroxyl groups, lignin colloidal spheres were prepared without chemical modification and then blended with pure cream to develop lignin-based sunscreens. Sunscreen containing 10 wt% lignin colloidal spheres of about 50 nm exhibited sun protection factor (SPF) value of 15. Inspired by the high efficiency of acoustic cavitation for initiating the polymerization reactions, lignin/chemical sunscreen nanocapsules were successfully prepared by one-step high intensity ultrasound. The lignin/chemical sunscreen nanocapsules present good photo, thermal, and storage stabilities. The SPF values of the creams containing 5 and 10 wt% lignin/chemical sunscreen nanocapsules reached 120 and 400 respectively, which are far higher than the SPF 60 exhibited by commercial sun cream containing >50 wt% chemical sunscreens.

**CELL 285**

Colloidal lignin particles towards gluing biological matrices

**Maija-Liisa Mattinen**, maija-liisa.mattinen@aalto.fi, Monica K. Osterberg. School of Chemical Engineering, Bioproducts and Biosystems, AALTO University, Espoo, Finland

For decades, intensive scientific research has been carried out to improve the efficiency of different adhesives. Basic understanding of the structure-property relationship of the basic components of adhesive is crucial for the successful sealing of the tissues in various physiological environments. Biomaterial processing industries produce different by-products such as lignin and proteins. Technologies for the formation stable lignin nanoparticles using proteins including peptide drug molecules as modifiers is an interesting approach to prepare functional adhesives for wound sealing and healing including gluing and modification of cellulosics matrices e.g. for medical textiles. Currently available tissue adhesives have several limitations as they must be safe and easy to use, have excellent adhesion properties depending on the surgical specialty and procedure including enough mechanical strength to support wound healing. Furthermore they have to be biodegradable, polymerize in a moist environment, metabolize gradually without rejection reactions, be inexpensive and to prevent tissue deformation. It is preposessed that colloidal lignin nanoparticles (CLPs) could be used as nanobuilding blocks to obtain above goals having global significance for tailoring novel biomaterials for medical and related applications e.g. in foods, cosmetics and chemical industry.

**CELL 286**

Lignin-based nanocarriers for the controlled release of agrochemicals

**Doungporn Yiamsawas**, doungporn@nanotec.or.th, Wiyong Kangwansapamorokn, Mongkol Pratwatsaowit, Daniel Crespy. (1) National Nanotechnology Center, Pathumthani, Thailand (2) Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, Thailand

Natural-based nanomaterials for drug-delivery have been widely explored in biomedical applications because they offer the possibility to target tumor cells and release therapeutics inside these cells. A similar concept can be applied for agriculture, in particular for plant protection and fertilization. Nanocarriers filled with agrochemicals could improve bioactivity, reduce toxicity and environmental pollution, and prolong the release time of agrochemicals. This presentation will highlight the various methods for the preparation of lignin-based nanocarriers for encapsulation of hydrophobic and hydrophilic agrochemicals. The release profiles and responsive behavior of the delivery systems will also be discussed.

**CELL 287**

Producing lignin nanoparticles directly from raw lignocelluloses at ≤ 80 °C in an aqueous system using a recyclable acid hydrotrope

**Junyong Zhu**, jzhu@fs.fed.us, USDA Forest Service, Madison, Wisconsin, United States

Here we present the discovery of the hydrotropic properties of a recyclable aromatic acid, p-tolueneisulfonic acid (p-TsOH), for potentially low-cost and efficient fractionation of wood through rapid and near-complete dissolution of lignin. Approximately 90% of poplar wood (NE22) lignin can be dissolved at 80 °C in 20 min. Efficient delignification using known hydrotropes such as sodium salts of p-TsOH have been achieved only at 150 °C or higher for over 10 h, or at 150 °C for 2 h with alkaline pulping. The dissolved lignin are relatively native state and can be easily precipitated as lignin nanoparticles simply by diluting the spent acid liquor to below the minimal hydrotrope concentration. Our NMR analyses of the dissolved lignin revealed that p-TsOH can depolymerize lignin via either bond cleavage and separate carbohydrate-free lignin from the wood. p-TsOH has a relatively low water solubility, which can facilitate efficient recovery simply using commercially proven crystallization technology by cooling the concentrated spent acid solution to ambient temperatures to achieve environmental sustainability through recycling of p-TsOH.
investigated using TEM and AFM. In order to evaluate its potential applications in electrode materials, the supercapacitor electrode was prepared using lignosulfonate nanosheets/graphene composites and their electrochemical properties were investigated. The results indicated that the electrochemical performances were dramatically enhanced with the addition of lignosulfonate nanosheets as compared with electrode materials with the presence of graphene only.

**CELL 290**

Spherical lignin particles for triggered release of anti-inflammatory drugs

Mika Sipponen1,2, mika.sipponen@aalto.fi, Heiko Lange1, Claudia Crestini1. (1) Department of Chemical Sciences and Technologies, University of Rome `Tor Vergata`, Rome, Italy (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

Spherical lignin particles offer a versatile platform for the development of advanced materials for controlled release of anti-inflammatory drugs used in the treatment of gastrointestinal diseases. For this application, the prerequisite is to use lignin with high purity, well-mixed organoleptic quality, and only biocompatible solvents. Following these criteria, we developed novel lignin particles and determined their structural stability and ability to carry and release anti-inflammatory drugs in a pH-dependent manner. Strategies to tailor the particles with triggered drug release properties are currently under development. The application of antioxidative lignin particles as carriers for anti-inflammatory drugs is also expected to offer synergistic effects in vivo.

**CELL 291**

Lignin-modified carbon nanotubes/graphene hybrid as efficient flame retardant

Kunlin Song, kunlin.song@gmail.com, Indroneil Ganguly, Ivan Eastin, Anthony Dichiera. University of Washington, Seattle, Washington, United States

To reduce fire hazards and expand high value applications of lignocellulosic materials, lignin-modified graphene nanoplatelets (GNPs) and multi-wall carbon nanotubes (CNTs) thin films were deposited by a Meyer rod process. Lignin promoted the aqueous dispersion of carbon nanomaterials, and served as a fixer to bridge the cellulose microfibers with carbon nanomaterials, which resulted in the formation of a compact layer protecting the cellulose substrate from the flame and preserving the paper integrity. Lightweight and highly flexible papers with increased gas impermeability were obtained by coating a protective layer of lignin-modified carbon nanomaterials in a randomly oriented and overlapped network structure. Assessment of the thermal and flammability properties of papers containing as low as 4 wt% coatings exhibited self-extinguishing behavior and yielded up to 83.5%, 87.7%, and 120°C reduction in weight loss, burning area, and maximum temperature, respectively, compared to the blank papers. Furthermore, papers coated with composites of GNPs and CNTs pre-adsorbed with lignin showed enhanced thermal stability and superior fire resistance than samples treated with either component alone. These outstanding flame retardant properties can be attributed to the synergistic effects between lignin, GNPs, and CNTs, enhancing physical barrier characteristics, formation of intumescent char, and thermal management of the material. These results provide potential opportunities of using lignin for the development of efficient, cost-effective, and environmentally friendly flame retardants.

**Functional Structures from Wood-Based Materials**

**CELL 292**

Novel polysaccharides for strength improvement and coatings for paper and paperboard structures

John Fisher, john.fisher@dupont.com. E.I. duPont Canada, Kingston, Ontario, Canada

Demand for improved performance of paper and board products is spurting the development of new additives. DuPont has applied its expertise in producing cost effective Industrial Biomaterials to design a family of new polysaccharide materials with unique morphologies and functionalities. These materials are produced from natural, sustainable feedstocks, and will be fully recyclable. This presentation will describe some of these new materials and how they can be used to improve the strength of paper and board structures in the wet end of the paper making process. Their unique morphology and chemical properties can also enable them to be used as coatings to improve printability and barrier properties in cellulose substrates.

**CELL 293**

Comparing approaches to very high wet adhesion between wet cellulose surfaces

Emil Gustafsson1, Emilagus@mcmaster.ca, Dong Yang2, Robert H. Patton1. (1) Chemical Engineering, McMaster University, Dundas, Ontario, Canada (2) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

Strong adhesive joints between wet cellulose surfaces requires that the cellulose surfaces are “primed” for adhesion and the presence of an effective wet adhesive between the wet, primed surfaces. Herein we compare: two priming approaches, TEMPO-oxidation and CMC grafting; two wet adhesive chemistries, glycosylated cationic polyacrylamide (G-CPAM) and polyamideamine
epichlorohydrin (PAE), and, two types of adhesion measurements, wet tensile strength of paper handsheets and the wet peel delamination force for laminates of regenerated cellulose. Both priming approaches increase the surface density of carbonyl groups, promoting adsorption of both cationic adhesive types and providing grafting sites for the PAE. The superior combination was G-CPAM on CNC grafted fibers. In addition to high wet strength after drying, this combination also gave significant never-dried wet strength, suggesting polyelectrolyte complexation of the cationic G-CPAM with anionic grafted CNC. Both the classic handsheet measurements and the cellulose delamination experiments showed the same trends. This comparison highlights the utility of delamination experiments which are faster, better defined, and more reproducible than handsheet testing.

CELL 294

Liquid flame spray (LFS) deposited nanoparticles on natural fibre based substrates for antimicrobial activity

Jarkko J Saarinen1, Jarkko.j.saarinen@abo.fi, Birkej K Jocelyn1, Janne Haapanen2, M Gunnels3, E Eerola4, Jyri Mäkelä5, (1) Laboratory of Paper Coating and Converting, Center for Functional Materials and Biological Interfaces (FunMat), Abo Akademi University, Turku, Finland (2) Aerosol Physics Laboratory, Tampere University of Technology, Tampere, Finland (3) Medical Microbiology and Immunology, University of Turku, Turku, Finland

Microbial infections impose major consequences on global, national, and individual level. For example, hospital acquired infections (HAIs) are a large problem in the western societies with costs up to billions of dollars. In the United States only, the HAIs result in approximately one million infections annually with significant morbidity and ca. 5% mortality (up to 25% in the intensive care units) [1].

In this work natural fibre based substrates such as paper and pulp were functionalized with metal and metal oxide nanoparticles for antimicrobial activity. We utilized a liquid flame spray (LFS) nanoparticle deposition [2] that is a versatile tool for depositing various nanoparticles on different substrates at an atmospheric condition. LFS can easily be up-scaled for a large-scale production with a roll-to-roll process flow.

We selected silver nanoparticles for a reference as shown in Fig. 1 in addition to photocatalytically active TiO2 and ZnO nanoparticles. The nanoparticles were deposited on pulp, release base paper, and polyethylene (PE) coated paperboard. The antimicrobial activity of the substrates was tested using a touch prepare test method with Escherichia coli (gram negative) and Staphylococcus aureus (gram positive) bacteria that mimics bacterial transfer from the surface.

The antimicrobial activity testing was complemented with a detailed physico-chemical characterization by using FESEM and XPS.

The nanoparticle coatings on natural fibre-based substrates show antimicrobial activity both against gram negative and positive bacteria. We believe that such antimicrobial, cost-effective, and disposable LFS nanoparticle coated natural fibre-based substrates will find many applications in the future.

Fig 1: FESEM image of Ag nanoparticle coated pulp fiber.

CELL 295

Tailored nano-latexes for modification of nanocelluloses: Compatabilizing and plasticizing effects

Joakim Engström1,2, joengst@kth.se, Fiona Hatton1, Assya Boujemaoui3, Carmen Cobo Sanchez1, Lars Wagberg4, Franool D’Agostino5, Munee L Lansalot5, Linda Fogelström3, Eva E Malmström5, Anna E. Carleyn7,1,2,1,2,1,2 1) Department of Chemistry, Sheffield University, Sheffield, United Kingdom (2) CPE Lyon Bat 308F, C2P2 CNRS/CPE/UEBL, Villeurbanne Cedex, France (3) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (4) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (5) Nanocellulose, RISE Research Institutes of Sweden Division Bioeconomy, Stockholm, Sweden

Cellulose is an interesting natural polymer due to its renewability, large abundance and mechanical properties. It has been shown that by adsorbing block copolymers onto its surface, cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) can be compatibilized with hydrophobic matrices in composites applications. In recent studies we have extended our work, using RAFT-mediated surfactant free emulsion polymerization and polymerization-induced self-assembly (PISA), to form different types of latex particles for cellulose modifications; as compatibilizers for PCL nanocomposites and in a “one-pot” mixing approach for cellulose-rich materials (above 75wt%), see Fig. 2. Latexes are tailored to have a hydrophilic, cationic corona based on 2-(dimethylamino)ethyl methacrylate) (DMAEMA) and a hydrophobic core of either poly(methyl methacrylate) (PMMA) or poly(ethyl-butyl) methacrylate) (PBMA), varying the degree of polymerization (DP), of the hydrophobic core. PMMA and PBMA were chosen as high and low Tg polymers, respectively, to investigate the effect of the core properties. Increasing the DP of the hydrophobic block (from 176 to 1410) increased the latex particle diameter from 35 to 140 nm. The effects together with the kinetics of the latex adsorption were studied on cellulose filter papers and in a QCM-D on CNF layers and cellulose model surfaces. The “one-pot” mixtures of 25 wt% PMMA latex (DP=1410) and CNF (75 wt%) resulted in up to 200% increase of the strain-at-break for the nanocomposites. The PBMA latex on the other hand was found to sufficiently compatibilize CNCS with PCL in nanocomposites, increasing the tensile strength (at 50% RH) from values of 25 MPa to 30 MPa.

Schematic illustration of RAFT-mediated surfactant-free emulsion polymerization and PISA to form latex particles of amphiphilic block copolymers with butyl methacrylate (BMA) or methyl methacrylate (MMA) in the core. The cationically charged nano-latex can be adsorbed onto nanocellulose as, compatibilizer in PCL nanocomposites or plasticizers in cellulose-rich materials (75% wt%).

CELL 296

Industrially relevant cationic starches: Interaction with cellulose thin films

Katriin Nieglaheli1, Angela Chemelli1, Thomas Grieser2, Heidemarie Raler4, Ulrich Hintl1, Stefan Speik1, stein@spiek@graz.at, (1) Institute for the Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria (2) Institute for Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria (3) University of Leoben, Leoben, Austria (4) Mond Group, Hausham, Austria

Abstract

Industrially relevant, commercially available cationic starches from different sources (potato, pea, corn) which feature rather low degrees of substitution ranging from 0.030 to 0.052 have been studied towards their behavior with cellulose thin films. Surface plasmon resonance spectroscopy under flow conditions using concentrations of 1.0 mg ml−1 and a flow rate of 25 ml min−1 was employed and revealed that all the investigated starches employed in this study were capable to efficiently interact with the slightly negatively charged cellulose surface leading to their irreversible deposition on the surface. As complementary techniques atomic force microscopy and x-ray photoelectron spectroscopy were used to confirm the presence of the starches on the cellulose film surface. Further, dynamic light scattering and size exclusion chromatography measurements were performed to correlate adsorbed amount, particle size and molecular weight of the starches to their interaction behavior.

CELL 297

Flow-assisted organization of nanostructured bio-based materials

Nitesh Mittal1, nitesh@kth.se, Fredrik Lundell2, Lars Wagberg2, My Hedhammar1, Daniel Soderberg1, (1) KTH Fibre Polymer Techn, Stockholm, Sweden (2) Department of Mechanics, KTH Royal Institute of Technology, Stockholm, Sweden (3) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (4) Division of Protein Technology, KTH Royal Institute of Technology, Stockholm, Sweden
The need for high-end multifunctional materials from bio-based resources has been resolved by a rapidly increasing population and accompanying environmental concerns. However, lack of scalable assembly methods has been a key block in manufacture of high-performance nanostructured materials. I would like to present material concepts using components from bio-based resources, to achieve extraordinary performance of the macroscopic materials. We utilized fluid-phase assembly process as it is the most promising method for producing large, ordered structures for nanoscale objects. I would like to brief our approach in context to different nanoscale building blocks from the bio-based resources.

**CELL 298**

Morphological and thermal characterization of polysaccharides/protein biocomposites as a function of alcohol and peroxide content

David Salas-de la Cruz, david.salas@camden.rutgers.edu, David Verrell, John Stanton, Chemistry, Rutgers University-Camden, Camden, New Jersey, United States

In biological systems, most structural materials are composites formed from a dispersed phase, typically biomacromolecules arranged in a hierarchically assembled by molecular interactions. For example, in wood, cellulose is the dispersed phase, and interacts within a matrix composed of xylan and lignin. In another example, in the exoskeleton of arthropods, chitin is the dispersed phase within a matrix of silk-like proteins. Recent reports characterizing the fabrication of biomaterial composites (biocomposites) using natural materials such as silk and cellulose have identified changes in physicochemical properties as a function of fabrication method and material composition. However, the relationship between hierarchical and secondary structures during materials formation is important but still astonishingly unclear. In this study, the effect of alcohol and peroxide content is evaluated to understand the morphological and thermal properties in cellulose/silk biocomposites using ionic liquids. Various techniques were implemented to investigate structural, morphological and thermal properties of the biocomposite films, including FTIR, SEM, TGA, DSC, AFM, Confocal Microscopy, and X-rays scattering. Results show that the type of coagulation agent has strong influence on the structure and thermal properties of the biocomposite. As the alcohol content increases the formation of beta sheets increase while maintaining a constant alpha-helix formation. On the other hand, low concentrations of peroxide seem to show a decrease in the beta sheets while maintaining a constant amount of alpha-helix as seen in the alcohols. Topological and textural imaging in combination with X-ray scattering provide information to support our findings. The overall characterization results confirm that the level of interaction between both polymeric chains can be tuned by fabrication method.

**CELL 299**

Maintenance of functional effectiveness of modified cellulose fibers during textile refining

Frank Wendler, Frank Meister, Frank Meister, (1) Chemical Research, Thuringian Institute for Textile and Plastics Research (ITTK), Rudolstadt, Thuringia, Germany (2) Smartpolymer GmbH, Rudolstadt, Thuringia, Germany

Cellulosic fibers enhance their potential as natural origin by implementation of functional agents compared to fuel-based fibers. Composites of cellulose and additional components of natural or synthetic origin are accessible via the Lyocell technology and draw rising attention for the creation of “High-tech-polyomers. Physical dissolving process of cellulose and the high loading capacity of the solution enable the incorporation of chemically different compounds, e.g., ceramics, carbon black, activated charcoal or superabsorbent polymers. Further, liquid lipophilic agents can be incorporated into the cellulose structure. Bound inside the cellulose network the functional agent has to develop its effect for longer time periods while textile processing steps give rise to desintegrate the agent or to release it. Stages of incorporation include admixing, binding inside the composite matrix by pressure and release by refining processes of fibers throughout the whole textile chain place high demands on the chemical agent. Especially, harsh stages inside the textile chain demand permanent fiber material with high durability to maintain the effectivity of incorporated agent. Increased temperatures over certain time periods, far-ranging pH values or pressure due to mechanical treatment have impact on textile properties and the bound functional agent. With the aid of insecticide permethrin as an oily, lipophilic substance the binding inside cellulose skeleton is elucidated within the scope of the study. Impacts on processing stages on leaching behavior as well as chemical transformation and degradation should be demonstrated. Measures to maintain the functional effectiveness in interaction with selected technical parameters of textile processes are explained.

**CELL 300**

Preparation and properties of solution cast films from pennycress protein isolate

Gordon W. Selling, gordon.selling@ars.usda.gov, Mía Hajojilla-Evangelista, William Hay, Kelly Ull, Gary Gross. NCAAR ARS USDA, Peoria, Illinois, United States

Pennyseed is a crop which may grow over the winter months may be a good candidate for biodiesel production due to the high oil content of the seed. All parts of the seed must be utilized in order to obtain the most value from the pennycress seed. High yield and very high purity pennycress protein isolate (PPI) was obtained using an improved pilot scale process. Solution cast films were prepared from formic acid solution. The films had good transparency but high color. Glycerol (GLY) was found to be a good plasticizer for PPI. Elongations up to 194% could be obtained at the highest level tested of GLY. At these high elongations tensile strength declined to 3.2 MPa. Increased humidity resulted in increased elongation and lower tensile strength. The Tg and heat deflection temperature for the PPI films were in the range of 75 and 117 °C respectively. Degradation began at around 170 °C; the films had good water and oxygen barrier performance. Given the overall balance of properties, PPI films may have value in film applications. This would especially be true in composite applications where exposure to moisture may be reduced.

**CELL 301**

Encapsulation of valuable algae-based compounds in biopolymeric nanoparticles

Sara Ortiz, Laura Rodas, Laura Morales, Claudia A. Valencia, José Campos-Terán, Izilda Arroyo-Maya, arroyo@correo.ceu.uam.mx, (1) UAM-Cuajimalpa, Mexico DF, Mexico (2) Procesos y Tecnología, Universidad Autónoma Metropolitana, Mexico City, Mexico (3) Instituto Tecnológico de Monterrey, Monterrey, Mexico

Nanoparticles of whey proteins (β-lactoglobulin, β-lactalbumin) prepared by desolvation in ethanol and glutaraldehyde crosslinking are promising carriers for bioactive compounds. The objective of this work was to study the use of these nanoparticles as delivery systems for phycocyanin (PC), which is one of the main pigments of the algae Spirulina. PC is a protein from the phycobiliprotein family characterized by its intense blue color and a structure that includes a non-protein component known as phycocyanobilin. PC scavenges reactive oxygen and nitrogen species and prevents oxidative damage that may explain its beneficial effects. The impact of the nanocapsulation of PC in protein-based nanoparticles was measured in terms of particle size and size distribution, surface charge, encapsulation efficiency and antioxidant activity. In all cases, a high average particle yield of 99.63% was obtained. Smaller sizes (<200 nm) can be obtained with the use of α-lactalbumin as wall material. These nanoparticles, with an isoelectric point of 3.7, are very stable at pH values >4.8, based on their ζ-potential, although their antioxidant activity is weak. The highest encapsulation efficiency for PC was around 60%. These results support the idea that biopolymers can be used to design degradable and functional nanoparticles for diverse delivery purposes.

**CELL 302**

Thermodynamics of algal growth substrates made from renewable macromolecules

Zahra Karimi, zah6004@auburn.edu, Joshua M. Passantino, Derryn W. Herring, Daniel P. Pantaloni, David Blersch, Virginia A. Davis, (1) Department of Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) Department of Industrial and Systems Engineering, Auburn University, Auburn, Alabama, United States (3) Department of Biosystems Engineering, Auburn University, Auburn, Alabama, United States

The overall objective of this research is to develop substrates for attached algal growth from polyacrylic acid (PLA) and PLA composites containing lignin and/or cellulose nanocrystals (CNC). Algae has the potential to produce significant economic impact in many sectors: biofuels, environmental remediation, and nutritional supplements. Algal cultivation on substrates promotes to increase product yield and process efficiency. However, limited fundamental scientific
understanding of algal attachment and growth is one of the major obstacles to designing high yield substrates that are species-selective. In this research, the surface energies of the renewable biomass substrates and various algal species were determined through sessile drop contact angle measurements. Substrate-algae thermodynamic interactions were modeled using the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) model to determine which algae-substrate pairs had the greatest theoretical thermodynamic attraction. The model results were then compared to experimental findings on algae-substrate attachment. The results demonstrate the effect of chemical composition on surface energy of the substrates, which ultimately results in different interaction energies between the algae and the substrates. In ongoing research, the effects of surface roughness and thermodynamic modeling of three-dimensional substrates are being explored.

CELL 303

Zinc-free synthetic isoprene rubber vulcanizates using wheat protein as an activator
Barbara L. DeBults1, ldebults@vt.edu, Renee Thompson2, Justin R. Barone2. (1) Macromolecular Science and Engineering and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (2) Biological Systems Engineering, Center for Soft Matter and Biological Physics, and Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

Tris(2-carboxyethyl)phosphine hydroxylid (THGd) was used in place of zinc oxide (Zno) and stearic acid to activate the sulfur vulcanization of synthetic polyisoprene rubber (IR). The protein-activated vulcanizates were characterized using differential scanning calorimetry (DSC), tensile testing, swelling experiments, and Fourier transform infrared spectroscopy (FTIR). All protein-activated compounds were successfully crosslinked, as determined by swelling experiments. As protein loading increased from 4 to 16 parts per hundred rubber (phr), the Young’s modulus increased while the relative crosslink density decreased. This suggested that as protein loading increased, the effectiveness of the curing reaction decreased and the additional protein served to reinforce the rubber. The curing kinetics were evaluated by DSC and found to be generally slower in the THGd-activated vulcanizates, i.e., longer cure times were required to achieve a similar degree of cure to the control. However, at low protein loading of 4 and 8 phr, the activation energy, Ea, required to reach a maximum cure rate was lower than the control. This study showed that THGd protein could successfully activate the curing reaction of synthetic IR, while also serving as a reinforcing filler. Thus, the potential for a completely zinc-free rubber curing system exists.

CELL 304

Crystallization of polypropylene in the presence of plant tissue
Patrick R. Navard1, patrick.navard@mines-paristech.fr, Jorid Girones1, Loan Vo1, Jean-Marc Haudin1, Lionel Freire1, Vixian Song1, Séverine Boyer1, Cécile Barnou1. (1) Mines ParisTech, Sophia Antipolis, France (2) IATE, INRA, Montpeller, France

First, natural fillers composed of cellulose, lignin and fillers with a varying lignin/cellulose ratio (flax, jute, curaua fibers and miscanthus stem fragments) were used to prepare composites with polypropylene using the same procedure, with or without a maleic anhydride-grafted polypropylene (MA-g-PP) coupling agent. A clear acceleration of the crystallization kinetics was observed in the presence of miscanthus stem fragments. A clear effect of the nature of the polymers present in the filler was observed. There is a direct relationship between the values of the Avrami kinetic constant for the six fillers and their lignin content, the more effective to enhance crystallization kinetics being pure cellulose. Lignin has no effect on the crystallization kinetics of polypropylene.

A second study detailed the role of vegetal tissues which were separated from maize stems. Clear differences were seen depending on the type of tissue (pith, parenchyma cell, vascular vessels, epidermis, sclerenchyma parts).

This study is enabling to identify key parameters in polypropylene transcristallinity in the presence of plant tissues.

CELL 305

Invasive plants in Western Europe as renewable raw materials for biofertilizing: The case study of Japanese knotweed
Antoine Hospied, antoine.hospied@ulg.ac.be, Quentin Schmetz, Aure olechel, University of Liege, Liege, Belgium

Japanese knotweed (Fallopia japonica) is a non-native invasive freshwater plant commonly found in Western Europe, notably along water bodies. In Belgium, our group works on the identification of valuable option for the valorization of this plant in a biofertilizing perspective. Japanese knotweed is indeed a complex lignocellulosic plant composed of about 35%, lignin (26%), hemicellulose (9%) and others (proteins, inorganics, secondary metabolites, etc.). The rheology of the plant is an attractive source of trans-resveratrol, a phenolic compound of great potential for high added value applications for cosmetics or para-pharmaceuticals.

Japanese knotweed is a complex heterogeneous matrix that requires pretreatment processes to individualize lignin from hemicellulose and cellulose for further valorization schemes. Many types of pretreatment allow such a fractionation, their efficiency depending on the structure and composition of the raw material, but mostly on the desired applications for the separated fractions. Our works have evidenced that a methodology combining solvents mixture and Brønsted acid could be a cost-effective option for the one-step recovery of almost all the valuable compounds found in the Japanese knotweed and for their subsequent valorization for niche markets. This pretreatment methodology was found particularly suited for the extraction of phenolic compounds

In (in particular resveratrol) in high yields and purity.

This contribution highlights the innovative applications of molecules extracted from an invasive plant and the benefits of this strategy in biofertilizing options. Valorization of secondary metabolites, production of high added value derivatives of lignin and cellulose are here presented and illustrated.

CELL 306

Utilization of aqueous phase of biomass pyrolysis for synthesis of novel olefins and polyolefins
Mehul Barde1,1, mrb0063@auburn.edu, Katrina Avery1,1, Charles W. Edmunds2, Nicole Labbé2, Maria L. Aued3. (1) Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States (3) Center for Polymers and Advanced Composites, Auburn University, Auburn, Alabama, United States

Aqueous stream of fast pyrolysis of wood biomass was considered as feedstock for monomer synthesis. GC-MS analysis indicated the presence of aliphatic organic compounds in aqueous phase, including aldehydes, ketones and alcohols. Olefination of bio-oil components was performed via different routes. Aldehydes and ketones were converted to ethylene-analogues via Wittig reaction. Alcohols and phenols were reacted with methacryloyl chloride to carry out methacrylation of hydroxy groups of the organic compounds. In another approach, maleic anhydride was used for derivatization of bio-liquid hydroxy compounds. The bio-liquid-based olefins were characterized by FTIR and DSC. Olefinated bio-oil was polymerized to produce plastic films.

The resulting polymers showed a wide range of properties depending on the olefination route. Polyolefin synthesis proved to be a potential, efficient method of valorization of aqueous phase of bio-oil. Bio-oil based polyolefins can be used in the biomedical and agricultural applications such as hydrogels and superabsorbent polymers.
Biobased Gels & Porous Materials

CELL 308

Structure-property relationship of nanocellulose gels

Lyza Mendoza. lyza.mendoza@monash.edu, Warren Batchelor, Gil Garnier. Chemical Engineering, Monash University, Melbourne, Victoria, Australia

Cellulose, the most abundant polymer occurring in nature, can be processed into carboxylated cellulose nanofibers which form biodegradable and biocompatible hydrogels. These nanocellulose hydrogels present interesting potential for high value products, particularly in food and biomedical applications. However, characterisation and fundamental understanding of their gelation mechanism are required to efficiently engineer their properties for specific applications. Through understanding their structure-property relationship, we can modify and functionalise hydrogels by optimising parameters such as fibre content, predicting their response to additives (salts and pH), and modifying surface composition.

Herein, we present methods to understand the gelation mechanism and structure-property relationship of hydrogels produced with TEMPO-oxidised cellulose nanofibres. Fibre aspect ratio and bulk material properties of the gels were measured using the sedimentation method and rheology, respectively. The strong viscoelastic response of the hydrogel predominantly arises from the entanglement of high aspect ratio fibres, which is also affected by the pulp source. The strength and stability of the gel also depends on the surface charge density of the carboxylated fibres. We found that the critical factors for the formation of stable colloidal gels are the critical length-scale and high surface charge density of the nanocellulose fibres.

Figure 1 illustrates the factors affecting the gelation of TEMPO-oxidised nanocellulose.

CELL 309

Novel preparation method of self-sustaining hydrogel using only cellulose nanofiber dispersion

Shin Suennaga. 17axz05g@shinsuhi-u.ac.jp, Mitsuuma Osada. Department of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano, Japan

Cellulose nanofibers (NFs) with widths of 3–4 nm and lengths of a few μm have been prepared by treating pulp with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals and exhibit outstanding mechanical properties; therefore, TEMPO-oxidized cellulose nanofibers (TOCNs) have attracted research interest in the field of materials chemistry. TOCN dispersion is consisted of network structure due to entanglement between NFs having high aspect ratio, however easily run off by applying large strain. To effectively use TOCN dispersion as wound dressing material, scaffolds, and seed growing mediums, it is needed to convert into a hydrogel which has high strength and can keep their shape, and the formation of the network structure by chemical and physical crosslinking is important. So far, the chemical crosslinking using epichlorohydrin and immersion into hydrochloric acid were carried out to prepare self-sustainable hydrogel. However, the use of these additives is not desirable in the view of toxicity and unclear behavior to human body. In this study, the preparation of self-sustaining hydrogel was achieved by only applying heat and pressure. The high-temperature and high-pressure treatment induced two effects for TOCN. First, glucose/glucuronate copolymer on external layer of TOCN was selectively hydrolyzed. Second, hydrophobic interaction worked between exposed crystalline cellulose nanofibers. The selective hydrolysis was confirmed by high-performance liquid chromatography and conductometric titration. Derivative thermogravimetric curve and X-ray diffraction pattern indicated that the hydrogel consisted of crystalline cellulose nanofibers mainly. This hydrogel dissolved in brown after high-temperature and high-pressure treatment and included some decomposition products, but the decomposition products can be eliminated from the hydrogel by immersion in distilled water. In conclusion, TOCN dispersions was converted into transparent and self-sustaining hydrogel without any additives through high-temperature and high-pressure treatment.

CELL 310

Tuning rheological properties of polysaccharide gels using hydrophobic cellulose nanocrystals

Rinat Nigmatullin1, Janet Scott2, Karen J. Edler1, Yaroslav Z. Kitymyk1, Jesus Angulo3, Stephen J. Eichhorn1, s.j.eichhorn@bristol.ac.uk. (1) Building 13, Centre for Sustainable Chemical Technologies, Bath, United Kingdom (2) Bristol Composites Institute, University of Bristol, Bristol, United Kingdom (3) School of Pharmacy, University of East Anglia, Norwich, United Kingdom

Starch is widely incorporated into processed foods, cosmetics, pharmaceutical formulations, etc. as a thickener, colloidal stabilizer, geling agent, bulking agent and as a water retention agent. Blending starch with other hydrocolloids into starch-based systems is a well-established approach to modify its physico-chemical and functional properties. In this contribution we explore the combination of corn starch and cellulose nanocrystals (CNC) for modification of rheological and textural properties of gel materials.

Sulfated CNCs (sCNC) produced by hydrolysis with sulfuric acid were further modified to introduce hydrophobic moieties onto their surface. Rheological properties of modified CNC dispersion/gels were studied using oscillatory rheology and steady flow viscometry. Similar to sCNC, transitions from isotropic suspensions to liquid crystalline systems and ultimately to gels were observed with an increase of modified CNCs. However, critical concentrations corresponding to these transitions were observed at lower concentrations compared with sCNC. Moreover, storage modulus and steady flow viscosity were significantly higher for modified CNC suspensions/gels than sCNC suspensions of the same concentrations. Surface modification is thought to facilitate interaction between CNCs due to hydrophobic interactions.

Gelation and viscoelastic behaviour of starch formulations with modified CNCs and sCNC were investigated. Replacing sCNC with modified CNCs in starch/CNC gels drastically changed rheological properties. Such changes in rheological properties are believed to arise due to formation of inclusion complexes between amylose and hydrophobized CNCs. Starch/CNC gels of wide range of rheological properties were achieved via variation of sCNC content and combination of sCNC and modified CNCs in different proportions.

CELL 311

Dynamic networks of cellulose nanofibres as a platform for tunable hydrogels, aerogels, and chemical modifications

Tobias Benselfelt1,2, benselfet@kth.se, Lars Wagberg1,2. (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Wallenberg Wood Science Center, Stockholm, Sweden

Nanopapers prepared from oxidized cellulose nanofibers swell dramatically in deionized water due to the osmotic pressure generated by the charged groups on the fibril surface. This is in many aspects considered as a disadvantage and something to prevent in order to utilize the mechanical properties of CNF in future materials. In this work we take an opposite approach and try to utilize the impressive swelling of charged CNF-films in order to create ideal networks that are hard to reach by traditional methods. Due to the ionic repulsion between the fibrils and between the fibrils and added highly charged anionic polyelectrolytes it is possible to create highly dynamic networks also at rather high CNC concentrations. These dynamic networks are used to tune the material properties of hydrogels and the subsequent freeze dried aerogels. The incorporation of small amounts of anionic polyelectrolytes, in this case alginate, also makes it possible to further enhance the swelling ability and to introduce a way to lock the desired hydrogel or to make the aerogel water resistant. The presented approach provides the possibility to tailor the dry content, density, mechanical properties as well as the shape and size of the hydrogels and aerogels with high accuracy. Furthermore, we study solvent exchange of the prepared hydrogels to create a platform for chemical modifications in different solvents or to enable critical or ambient drying to produce aerogels without lyophilization. In conclusion, we present different tunable materials from cellulose nanofibers to be used as a foundation for advanced functional materials such as electrically or biomedically interactive devices.

Image of freestanding physical hydrogels of CNF and alginate tuned to different dry content in the range of 0.5 to 3 wt%.

CELL 312

Sorghum protein based biocomposites reinforced by cellulose nanowhiskers: Effect of hydrolysis time

Wei Lü1, louisa.lew@vpr.163.com, Bingnan Mu1, Yai Yang1. (1) UCL Dept of Biological Sys Eng, Lincoln, Nebraska, United States (2) University of Nebraska–Lincoln, Lincoln, Nebraska, United States (3) University of Nebraska-Lincoln, Lincoln, Nebraska, United States

Biocomposite films based on sorghum protein reinforced by cellulose nanowhiskers were prepared by solvent casting method. Since research interests have been focused on exploiting bio-polymers from agricultural wastes or by-products, sorghum distillers grains, with its special feature of large availability and low prices, has been a potential candidate for protein sources. Current products based on sorghum protein possess inferior tensile properties due to damages to backbones during extraction of the highly crosslinked protein. Therefore, cellulose nanowhiskers were hydrolyzed for different length of time with sulfuric acid and used as reinforcing materials. The effect of hydrolysis time on the structure and properties of different cellulose nanowhiskers and their reinforcing effects on the sorghum protein based biocomposites were systematically studied. The interactions between sorghum protein and cellulose nano fillers were characterized by rheology study. Since the interactions were mainly attributed to hydrogen bondings and...
Electrostatic forces, crystal size of sorghum protein based biocomposites reinforced by different cellulose nanowhiskers and surface charges (as sulfate ester groups) of cellulose nanowhiskers with different hydrolysis extent were further investigated by XRD and ICP. SEM was used to analyze dispersion and adhesion of different cellulose nanowhiskers in sorghum protein based biocomposites. It was found that the improved interfacial interactions not only benefited the formation of percolating nanofiller network in sorghum protein matrix, but also the effective interfacial stress transfer, thus leading to the significantly improved mechanical properties of the biocomposites. A relationship between tensile strength of sorghum protein based biocomposites and three factors, size of cellulose nanowhiskers, surface charges of cellulose nanowhiskers as well as crystal size of biocomposites, were set up. With this relationship, selection of proper hydrolysis time of cellulose nanowhiskers as reinforcing materials would not only expand the applications of sorghum protein in food packaging, tissue engineering and drug delivery areas, but also help to develop high performance composites derived from other protein materials.

CELL 313

Cellulose-based gel beads for quantifying the swelling behavior of plant fibers

Pernilla Karlsson, pemkar@ki.se, Tomas Larsson, Lars Wågberg1, (1) Invenenta AB, Stockholm, Sweden (2) KTH Fibre Polymer Techn, Stockholm, Sweden (3) KTH Royal Institute of Technology, Stockholm, Sweden

To obtain a successful utilization of cellulose as a component in new materials a fundamental knowledge about their interaction with moist air or condensed water is necessary. There is a need to be able to predetermine the change in materials properties under various environmental conditions. Cellulose fibres are however difficult to study due to the variety of the fibres both regarding chemistry and morphology and there is therefore a need to develop a model cellulose material that can be studied regarding the water sorption and the irreversible change in swelling upon drying of the material.

To solve this problem macroscopic spherical cellulose-based hydrogel beads with a diameter of 2–3 mm were produced using cellulose-rich pulp dissolved in the DMA/CDI-system followed by a special precipitation step. A carboxymethylation of the pulp was performed to introduce charges in the final gel beads. By using NMR and X-ray scattering it was shown that the water swollen gel beads consist of a non-crystalline cellulose network where the scattering objects are colloidal entities of around 20 nm in diameter. By exposing the gel beads to different pH and ionic strengths it was also shown that they behave like a polyelectrolyte gel in the same manner as the plant fiber wall i.e. the swelling is affected when changing the pH and/or adding salt.

The gel beads have also proven to be an excellent model material for studying the non-ionic contribution to the water uptake in cellulose-rich substrates. Despite a considerable work on clarifying the ion-induced swelling of cellulose hydrogels, there is still a very limited knowledge about the factors controlling the non-ionic swelling of the hydrogels which in fact is the dominating factor controlling the swelling. The non-ionic water retaining ability of the cellulosic network was studied by placing the gel beads in solutions with high molecular weight dextran at different concentrations. The increase in concentration of the dextran created an increased osmotic stress on the gel beads which in turn induced a change in structure leading to a draining of water at around 17 KPa. However the gel beads were not fully drained until an osmotic pressure of approx. 4.9 MPa was applied. In an attempt of further separating this water retaining ability in an ionic, a non-ionic and a mechanical network strength contribution the water activity of gel beads with different charge densities and concentrations of cellulose have been studied.

CELL 314

3D printing functional nanocellulose hydrogels

Olivier Fourmann, Gilberto Siqueira, Gilberto.siqueira@empa.ch, Michael Hausmann, Mark Schubert, Tanja Zimmermann. Applied Wood Materials, Empa, Dubendorf, Switzerland

The interest for use of nanocelluloses as reinforcing building-blocks in polymers composites is constantly increasing mainly due to their exceptional mechanical properties. The high number of reactive hydroxyl groups (–OH) available on the surfaces of such nanomaterials make them highly prone to chemical functionalization, which increases their compatibility with varied polymers matrices and allows for the development of materials with specific functionality as anti-microbial properties.

In this work, we demonstrated how to prepare high-cellulose-content inks to achieve successful 3D printing of cellular-structured hydrogels. The effects of high concentration of CNC within the mixtures on the rheological properties of inks as well as on the final mechanical properties of the printed materials were evaluated. The alignment of CNC proven by 2D WAXS measurements showed that a high degree of ordering (up to 86 %) was achieved by combining the right printing parameters and ink composition. The anisotropic swelling of the printed hydrogels could be correlated to the alignment of anisotropic cellulose particles. Our approach can be utilized by a great variety of monomers and therefore hydrogels with complex shapes and programmable reinforcement can be envisaged without the need of extra inorganic and/or synthetic rheological modifiers. By introducing anti-microbial properties to the hydrogels, it was possible to broaden their applications in biomedical fields.

CELL 315

Nanostructured hydrogels for potential application in 3-D bioprinting

Nuno H. Silva, Carla Vilela, Ricardo J. Pinto, Carmen Freire, cfreire@ua.pt. University of Aveiro, Aveiro Institute of Materials, Aveiro, Portugal

3D bioprinting of living tissue constructs, with specific shapes and functionalities, to repair or replace damaged parts of the human body, as well as to be used in diseases research and drug testing, is developing as a cutting edge approach in medicine and pharmaceutical research. However, the availability of biomics, i.e. the cell-laden biomaterials that are deposited by the bioprinters, with good bioprintability, high cell density and mechanical properties, is still limited and considered one of the main restrictions in this field. In this communication, we will describe the preparation and characterization of innovative bio-based nanostructured hydrogel biomics, for 3D printing of living tissues.

Plant Heteropolysaccharides: Interactions within Lignocellulosics, New Modifications & Future Applications

CELL 316

Safety considerations of softwood galactoglucomannans in food use

Leena Pilkkanen, Marina Heinonen, Kiri S. Mikkonen, kiri.s.mikkonen@helsinki.fi. University of Helsinki, Helsinki, Finland

A growing population and concern over the sufficiency of natural resources for feeding this population has motivated researchers and industries to search for alternative and complementary sources of food ingredients and additives. Numerious plant species and parts of plants are explored as raw materials for food production. An interesting example is wood; to date, few wood-based additives or ingredients are authorized for food use. Wood hemicelluloses, such as softwood galactoglucomannans (GGM), constitute an abundant bioresource that shows a highly potential functionality in edible materials. GGM—“spruce gum”—acts as a multi-functional emulsifier and stabilizer, and it could be used in various processed food products, replacing less effective, conventional emulsifiers. Before new materials can be released onto the food market, their safety must be evaluated, according to legislation. This study focuses on the safety aspects that must be considered before polysaccharide- and phenolic-rich plant extracts can be awarded the status of authorized food ingredients. GGM is presented as a case study and examples are given of plant-based polysaccharides that are already authorized for food purposes. GGM, an abundant wood-based hydrolactic, is envisioned as a future food ingredient that may pave the way for the safety evaluation and commercialization of other potential polysaccharide-based plant extracts.

CELL 317

Extraction of distinct populations of bioactive arabinoxylans from wheat bran using sequential chemo-enzymatic processes

Amparo Jimenez Quero, amparoq@iith.se. Reskand C. Rudjito, Antonio Martinez-Abad, Andrea C. Rothes, Francisco Vilaplana. Glycoscience, KTH Royal Institute of Technology, Stockholm, Sweden

Wheat bran is a major by-product of cereal production that can be used for advanced nutritional and material applications. Due to its content of valuable biomacromolecules (e.g. polysaccharides and phenolic compounds), wheat bran has gained renewed interest as a raw material to be used in second-generation biorefineries. Wheat bran has a total carbohydrate content of approximately 55-60%, of which 40-45% correspond to hemicelluloses, 15-20% protein, 5 fats and 10-12% phenolic lignin (Figure 1a). Arabinoxylans (AXs) are the most abundant hemicelluloses in cereals, consisting of a backbone of (1→4)-linked β-D-Xylp units, substituted by α-L-Araf in O-2 and/or O-3 positions to different extents and intramolecular distributions, depending on the biological source and tissue (Figure 1b). The L-Araf residues can be further substituted by phenolic compounds (e.g. ferulic acid), which can dimerise creating a crosslinked covalent supramolecular architecture. Cereal AXs have been classified in water-extractable (WE-AX) and water-unextractable (WU-AX) (Figure 1c). A sequential process using subcritical water, membrane filtration and selective enzymatic treatments has been designed for the combined fractionation of functional high molecular mass hemicelluloses and oligosaccharides. This process preserves the inherent fermentable functionalities. Feruloylated arabinoxylans (F-AX) with significant radical scavenging activity can be isolated from the subcritical water extract. Valuable feruloylated arabinoxylans (FAXoS) can be further isolated from the crosslinked residue using xylanolytic enzymes. Finally, subsequent extractions using alkali or DMSO solutions are able to distinctly isolate different arabinoxylan populations from the wheat bran. The oligo- and polysaccharide fractions isolated from these sequential processes show great potential for use in food and biomedical applications as prebiotic or platform chemicals, and as polymeric matrices for carbohydrate-based materials.
Spruce galactoglucomannan stabilized emulsions are potential carriers for bioactive compounds

Hongbo Zhao1, hbo.zhao@outlook.com, Kiri S. Mikkonen1, Anna-Maja Lampi2, Petri Koppeläinen1, Mari Lehtonen1. (1) University of Helsinki, Helsinki, Finland (2) Lulea natural resources institute Finland, Helsinki, Finland

Developing of functional foods or edible health care products requires the design of suitable delivery system to protect, carry and release bioactive compounds, such as polyunsaturated fatty acids, tocopherols and carotenoids. Emulsion technology is found to be a useful tool to improve the delivery of lipophilic bioactive compounds. Spruce galactoglucomannans (GGM) are wood hemicelluloses that can be recovered at high quantity by lignocellulosic refining processes, such as with pressurized hot water extraction. GGM are bio-based, novel and sustainable compounds, which have the ability to efficiently emulsify and physically stabilize oil-in-water emulsions. In addition, lipid oxidation in GGM-stabilized emulsions is exceptionally inhibited. These features make GGM attractive alternatives for the conventional stabilizers of emulsions used in food applications.

In this study, we investigated the applicability of GGM-stabilized emulsions for the delivery of polyunsaturated fatty acids by pressed oil. Changes occurring in the emulsion stability and bio-accessibility of lipids were investigated during in vitro digestion. The in vitro model constituted of oral, gastric and small intestinal phases. GGM-stabilized emulsions retained their morphology during oral and gastric phases. In small intestinal phase, GGM did not inhibit the action of pancreatic lipases but tracyglycerols were hydrolyzed efficiently into free fatty acids. At the same time, the oil droplets were disrupted. GGM remained stable during the digestion and no significant release of phenolic compounds, free mono-, di-, or oligosaccharides were detected. Thus, GGM-stabilized emulsions are potential delivery systems for bioactive compounds.

Enzymatic modification of corn bran arabinxyloylan alters the in vitro fecal fermentation profiles by human gut microbiota

Xiaowei Zhang, zha1983@purdue.edu, Bruce Hamaker. Whittier Center for Carbohydrate Research and Department of Food Science, Purdue University, West Lafayette, Indiana, United States

The human gut microbiota composition is related to a number of chronic diseases such as obesity, type 2 diabetes, and inflammatory bowel disease. Corn bran arabinoylan (CAX) could be a desirable dietary fiber to modulate the gut microbiota composition as it has diverse structures. The hypothesis of this study was that enzymatic modification of CAX improves the metabolic activity of the human gut microbiota. In this study, CAX was solubilized in different concentrations of NaOH, and products either treated with feruloyl esterase treatment further deplete the ferulic acid in CAX or with lactase to re-crosslink CAX. Monosaccharides analysis by gas chromatography showed that neutral sugars of CAX were 16% arabinose, 75% xylose, 5% galactose and 4% of glucose. The measurement of gas production of these three samples from in vitro fecal fermentation revealed that CAX had significantly higher gas production than the ferulic acid-depleted CAX (FAD-CAX) and crosslinked CAX. Notably, FAD-CAX had substantially higher acetate (58.1 ± 3.6 mM), propionate (34.5 ± 2.0 mM) and butyrate (6.3 ± 0.5 mM) production than CAX, which was 41.9 ± 1.9 mM, 22.2 ± 1.0 mM and 4.3 ± 0.2 mM at 24, respectively. Additionally, crosslinked CAX had a significantly higher butyrate ratio (6.8%) than CAX (6.3%). The results indicate that the presence of ferulic acid esters and di-ferulate crosslinks alter CAX metabolism by gut microbiota. This interesting finding suggests a strategy to improve the utilization of dietary fiber by gut microbiota through enzyme treatment.

Heteropolysaccharides recovered from plant biomass have great utilization potential as future alternatives to conventional oil-based products. In biorefining processes, several constituents of the biomass need to be recovered to prevent the formation of waste fractions. Key enabling technologies include pathways for the efficient recovery of the major biopolymer fractions from plant biomass, and their conversion to functional materials such as bio-based plastics and composites.

Many challenges need to be overcome to realize this concept. The interactions between cellulose and heteropolysaccharides in the biomass need to be fully understood and the separation of different biomass components requires methods that are efficient without causing unwanted modifications of the polysaccharides’ structures, molecular weights or properties.

Many polysaccharides are not thermoplastic but very brittle, limiting their application as bioplastics. In addition, the inherent hydrophilicity of many polysaccharides makes them typically poorly miscible with conventional bulk plastics, limiting their application in composites. Chemical modifications of the polysaccharides may help improve the thermoplasticity, moldability and blend compatibility.

Here, viable protocols for the recovery of heteropolysaccharides from plant biomass will be presented along with strategies for chemical modifications of polysaccharides. We produced modified heteropolysaccharides, for example grafted hemicleillulosics, which became significantly more hydrophobic and exhibited a thermoplastic behavior. Bioplastic films, filaments and composites based on plant heteropolysaccharides will be presented.

Xylan nanotiles

Amanda M. Johnson1, amanda.marie.j@gmail.com, Muzaffer Karaaslan2, Scott Renneckar3, Shaen Mansfield4, Fanide Unda1. (1) University of British Columbia, Vancouver, British Columbia, Canada (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) Energy Science and Engineering, University of Tennessee, Knoxville, Tennessee, United States (4) Chemical Engineering, Aalto University, Helsinki, Finland (5) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Biopolymers such as xylan have been noted to self-assemble into unique nanostructures. However, characteristics that lead to assembly require further study. The objective of this research was to characterize chain-assembly of xylan into nanoparticles with potential use in bioplastic films. The crystalization of two xylan-based polysaccharides were investigated based on their distinct structural features. The sources of the xylans were esparto grass and birch wood, with each material further fractionated into water soluble and water insoluble fractions. Under controlled conditions, certain xylans crystallized into hexagonal lattices. Crystals were proven to be durable when sonicated and their thermal stability were compared to amorphous xylan. Crystal dimensions were determined using x-ray powder diffraction. Peak-Force Quantitative Nanoscale Atomic Force microscopy and transmission electron microscopy characterized their mechanical properties and further measurements were made to determine size and size distributions of the samples. Xylan nanotiles were then mixed into films using chitosan and amorphous xylan as the matrix. The resulting films were investigated for their tensile properties, water vapour transmission rate, and swelling in water. This work presents a novel nanomaterial - xylan nanotiles - with potential applications in the plastics industry. Using renewable materials such as xylan in plastics holds great economic promise for the emerging bioeconomy and could reduce dependence on petroleum.

Insights into hemicellulose-cellulose interactions from thermochemical pretreatment of model composite materials

Riddhi Shah1, rnah10@vols.utk.edu, Daisuke Sawada2, Barbara Evans3, Sai Venkatesh Pingali1, Brian H. Davison1, Hugh M. O’Neill1. (1) Oak Ridge Natl Lab, Knoxville, Tennessee, United States (2) Biology and Soft Matter Division, Oak Ridge Natl Lab, Oak Ridge, Tennessee, United States (3) Energy Science and Engineering, University of Tennessee, Knoxville, Oak Ridge, Tennessee, United States (4) Chemical Engineering, Aalto University, Helsinki, Finland (5) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Thermochemical pretreatment of biomass results in structural reorganization of cell wall polymers that help in breaking down the cell wall. However, the impact of pretreatment on biomass is not fully understood due to the variable cell wall composition and multifaceted interaction between polymers and solvents. Model systems that mimic cell wall polymers potentially can help in understanding polymer-polymer interactions.

In this study, model hemicellulose-cellulose composites were prepared by synthesizing bacterial cellulose in presence of glucosamnan or xyloglucan dissolved in the growth media. Small-angle neutron scattering (SANS) was used to study structural changes in the composites as a result of dilute acid pretreatment (DAP). By growing deuterium labeled cellulose in the presence of hydrogenated hemicellulose it was possible to deconvolute the scattering signatures of the two components. No significant change in the crystallinity and glucon chain packing was observed in the DAP cellulose by X-ray diffraction (XRD). However, at the nanoscale, DAP cellulose showed a collapse in structure as indicated by a decrease in R_h from 250A to 130 A and a change of power law exponent (γ) from 2.77 to 3.13. This was interpreted as expulsion of water from the space between microfibris resulting in formation of a tightly packed macrofibril. In addition, the cellulose network after DAP show less entanglement than in the untreated cellulose.
Addition of xyloglucan (XG) decreased cellulose crystallinity in the composite material and altered the glucan chain packing in the microfibrils as determined by analysis of the XRD pattern. After removal of the XG by DAP, the nanoscale cellulose structure showed minimal change but the crystallinity increased. On the other hand, in composites formed using guaianolide (GM) the structural changes that occurred due to DAP were similar to the cellulose only samples. However, the cellulose network of the pretreated composite was more entangled (on 2.8%) than the cellulose only counterpart (on 2.2).

Our results show that XG and GM interact with the cellulose network differently. XG directly interacts with the microfibrils that comprise the microfibrils, while GM only interacts at the surface of the microfibrils. This study provides insight into cellulose-carbohydrate interactions and may help in developing better extraction processes for cell wall polymers.

**CELL 323**

Solubility and adsorption of different xyloglucan fractions to model surfaces

Saina Kishani1,2, sainakf@kth.se, Jakob Wohletz4, Francisco Vilaplana2, Lars Wegberg2, (1) Fiber and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Glycoscience, KTH Royal Institute of Technology, Stockholm, Sweden (3) Wallenberg Wood Science Center, Stockholm, Sweden (4) KTH Royal Institute of Technology, Stockholm, Sweden

A fundamental knowledge of the factors controlling the solubility of biopolymers in solutions is essential in order to provide a basis for the different types of composites. Xyloglucans extracted from Tamarind seeds are a group of neutral biopolymers that have been used as a food thickener and also shown big promise as an additive in papermaking. In order to clarify the interaction between these biopolymers and different model surfaces, it was essential to initially investigate the solubility behavior of a range of xyloglucan fractions with different molar masses. This was conducted by determining the size and molar mass of the different fractions by Dynamic Light Scattering (DLS) at different temperatures and concentrations, and Size Exclusion Chromatography (SEC), respectively. A detailed analysis of both molecular size and molar mass distributions shows that the solubility is significantly influenced by the molar mass, the temperature, and the concentration. The results show that the solubility of the selected biopolymer decreases by an increase in concentration and molar mass. On the other hand, the solubility increases with the temperature in the range between 30 and 40 °C. As the solubility decreases the xyloglucan polymers are associated into larger clusters and the morphology and size of these have been further investigated using Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). These results are in agreement with the size measured by DLS. Following these solubility studies, the adsorption behavior of the selected xyloglucan fractions onto model surfaces was investigated both using quartz crystal microbalance investigations (QCM) and molecular dynamic simulation. By combining the results from the solubility studies and the adsorption investigations it was possible to estimate how the change in solubility of the polymer influenced the adsorption of the polymer and to compare this effect to the enthalpy and entropy change upon adsorption of the polymer at the cellulosewater interface.

Lignin: From Fundamentals to New Materials & Applications

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Against all odds: Carbon nanofibers from unmodified low molecular weight lignin fractions

Reza Ebrahim Majdar1, Heiko Lange2, heiko.lange@unimana2.it, Francesco Basoli1, Marcella Trombetta1, Claudia Creatini1, (1) Department of Chemical Sciences and Technologies, University of Rome ‘Tor Vergata’, Rome, Italy (2) Departmental Faculty of Engineering, Campus Bio-Medico University of Rome, Rome, Italy (3) Department of Pulp and Paper Engineering, Gorgan University of Agricultural Sciences and Natural Resources, Teheran, Iran (the Islamic Republic of)

Despite the prevailing general idea that manufacturing lignin-based carbon fibres via an electrospinning process requires high molecular weight lignin or lignin fractions, carbon nanofibers from low molecular weight lignin have been realized, without addition of any supportive high molecular weight polymer. Two technical lignins, namely softwood kraft lignin and wheat straw organosolv lignin were fractionated by a single-step solvent extraction. Parent lignins and resulting fractions were thoroughly characterized by means of GPC, FT-IR, quantitative 13C NMR, H, O, S, DSC and TGA. Using optimized spinning solutions and electrospinning process parameters, lignin fibres from lower molecular weight fractions were realised. Uniform and bead-free fibres in both random and aligned mode were confirmed by SEM analyses. Various regimes were further performed for well-defined thermostabilised and carbonised fibres. Structural, thermal and morphological properties of the starting lignins and derived carbon fibres were determined. The accumulated results of this research effort suggest eventually a set of rationales, on the basis of which the proposal of suitable lignins for carbon nanofiber formation could be based.

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Ultrathin nanofibrous lignin aerogels with outstanding shape-recovery properties

Mi-Jung Cho, jomi9612@gmail.com, Muzaffer Karaaslan, Han Wang, Scott Rennecker, Department of Wood Science, University of British Columbia, Vancouver, British Columbia, Canada

Many natural materials are noted to be lightweight, tough and resilient. Nano- and micro-scale fibers are a common structural motif found in many of these systems that give rise to interesting properties. Electrospun fibers have great potential to become innovative fibrous material products that mimic aspects of natural materials. Lignin-based nanofiber mats composed of 99 wt.% softwood kraft lignin were transformed into three dimensional (3D) fibrous aerogels with a novel method without using toxic reagents. In addition, the effects of incorporating nanocrystalline cellulose (NCC) on the properties of aerogels were investigated. The resulting ultrathin aerogels were composed of a network of short nanofibers and showed outstanding shape recovery properties. Further, we report the compressive elasticity of the lignin aerogels as a function of fiber diameter, NCC loading, and thermal heat treatment. This work portrays a novel method to form lignin-based materials fabricated through electrospinning by exploiting the inherent thermal stability of lignin.

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Carbon fibers made from cellulose-lignin hybrid filaments

Michael Hummel1, michael.hummel@aalto.fi, Mikaela Tregren2, Daisuke Sawada3, Herbert Siirola4, Holme Bjørn1, (1) Aalto University, Espoo, Finland (2) Forest Products Technology, Aalto University, Espoo, Finland (3) Deakin University, Geelong, Victoria, Australia

A global stride to increase fuel efficiency and reduce emissions has led to a steep increase in the use of carbon fibre composites. The outstanding weight-to-strength ratio of carbon fibres (CFs) allows for the production of high-performance lightweight composite material as substitute for heavy metal structural parts. However, the prevailing high costs of PAN-derived CFs prevent their widespread use in high-volume applications. Cellulose and lignin have both been considered as raw material for CF-production since the early days of CF research. Inferior mechanical properties of the first generation bio-derived CFs led to the discontinuation of attempts to use bio-derived precursor materials. Driven by the emergence of new technologies and a better understanding of biomass processing, research on bio-based carbon fibers has experienced a renaissance during the past decade. Most studies have focused on either cellulose or lignin. Herein, we report on the preparation of cellulose and lignin hybrid fibers and their potential as CF precursor. It was found that the bi-component matrix shows an altered stabilization and carbonization behavior, resulting in a higher carbon yield and better mechanical properties. The pyrolysis mechanism was studied through thermogravimetric analyses coupled with FTIR spectroscopic analyses of the gas phase and revealed synergistic effects. The filaments were then carbonized both in a stationary and continuous manner and the resulting properties were assessed.

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Dry-jet wet-spin lignin-based carbon fibre precursors: Phenomena and properties

Jenny Bengtsson1,2, jenny.bengtsson@swerea.se, Kerstin Jedver2, Tobias Köhnke1, Hans Trefry1, (1) Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden (2) Biobased fibres, Swerea IVF, Malmö, Sweden

To be able to meet regulations regarding fuel economy for cars, the automotive industry is searching for new lightweight materials. One opportunity is high strength, carbon fibre reinforced
Electrochemical conversion of Kraft-lignin to valuable products

Siegfried R. Waldvogel, waldvogel@uni-mainz.de, Michael Zirnes. Johannes Gutenberg University Mainz, Mainz, Germany

In the past century, petroleum became the primary feedstock for the industrial production of organic chemicals. The use of fossil raw materials is nowadays questionable due to the increasing environmental awareness in society and the guiding principle of "sustainable development" to which the chemical industry commits itself. Biomass seems to be a promising alternative as renewable and sustainable source for fuels and chemicals. Furthermore, organic electrochemistry is an ecological and powerful approach. Kraft lignin is a waste product from the dominating Kraft pulping process for cellulose production. The polyphenolic structure qualifies it as a potential sustainable feedstock for aromatic fine chemicals. Due to the inertness and degradation robustness of the Kraft lignin it is currently only inerminated for energy recovery. We investigated an electrochemical method for the highly selective production of the aromatic fine chemical vanillin form Kraft lignin. Thereby, the anodic degradation takes place at activated NiP-foil electrodes and the electrolysis was optimized for temperatures below 100°C. Moreover, we present an easy protocol for adsorption and selective desorption of low weight phenolic compounds from black liquor (waste stream from the Kraft pulping process). Employing ion exchange resins gave rise to a selective removal of low molecular weight phenols from the strongly alkaline electrolyte without acidification and precipitation of remaining lignin. The depeled black liquor was also electrochemically treated to breakdown the containing lignin and to maximize the yield of vanillin.

Lignin degradation using recyclable formate ionic liquids and microwave

Jinhua Dai, daijinhua@gmail.com, Antonio Patti, Kei Saito. School of Chemistry, Monash University, Clayton, Victoria, Australia

Lignin has been widely studied as a sustainable source of renewable materials, particularly aromatic feedstock chemicals, which are in great and increasing need in the world. Lignin oxidation and depolymerisation presents a promising approach to produce functionalized phenolic products. In this work, two novel pathways of oxidative degradation of lignin have been investigated. The first strategy is that oxidize lignin with copper acetate, which was then depolymerised by a formate ionic liquid resulting in ethyl acetate soluble and also water-soluble depolymerised lignin products. The β-O-4 bonds in lignin were oxidized and then depolymerised by aqueous ionic liquid, 2-hydroxy ethylammonium formate, at the temperature of 110°C for 24 hours. 2-Hydroxy ethylammonium formate, which could dissolve lignin acting as a solvent, was found to also catalyse the depolymerisation of the oxidised lignin. The second strategy is using copper acetate as a catalyst to proceed the oxidative depolymerisation with the assistant of microwave. Lignin was successfully depolymerised in these two methods and depolymerised products were also characterised.

Oxidized lignin was depolymerised by a recyclable formate ionic liquids. Another strategy is using copper sulfate and hydrogen peroxide to depolymerise lignin under the irradiation of microwave.

Aerobic vanadium catalysis for lignin valorization: A bottom-up approach

G Licini, giulia.licini@unipd.it. Chemical Sciences, University of Padova, Padova, Italy

Lignocellulosic biomass is an important renewable feedstock for the production of chemicals, fuels and energy. With its unique structure, lignin can be regarded as the major aromatic resource of the bio-based economy and, therefore, a wide variety of aromatic compounds may result from its efficient valorization. However, due to its complex nature, inert resistance to chemical reactivity and the lack of suitable conversion technologies, selective lignin depolymerization to value-added products still remains a challenge. In particular, the development of robust catalysts that selectively target C-C bonds cleavage in lignin structure can be a key in overcoming the problem. Here we will report on how vanadium(V) amino triphenolate complexes (TPAs-V) are good candidates to achieve such ambitious goals in a very active and selective manner under rather mild reaction conditions (Figure 1).

Specifically, the reactivity of these complexes under catalytic aerobic conditions with different classes of lignin model substrates such as diols, 1,2-hydroxyethers and more complex lignin substructures will be presented, together with preliminary experiments with lignin samples. In particular we will report on reactions carried out in a semi-continuous stirred glass autoclave reactor at 4 atm air pressure (flow rate 150 mL/min) which allowed to decreases, in the case of 1,2-diols, the catalyst loading down to 0.001 mol% reaching TOFs ≤ 71000 and TOFs up to 4200 h⁻¹. Experimental evidence and DFT calculations for the elucidation on the reaction mechanism will be presented as well as preliminary experiments related to the aerobic C-C bond cleavage of 1,2-diols in aqueous medium in the presence of surfactants.
The interest for cellulose nanocrystals and nanofibrils is exponentially increased since last decade thanks to their industrialization. In addition to their low density, high aspect ratio, high stiffness and Young's modulus and chemically reactive surface, this material is well known for its specific high surface. Thanks to these particular properties, cellulose nanomaterials can be used within a wide variety of applications. Coating is one of the promising applications for nanocellulose mainly for barrier applications in packaging. Indeed new bio-based but also high performance solutions are expected in food packaging. Unfortunately, up to now, high barrier solutions can be provided but they always require a layer of thermosealing polymer which is usually fossil based. These multilayer materials are also more complicate to handle when end of life is considered. One solution would be to propose cellulose materials which could be welded easily. Except thermosealing, ultrasounds welding have been developed in plastic industry last years. This study is a proof of concept that nanocellulosic materials can be welded by ultrasounds. Several nanocellulosic materials were firstly designed and characterized, i.e. from classic cellulose nanocrystals and nanofibrils to functionalized CNC by esterification with lauric acid. Then model films were prepared and characterized by ultrasounds. Process parameters were optimized; the successful welding were obtained and mechanically characterized. These very positive results have been patented and open the door for new solutions in welding of biobased materials.

Cellulose nanofibers from elephant manure

The interest in cellulose fibers, in particular micro- or nanofibrillated cellulose, utilized in paper and composite materials as alternative to conventional fibre materials, has recently grown significantly. Thereby, particularly in countries without access to large forest areas, an alternative to wood as raw material for natural fibres is highly desirable. In order to promote an environmentally sustainable, widely available and cheap raw material, elephant manure was proposed as potential source. As elephants digest only 30 to 40% of their diet, their manure contains large quantities of fibrous cellulose material. In addition, the mechanical, acidic and enzymatic pre-treatment during ingestation and digestion, respectively, reduced its thickness. This makes it a very attractive candidate for the use as precursor for the production of micro- or even nanofibrillated cellulose. Nanocelluloses are commonly prepared by mechanical disintegration of plant material, optionally with chemical pretreatment, thus requiring a lot of energy and chemicals during the fibillation process. Therefore, utilizing the elephant as the first-stage bioresource for the delignification of cellulose fibers by mechanical and chemical means would constitute an energy-efficient approach.

We demonstrate that by chemical purification of elephant manure, microfibrillated cellulose with controllable properties can be isolated. The fibers were characterized regarding their cellulose content and physico-chemical properties in order to optimize the extraction process. Optimized fibers were initially used for the preparation of papers that were characterized regarding their physico-chemical and mechanical properties and served as reference material. Moreover, the fibers were further mechanically refined and papers produced from these refined elephant manure nanofibrils that were compared to the non-refined elephant manure papers and cellulose nanofibers.

Thermal and electrical properties of TEMPO-oxidized nanocellulose films with quaternary alkylammonium carboxylates

Self-standing films of fibrillated cellulose microfibrils, or nanofibrils show high transparency, high strength and low thermal expansions. Therefore, the nanocelluloses films are promising materials for the substrates of electric devices, and then thermal and electric properties of nanocellulose films have been recently explored to apply in the fields of electronics. It has been reported that the nanocellulose films and aerogels show the low thermal conductivity. According to the previous reports, the organized structures of nanocellulose films or aerogels have a great influence on their thermal conductivity. The nanocellulose films also have low electric conductivity. When the nanocellulose films are modified with highly conductive materials, the optical transparency and mechanical strengths of the films would be reduced. Therefore, there is still a need to control the thermal and electric properties of the nanocellulose films without changing their high transparency and high strengths. Nanofibrils with ~3 nm widths can be prepared through the TEMPO-mediated oxidation system. TEMPO-oxidized nanocelluloses can be dispersed in water as individual nanofibrils due to the densely introduced carbohydrate groups on their surfaces. The films prepared from the water dispersions of TEMPO-oxidized nanocelluloses show high transparency, high strengths and high barrier properties. The carbonyl groups of the TEMPO-oxidized nanocelluloses provide places to modify the nanocellulose surfaces. Moreover, counter-ions of the carbonyl groups can be simply changed to various ions. The dispersibility of the TEMPO-oxidized nanocelluloses in solvents and material properties of their films can be controlled by the counter-ions of the carbonyls of the TEMPO-oxidized nanocelluloses. In our previous study, TEMPO-oxidized nanocelluloses with quaternary alkylammonium (QA) carboxylates showed high transparency and high strength. Moreover, TEMPO-oxidized nanocelluloses can be modified with high polar materials. The strong polar interactions of the hydrogen bonds between the QA carboxylates and cellulose hydroxyls (C=O and/or O−H) were characterized. The results were related to the film structures and interfacial interactions between nanocelluloses using X-ray diffraction measurements and the solid-state 13C cross-polarization/magic-angle spinning nuclear magnetic resonance analysis of the films.

Poly saccharide film as a ductile substrate for gas phase treatment

Self-standing films from polysaccharides are one current topic of interests in the cellulose community. Films out of cellulose fibrils have a propitious promise of strength, flexibility and resistance towards gas permeation whereas films made from cellulose nanofibril subunits, cellulose nanocrystals, exhibit organization leading to intense chiral nematic phases, and breathtaking visual effects. There is a need for facile surface treatment of modern polysaccharide films for majority of applications including shielding, sensing, packaging. Here we discuss a case of gas phase treatment of a self-standing film of cellulose fibrils. First of all, the fibrils were oxidized with periodate ion to modify their surface chemistry and induce film formation. The ductile film was then exposed to gas phase modification to alter the chemistry of the film surface. Due to the dense structure the films exhibited restricted gas permeation. This was utilized for creating a Janus-type film with two functionalities. Using the selfstanding film enabled to perform otherwise degradative post treatments without negatively affecting the film physical properties. Applications for such films and possibilities of gas phase treatment of polysaccharide films will be discussed.
We have shown that the nature of the molecular chain orientation (induced by injection processing), as seen in the graph, and the polymer-plasticizer miscibility are keys for controlling ultimate properties and the studied hardening regime.

Finally, in order to study their damage mechanisms, these plasticized polymers are tested in fatigue at different stress level. Following a well-improved strategy [6], characterizations by X-ray scattering, electronic microscopy and tomography enabled us to study their fatigue damage from nanometric scale to the micronic scale.

Graph 1 Effect of the orientation on strain hardening regime in CDA+30%TA under tensile testing

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Novel method for producing formable low-density materials from self-assembled cellulose nanofibrils

Hugo S. Françon1, francon@kth.se, Johan Erlendsson2, Verónica López Durán1, Hjalmar Granberg1, Lars Wagberg1. (1) KTH Fibre Polymer Techn, Stockholm, Sweden (2) RISE Bioeconomy, Stockholm, Sweden

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. However, aerogel preparation procedures often rely on freeze-drying, which is an evident obstacle to an up-scaling of the aerogel manufacturing.

In the present work, we have developed a so-called freeze-linking method where wet resilient aerogels can be prepared by a simple freezing step. By applying this method along with a simple casting procedure using 3D-printed moulds, CNF-based aerogels can be freely shaped and designed. We have demonstrated a large variety of unique shapes by using these specially designed 3D printed molds, as shown in figure 1. These 3D wet resilient aerogels also showed subsequent well-forming ability and shape recovery behavior, thus enabling even more complex forming methods.

The intrinsic properties of such aerogels, along with their ease of production, could make them suitable for wide application areas. Following this approach, three distinct potential applications were studied. First, structural materials were produced by making low density and stiff core-shell biocomposites. Then, these aerogels were used as cell growth substrates to demonstrate their potential as templates for tissue engineering. Finally, electrochemical devices were produced using the unique combination of formability, adsorption and wet-stability of the material.

Figure 1: Nanocellulose aerogels of different shapes obtained with the freeze-linking method.

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Nano-FTIR spectroscopy: Nanoscale resolved infrared spectroscopy of individual CNC fibers and thin films

Tobias Gokus, tobias.gokus@neaspec.com, Philip Schäfer. neaspec GmbH, Martinsried, Bayern, Germany

Nano-FTIR is an emerging new optical super resolution microscopy technique that enables IR spectroscopy and chemical mapping with 20 nm spatial resolution. Nano-FTIR employs an externally IR-illuminated metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically tip-scattered light simultaneous to AFM imaging yields nanoscale resolved near-field images. Utilizing broadband laser sources like a mid-IR supercontinuum laser for tip illumination and interferometric light detection analogous to classical FTIR spectroscopy, enables near-field spectroscopic measurements with nanometer scale spatial resolution. Recently, nanoscale chemical characterization of multicomponent thin film polymer blends and probing of secondary structure in individual protein fibrils have been successfully demonstrated.

Here we demonstrate for the first time nano-FTIR spectroscopy and nanoscaled resolved infrared mapping of a thin crystalline cellulose nanofibers (CNC) film and individual fibers. Nano-FTIR spectra are reproducible and are in good agreement with conventional FTIR spectra from similar materials. Remarkably, the nano-FTIR reveal distinct difference between single fiber spectra and the film spectra. The ratio between the group of bands in the 1100-1150 cm⁻¹ spectral range (C-O, C-C backbone) and the group of 1300-1400 cm⁻¹ bands is about 3 times larger for the film spectra compared to the fiber spectra. This observation can be explained in terms of the intrinsic polarization selectivity and thus molecular orientation sensitivity of nano-FTIR.

a) AFM topography image of CNC fibers deposited on a silicon substrate b) Simultaneously recorded infrared near-field image (integrated intensity) of the same sample as in Fig. 1. a) Nano-FTIR spectra recorded on individual nanofibers and at a location on the CNC film marked in a).

Nano-FTIR spectroscopy reveals characteristic absorption bands of nanocellulose in the fingerprint region between 800-1400 cm⁻¹.

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

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Colloidal behavior of aqueous dispersions of cellulose nanofibrils

Malin Nordenstrom1, nordenst@kth.se, Lars Wagberg1. (1) KTH Fibre Polymer Techn, Stockholm, Sweden (2) KTH Royal Institute of Technology, Stockholm, Sweden

Cellulose nanofibrils (CNF) have been given extensive attention as reinforcing agents in biocomposites because of their outstanding mechanical properties. In order to maximize the benefit of the inherent properties of CNF it is important to achieve a good dispersion and distribution of the CNF in the composite. This is not a trivial task due to the complicated phase behavior of CNF. Nanocellulose-based materials are commonly formed from aqueous dispersions and the colloidal stability of the particles is highly sensitive to changes in the particle concentration or the chemical environment. Depending on the concentration of CNF, the loss of colloidal stability can lead either to a chaotic particle aggregation or to the formation of a non-flowing volume-spanning arrested state. A chaotic aggregation must naturally be avoided in the material preparation. In order to optimize the processes involved in preparing CNF materials it is hence crucial to understand the colloidal behavior of the particles. The colloidal interactions in highly charged CNF dispersions cannot be explained by the classical DLVO theory and therefore it is necessary to develop new models that can fully describe their colloidal behavior.

In our work we study the colloidal behavior of CNF upon changes in particle concentration and chemical environment, and how it changes with the surface charge density, the type of surface charge and the aspect ratio of the particles. We also put substantial focus on understanding how
the colloidal interactions in CNF systems are affected by the choice of counterion to the charges of CNF, by studying the effect on colloidal behavior when changing counterion valency or size. This is achieved by measuring the interaction forces between CNF-coated surfaces immersed in different salt solutions, using colloidal probe AFM. The goal is to use the results obtained in the experiments to formulate new models for describing the colloidal properties of CNF.

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Imparting moisture resistance to transparent nematic i-CNF aerogels by scCO$_2$-antisolvent coating of the interior with ultrathin PMMA layers

Sven Piapprat$^a$, Sakeena Quraishi$^b$, Jean-Marie Nedelec$^b$, Johannes Konnerth$^c$, Harald Renhof$^d$, Helga Lichtenegger$^e$, Falk Wolfgang Liebner$^f$, Falk Liebner@boku.ac.at. (1) Division of Chemistry of Renewable Resources, Boku University Vienna, Tulln an der Donau, Austria (2) Division of Chemistry of Renewable Resources, BOKU University Vienna, Tulln an der Donau, Austria (3) Division of Chemistry of Renewable Resources, BOKU University Vienna, Tulln an der Donau, Austria (4) Institute of Wood Technology and Renewable Resources, BOKU University Vienna, Tulln an der Donau, Austria (5) Institute of Physics and Materials Science, BOKU University Vienna, Vienna, Austria (7) CNFS, Sigma-Clement, ICFG, Universite Clement-Auvergne, Clermont-Austria

A facile approach for adding moisture resistance to transparent nematic aerogels composed of individualized cellulose nanofibrils (i-CNF) at full preservation of the anisotropic aerogel structure is presented. Sequential nitroxy-mediated oxidation and mechanical cellulose fiber delamination was applied to obtain i-CNF dispersions in water. Nematic ordering caused by repulsive forces between i-CNF surface carbonyl groups was set by acid-induced hydrogen bonding and gelation, respectively. Solvent exchange to acetone, impregnation with the PMMA, scCO$_2$-mediated anti-solvent precipitation of the secondary polymer and scCO$_2$ extraction of interstitial acetone afforded highly hydrophobic nanocomposite aerogels. Birefringence studies utilizing polarized light and the Michel-Levy Chart to evaluate interference pattern revealed that nematic i-CNF ordering is virtually not affected by the respective surface modification and scCO$_2$ drying steps. Morphological studies provide evidence that the large internal surface (>500 m$^2$ g$^{-1}$) of the hybrid aerogels consists of a homogeneous ultrathin PMMA (mono)layer that does virtually not affect the high porosity (98.9%) and transparency (>77% transmission, 600 nm, 2.13 mm thickness) inherent to i-CNF aerogels. The obtained materials exhibited excellent resistance towards moisture as apparent from the high water content angle (119.4° ± 7.5°). As PMMA imparts the aerogels stiffness and hydrophobicity, aggregation of nanofibrils in moist environment or under vacuum conditions can be avoided even at ultra-low densities as low as 9.6 mg cm$^{-3}$.

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Formulation and composition effects in phase transitions of emulsions stabilized by cellulose nanofibrils and an ionic surfactant

Sgli Huan$^1$, Shingo Yokot$^a$, Long Bai$^1$, Marko Ago$^1$, Maryam Borghi$^1$, Tetsuo Kondo$^2$, Orlando Rojas$^3$, orlando.rojas@aalto.fi. (1) Bioproducts and biobioystems, Aalto University, Espoo, Finland (2) Kyushu University, Fukuoka, Japan (3) Applied Physics, Aalto University, Espoo, Finland

Cellulose nanofibrils (CNF) offer great prospects as a natural stabilizer of colloidal dispersions and complex fluids for multiple applications. In this study, emulsions can be successfully obtained by blending oil and aqueous phases in the presence of an ionic surfactant and a bio-based co-stabilizer. Sodium dodecyl sulfate, SDS, was used as emulsifier of oil-in-water, bi-continuous and water-in-oil emulsions that were further co-stabilized by addition of CNF. Two types of morphologies were investigated by using CNF derived from microfluidization and aqueous counter-ion co-solation processes, which revealed some subtle differences in interfacial activity. The adsorption properties of SDS in both, CNF dispersions and emulsions, as well as the influence of composition (CNF and SDS concentration) and formulation (ionic strength, oil and CNF types) on the phase behavior were elucidated and described in the framework of Winsor systems. Results have demonstrated that the function of CNF in stabilizing oil droplets originates from the synergistic effect of long fibrous chains, negative surface charge and the network-like structure. The phase transition behavior was mainly controlled by salinity. At low salinity, the phase transition of emulsions containing CNF and SDS at low concentrations was controlled by molecular transfer in the oil-in-water system. Irregular droplets and bi-continuous morphologies were observed at medium and high salinity for systems containing high CNF and SDS concentrations. Water-in-oil emulsions were only possible at high salinity and SDS concentrations in the presence of small amounts of CNF. The control of emulsion morphology and stability by addition of CNF opens the possibility to develop environmentally-friendly multiple phase systems that display high stability and respond to ionic strength following the expectations of classical emulsion systems.

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Cellulose nanofibrils in ice cream: An analysis of its influence in the matrix structure

Jorge A. Velasquez$^1$, jorgeandres.velasquez@alfa.upb.edu.co, Catalina Gomez Hoyos$^2$, Valeria Escovar$^1$, Ana Maria Hernández$^1$, Diego Takahashi$^1$, Robin Zuluaga Gallego$^1$, (1) Chemical engineering, Universidad Pontificia Bolivariana, Medellín, Colombia (2) Facultad de Ingeniería Agrícola, Universidad Pontificia Bolivariana, Medellín, Antioquia, Colombia (3) Programa de ingeniería en nanotecnología, Universidad Pontificia Bolivariana, Medellín, Antioquia, Colombia (4) Department of Food Science, University of Guelph, Guelph, Ontario, Canada (5) Facultad de Ingeniería Textil, Universidad Pontificia Bolivariana, Medellín, Antioquia, Colombia

Deconstruction of the hierarchical structure of plant-derived cellulose yields cellulose nanofibrils (CNFs), known for its fascinating properties, such as a viscosity in the order of 10$^2$ Pa.s for 5.9 wt.% suspensions, hydrophilic nature and an ability to form enlarget networks. Coupled to its character as an insoluble fiber, CNFs become an interesting alternative for its use in the food industry. Different studies have indicated its potential use in pastry dough, hamburgers and ice creams, among other products. Its application in the ice cream industry is interesting as this product loses its quality due to fluctuating storage temperatures and ice crystal growth; this effect is more critical in low-fat formulations, which are not supported by a fat network. CNFs have been used to decrease the melting rate of ice cream formulations without affecting its texture, although the mechanism of action has not been studied yet. The present work attempts to explain the influence of unmodified CNFs from banana bunches in the structure of ice cream and its correlation to the physical and sensory properties of the final product. To this end, different formulations were studied with fat contents of 5 and 10 wt.%, and CNFs concentrations of 0.15 and 0.3 wt.%. Samples were evaluated for their rheological, thermal and structural properties. Results indicate that CNFs kinetically stabilized the ice cream structure without modifying ice crystal growth, decreased melting rates of the 10 wt.% fat formulation and improved the textural sensation in the 5 wt.% sample. This suggested that CNFs affect the colloidal network structure of ice cream, while showing little influence on the aqueous phase.

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Use of cellulose nanofibrils as replacement of xanthan gum in water based drilling fluids for Argentina shale

Yurany A. Villada Villeda$^1$, Maria Celeste Iglesias$^2$, Natalia Hazi$^3$, Marisa Soledad Pernier$^4$, Eleonora Erdtmann$^5$, Diana Estenoz$^6$, destenoz@santafe-conicet.gov.ar. (1) INTEC (UNL-CONICET), Santa Fe, Argentina (2) Auburn University, Auburn, Alabama, United States (3) INTEC (Instituto de Desarrollo Tecnológico para la Industria Química), Santa Fe, Santa Fe, Argentina (4) Universidad Nacional del Litoral, Santa Fe, Santa Fe, Argentina (5) ITBA (Instituto Tecnológico de Buenos Aires), Santa Fe, Santa Fe, Argentina

Drilling fluids play critical role in oil and gas drilling operations, such as cleaning and stabilizing of well, suspending and carrying out cuttings, reducing friction between formation and drilling tools, among others. Successful drilling operations are highly dependent on the selection of fluids with pre-specified properties, which are mainly determined by their rheological and filtration properties. On the basis of the composition, fluids are classified in two groups: water-based muds (WBM), and oil-based muds (OBM). OBMs exhibit high performance but present some disadvantages related to the environmental impact, cost and negative effects on cementing. From an environmental point of view, the use of WBM represents an attractive alternative. In recent years, different natural polymers, synthetic polymers and inorganic nanoparticles have been used as additives in WBM to improve rheological and filtration properties. Nowadays, there is an increasing interest in designing new formulations for WBM using additives from renewable and biodegradable sources. In this sense, the use of cellulose nanofibrils (CNF) is a promising alternative. CNF is obtained from different resources, such as wood, plants, marine animals, algae and bacteria and processed by using only mechanical treatments or combining mechanical treatments with enzymatical or chemical pre-treatments. In this work the use of cellulose without lignin (CNF-1) and cellulose with lignin (CNF-2) as...
replacement of xantham gum (XGO) in WBMs for Argentina shale was studied. The effect of the CNFs concentration on the rheological properties was analyzed. The rheometric characterization of the fluids was complemented with the structural analysis and rheological model.

A shear-thinning behavior with notable effect on the concentration of CNFs was observed. Also, mud rheological properties very close to the base mud were achieved for composition of PAC = 8.00 g/l and CNF = 3.00 g/l. Structural changes were assessed by SEM and a high particle agglomeration and a film formation due to the presence of CNF were observed. Additionally, results indicated that CNF1 exhibited more viscosifying characteristics in WBMs, and CNF2 improved filtration properties. The Sisko model was used to determine rheological parameters.

CELL 345

Nano-cellulose from wood residues for water-based polymer reinforcement

George Cheng1, jcp0007@auburn.edu, Brian Va1, Liang Wei2, Nicole Stark2, (1) Auburn University, Auburn, Alabama, United States (2) USDA Forest Service Forest Products Laboratory, Madison, Wisconsin, United States

Cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs) were isolated from wood residues including wood dust and wood pulp fibers from small diameter logs by mechanical and chemical processes, respectively. Both CNF and CNC were used to reinforce water-based polymers, including poly(vinyl alcohol) (PVA) and polyethylene oxide (PEO) in this study. The cellulose nanocomposites were prepared using film casting method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis, and tensile testing were used to investigate the water absorption and its nanocomposites. Most CNF composites had higher strength and modulus than those of CNC composites. Significant differences of thermal behavior were observed according to the amount of nanocellulose used as reinforcement. These nanocomposites can be used for medical, packaging and other applications, which could be benefit for both forest products and packaging industries.

CELL 346

Antibacterial membranes based on N-halamine/quaternary ammonium salts modified nano-crystalline cellulose

Xuehong Ren1, xuehong@hotmail.com, Ying Liu1, Yan Zhang2, Tung-Shi Huang3, (1) College of Textile and Clothing, Jiangnan University, Wuxi Jiangsu, China (2) Auburn University, Auburn, Alabama, United States

Nano-crystalline cellulose (NCC) has generated much attention recently and has great potential in many applications due to its availability, high specific surface area, biodegradability, biocompatibility and reproducibility. While, many studies have shown that NCC is able to serve as film reinforcement and has been incorporated into cellulose acetate, polyurethane, polyvinyl alcohol, and poly (lactic acid) matrices to prepare composite membranes. Few research has been performed on the functional modifications of NCC prior to forming composites. In this study, noncyclic N-halamine precursor, cyclic N-halamine precursor, and quaternary ammonium salts with different chain lengths were used to chemically modify NCC particles, and the modified NCC particles were incorporated into CA film, CS/PVA composite film, and chitosan film, respectively. In the antibacterial efficacy test, the results showed that all these three types of films demonstrated good biocidal property. The mechanical, thermal, and cytocompatibility of the composite films were also evaluated. The bio-based nanocomposite films with good antibacterial properties could have potential applications in packaging materials.

CELL 347

Environmental benign and salt-free reactive dying of cellulose using a cottonseed oil/water system to achieve high dye fixation

Bingnan Mu1, bingnan.mu@huskers.unl.edu, Heian Xu1, Yi’ji Yang2, (1) UNL Dept of Biological Sys Eng, Lincoln, Nebraska, United States (2) University of Nebraska-Lincoln, Lincoln, Nebraska, United States (3) Jiangnan University, Wuxi, China

A cottonseed oil/water system for low-dye reactive dying of cotton with higher dye fixation than and as good dyeing quality as conventional aqueous dyeing. Conventional aqueous reactive dying of cotton suffers low dye fixation and generates large quantities of wastewater containing high concentrations of hydrolyzed dyes and salts. Some new reactive dying methods, like dyeings with cellulose nanocrystals, supercritical CO2, and all-organic solvents, could not get complete success due to some limitations such as light shade, low potential for commercialization and environmental pollution. This cottonseed oil/water dying system uses a large portion of biodegradable cottonseed oil to disperse reactive dyes, and a small portion of water to swell cotton and fix dyes with alkali. In this system, % exhaustion of dye was 100%, and % fixation of dye was 92%. Resultantly, discharges of dyes and salts from the cottonseed oil/water system were decreased by 85% and 97%, respectively, comparing to that from the conventional aqueous system. More than 99.5% of property, The mechanical strength, thermal stability, and in vitro cytocompatibility of the composite films were also evaluated. The bio-based nanocomposite films with good antibacterial properties could have potential applications in packaging materials.

CELL 348

Biobased Gels & Porous Materials

Martin Gercke1, martin.gercke@uni-jena.de, Markus Wüster2, Astrid Enkelmann1, Gerlinde Schneider3, Margit Schuler3, Thomas J. Heinze1, (1) Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University of Jena, Jena, Germany (2) Department of Natural Sciences, Bonn-Rhein-Sieg University of Applied Sciences, Rheinbach, Germany (3) Department of Otolaryngology, Laboratory for Biomaterials, University Hospital Jena, Jena, Germany

Hydrogels are highly attractive for biomedical applications such as tissue engineering and drug delivery. Polysaccharide based materials have inherent advantages over synthetic ones such as inherent biocompatibility and facile preparation of the hydrogels by self-assembling. Agarose hydrogels are of particular interest because they are non-cytotoxic and easy to prepare. Key for their use in advanced applications is the functionalization of the materials to tune their physical, chemical, and biological properties. Two approaches towards functional agarose hydrogels are presented: defined chemical derivatization of agarose and formation of composites with inorganic- or polysaccharide based additives.

Different types of novel agarose derivatives were obtained by homogeneous functionalization of agarose. Acido modified agaroses are valuable reactive compounds that can be further functionalized by "click-chemistry". Agarose sulfates are expected to show beneficial biological properties. Both derivatives formed hydrogels depending on the molecular structure that was used. Inorganic hybrid hydrogels were prepared by in situ precipitation of hydroxyapatite within the agarose hydrogel matrix. The chemical composition, morphology, and swelling behavior of these novel materials were evaluated by XRD, SAXS, FTIR spectroscopy, and SEM. The agarose- hydrogels showed improved properties in comparison with pure agarose hydrogels due to the unique mechanical and biological properties. It was possible to facilitate time-released release of drug analogues for receptor ligands that enable differentiation of human adult menenchymal stem cells towards bone formation. Hydrogel nanocomposites were prepared by (i) incorporation of functional polysaccharide based nanoparticles within agarose hydrogels and (ii) in situ self-assembling of polysaccharide derivatives within the porous agarose matrix. The approach is used to tune properties such as hydrophobicity and surface area and to implement functionalities.

Multifunctional hyaluronic acid based hydrogel with enzymatically embedded silverlignin nanoparticles

Silvia Pérez Rafael, silvia.perez-rafael@gmail.com, Kristina Ivanova, Ilayo Stefanov, Tzanko Tzanov. Chemical Engineering, Universitat Politècnica de Catalunya, Terrassa (PC 08222), Barcelona, Spain

Silver nanoparticles (Ag-NPs) have been among the most commonly used nano-materials in our health care system, widely used in a range of biomedical applications, including diagnosis, treatment, drug delivery, medical device coating and for personal health care. Ag-NPs present unique physicochemical properties such as antibacterial, antifungal, antiviral and anti-inflammatory activity. In this matter, bionanocomposites materials, formed by the combination of natural polymers and inorganic components, like hybrid Ag-NPs, represents an important stake in scientific research offering the combined properties inherent to the natural biopolymers and inorganic nanoparticles. Meanwhile, hyaluronic acid (HA), an immunonelutral polysaccharide ubiquitously present in the human body, is an attractive starting materials since can be chemically modified through its reactive functional groups and transformed into many physical forms (viscoelastic solutions, soft or stiff hydrogels or even nanoparticulate fluids) as a biocompatible platform for a wide range of biomedical applications.

Multifunctional hydrogels were enzymatically generated by the crosslinking reaction between silver lignin nanoparticles (Ag-Lig-NPs) and thiolated hyaluronic acid (HA-SH). First, Ag-Lig-NPs were synthesized using a green, eco-friendly procedure from aqueous AgNO3 solution with lignin, one of the most abundant biopolymers in nature, serving as a dual reducing and capping agent. Afterwards, the multiple functional groups present in lignin, mainly phenolic hydroxyls, serve as active groups to crosslink with thiol groups from HA by the action of the enzyme laccase. The morphology, swelling properties, and rheological characteristics of the performed HA hydrogels with embedded Ag-Lig-NPs together with their stability, control over MMP and MPO and cellular ROS scavenging were investigated. Finally, the potential toxicology, the silver release from the
hydrogel matrix, the anti-inflammatory effect and the antibacterial activity in front of different bacterial stains were addressed to explore their potential biomedical applications.

**CELL 350**

Developing renewable and high strength hydrogels by incorporating lignin

Kalavathy Rajan1, khran@jutk.edu, David P. Harper1, Timothy G. Riets1, Danielle Jule Carrier2, Nicole Labbé1, Stephen C. Chimley1, (1) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States (2) BioSci, Engineering & Soil Science, The University of Tennessee, Knoxville, Tennessee, United States

Synthesizing lignin-based copolymers would valorize a major co-product stream from pulp mills and bio-refineries, as well as reduce the dependence on petrochemicals-based consumer goods. In this study, we used organosolv lignin (OSL) isolated from hybrid poplar (Populus trichocarpa x P. deltoides) to generate lignin-containing methacrylate hydrogels. The copolymer hydrogels were synthesized by grafting 2-hydroxethyl methacrylate (HEMA) onto modified OSL by free radical polymerization. The OSL-HEMA hydrogels were synthesized with different ratios of OSL i.e. 0, 10, 20 and 40% (w/w). Copolymerization with OSL led to an increase in crosslinking density of the poly-HEMA-based hydrogels, which in turn affected their material properties. The OSL-HEMA hydrogels displayed up to 39% improvement in water retention, 20% increase in thermal resistance and up to 3-fold increase in magnitude of shear moduli (G', G''), when compared to the control. The properties of OSL-HEMA hydrogels, such as water retention, could be tuned by altering the degree of lignin Or group modification and the ratio of modified lignin to HEMA.

Microbial glycolipid, the gelling conditions of which in water have never been described, have a great potential in this field; in fact, microbial glycolipid are obtained from renewable resources, they are biocompatible, non-cytotoxic and they exhibit astonishing self-assembly properties in water. This contribution discusses the self-assembly properties of selected microbial glycolipids and their hydrogel-forming properties. The self-assembly will be shown via SAXS and cryo-TEM experiments, while the gelling properties will be analyzed using time, temperature and pH-resolved rheology experiments.

**CELL 352**

Controlling the nanomorphology of anisotropic cellulose II aerogels by diffusion-driven gradual molecular self-assembly in a templating solvent

Sven Pappert1, Harald Reinholde, Helga Lichtenegger1, Falk Wolfgang Lieberme, falk.liebme@boku.ac.at, (1) Dept of Chemistry, Boku University Vienna, TuIn an der Donau, Austria (2) Institute of Physics and Materials Science, BOKU University Vienna, Vienna, Austria

Biopolymer-based aerogels constitute an emerging class of materials whose intriguing properties including low weight, high interconnected porosity and large specific surface literally invite to be used in a multitude of applications. Cellulose II lyogels and aerogels are of particular interest in this regard, last but not least owing to the abundance of cellulose, its largely homogeneous structure and the comparatively facile methods required to prepare gels and aerogels. However, controlled tuning of the properties of cellulose II gels and aerogels was hitherto barely possible, even though systematic studies have shown that both the cellulose solvent and surfactants - the latter used to coagulate cellulose from solution state - decide about the type of phase separation occurring during cellulose coagulation and have thus an important impact on the type of nanomorphology formed. This paper reports a novel, simple and energy efficient route towards anisotropic cellulose II gels of controlled nanomorphology employing diffusion-driven gradual molecular self-assembly in an appropriate templating cellulose solvent. Comprehensive time-resolved SAXS studies during the diffusion-driven coagulation process complemented by light microscopy and SEM revealed the development of a symmetric radially ordered structure during gelation. As the formed anisotropic structure can be preserved throughout conversion to aerogels, the presented approach has a great potential for controlled synthesis of bioinspired open-porous materials of complex morphology.

**CELL 353**

Microstructural dynamics and rheology of foeculated micro/nanofibrillated cellulose suspensions

Emily Faccchine, efacchin@ncsu.edu, Orlando J. Rojas, Saad Khan, NC State University, Raleigh, North Carolina, United States

Aqueous suspensions of micro/nanofibrillated cellulose are known to exhibit gel-like behavior at low concentrations. The physical gel properties are a result of extensive hydrogen bonding, fibril entanglement, and flocculation. In this work, we used dynamic oscillatory rheology and steady shear rheometry to assess the microstructural behavior. Three phenomena were studied at length: (1) flow instability in the form of a deviation from typical shear-thinning viscosity at intermediate shear rates (1–10 s–1), (2) reduced structural recovery after breakdown under intermediate values of oscillatory shear (0–5 Pa), (3) yield stress of the system as measured by two different rheological methods. These dynamic behaviors provide insight to the fundamental structure of the suspension, which behaves in the manner of a highly flocculated system. Furthermore, the properties of MNFC were compared with a system of (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO)-oxidized cellulose nanofibers (CNF), which differ from MNFC in their smaller cross section and negative surface charge. The properties reported here are the TEMPO-CNFSuspension. Between these two related systems, yield stress, floc dynamics, and critical concentration of gel formation were compared and analyzed.

**CELL 354**

Spreading of water in low density nanocellulose networks: From capillaries to specific surface area

Lars Wagberg1, wagberg@kh.se, Hjalmar Granberg2, Johan Erlandson2, Hugo Francon, Fangxin Zou1, Rebecca Östman1, (1) KTH Fibre Polymer Techn, Stockholm, Sweden (2) RISE Bioeconomy, Stockholm, Sweden

The development of low density, wet-resilient networks of nanocelluloses has opened up new possibilities for the use of cellulose in absorbent products applications. In many of these applications the materials should induce a fast fluid spreading and hold the absorbed liquid under an externally applied load. In existing products these functions are separately controlled by a fibrous network and liquid holding gels. In a recent development we have shown that it is possible to prepare wet resilient, high porosity and high specific surface area networks from Cellulose Nanofibrated (CNFs) through a freeze-linking procedure1. By using specially 3D-printed moulds together with this freeze-linking procedure it is also possible to prepare basically any shape of the CNF networks.

In the present investigation we have prepared highly wet resilient, cylindrically shaped samples of the CNF, see figure, with a porosity higher than 97 %. A high speed camera was used to quantify the spreading with high accuracy.

A Lucas-Washburn evaluation of the data was too simple for describing the liquid flow in the cylinders. Instead a Kozeny-Carman approach was used where the spreading pressure in the networks was linked to the specific surface area of the CNF in these materials. It was possible to estimate the specific surface area which was found to be between 49 and 96 m2/g depending on the preparation conditions. The freeze-linked samples were able to hold close to 40 g water/g of
Typical shapes of the cylindrically shaped CNF-networks. The diameters of the cylinders are 5 mm.

**CELL 355**

**Low-cost and chemically stable quaternary ammonium salts for cellulose homogenisation**

Gabriel J. Partl, gabriel.partl@helsinki.fi, Sofia Välimäki, Jussi K. Helmnen, Daniel Rico del Cerro, Ilkka A. Koppelänen, Alistair King. Department of Chemistry, University of Helsinki, Helsinki, Finland

In continuation of our long-standing interest in Ionic Liquids (ILs) and biopolymers, an effort pertaining to the synthesis and characterization of quaternary ammonium ILs and related salts, with the ability to dissolve cellulose, was undertaken. Special focus was placed on finding exceptionally stable and low-cost ammonium salts that do not degrade under the conditions applied for cellulose homogenization. It has so far been a challenge to find thermally stable salts that might tolerate dissolution and recycling conditions, such as to avoid liquid losses or decomposition of cellulose. Striving for an economic approach, simple, selective (in the case of compounds containing more than one nitrogen atom) and high-yield synthesis conditions were sought out. A series of cations were identified that reduce the propensity for decomposition via Hoffmann elimination or nucleophilic attack at alpha positions on ammonium salts. Stability of the quaternary ammonium halides, acetates and hydroxides were assessed through thermogravimetric analysis (TGA) and NMR studies. The dissolution capability of cellulose, in the electrolytes of these salts, was then determined.

**Advances in Bacterial (Nano)Cellulose Research**

**CELL 356**

**From comparative genomics to BNC structural variants production**

Katarzyna Kubiak, katarzyna.kubiak@uiodz.pl, Malgorzata Ryngajllo, Paulina Jacek, Marzena Jedrzejczak-Krężpowska, Stanislaw Bielecki. Institute of Technical Biochemistry, Lodz University of Technology, Lodz, Poland

Bacterial cellulose over-producing bacteria in great majority belong to Komagataeibacter genera. Even though the bacteria were first reported over hundred years ago there are a lot of misunderstandings in the literature due to great diversity in strains phenotypes and not clear, dynamic taxonomic classification. We have made wide comparative genomic studies in order to find core genome of BNC producers and point out main fields of their diversity. Analysis done with 19 complete genomes of diverse strains from Komagataeibacter genus have proven very clear composition of this taxon of two major clades, the xylinus and the hansenii group. Some aspects of genomes flexibility mechanisms (genomic islands (GI), insertion sequences (IS), and CRISP-Cas loci) will be shown. Furthermore, we were able to identify, which functional groups of genes are well conserved and which most probably gives contribution into the Komagataeibacter strains’ diversity. Among others, we found interesting variety in exopolysaccharide production related genes. We bring evidence, that reported before leven and acetan production is not a common feature among cellulose producing strains. Finally, in our opinion especially interesting is poor conservation in c-di-GMP regulatory network genes in studied genus. Present data indicate great need of better understanding of this important regulatory pathway, as in each tested strain there was more genes than canonical 3 cdg operons, furthermore, more even operons were not well conserved. Genomic studies ongoing in our laboratory continuously deliver new data enabling BNC-producing strain engineering. An example of such approach, resulting in structural changes in cellulose fiber organization will be presented. Both disruption and overexpressing mutants will be characterized and possible applications of material obtained from their cultures will be suggested during the talk.

**CELL 357**

**Simulations of cellulose synthesis in bacteria suggested a primer-independent mechanism**

Hui Yang, hyang2016@gmail.com, Ming Tien, Yoarosla G. Yingling, James D. Kubicki. (1) Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States (2) Geological Sciences, University of Texas at El Paso, El Paso, Texas, United States (3) Department of Biology, The Pennsylvania State University, State College, Pennsylvania, United States (4) Department of Biochemistry and Molecular Biology, The Pennsylvania State University, State College, Pennsylvania, United States

Cellulose the most abundant renewable hydrocarbon source on Earth and thus is of central interest for bioethanol. Cellulose is composed of β-1,4-linked glucose units and is synthesized by both plants and microbes. Bacteria produce cellulose via a protein complex consisting of BcsA and BcsB. The first crystal structure of BcsAB was obtained from the bacterial enzyme from R. sphaeroides recently. BcsA is the catalytically active subunit responsible for the formation of bacterial cellulose and its translocation across the inner membrane. Within BcsA is a channel from which the cellulose strand is extruded during the course of synthesis. Herein, we have investigated the cellulose synthesis and its processivity within BcsAB using molecular dynamics (MD) simulations and the hybrid quantum mechanics and molecular mechanics (QM/MM) approach. Our results suggested that initiation of cellulose synthesis in bacteria CESA is primer-independent.

**CELL 358**

**Modification of bacterial nanocellulose – in terms of (bio)molecular aspect and its application**

Przemyslaw P. Rytczak, Malgorzata Ryngajllo, Izabela Cielecka, Stanislaw Bielecki, stanislaw.bielecki@uiodz.pl, Institute of Technical Biochemistry, Lodz University of Technology, Lodz, Poland

Bacterial nanocellulose (BNC) is an excellent alternative to synthetic polymers, which still, despite their various unquestionable advantages, may cause excessive immune response and in long-term applications often do not fulfill adequately their functions. Bionanocellulose, as a natural polymer of excellent chemical purity, has a chance to become a competitive product, successfully applied in various field especially in biomedicine. Furthermore, understanding the molecular aspects of cellulose biosynthesis and factors that determine its structure and properties is the basis for obtaining highly useful products with desired properties. The presentation will focus on new achievements in the field of bacterial nanocellulose synthesis and applications obtained by -omics studies of the producing strain as well as by in situ and ex situ modification applying to a new type of BNC wound dressing material with increased sorption properties and mechanical strength and tracheal prosthesis completely made from BNC. The new types of BNC dressings were prepared by the addition of hydroxyethyl cellulose (HEC) and carboxymethylcellulose (CMC) media or ex situ modification through generation of its composites with polyol. The obtained composites have significantly increased absorption properties and mechanical strength compared to non-modified cellulose. Additionally, the composites were tested in vitro using skin cell lines (fibroblast and keratinocytes).

Another achievement concerns a tracheal prosthesis made from BioNanoCellulose obtained under the production culture of Komagataeibacter bacteria, in the form of a tube-shaped segment with its inner diameter equal to the diameter of the human trachea interior. The prosthesis being a composite of native and mercerized BNC is intended to replace part of the natural trachea affected as a result of injury or disease.

**CELL 359**

**Design of bacterial nanocellulose materials using a novel matrix technology**

Dieter O. Klemm, dieter.klemm@uni-jena.de, Friederike Kramer, Sandor Nietzsche, Katrin Petroski-Weigle, Thomas Richter, (1) Nanocellulose RAD, Polymer Jena Association, Weimar, Germany (2) Center for Electron Microscopy, University Hospital Jena, Jena, Germany (3) Jenplpoy Materials, Jena, Germany

A novel matrix technology (Mobil Matrix Technology) allows the design of shape, dimensions, surface properties and nanofiber network structure of bacterial nanocellulose (BNC) hydrogel bodies. By repeated dipping of templates (combined in a matrix) between air space and liquid culture in a bioreactor BNC is formed layer by layer only at the templates. The result are self-contained layers because of the air contact after each immersion step. Nevertheless, the connection between these single self-contained layers is so strong that the hydrogel assembled does not delaminate. The technology is useful for preparation of flat and tubular BNC. One important method for structure characterization represents scanning electron microscopy. Moreover, the layer by layer formation is also useful for coating different materials with BNC layers as well as the composite formation of BNC with additives, e.g. nanofibrilated cellulose from wood and synthetic polymers. Examples are presented.
Fermentation and purification process scale-up for bacteria derived nanocellulose in medical device industry

Wojciech Czaja, wczaja@its.jgj.com, Erica Shawar, Damic W. Inselman. Biomaterials, DePuySynthes, West Chester, Pennsylvania, United States

Development of an efficient and stable large volume fermentation process has been considered as a limiting factor for the rapid development of novel products comprised of bacterially derived nanocellulose (BNC). Both high volume (Consumer market) and lower volume (Medical device market) products composed from BNC require the establishment of a stable manufacturing process that could ensure supply chain continuity while meeting worldwide market demands. Consequently, the successful scaling of BNC pellicle production during fermentation requires subsequent scale up of the purification processes that could render materials into nonpyrogenic implantable materials. The purification processes are fully validated prior to regulatory approval and further product availability for doctors and patients. As process validation efforts are not trivial and can often be complex and time consuming it is advisable to focus on the most critical to quality parameters when strategizing your scale up approach. A successful scale up of fermentation process in 20L bioreactor has been accomplished that resulted in manufacturing of 150 pellicles meeting the requirements for product release, process validation, and regulatory agencies.

Novel multi-layered drug delivery systems based on bacterial nanocellulose for skin treatment

Carmen Freire1, cfreire2011@gmail.com, Carla Vilela1, Cátia Rodrigues1, Daniela Fonseca2, Amendo Silva2,3,1 (1) University of Aveiro, Aveiro Institute of Materials, Aveiro, Portugal (2) University of Aveiro, Aveiro, Portugal

Bacterial nanocellulose (BNC) is a promising source of new functional and sustainable nanomaterials for myriad applications. The use of this highly pure and peculiar form of cellulose in the biomedical field, particularly in drug delivery, has become an active area of research and development as a result of the potential of this nanomaterials structure as a drug carrier for both oral and transdermal drug delivery.[1]

In this communication, recent research efforts on BNC-based membranes for drug delivery performed in our group will be presented with focus on multilayered based BNC systems for dermal application.

Epicyte – A new advanced wound dressing made from bacterial cellulose

Dana Kralisch1,2, dana.kralisch@uni-jena.de, Nadine Hessler2, Martin Funk2, Franz Schubert1, (1) JenaCell GmbH, Jena, Germany (2) Institut of Pharmaceutical Technology, FSU Jena, Jena, Germany (3) Bioskinco GmbH, Würzburg, Germany

The new advanced wound dressing “epicyte” made from bacterial cellulose will be introduced. Its production in an I-protected (semi-)continuous biotechnological production process, the so called Horizontal-Lift-Reactor (HoLR)-process [1], performed under ISO 13485 standards, customizes material properties which are highly suited for modern wound treatment. First hand experiences and case studies of medical application of epicyte for the treatment of burn injuries, gathered in close collaboration with specialized burn centres worldwide, will be presented and discussed in detail.

Biocellulosis as scaffold for tissue regeneration in modern surgery

Falk Rauchfuss, Falk.Rauchfuss@med.uni-jena.de, Jena University Hospital, Jena, Germany

Despite significant advances in surgery, there is an urgent need for biomaterials which can be implanted in tissue defects. Especially in abdominal surgery and urology, defects in organs like the bile duct, the esophagus, the ureter, the urinary bladder and the urethra are difficult to cure. In most cases, there are only extra-anatomical surgical procedures which can be performed to treat such a loss of tissue substance. These operations often go along with scarred stenosis, recurrent infections and, subsequently, the need of expensive antibiotic therapies.

Biocellulosis as graft. After such defects either implanted as patch or, in a tubular form, as complete graft in hollow organs.

In our own workgroup, we established a large animal model to evaluate biocellulosis as bile duct graft. After section of the extrahepatic bile duct, a biocellulosis tube was interposed (performing end-to-end anastomosis on both sides), which was stabilized with a commercially available stent. After a time period of twelve weeks, the animals were sacrificed and the operation site was evaluated. The bile duct defect was fully restored since the extrahelical bile duct was completely regenerated over the biocellulosis tube, which lied loose with the “neo”-bile duct lumen.
Novel biobased epoxy resins from depolymerized native lignin

Daniel van de Pas1, Daniel v.d. Pas2, Simon M.R. van der Vlugt3, (1) Scion, Rotorua, New Zealand (2) Norelco Research, Inc., Blaine, Minnesota, United States (3) Scion, Rotorua, New Zealand

The growth of the biobased economy has fueled interest in replacing non-renewable polymers with sustainable alternatives. Epoxy resins represent a major class of thermosetting polymers that are largely synthesized from the petrochemical-derived precursor bisphenol A. Lignin offers a potential biobased alternative to bisphenol A, however developing lignin-based epoxy resins that can outperform bisphenol A resins has proved scientifically challenging. Traditional pulping methods for extracting lignin from lignocellulosic biomass can heavily modify the chemical structure of the lignin, making it difficult to process into epoxy resins with desirable properties. In our research, we have taken advantage of the inherent properties of native lignin found in wood in producing a bio-derived polyphenol which is a more suitable precursor to high quality epoxy resins. Using mild hydrolysis methods, we selectively depolymerized native lignin within pine wood to give high yields of a well-defined mixture of monomers and oligomers with reactive phenolic groups. These products were reacted with epichlorohydrin to give epoxy prepolymer for subsequent blending with bisphenol A or glycerol-based epoxy prepolymer. The blended resins were cured, and their thermal and mechanical properties compared to an industry standard epoxy resin based on bisphenol A. Partial or full replacement of the bisphenol A component with these biobased epoxy prepolymer gave novel resins with improved flexural properties. The results indicated that depolymerized native lignin has potential for producing new high performance biobased epoxy resins.

A retrosynthetic perspective on new thermoset resin applications based on industrial Kraft lignin

Marcus Jawerth1, mjawerth@lth.se, Mats K. Johansson2, Stefan Lundmark3, Claudio Gioia4, Martin Lewok1, (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Royal Inst of Tech, Stockholm, Sweden (3) Perstorp AB, Perstorp, Sweden

Renewable constituents for thermosetting resins have gained interest due to increased environmental awareness in society. In many applications it is important to form strong, rigid, and temperature resistant materials. These properties are normally provided by aromatic structures, i.e. Bisphenol-A or isophthalic acid, in thermosets. However, aromatic building blocks for material applications are largely derived from crude oil. This makes aromatic structures derived from renewable resources attractive for new bio-based polymer systems if suitable structures can be retrieved. Kraft lignin is a renewable feedstock in abundance that could be utilized in these kinds of resins. The inherent aromatic structure of lignin can provide a suitable raw material for high Tg thermoset resins. Kraft lignin is however notorious for its heterogeneity in both structure and molecular weight thus needs to be treated before it can be used in thermosetting applications. A way to obtain the desired properties is by applying using solvents that are considered green and different fractions are achieved. The lignin fractions have various functional groups that allows for chemical modification, predominantly represented by phenol, carboxylic acids and carboxylic acids. Thus, solvent fractionation can be considered a tool to retrieve lignin fractions resembling similar structures as in traditional thermoset resins with regards to Mw and functional group density. Each of these functional groups can then be considered as handles for chemical modification. A high degree of control over the chemical modifications is important when utilizing lignin in material applications in order to be able to achieve the properties that are desired. In this study, the ethanol soluble fraction of softwood Kraft lignin has been converted selectively on phenolic hydroxyl substitution of 95% under benign and scalable conditions and is thoroughly characterized. The chemically modified lignin fraction has furthermore been used in thiol-ene thermosetting systems to validate the potential of using this resource for thermoset resin applications.

Lignin-caused performance improvements of poly(lactic acid)/CNCs composites

Liqing Wei1, Umesh P. Agarwala2, sagarwala@fs.fed.us, Laurent Matuana2, Ron Sabo1, Nicole Stark1, (1) Forest Products Laboratory, USDA FS, Madison, Wisconsin, United States, (2) Michigan State University, East Lansing, Michigan, United States

Cellulose nanocrystals (CNCs) are renewable green materials and have been used as reinforcing agents in polymer composites. However, poor interaction and compatibility between CNCs and hydrophobic polymers lead to composites that have poor mechanical properties. Additionally, CNCs aggregate during drying, which reduces their dispersion in a matrix. To address these issues, composites of high lignin containing CNCs (HLCNCs), fr...
Microelectromechanical systems (MEMS) are a ubiquitous part of a multitude of industries including transportation, communication, medical diagnostics, and consumer products. Since the MEMS industry evolved from the integrated circuit industry, the majority are made from silicon which requires energy intensive, time consuming processing with harsh chemicals. We have developed a process for producing standard MEMS devices from cellulose nanocrystal (CNC) films. CNC provide the advantages of less energy intensive, more environmentally benign processing, as well as the ability to easily tailor surface chemistry as well as optical and mechanical properties. A test platform of multiple MEMS structures including cantilever arrays, doubly clamped beams, residual stress testers, and mechanical strength testers were fabricated from shear aligned CNC films using lithography. Nanoindentation, electrostatic actuation, and scanning electron/polarized optical microscopy revealed unique anisotropic optical and mechanical properties of aligned CNC at these micron scale structures. The films have an elastic modulus of ~60 GPa which is the same order of magnitude as silicon. One of the most promising applications for CNC MEMS is in biosensing. We report the performance of CNC cantilever arrays in the detection of model cancer biomarkers. These results highlight the potential for using CNC as a renewable and green alternative for broad application of MEMS with tailorable mechanical, optical, and surface properties unlike silicon.

### CELL 372

**Cellulose nanocrystal (CNC) microelectromechanical systems (MEMS) for biosensing**

**Partha Saha, Robert Ashurst, Virginia A. Davis, davisva@auburn.edu. Department of Chemical Engineering, Auburn University, Auburn, Alabama, United States**

Cellulose and hemicelluloses are the most abundant bio-macromolecules found in nature and they constitute a renewable and biodegradable resource with great potential as building blocks for future technologies. A technology which can be utilized for assembly of building blocks is 3D printing. There is a large interest in 3D printing since it challenges the way of traditionally processing materials and enables the production of customizable products with complex design and an efficient use of materials. We have found that 3D printers developed for printing with liquids are suitable for the assembly of wood biopolymers to obtain constructs which resemble the hierarchical structures found in wood. Inks based on cellulose and crosslinkable hemicelluloses were developed that meet the requirements for 3D printing: they have high viscosity, are shear thinning and form hydrogels upon crosslinking. By 3D printing of all wood based inks we have focused on mimicking specific functions in wood that contribute to its mechanical properties: the cell wall architecture, the fibril angle in the cell wall and the crosslinked matrix of hemicellulose and lignin. Combining the technology of 3D printing with wood biopolymers and the knowledge of the plant-cell wall will lead to new fascinating materials that are strong, smart and renewable!

### CELL 373

**Derivatization and processing of biodegradable polymers into biomaterials**

Tamilvelan Mohan1,2, Tina Mauer1, Manja Kurečič-Ravić2, Rupert Kargl2,4, Thomas Elschnig2, Thomas J. Heinze1, Karin Stanina Kleinschek1,2, karin.stanina@um.si (1) Laboratory for Characterization and Processing of Polymers (LCPP), Faculty of Mechanical Engineering, University of Maribor, Maribor, Slovenia (2) Institute for Organic Chemistry and Macromolecular Chemistry Center of Excellence for Polysaccharide Research, Friedrich Schiller University of Jena, Jena, Germany (3) Institute of Chemistry, University of Graz, Graz, Austria (4) Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Graz, Austria

Polymer based biomaterials possess many advantages. Among others it is their flexible processibility into various shapes employing a broad range of forming methods known for polymers. For thermoplastic materials this includes melt-extrusion into three dimensional objects whereas solution processing (nuclear emulsion, nanoprecipitation, spin-coating, electropinning etc.) can be used if proper solvents are available and solution parameters are in a desired range. Polymeric biomaterials are of further interest since their chemical composition and structure can be influenced in a wide range by derivatization reactions. Though the polymer backbone of natural e.g. polysaccharides is "pre-defined", homogeneous or heterogeneous derivatization allows for a targeted change in their properties. This lecture will give examples on what kind of reactions and surface modifications can be performed with biodegradable polymers and how these materials can be processed into various shapes. The presentation also includes results on the evaluation of biological efficacies of selected materials based on esters, ethers and amide derivatives of biodegradable or bio-based polymers with an emphasis on polysaccharides.

### CELL 374

**Polymer analogous reactions comparing polysaccharides with polyvinylalcoholes**

Ana Bratul1, Karin Stanina Kleinschek1,2, Rupert Kargl2,4, rupert.kargl@um.si. (1) Laboratory for Characterization and Processing of Polymers (LCPP), Faculty of Mechanical Engineering, University of Maribor, Maribor, Slovenia (2) Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Graz, Austria

Homogeneous and heterogeneous polymer analogous derivatization reactions are powerful means of increasing the property range and applicability of polysaccharides and synthetic polymers with amino-acids or peptides was used to produce bioactive materials of interest. The reactivity of natural polysaccharides was compared with those of polyvinyl alcohols (PVA) in order to increase understanding and estimate the influence of the polymer backbone on the outcome of the reaction and the final properties. Aminoacids and peptides were bound to the polymers via homogeneous esterification reactions in organic solvents employing proper activating reagent. The necessity of protecting groups was evaluated and protocols for their removal were established. Detailed analyses of the degree of substitution (DS) was performed by change titration, NMR and IR-spectroscopy. Selected obtained materials were evaluated with respect to their bioactivity using cell viability tests. Common material forming techniques for polymers (nanoprecipitation of Polymers (LCPP), Monoetching etc.) can be used if proper solvents are available and solution parameters are in a desired range. Polymeric biomaterials are of further interest since their chemical composition and structure can be influenced in a wide range by derivatization reactions. Though the polymer backbone of natural e.g. polysaccharides is "pre-defined", homogeneous or heterogeneous derivatization allows for a targeted change in their properties. This lecture will give examples on what kind of reactions and surface modifications can be performed with biodegradable polymers and how these materials can be processed into various shapes. The presentation also includes results on the evaluation of biological efficacies of selected materials based on esters, ethers and amide derivatives of biodegradable or bio-based polymers with an emphasis on polysaccharides.

### CELL 375

**3D printing wood – a biomimetic approach**

Kaja Markstedt1, kaja@chalmers.se, Paul Gatenholm1, (1) Chemical Biological Engineering/Biopolymer, Chalmers University of Technology, Göteborg, Sweden (2) Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden

Cellulose and hemicelluloses are the most abundant bio-macromolecules found in nature and they constitute a renewable and biodegradable resource with great potential as building blocks for future technologies. A technology which can be utilized for assembly of building blocks is 3D printing. There is a large interest in 3D printing since it challenges the way of traditionally processing materials and enables the production of customizable products with complex design and an efficient use of materials. We have found that 3D printers developed for printing with liquids are suitable for the assembly of wood biopolymers to obtain constructs which resemble the hierarchical structures found in wood. Inks based on cellulose and crosslinkable hemicelluloses were developed that meet the requirements for 3D printing: they have high viscosity, are shear thinning and form hydrogels upon crosslinking. By 3D printing of all wood based inks we have focused on mimicking specific functions in wood that contribute to its mechanical properties: the cell wall architecture, the fibril angle in the cell wall and the crosslinked matrix of hemicellulose and lignin. Combining the technology of 3D printing with wood biopolymers and the knowledge of the plant-cell wall will lead to new fascinating materials that are strong, smart and renewable!

![Crosslinked hemicellulose](from_31_to_40_printed.png) Figure 1. Examples of functions mimicked in wood: crosslinkable hemicelluloses, honeycomb cell architecture and fibril angle of the secondary cell wall.

### CELL 376

**Cellulose nanocrystals for fabricating biomimetic carilage**

Anaswatha V. Kumar1, Kyungjin Lee2, Hong Liang2, Amir Asadi2, amir.asadi@tamu.edu, (1) Texas A&M University, College Station, Texas, United States (2) Mechanical Eng, Texas A&M University, College Station, Texas, United States

A longer lifespan for future joint repair rely on developing new materials for artifical cartilage capable of mimicking the real behavior of a natural one. It is necessary that materials used for cartilage to be biocompatible ensuring that the body immune system would not reject it, lubricious and wear resistant whose wear debris are biodegradable. We develop a new nanocomposite material of polytetraethylene carbonate (PTMC), hydroxyapatite (HAP) and cellulose nanocrystals (CNC) to mimic real cartilage. CNC are cellulose-based whisker-shaped particles (typically, 3–5 nm in width and 5–500 nm in length) obtained from wood and plants and their low density, sustainability, high aspect ratio, high mechanical properties, low toxicity, bio compatibility and biodegradability make them attractive for reinforcement of polymers used in biomedical applications. We showed that our developed cartilage is able to mimic a natural one in terms of mechanical properties, friction coefficient and surface elastic behavior. Our result enlighten a path forward using cellulose nanomaterials as promising materials in fabricating cartilages with longer lifespans that reduce the number of surgeries required for repairing the joints and hence lower the cost and risk of surgeries and patient’s pain and discomfort.

### CELL 377

**Cellulose nanofibers from wood as a new substrate for covalent immobilization of pro-drug molecule by click chemistry**

Hippolyte Durand1, Hippolyte.durand@ip2.grenoble-inp.fr, Elisa Zen2, Isabelle Baussare2, Marine Demoursnay3, Sébastien Fort1, Narcis Balasa1, Julien Bras2, (1) CERMAV, Grenoble Cedex 9, France (2) Univ. Grenoble Alpes - Grenoble INP - LGP2, Grenoble, France (3) CTP, Grenoble, France (4) Univ. Grenoble Alpes, CNRS, DPM, Grenoble, France

Cellulose Nanofibers (CNF) from wood are more and more investigated for their outstanding properties (high specific area, low density, excellent mechanical properties and chemical reactivity) besides their character of renewable resource. Such fibrils of 5-20nm in width and 1-5µm long are able to form highly entangled networks, resulting in films with high mechanical and bio compatibility properties that make them interesting candidates for a number of applications, as seen recently in the biomedical field. The possibility to further expand the CNF use by tailoring their surface properties and functions has also been intensely explored in the last decade. This paper reports two different modifications of either native CNF or TEMPO-oxidized CNF. The latter were grafted with furfuryl amine, through a peptide linkage formed with the carboxylic acid moieties. On the other hand, an esterification reaction between carboxylic acid of compounds (which also bears maleimide function) and hydroxyl groups of non-oxidized CNF was conducted. Surface modifications of CNF were confirmed by FTIR, conductometric titration and solid state C13-NMR. Two types of functionalized CNF were produced: furane-CN and maleimide-CN. This first modification pre-activated CNF for further grafting with a bioactive molecule. Metronidazole was the starting molecule to produce modified drug (=pro-drug) with either maleimide or thiol function that can be coupled with the afore-mentioned two types of CNF by click chemistry (Thiol-ENE and Diels & Alder types). The coupling efficiency has been confirmed by FTIR, elemental analysis and solid state C13-NMR.

### CELL 378

**Metronidazole as a starting molecule to produce modified drug (=pro-drug) with either maleimide or thiol function that can be coupled with the afore-mentioned two types of CNF by click chemistry (Thiol-ENE and Diels & Alder types). The coupling efficiency has been confirmed by FTIR, elemental analysis and solid state C13-NMR.**

![Metronidazole](from_31_to_40_printed.png)
This new coupling has been successful in both case and open the gate for new CNF based drug release system sensitive to specific stimuli, like enzyme activity in the human body.

**CELL 378**

**Acquiring antibacterial and hemostatic properties for polypropylene nonwovens via layer-by-layer surface modification using soybean protein**

Abdelrahman M. Abdelgawad1, aadbelegi@gcsu.edu, Consuelo Fritz1, Orlando J. Rojas2,3, (1) North Carolina State University, Raleigh, North Carolina, United States (2) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States (3) Textile Research Division, National Research Center, Cairo, Egypt — Select One —, Egypt (4) Department of Forest Products Technology, Aalto University, Alto, Finland

Polypropylene (PP) nonwovens are very important textile material. It is widely used in medical and medicinal products. Modification of the wetting behavior of its hydrophobic surface is essential to control fluid interactions, adhesion, transport processes, sensing, etc. The current work investigates the development of antibacterial/hemostatic material based on polypropylene nonwoven using soybean protein isolate (SPI). A layer by layer technique was applied to impart the desired properties. In the first layer, a cationic surfactant, diocetyl(dimethylammonium bromide (DODA) was adsorbed onto PP surface prior to the protein deposition to enhance its wettability. Then an antibacterial layer of silver nanoparticles/soybean protein isolate, was acquired to the surface of PP. Separately, nano-sized silver metal was synthesized in high concentration in less than five minutes via solid state grinding of silver salt and soybean protein. A third layer contains thornin protein was absorbed to the surface of PP to attain a hemostatic properties to the system. The adsorption of soybean protein onto DODA-treated PP leads to significant improvement in water wettability and a shift in the contact angle from 128° to completely wettable surfaces (0°). The formation of nanostructured silver was elucidated by using complementary spectroscopy and imaging techniques, including UV-vis, SEM, X-Ray Diffraction, TEM, and Surface Chemical Composition. Finally, the reactivity of loaded thornin protein was confirmed by the exposure of the treated PP nonwovens to fibrinogen protein. Thrombin was released from the system and fibrin gel was formed on the surface of PP nonwoven. The developed system showed interesting behavior and could be used as antibacterial/hemostatic wound dressing material.

**CELL 379**

**Construction of chitosan/rectorite/cellulose nanofibers composites and their applications in biomedical materials**

Yumin Du1, duyumin@whu.edu.cn, Ang Lyu2, Huimin Gao1,3, Xiaowen Shi1, (1) Center of Research on Biomass Resource, Wuhan University, Wuhan Hubei, China (2) College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China

Chitosan (CS)/rectorite (REC)/cellulose nanofibers (CNFs) composite films were fabricated, and their structure, mechanical properties, anti-UV and anti-bacteria properties were characterized. CNFs were prepared from waste brown algae, and a 20 ml 1% CNFs suspension was poured into a circular mold with diameter of 10 cm and dried at 50°C to obtain CNFs film. The film was immersed in 2% chitosan/rectorite solution, and then were dried to obtain CS/REC/CNFs films. CS/REC films reinforced with CNFs possessed higher tensile strength, good anti-UV and anti-bacteria properties. The tensile strength (σs) of the CS/REC/CNFs films were much better than CS and CS/REC films, and their anti-UV properties were lower than CS/REC film, but were much higher than CS film and CNFs film, indicating that REC in the CS/REC/CNFs films contributed to the anti-UV function. More importantly, the CS/REC/CNFs films exhibited very evident antibacteria effect. The large surface area and biocompatibility of CNFs increased the absorption on bacteria, and then CS around REC inhibited the growth of bacteria. These composite films possessed promising applications in the biomedical and packaging materials.

**CELL 380**

**Hybrid nanocelluloses to design functional emulsions**

Isabelle Capron1, Isabelle.capron@inra.fr, Jean-Bruno Mougel1,2, Olivier Chauveau3, Académie Cathala1, Patricia Bertononi1, Néwaj Shaarafy2,1 (1) IMN-CNRS, Nantes, France (2) BIA, INRA, Nantes, France

Nanocelluloses offer interesting assembling properties that allow building original multidimensional architectures. Notably they proved to stabilize oil/water interfaces and form the so-called Pickering emulsions, replacing surfactants from formulations. However, their uses are limited by their physical properties. Their modification or association with nanoparticles with complementary properties is an underestimated way to develop multifunctional original architectures. The present strategy consists in forming hybrid particles by combining cellulose nanocrystals (CNC) with other nanoparticles such as carbon nanotubes in order to get conductivity or titanium dioxide (TiO2) nanoparticles used for their remarkable photocatalytic and pigments properties. It is shown that oil-in-water Pickering emulsions can be prepared with the hybrid particles adsorbed at the interface as the unique stabilizers. For example CNC-TiO2 hybrid nanoparticles are prepared and tested for anti-UV filters. Such hybrids may serve as an ideal alternative to the conventionally used inorganic filters and stabilizers in a large range of applications. This strategy to achieve versatile functional emulsions can be addressed to a large range of properties.

**CELL 381**

**Nanocellulose derivatives: A comparative study of nanocelluloses from wood- and vegetable-based raw materials**

Nikolaos Pahimanolis, npahimanolis@gmail.com, Jason McKee, Henkki Mertaniemi, Antti Luukenen, Betulium Ltd, Espoo, Finland

Development of vegetable-based (i.e. parenchymal cellulose) nanocellulose derivatives has recently offered a paradigm shift from the traditional wood-based (i.e. secondary cell wall cellulose) products. Especially, processing non-food agroindustry side streams using Betulium’s biofinery concept has been demonstrated to be a cost-effective and sustainable method to produce a variety of native and chemically derivatized nanocellulose grades. In this study, we provide a comparative examination of native non-derivatized, anionic, cationic, and other derivatized nanocelluloses and sies processed from parenchymal cellulosics and secondary cell wall cellulosics. Rheological characterization was used to study the yield-strain and viscosity profiles; electron microscopy to study the fibril dimensions; and, titration to determine the degree of substitution. Turbidity was measured to study the homogeneity; and, finally, tensile measurements of cast films were used compare mechanical properties of the different nanocellulose types. Based on the experimental results, the similarities and differences between the derivatized grades and raw materials are highlighted. Furthermore, the differences in the process parameters and chemical usage resulting from the cell wall type are discussed. We see that the results help differentiate between different derivatized nanocellulose grades and raw materials, allowing the academia and industry to choose the most suitable grades for their research and development activities.

**CELL 382**

**Control of Pickering emulsion properties by the structural characteristics of nanocelluloses**

Clara Jimenez Saelices, clara.jimenez-saelices@inra.fr, Isabelle Capron, INRA, NANTES, France

Pickering emulsions are dispersions systems where two immiscible liquids are stabilized by colloidal solid particles. Cellulosic nanocrystals (CNC) and nanofibrillated cellulose (NFC) are both known to stabilize oil/water interfaces despite being non-surface active nanoparticles. In this work, we study the emulsion’s characteristics and properties as a function of particle size, shape and raw materials are highlighted. Furthermore, the differences in the process parameters and chemical usage resulting from the cell wall type are discussed. We see that the results help differentiate between different derivatized nanocellulose grades and raw materials, allowing the academia and industry to choose the most suitable grades for their research and development activities.
TEMPO NFC stabilized Pickering emulsions have excellent characteristics to form strong porous aerogels with thermal superinsulating properties.

Photomicrographs of emulsions stabilized by cellulose nanocrystal (CNC) and nanofibrillated cellulose (NFC)

CELL 383

Continuous filaments from cellulose with impressive wet strength

Anurodh Tripathi1, atirpat2@ncsu.edu, Manko Aga1, Saad Khan2, khan@ncsu.edu, Orlando Rijgers1. (1) Aalto university, Espoo, Finland (2) Chemical and Biomolecular Engineering, North Carolina State University, Durham, North Carolina, United States

The changing climate pattern necessitates us to go sustainable and renewable. However, to make renewable materials like cellulose and lignin commercially attractive, a fast and inexpensive processing is required to produce a high-performance material. We propose a one-step chemical modification to cellulose pulp, by which continuous filaments can be produced by wet-spinning the modified cellulose pulp in a benign non-solvent: water. With the right spinning conditions, the filaments from cellulose can have high tensile modulus strain, that can reach up to 5 GPa and 30% respectively. More important, the modification imparts impressive wet-strength to these filaments, such that their mechanical properties do not deteriorate even after immersing them in water for 24 h.

CELL 384

Sustainable bio-ethanol production from crystalline cellulose promoted by Pd/Fe3O4 catalyst

Bianca Guminá1, bianca.gumina@gmail.com, Francesco Maunuelio2, Claudia Espro2, Rossario Pietro Paolo1, Signorino Galavagno1. (1) Department of Civil, Energy, Environmental and Materials Engineering (DCEAM), Mediterranea University of Reggio Calabria, Reggio di Calabria, Italy (2) Department of Engineering, University of Messina, Messina, Italy

The direct cellulose conversion into valuable chemicals is currently one of the main challenges in green chemistry, since its transformation consists of multiple steps including hydrolysis to glucose, followed by the hydrogenation of glucose to polyols.

The aim of our work is the one-pot conversion of crystalline cellulose into valuable products, in water, in mild operative conditions, promoted by Pd/Fe3O4 catalyst. This process is also feasible under auto-hydrogenolysis conditions, without the direct addition of a reducing agent, because the hydrogen necessary for the hydrogenolysis is supplied from the aqueous-phase reforming (APR) and water-gas-shift (WGS) processes.

The Pd/Fe3O4 catalyst has been recently investigated for its advanced performance in several catalytic reactions including hydrogenolysis, catalytic transfer hydrogenolysis of polyols and APR of C3-C2 polyols. The one-pot conversion of microcrystalline cellulose over the bimetallic Pd/Fe3O4 catalyst, has been performed either using molecular H2, as direct reducing agent, as well as under auto-hydrogenolysis conditions, where the hydrogen for hydrogenolysis reactions is derived from the APR and WGS processes. The cellulotic substrate used in this study was not subjected to any pretreatment. The crystalline cellulose was easily converted in the temperature range investigated (180-240°C) and the liquid phase mainly includes 1,2-propanediol, butanediols and ethanol. The increase in the reaction temperature produces higher conversion as well as a higher selectivity to ethanol. The Pd/Fe3O4 catalyst exhibited a great activity in the direct conversion of the crystalline cellulose into short chain molecules (C4-C2) and lead to an increasing preferential formation of ethanol, which overcomes the 60% selectivity at 240°C, both in presence and in absence of molecular H2 addition. These findings could have significant implications for the sustainable bio-ethanol production feasible in only one step by using lignocellulosic biomasses as starting raw material.

CELL 385

Study of biopolymeric hydrogel interactions with photodynamic systems

Diego Gómez-Maldonado1, Diego0023@gmail.com, Roxana López-Simeon2, Antonio Topete Camacho3, Jose Campos-Terán1, jcamps@correo.uan.mx. (1) Forest Products Development Center, School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama. United States (2) Department of Civil Engineering, University Autónoma Metropolitana-Cuajimalpa, Ciudad de México, Mexico (3) Posgrado en Ciencias Naturales e Ingeniería, Universidad Autónoma Metropolitana-Cuajimalpa, Ciudad de México, Mexico (4) Departamento de Fisiología, Centro Universitario de Ciencias de la Salud, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico (5) Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana-Cuajimalpa, Ciudad de México, Mexico

Understanding the surface interactions between different components could help us to glimpse the best and most efficient ways of surface attachment and therefore the design of these materials for the different applications. Hydrogels, especially those made with natural polymers like alginate and chitosan, are attractive materials due to their bioactive properties and biocompatibility. Gold nanoparticles had proven to have good interactions with diverse polymers, and mainly they have been used for modifying some structural or physicochemical properties of the hydrogels formed with them. In this work, three different types of nanoparticles were used; the first were 7 nm gold nanoparticles, then 120 nm of nanoshells with poly(lactic-co-glycolic acid)-chitosan core, and finally, the latter but adding bovine serum albumin protein as a surface modifier. These nanoparticles have been studied for photodynamic therapies and cancer treatment.

To evaluate the modification of the surface and viscoelastic properties of alginate, chitosan and a 1:1 blend hydrogels with these nanoparticles systems, measurements were made in Quartz Crystal Microbalance with Dissipation and in Surface Plasmon Resonance at different concentrations. These modifications were also observed by Fourier Transform Infrared, Scanning Electronic and Atomic Force Microscopy.

The main trend observed was that chitosan hydrogels presented three times more adsorption of the nanoparticle systems without a meaningful change in its viscoelastic properties, while alginate presented important stiffness changes once it had interacted with the gold nanoparticles. This is most probably to the exchange of the citrate groups that serve as surface stabilizers. Finally, the blend presents an improved adsorption as compared to alginate alone, but still presents some changes in the dissipation factor.

CELL 386

Cellulose surface modification using polysaccharide multfunctional systems

Iris Beatriz Vega Erramuspe1,2, bvega@abo.fi, Maria Soledad Perea3, Thomas J. Heinze1,2, Pedro E. Fardh1, (1) Abo Akademi University, Turku, Finland (2) Friedrich Schiller University of Jena, Jena, Germany (3) Auburn University, Auburn, Alabama, United States (4) KU Leuven University, Leuven, Belgium

 Bleached cellulose pulp fibers with large surface area (<130 m2/g) are excellent templates for the self-assembly of polyelectrolyte systems with cationic net charge. Moreover, they are biocompatible and produced from renewable sources, available on the large scale at lower costs than synthetic fibers, and show excellent mechanical properties. Taking advantage of these characteristics, an intensive research work has been conducted in the recent decades on the look out for a wide variety of novel materials and innovative solutions, using cellulose fibers as raw material. Thus, a wide variety of materials have been developed, either at the laboratory and on the large scale (e.g. paper packaging materials with antibacterial properties). In many cases, using cost-effective processes with low environmental impact. The present work describes a simple, controlled, and efficient method for fiber surface modification of bleached pulp fibers, using multifunctional polysaccharide derivatives in aqueous solution. The modified fibers where further used as an efficient template for enzyme immobilization. The characterization of the mentioned fibers was assessed by using Time-of-Flight Secondary Ion Mass Spectrometry, and X-ray Photoelectron Spectroscopy. In addition, Stimulated Emission Depolarization Microscopy and Two-Dimensional Fluorescence Microscopy were useful tools to study the distribution of the biocatalysts on the fiber surfaces. The enzyme activity of the resulting fibers was assessed by UV-vis spectroscopy.
Due to the biocatalytic activity, the modified fibers might find application in different areas such as water remediation or paper packaging with antimicrobial properties. Moreover, by using the same approach, a broad range of novel materials and new bioprocesses could be tested, if the correct biocatalysts are selected for the corresponding target applications of the modified fibers.

**CELL 387**

**Stabilization of cellulose nanocrystal-based Pickering emulsion induced by cellulose nanofibrils: Impact of depletion effect on the phase behavior of emulsion droplets**

Long Bai, Siqi Huan, Wenchao Xiang, Orlando Rojas, Orlando.rojas@aalto.fi, Bioproducts and biosystems, Aalto University, Espoo, Finland

Nanocellulose is the most abundant natural shape-anisotropic nanoparticle extracted from plant cell walls, offering promising prospects as a particle stabilizer of Pickering colloids and emulsions for applications in food, cosmetics, and green materials. In this study, cellulose nanofibrils (CNF) was used as a depletion stabilization inducer to stabilize cellulose nanocrystal-based low-oil-concentration Pickering emulsions with droplet size being micrometers. Ultra-long, thin, and flexible CNF was mainly distributed in aqueous phase as flocs, showing a high efficiency to induce concentration-dependent depletion effect. Upon increasing the concentration of CNF, the creaming behavior of CNC-stabilized Pickering emulsions transformed from regular creaming without flocculation (low CNF), over creaming containing highly flocculated droplets (medium CNF), to stable emulsions with small-sized droplet aggregates (high CNF). The droplets flocculation at medium CNF was mainly induced by depletion flocculation. Above critical stabilization concentration, the size of flocculated droplets becomes independent of CNF concentration, and emulsion stabilization was achieved by depletion stabilization and emulsion gel mechanism. The universal feasibility of current system was demonstrated by employing dodecan as oil phase, displaying similar droplet phase behavior as sunflower oil. The depletion interaction in Pickering emulsions induced by rod-like biopolymer was proved to be rod-length dependent. The findings could be of importance to researches and applications of flexible biopolymers in all-natural label-friendly Pickering colloidal dispersions. The results of this study also provide valuable information for food-grade emulsion manufacturers who would like to use all-natural materials within their products to realize high-stability, low-oil-concentration, and fluid-like emulsion products, e.g., beverage or soft drinks.

Schematic illustration (not to scale) of manufacturing process for stable CNC-based Pickering emulsions via adding CNF and its corresponding stabilization mechanism

**Biobased Gels & Porous Materials**

**CELL 388**

**Cellulose nanofibril hydrogels as scaffolds for tissue engineering**

Kristin Syverud\(^1\), Kristin.syarued@pdi.no, Elinor Hegge\(^2\), Ahmad Rashid\(^3\), Kamal Mustafa\(^4\),
\(^1\) RISE PFI, Trondheim, Norway \(^2\) NTNU, Trondheim, Norway \(^3\) University of Bergen, Bergen, Norway

The purpose of tissue engineering is to regenerate damaged tissue by interplay between stem cells, nutrients and signal molecules, and an artificially created scaffold. We build the scaffold from wood derived cellulose nanofibrils (CNF). In tissue engineering, the micro-environment in the extracellular matrix (ECM) is mimicked. Several factors are important for a successful result. The scaffold must not induce cytotoxicity, the hydrogel or porous structure must be cell friendly and allow for cell growth and vascularization, the stiffness of the scaffold should be similar to the tissue to be regenerated, the surface chemistry should promote cell adhesion, migration and proliferation, and finally, the scaffold should gradually degrade when new tissue is formed. Various types of CNF have been studied, and also combinations with gelatin and alginate. Mechanical properties of the scaffolds are important for cell differentiation and will be reported. The effect of using two different surface chemistries, TEMPO oxidized CNF (TO-CNPF) and carboxymethylated CNF (CM-CNPF) on mouse fibroblast cell adhesion and proliferation was investigated. TEMPO oxidized CNF was characterized with respect to content of functional groups of CNFs, CNF morphologies and rheological properties of the hydrogels. In vitro studies show that the TO-CNPF hydrogel promotes cell spreading and characteristic morphology of fibroblast cells.

**CELL 389**

**Development of nanostructured systems based on poly (3,4-ethylenedioxythiophene) (PEDOT) aerogels of starch-­carrageenan for biomedical applications**

Roy Zamora, rzamorasequeira@ina.ac.cr. INA, San José, Costa Rica

A new generation of smart electroactive biomaterials is being sought to allow the direct delivery of electrical, electrochemical and electromechanical, that allow to improve the applications in this field. PEDOT (poly(3,4-ethylenedioxythiophene)) is a conductive and electrochemically switchable polymer when doped with various compounds, can stimulate the tissues that require electrical stimulation, such as nerve cells and skeletal muscle. Nanostructureization of PEDOT in the form of aerogels can enhance biological and electrical properties to the material, as well as adequate electrical stimulation, not only generates a more controlled location of cells, but also provides adequate microenvironment for synergistic action between biophysical and adhesion, proliferation and directional growth compared with pure BC hydrogel when coupling with NHI3T3 cell co-culture with electrical stimulation. Collectively, results suggested that the functional
electroactive BC/Ti$_3$C$_2$-MXene composite hydrogels can be useful as skin wound dressing, further contributing to skin tissue repair and regeneration.

Fig.1 Scheme of BC/Ti$_3$C$_2$-MXene hydrogel fabrication

Cell biocompatibility. (a) Alarna Blue assay, (b) LDH assay.

Fig.2 NIH3T3 cells biocompatibility. (a) Alarna Blue assay, (b) LDH assay.

In this work, naturally-derived porous chitosan microspheres (CSMs) free of toxic crosslinking and porogenic agents were developed, which allowed cell attachment, growth and cell-cell interactions in the internal pores. Firstly, CSM with a macroporous structure were prepared through a combination method of emulsification and thermally induced phase separation (Fig.1). The morphology of CSM were studied, followed by the evaluations of cytotoxicity and blood compatibility (Fig.2). Then, L-02 was used to evaluate CSM as microcarriers for 3D cell culture. SEM and LSCM combining Live/Dead assay indicated the hepatocytes could well adhere and grow into the pores besides on the outer surface of the CSM. Furthermore, the liver function studies including the expressions of related genes and proteins, albumin secretion and urea synthesis demonstrated that the metabolism of hepatocytes cultured with CSM were normal compared with the free cells. To the best of our knowledge, this work presents the first report that cell attachment and growth as well as the cell-cell interactions were observed in the internal pores of CSM, indicating a "real" 3D cell culture with the potential high cell activity and density. Together with the green and sustainable nature and superior biocompatibility and safety, these porous CSM may have great potential as cell microcarriers for 3D cell culture in biomedical applications.

Microspheres with porous structures have been applied as microcarriers for cell culture in past decades. However, the utilization of internal pores in microcarriers for cell attachment, growth and interactions has been rarely reported. Meanwhile, microcarriers from green and sustainable raw materials are on an increasing demand in terms of biocompatibility, safety and abundant source. In this work, naturally-derived porous chitosan microspheres (CSM) free of toxic crosslinking and porogenic agents were developed, which allowed cell attachment, growth and cell-cell interactions in the internal pores. Firstly, CSM with a macroporous structure were prepared through a combination method of emulsification and thermally induced phase separation (Fig.1). The morphology of CSM were studied, followed by the evaluations of cytotoxicity and blood compatibility (Fig.2). Then, L-02 was used to evaluate CSM as microcarriers for 3D cell culture. SEM and LSCM combining Live/Dead assay indicated the hepatocytes could well adhere and grow into the pores besides on the outer surface of the CSM. Furthermore, the liver function studies including the expressions of related genes and proteins, albumin secretion and urea synthesis demonstrated that the metabolism of hepatocytes cultured with CSM were normal compared with the free cells. To the best of our knowledge, this work presents the first report that cell attachment and growth as well as the cell-cell interactions were observed in the internal pores of CSM, indicating a "real" 3D cell culture with the potential high cell activity and density. Together with the green and sustainable nature and superior biocompatibility and safety, these porous CSM may have great potential as cell microcarriers for 3D cell culture in biomedical applications.

While injectable hydrogels have several advantages in the context of experimental medicine and tissue engineering, their relatively weak mechanical properties and isotropic network structure often limit their practical applications or translation to clinical use. By physically incorporating rigid high aspect ratio cellulose nanocrystals (CNCs) into hydrazone crosslinked poly (oligoethylene glycol methacrylate) (POEGMA) hydrogels, we have shown an ability to significantly enhance the mechanical performance of these injectable gels. Furthermore, by utilizing the diamagnetic susceptibility of CNCs, their in situ alignment may be controlled via the application of an external magnetic field, leading to the first example of an injectable hydrogel with nanoscale anisotropy. Increasing both the field strength (0–1.2 T) and CNC concentration (0.2–1.65 wt%) leads to enhanced nanocrystal alignment, as determined via small angle x-ray scattering (SAXS). CNC alignment occurs rapidly (< 2 min) during POEGMA network gelation, and is "frozen" within the nanocomposite hydrogel due to extensive chemical crosslinking. These readily tunable anisotropic hydrogels are capable of directing the in situ growth and differentiation of skeletal muscle myoblasts to form highly aligned myotubes, showing promise as a minimally invasive scaffold for muscle tissue engineering.

Fig.2 Morphological and biological property of CSM: (A) and (B) SEM image of CSM; (C) Blood capability of CSM; (D) Cytotoxicity of CSM.

Injectable anisotropic cellulose nanocrystal hydrogels as a platform for functional tissue engineering applications

Kevin J. De France$^1$, k.j.defrance@gmail.com, Kevin Yager$^3$, Katelyn Chan$^1$, Branton Corbett$^1$, Emily D. Cranston$^1$, Todd Hoare$^3$. (1) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (2) J.Hodgins Eng, McMaster University, Hamilton, Ontario, Canada (3) Brookhaven National Institute, Upton, New York, United States

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Nanocellulose based materials in liquid for stem cell growth monitoring

Julien Bras1, Julien.Bras@grenoble-inp.fr, Megan Smyth2, Catherine Picart2, Johan Fastet2. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Univ. Grenoble Alpes - Grenoble INP - LGP2, Grenoble, France

The research field of biocompatible materials encompasses many aspects and types of materials from polymers to bioceramic microspheres. Studied since the 1950s, biomaterials are now used in a variety of applications such as: artificial joint implants, tissue engineering, drug release monitoring, and cell therapy. One of the most common motifs to influence cell behavior in the presence of biomaterials is to change the mechanical properties of the biomaterial substrate. This oral presentation will propose an overview of our project entitled CellDiff (2014-2017). It was hypothesized that nanocellulose-based substrates could be fabricated with various elastic modulus to change the characteristics of MSCs. All stages of material development from creating high-value added nanocomposites and their effect on stem cell behavior in culture were performed during this research. Cellulose nanofibril films were prepared and their mechanical properties in liquid were tuned by drying procedure. Cell growth was much higher with stiffer CNF films. Composites with alginates and cellulose nanocrystals were also prepared and different stiffness values were achieved with modifying the percentage of CNC and CaCl2 content. Such difference was then correlated to cell growth values. All these results will open new high value added application for nanocellulose based materials.

Hemocompatibility of porous sulfonated Cladophora cellulose beads towards a blood purification material with anticoagulant properties

Igor Rocha, iiguroch8@gmail.com, Natalia Fernaz, Albert Mihranyan, Maria Strömme, Jonas Lindh. Nanotechnology and Functional Materials, Uppsala University, Uppsala, Sweden

Cellulose beads are a very versatile class of materials which unites the high chemical modification capacity and mechanical properties of cellulose with the properties derived from the round shaped structure, which are well suited for applications involving filtration of liquids in packed columns as for blood purification devices. In this work, we studied sulfonated cellulose beads from Cladophora green algae regarding blood compatibility in relation with the physicochemical properties. A one-pot aqueous persulfate oxidation producing 1-10 μm diaethylether cellulose beads followed by sulfonation and reduction led to a highly charged material with 90 m²/g of surface area and 0.20 cm²/g of total pore volume. The interaction of this material with whole human blood showed a decrease in coagulation activation, an increase in complement activation and very low hemolytic activity when compared to the unmodified Cladophora cellulose. These results make the modified beads very promising candidates for being used as a platform for blood purification procedures with anticoagulant properties.

Advances in Bacterial (Nano)Cellulose Research

Surface microstructured bacterial nano-cellulose for anti-adhesive and anti-fibrotic protection of medical devices

Aldo Ferrari1, aferran@eth.ch, Simone Bottarí2, Francesco Robotti3, Giovanni Pellegrini3, Dimos Poulikakos1, Christoph Starck1. (1) O-MAVT, ETH Zurich, Zurich, Switzerland (2) Wyss Institute, ETH Zurich, Zurich, Switzerland (3) DHZB, Berlin, Germany

The size and geometry of topographical features presented on the surface of implanted materials represents a complementary signal which is read by cells mediating the inflammatory response to foreign bodies, independently from other biochemical properties of the substrate. For this reason the structuring of protective anti-fibrotic layers made of bacterial nano-cellulose provides an ideal access to counteract fibrotic encapsulation and capsular contraction.

Here, we explore a rational design of surface modifications in the sub-micron and micron range to optimize a topography comprised of a symmetrical array of hexagonal pits able to interfere with focal adhesion establishment and maturation in human fibroblasts and macrophages. When implemented on bacterial nano-cellulose in vitro, by means of Guided Assembly-Based Bioolithography (GAB), the anti-adhesive topography significantly reduces the adhesion of cells and their physical activation toward effectors of fibrotic activity. In addition, long-term interaction of the cells with anti-adhesive topographies markedly hampers cell proliferation, functionally linking to the natural progress of the cell cycle.

This solution for reduction in cell adhesion can be implemented to body implants as an additive protective conformal layer. In vivo tests in large animals demonstrate the stability of the protective layer and its performance in drastically reducing foreign body reaction against silicons, metals and plastic substitutes. Altogether these results establish topographically-modified bacterial nano-cellulose as an optimal anti-adhesive and anti-fibrotic protection supporting the long term integration of body implants.

Bacterial nanocellulose: A natural biopolymer for controlled drug delivery

Dagmar Fischer, jessica.hiepe@uni-jena.de. Department of Pharmaceutical Technology, Friedrich-Schiller-University Jena, Jena, Germany

Bacterial nanocellulose (BNC) is an innovative biofabricated material, generated in a biotechnological process by Komagatella bacter. Bacteria strains from glucose and consisting of about 1% cellulose and 99% water. Although the chemical formula is identical to plant cellulose, the material favours totally different, but outstanding material characteristics due to the three-dimensional network of nano-sized fibres. The interest in BNC as drug delivery system dramatically increased during the last years, as BNC is expected to hold a large amount of active ingredients due to the nano-sized 3D network resulting in an enormous surface area-to-volume ratio. However, the highly hydrophilic character limited a broad application, especially for the delivery of lipophilic drugs as well as for long-term applications. We developed different loading techniques to accomplish a controlled immediate and sustained drug release from several hours to weeks using BNC produced under lab-scale as well as under high throughput conditions. Native BNC, hybrid systems with thermo-responsive block-copolymers Poloxamers, as well as lipid-modified BNC were established. Depending on the type of modification, not only the drug release profile, but also superior material properties such as high compression stability and water binding could be achieved. Using the antiseptic octenidine as model drug for wound dressings, the antimicrobial activity against Staphylococcus aureus and Pseudomonas aeruginosa was not changed by the use of the modified BNC. The release of natural lipophilic active ingredients like coenzyme Q10, curcumin or frankincense could be controlled for dental BNC applications. Excellent biocompatibility of the loaded BNC could be demonstrated in vitro in keratinocytes as well as ex vivo in a shell-less hen’s egg model.

In conclusion, BNC can be tailored as immediate and sustained drug release system for ready-to-use and patient-designed bedside applications e.g. for dental wound treatment, cosmetics or the use as implant.

Nanocelluloses from cotton waste, bacterial nanocellulose and glycidyl methacrylate grafting: specific adsorption properties towards target molecules

Elena Vismara1, elena.vismara@polimi.it, Chiara Bongio2, Giangiacomo Tomi3. (1) Politecnico di Milano, Milano, Italy (2) Giuliana Ronzoni Institute, Milano, Italy

Oxidized (ONC) and hydrolyzed (HNC) crystalline nanocelluloses were prepared from a high-grade pure industrial cotton waste fibre (CFT). They were grafted by glycidyl methacrylate (GMA) with a Fenton-type reaction, affording crystalline ONC-GMA and HNC-GMA, with molar substitution (MS) in the range of 1.3–2.2, where the GMA appendages did not substantially affect the crystallinity degree. Modified and unmodified nanocelluloses (NCs) were tested with respect to adsorption of amoxicillin (AM) and beta-naphtol (NPT). ONC and ONC-GMA adsorbed AM in large amounts. HNC adsorbed AM only when grafted with GMA. ONC, ONC-GMA, and HNC-GMA can be developed as renewable nanomaterials to remove AM from wastewater. ONC-GMA and HNC-GMA showed moderate capability to remove beta-naphtol from water. Bacterial NC (BNC) grafting afforded BNC-GMA with molar substitution (MS) in the range of 0.25–2.5. Until MS reached ca. 1.7, BNC-GMA maintained the hydrogel state. Higher MS transformed it into a powder. BNC and BNC-GMA were tested in adsorption and release processes of amoxicillin and vancomycin (VC). BNC adsorbed and released good amounts of AM, BNC-GMA with MS = 0.28 adsorbed and released VC worse than BNC and BNC-GMA with MS = 0.28. BNCs loaded with VC could be developed as biocompatible wound dressing nanomaterials and tissue engineering scaffolds, while BNCs loaded with AM could be developed as drug delivery nanomaterials. All the tested NCs are crystalline in the range of 55–72%.
In this study, we report the mechanical performance of BC-reinforced poly(methyl methacrylate) (PMMA) composites with a thickness of 3 mm. The composites were prepared by replacing the fibres, with 5, 25 g.m² and 50 g.m² BC nanopapers, respectively. The low grammage paper was proven quicker to produce because of a filtration time cut by a third and possessed the highest porosity (78%). Tensile properties of the nanopapers were found to drop with lower grammages resulting in the 5 g.m² 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.m² BC nanopapers, with a tensile strength and modulus around 100 MPa and 11 GPa respectively, possessed tensile properties equivalent to that of composites made with higher grammage BC nanopapers. This was due to the increased porosity of the papers, as grammage was lowered, that lead to an improvement enhancement. A higher PLA crystallinity, due to an increased contact area with nanocellulose fibres, was also found with 3 ply BC nanopaper. A comparison between the tensile modulus of the composite and predictions from the rule of mixture and the Cox-Gordon exchange procedure will be given during the presentation.

**Fracture resistance of bacterial cellulose-reinforced poly(methyl methacrylate) composites**

**CELL 403**

**Ultra-low grammage bacterial cellulose nanofiber-reinforced polylactide composite laminates**

Martin Hervy, Frederic Boek, Koon-Yang Lee, Koonyang.lee@imperial.ac.uk. (1) Aeronautics, Imperial College London, London, United Kingdom (2) Department of Aeronautics, Imperial College London, London, United Kingdom

Cellulose is the most abundant polymer on earth and can be found in plants or animals but is also produced by the Gluconacetobacter 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 1.63 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 capital to the manufacture high fibre loading fractions (>30 vol.) polymer composites capable of rivaling commercial plastic materials. Yet, currently, the tensile properties of such composites are owed to the nanopaper instead of the much higher tensile properties of a single cellulose nanofibre. Achieving impregnation of the nanopaper by the matrix is a critical step in utilising the single cellulose nanofiber tensile properties. In order to ease the network impregnation, we investigated in this study the use of low grammage bacterial cellulose nanopapers to produce BC-reinforced polylactide composites.

Four bacterial cellulose (BC) nanopaper reinforced polylactide laminated composites containing 50 g.m² of BC nanopapers were produced using 10, 5, 2 and 1 layer of 5 g.m², 10 g.m², 25 g.m² and 50 g.m² BC nanopapers, respectively. The low grammage paper were proven quicker to produce because of a filtration time cut by a third and possessed the highest porosity (78%). Tensile properties of the nanopapers were found to drop with lower grammages resulting in the 5 g.m² 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.m² BC nanopapers, with a tensile strength and modulus around 100 MPa and 11 GPa respectively, possessed tensile properties equivalent to that of composites made with higher grammage BC nanopapers. This was due to the increased porosity of the papers, 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 with 3 ply BC nanopaper. A comparison between the tensile modulus of the composite and predictions from the rule of mixture and the Cox-Gordon model is also discussed in the presentation.

**Lignin: From Fundamentals to New Materials & Applications**

**CELL 404**

**Enzymatic lignin modification without solvents in water-soluble alkaline conditions**

Matti W. Heikila, matti.metgen.com, Klaara Birikh, klara.birikh@metgen.com, Toni Gronroos, toni@metgen.com. (1) Technology, MetGen, Kaarina, Finland (2) R&D, MetGen, Kaarina, Finland

Main hurdles of lignin valorization are its diverse chemical composition, recalcitrance, and poor solubility in high pH and branched structure. Controlled fragmentation of lignin could lead to its use in higher value products such as binders, coatings, fillers and more.
Oxidative enzymes have long been proposed as a potentially promising tool in lignin depolymerization. However, their application was limited to ambient pH, where lignin is poorly soluble in water.

MetGen Oy, an enzyme development company from Finland, developed and brought to market several lignin oxidizing enzymes, including an extremely lignin oxidizable metZyme® LIGNO that can function at pH as high as eleven and at elevated temperatures, addressing lignin at its water-soluble state. In this article, main characteristics of this enzyme as well as its action on bulk lignin coming from industrial processes are demonstrated. Presently, a genetically evolved commercially produced bacterial laccase is functional and stable at pH 11 demonstrating its use in reactor-scale lignin depolymerization.

Lignin modification by MetZyme® LIGNO was studied in different process conditions, and reaction products were characterized by size exclusion chromatography, dynamic light scattering, and UV-spectroscopy.

Depolymerization prevails in alkaline conditions and aeration. Under these conditions, not only the molecular weight but also solubility in water and solvents as well as water dispersion properties of lignin were altered as observed by the particle size of solubilized lignin.

In addition, more alkaline conditions proved to be more efficient for enzyme-assisted chemical activation (demethylation) of lignin. Importantly, solvent-free soluble lignin fragmentation allowed for robust industrial membrane separation technologies to be applicable for product fractionation.

These enzyme-based solutions open new opportunities for biofinery lignin valorization thus paving the way for economically viable biofinery business.

**CELL 405**

Lignin-rich residues originated from a range of pretreatments: Structural characterization and anaerobic microbial biomass production

Daniel Girma Mulat, daniel.girma.mulat@nmbu.no, Janka Dibdiakova, Mihaela Tanase Opeda, Svein Jarle Horn, (1) Chemistry, Biotechnology and Food Science, Norwegian University of Life Science, Ås, N/A, Norway (2) Norwegian Institute of Bioeconomy Research, Ås, N/A, Norway (3) Research Institutes of Sweden-Paper and Fibre Research Institute (RISE-PFI), Trondheim, N/A, Norway (4) Norwegian University of Life Science, Ås, Norway

Lignin-rich residues generated after enzymatic solubilization of polysaccharides in lignocellulosic biomass are mostly burned to generate process heat due to the inherent heterogeneity and recalcitrance of lignin. Valorization of lignin towards high volume applications like biomethane production via anaerobic digestion (AD) is important to increase the output of fuels from emerging biofineries. In nature, some soil bacteria have shown the potential to degrade lignin even under anaerobic conditions, but studies on the fate of lignin degradation in engineered AD systems are very limited. In this study, a range of birch and spruce lignin-rich residues originated from low-temperature sulphonation (LTS) pretreatment, and after enzymatic removal of the carbohydrate fraction of steam explosion (SE) and hot-water extraction (HWE) pretreated birch and spruce were used for biomethane production in AD. NMR, pyrolysis-GC/MS, FT-IR and thermogravimetric analysis of lignin showed that the different lignin preparation methods considerably affected the lignin content, structure and thermal properties. Our AD results showed that degradation of part of the lignin such as lignin-carbohydrate complex and pseudo-lignin along the carbohydrates impurities in the lignin-rich residues contributed to biomethane production. Aromatic compounds and volatile fatty acids were identified as lignin metabolites, suggesting lignin biodegradation in AD. The estimated energy output of bioethanol from SE pretreated birch was 4.9 MJ/kg, while subsequent biomethane production of the SE lignin-rich residues may yield of 3.2 MJ/kg. This shows biomethane production from lignin-rich residues in a biofinery setting has a potential to maximize the output of energy carriers from lignocellulosic. This study also shows the benefits of using advanced analytical techniques to study the degradation mechanisms of lignin during AD.

**CELL 406**

Laccase treatment as means to improve membrane filterability of lignin-containing birch hot water extract

Anna K. Kalliola, anna.kalliola@etl.f, Tarja Tamminen, Jussi Lahti, Tiina Virtanen, Mari Kallioinen, Heiko Lange, Claudia Crestini, (1) Department of Chemical Sciences and Technology, University of Rome “Tor Vergata”, Rome, Italy (2) Biocatalysis and Depolymerisation Chemistry, VTT Technical Research Centre of Finland Ltd., Espoo, Finland (3) LUT School of Engineering Science, Lappeenranta University of Technology, Lappeenranta, Finland

Ultrapurification is one of the key technologies in recovery of hemicelluloses and lignin from wood extractions. However, the commercial membranes available are often hydrophobic and thus very susceptible to fouling by lignin residues. In this work laccase catalyzed oxygen oxidation is applied to alter the structure of native like lignin into less fouling form to enhance the separation processes for recovery of the valuable compounds. Xylan rich hot water extract from birch chips was used as raw material in the experiments. The actual lignin content in the slightly acidic extract was 3.5 g/L. The dissolved lignin was oligomeric, based on its small molar mass 700 g/mol, determined by alkali SEC.

A commercial laccase preparation from Trametes sp., Laccase M120 was concentrated and used to treat the extract under 60 °C in the presence of oxygen (co-substrate). The laccase was found to be active towards lignin in the extract within a rather short delays (15 min) with dosing of 500 ml of lignin (protein 0.06 w/v of lignin). The alteration of lignin structure was measured directly from the filtrate as increased molar mass and slightly increased share of conjugated phenols. The treatment changed extract color into brownish and caused agglomeration of lignin. The lignin being not soluble any more was isolated and characterized by 13C NMR. It was shown that the laccase treatment significantly improved the filterability of the extract with polyethylenesulfone membranes.

Immobilization of the concentrated laccase M120 on carrier materials was experimented as means to develop catalytically active lignin-stable filtration systems. Two different immobilization methods were tested: Firstly via electrospinning into polyethersulfone nanofibers and secondly via linker chemistry onto alumina pellets or onto membrane spacer made of polypropylene. Based on the preliminary results, immobilization onto alumina pellets is the simplest way to implement laccase treatment to improve filterability.

**CELL 407**

Enzymatic modification of lignin by fungal laccases

Anne S. Meyer, am@dtu.dk, Meijan Kabel, Line Munk, (1) Center for BioProcess Engineering, Technical University of Denmark, Lyngby, Denmark (2) Chemical and biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark (3) Wageningen University, Wageningen, Netherlands

Laccases, EC 1.10.3.2, CAZY family AA11, are blue multicopper oxidases that catalyze oxidation of menaquinones and other electron-rich substrates during concomitant reduction of O2 to H2O. Laccases produced by white-rot fungi (Basidiomycetes) currently receive high research attention due to their apparent ability to catalyze modification of lignin and lignin-derived substances and in this way assist in biofining of plant biomass. The T1 copper site in the enzyme and the redox potential define the ability of the enzyme to catalyze the abstraction of electrons from phenolic substrates, and the trinuclear cluster allows for the remarkable copper-catalyzed oxidation reaction which can be exploited for modification and functionalization of lignin. The range of substrates that can be oxidized by laccases can be expanded by mediators that are believed to function as electron shuttles. However, recently, we discovered that fungal laccases could catalyze grafting of -OH type mediators, HPI (N-hydroxyacetanilide) and HBT (1-hydroxybenzotriazole), to lignin. HPI grafted better than HBT. We suggest that this laccase catalyzed grafting is a result of radical-radical coupling mechanisms involving laccase catalyzed oxidation of the mediator followed by either direct or indirect catalytic oxidation of lignin moieties. These data open up for new biofining uses for lignin by laccase-assisted modification.

**CELL 408**

Towards more uniform technical lignin

Li-Yang Liu, liyang.liu@alumni.ubc.ca, Noppadon Sathitsukhon, Mi-Jung Cho, Sudip Chowdhury, Scott Renneckar, (1) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (2) RD, Stratamatte Valley Company, Eugene, Oregon, United States (3) Department of Chemical Engineering, University of Louisville, Vancouver, British Columbia, Canada

Although lignin is the second most abundant biopolymer after cellulose, it has limited commercial application partly because of its non-uniform structure after isolation. In this study, to obtain a more uniform lignin structure, a safe, and green derivative, sodium hydroxide assisted carbonate (EC) was used to modify the aromatic hydroxyl groups of acetic soluble Kraft lignin. Reaction variables were studied such as temperature, time, solvent, catalysis types, and the amount of EC and catalysis; this hydroxyethylation reaction was optimized based on the analysis of 13C Nuclear Magnetic Resonance (NMR) spectroscopy. The structural changes to the lignin and conversion efficiency were further studied by 1H, 13C NMR and Fourier transform infrared spectroscopy. Overall, this solvent-free reaction provided a novel route to prepare uniform lignin functionality at 90~120 °C, 3-5 hours, and a small amount of catalysis and EC. This hydroxyethylation generally converted the functional groups into about 35% primary aliphatic hydroxyl groups (AOHs). The reaction led to larger molecular weight and enhanced thermal stabilities for the lignin derivatives, while having a small reduction in the glass transition
Carbon fibers derived from fractionated-solvated lignin

Jing Jin1, Junhuan Ding2, Adam Kleef3, Mark C. Thes1, Amor D. Ogale1,2, ogale@clemson.edu.
(1) Clemson Univ, Clemson, South Carolina, United States (2) Chemical engineering, Clemson University, Clemson, South Carolina, United States

Carbon fibers (CFs) possess outstanding specific strength and modulus. Therefore, they are used commercially in structural composite applications (viz. aerospace) for enhanced performance and fuel efficiency, resulting from superior strength-to-weight ratio. The vast majority of commercial CFs are currently produced from a synthetic precursor, polycyclohexilimine (PAN), via wet-spinning. The cost of PAN precursor not only contributes to about 50% of CF costs, but the cyamide groups generate toxic by-products (viz. hydrogen cyanide) during heat-treatment. Thus, bio-derived CF precursors are of increasing interest from an environmental perspective.

Among renewable feedstocks, lignin is an important potential precursor for carbon fibers. Although lignin is readily available as an inexpensive by-product, it is too high in metal impurities. Therefore, a renewable solvent system, Aqueous Lignin Purification with Hot Acids (ALPHA), consisting of hot-acetic acid-water mixture has been developed to purify, fractionate, and solvate kraft lignins. The ash content of the kraft lignin purified by this continuous flow ALPHA process was below 0.1%, which is lower than unfractionated kraft lignin and other organosolv lignins. Using different molecular weight fractions of the solvated lignin, direct dry-spinning of lignin precursor fibers was accomplished at temperatures ranging up to 229°C. The precursor fibers were converted to carbon fibers by thermal oxidative stabilization and carbonization under tension to improve molecular orientation. The resulting CFs possessed a tensile strength of 1.3±0.3 GPa and modulus of 86±8.8 GPa, the highest combination of strength and modulus of CFs derived from lignin. The fractionated ultra-pre and high molecular weight precursors led to better carbon structure formation, which in turn leads to the improved carbon fiber properties.

Expanding capability of 13C NMR spectroscopy in comprehensive lignin analysis

Mikhail Balakshin1, balakshin@hotmail.com, Evelyn A. Capanalera1,1, (1) Chemistry, Univ. of Natural Resources and Life Sciences, BOKU, Vienna, Austria (2) Wood and Paper Science, North Carolina State University, Apex, North Carolina, United States (3) Biorefining and Energy, RISE Bioeconomy, Stockholm, Sweden

Quantitative 13C NMR is one of the most powerful techniques in comprehensive lignin analysis. However, its high potential is often underutilized. In this paper we present different ways for quantification of a variety of lignin structural units and discuss different aspects of the method, such as productivity, reproducibility and the accuracy of the quantification of specific lignin units. Modified wood lignins (MWW) with very low sugar content isolated from 14 soft- and hardwood species were used as a baseline for method validation. Good correlations were found for different independent methods of the quantification of major lignin moieties. This indicates good reliability of the method not only for relative comparison of various lignin structures, but also in the absolute terms (per monomeric lignin unit).

Furthermore, the quantitative 13C NMR approach was modified for the analysis of different types of technical lignins, which was more complex than the analysis of the native lignins. Various technical lignins originated from different pulp and bioenergy processes were characterized. The statistical data allowed for evaluating the accuracy in the quantification of different lignin units, which was different from that obtained for native lignins. More than 40 structural characteristics of native lignins and about 30 values for technical lignins were obtained on routine base. In addition, lignin moieties specific for certain lignin types could be also quantified. At the same time, limitations of the 13C NMR method will be discussed.

Fungal growth and enzyme production on alkali lignin from grasses

Marianne Doux1, mariane.doux@etu.univ-amu.fr, David Navarro2,3, Sana Rauchoe1, Craig Faddis1, craig.faddis@etu.univ-amu.fr. (1) INRA UMR 1163 Biodiversity and Biotechnology of Fungi, Aix Marseille Université, Marseille, France (2) CRM-CF, INRA, Marseille, France

Eleven species of filamentous fungi belonging to the Polyporaceae (10 strains) and Hypocreaceae (1 strain) families from the Centre International de Recherches Microbiennes-Champignons Filamentaux (CIRM-CF) cultivation collection were isolated based on sequential liquid and solid-state NMR analysis and growth on lignosulphonate. The fungal strains were screened for their ability to grow on both agar plates and liquid media containing commercial alkali lignin from grasses, and for the production of ligninolytic enzymes. Previously it was considered that fungi could not grow well on lignin alone. The strains showed differences in their growth rates in the presence of lignin, especially in liquid cultures, and also differences in the secretion of laccase and/or lignin peroxidase activities. Further analysis of the secretomes produced by a further selection of these fungi will be presented and the different enzymatic mechanisms employed by filamentous fungi for the deconstruction of lignocellulosic biomasses, and in particular lignin, will be discussed.

Functional Structures from Wood-Based Materials

Ductile and thermoplastic cellulose with novel application and design opportunities

Per A. Larsson1,2, per@kth.se, Eric Lim1,2, Giada Lo Re1,2, Sören Olsrud1,2, Lars Wagberg1,2, (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) BiMac Innovation, KTH Royal Institute of Technology, Stockholm, Sweden

Cellulosic fibres are ubiquitous in our daily life and a key material in the sustainable society of tomorrow. However, there are inherent features of cellulosic fibres and cellulose-based materials that limit their applicability. One such feature is the lack of ductility and (thermo)plasticity, which consequently limits the design possibilities to two-dimensional sheets and by creasing and/or folding thereof formed geometries. Many approaches have been attempted to facilitate formability of cellulose fibres and cellulose nanofibrils to complex geometries, such as chemical modifications and composite approaches. The challenge in the first approach is to keep fibres intact for maintained wet-processing and papermaking, and in the latter approach the addition of cellulose typically below 50 wt%, i.e. forming a fibre-reinforced composite that typically contains a non-biodegradable polymer matrix. In the present work, we present a concept where cellulosic fibres are partly chemically modified to ductile, thermoplastic dialcohol cellulose, thereby facilitating not only maintained fibre processing to form ductile sheets, but also melt-processing of these fibres with or without any additional components. This obviously opens for a completely new type of cellulose-based materials, which was demonstrated by hydroforming of paper sheets into double-curved structures and extrusion and injection moulding into test pieces suitable for tensile testing.

Enhanced functional properties of co-exfoliated graphene doped microfibrillated cellulose composites

Josaphat Phiri1, josaphat.phiri@aalto.fi, Leena-Sisko Johansson1, Patrick Gene1,2, Thad C. Maloney1, (1) Aalto University, Espoo, Finland (2) Omya International AG, Oltingen, Switzerland

The excellent functional properties of graphene and micro nanofibrillated cellulose (MNFC) offer plenty of possibilities for a wide range of applications in composite materials. In this study, we show highly ordered approached to create graphene/microfibrillated cellulose (MFC) composite films prepared by a simple method of co-exfoliation of graphite in MFC suspension under high shear exhibiting enhanced properties in comparison to individual material suspension mixing. The co-exfoliation method promotes a homogeneous dispersion of hydrophobic graphene in the MFC matrix, and the composites produced show improved thermal, electrical and mechanical properties. The highest tensile strength (120 MPa) and Young's modulus (24 GPa) were achieved at 0.5 wt% loading for the co-exfoliated graphene/MFC composites while for the suspension mixing composites 92 MPa and 20 GPa, respectively. They also showed a high electrical conductivity of 2.4 S m−1 at 9 wt% loading in comparison to 1.8 S m−1 for the suspension mixed composites. This simple method for the fabrication of graphene/MFC composites with enhanced controlled functional properties can prove to be industrially beneficial, and adopting this production method is expected to open a new route for potential novel applications of materials based largely on renewable resources, for example in energy storage devices, barrier films, packaging, printed electronics etc.

Bio-based fire retardant and its application in cellulose-based thermal insulation materials

Chao Zheng1, chaoz1987@kth.se, Dongfang Li, Monica K. Ek. Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

Thermal insulation plays a very important role in maximizing the energy efficiency of buildings. Cellulose-based thermal insulation materials made from cellulosic fibres have advantages over the oil-based raw materials from a sustainability point of view. However, low-density cellulosic thermal insulation materials have a poor fire retardancy that has a negative effect on the safety of insulation. In this work, bio-based fire retardants modified from lignin, and mechanical pulp were used to prepare cellulose-fiber-based insulation foams, and these foams showed promising fire retardancy.

Application of nanocotton and nanocollagen on cotton/polyester blend fabric using layer-by-layer (LBL) technique

Salah M. Mansour1, salahmansour6042@hotmail.com. Chemistry, cotton research institute, Cairo, Egypt

This research aimed to application of prepared microcrystalline cellulose from the short fibers forming from snap of long fiber during the spinning processes made by acid hydrolysis, and nanocollagen prepared by the reduction technique with plant extracts. LBL technique incorporated
to nanomaterials was used for applying a thin nanocomposite on cotton-polyester fabric surface and wide range of functionalities has been imparted to the fabric. LBL process was carried out using microwave irrigation treatment. The deposition cycle was repeated until 16 blayers. The result showed that the deposited blend exhibited a better UV protection and a significant flame retardancy in comparison to untreated blend. The results obtained revealed that the treated sample gave better wettability and air permeability and made the fabric more comfortable. Other properties of the treated fabric such as tensile strength, elongation at break, crease recovery angle, color measurements (K/S, Hue, and Chroma), and fastness properties (Washing, light, and perspiration) was measured and the results showed enhancement compared with the untreated samples. The microwave technique gives very good results than the conventional one.

**CELL 416**

From vapour to gag: Optimising cellulose degradation with gaseous HCl

Timo Pääkkönen1, timo.paakkonen@aalto.fi, Eero Kontturi2, (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Forest Products Technology, Aalto University, Aalto, Finland

A new technique for cellulose nanocrystal (CNC) production based on hydrolysis with hydrogen chloride vapor is introduced. We further developed the existing technique based on HCl vapor pressure with a reactor that can be applied to the degradation of cellulose with pressurized HCl (99.8 %) gas. Leveling-off degree of polymerization (LOPD) level of CNC is better than the control. This technique is a promising candidate for large scale production of CNCS with high yields, minimal water consumption, and short reaction times. Furthermore, recycling of the gas is effortless because it spontaneously desorbs from the fibers after being removed from the HCl atmosphere.

**CELL 417**

Preparation of cellulose nanofibers using a combination of lytic polysaccharidase monooxygenase (LPMO) enzymatic treatment and chemical modification

Ana Villares1, ana.villares@inra.fr, Celine Moreau2, Mireille Hao3,1, Jean-Guy Berin1,2, Bernard Cathala1, (1) UR1268 Bipolyméres Interactions Assemblages, INRA, Nantes, 44316, France (2) UMR 1163 Biodiversité et Biotechnologie Foncières, INRA, Marseille, France (3) Polytech Marseille, Faculté des Sciences de Luminy, Marseille, France

Lytic polysaccharidase monooxygenase (LPMO) enzymes are a new class of microbial enzymes that cleave cellulose by an oxidative mechanism. They are classified into the auxiliary activity (AA) family from the CAZy database. A99 LPMOs are key players of wood decay by filamentous fungi. These enzymes have a β-sandwich fold structure with a planar surface to which cellulose can bind, and their active center consists of a type II copper coordinated by a histidine brace. From CAZy database, A99 LPMOs are classified into nine families.

In this work, we used LPMO enzymes as a tool for facilitating the disruption of cellulose fibers and the production of cellulose nanofibers. We studied the action of two LPMO enzymes from the coproinophilic ascomycete Podospora anserina (PalPMO09H and PalPMO09E) that were produced heterologously. In previous studies we have shown that the action of A99 LPMOs followed by mechanical treatment allowed efficient disruption of cellulose fibers. The enzyme PalPMO09H is known to introduce an oxidized group on C4 and eventually on C1 whereas PalPMO09E acts only on C1. Kraft pulp fibers were treated with each LPMO using ascorbate as electron donor. After the enzymatic step, cellulose fibers were carboxymethylated with chloroacetic acid in NaOH. Carboxymethylation favored fiber disruption by the repulsion between negative charges from the carboxylic acid groups.

After enzymatic action and carboxymethylation, no mechanical treatment was required for disrupting cellulose fibers. Compared to control samples, both PalPMO09H- and PalPMO09E-treated fibers showed intense fibrillation and dispersions were very viscous. Moreover, films fabricated by casting LPMO-treated dispersions showed higher transparency than control films. This work demonstrates that LPMO enzymes can be viewed as promising candidates for the preparation of nanocelluloses, facilitating the fiber disruption. Carboxymethylation is not only a good strategy for fibrillating cellulose but also gives more insight into the action of LPMO enzymes.

**CELL 418**

Stabilization kinetics of polycationic/lignin/cellulose nanocrystals composite fibers

Hulbin Chang1, hulbin.chang@patech.edu, Jeffrey Luo1, H. C. Lia1, Satish Kumar1, (1) Georgia Institute of Technology, Atlanta, Georgia, United States (2) Georgia Tech, Atlanta, Georgia, United States (3) Material Science Engr, Georgia Tech, Atlanta, Georgia, United States

Stabilization process is critical for the production of high quality carbon fiber from polycationonite (PAN) fibers. Cellulose nanocrystals (CNCs), which are recyclable materials and have high mechanical properties, is used to reinforce PAN fibers. In this study, the structural evolution and thermal behavior of PAN and PANCNC during thermal stabilization were studied. Azimuthal scans of wide-angle X-ray diffraction showed that stabilized PANCNC fibers exhibit higher orientation of ladder polymer as compared to the PAN fibers. Thermal stabilization reactions including oxidation, cyclization and crosslinking were individually studied by differential scanning calorimetry (DSC). Based on the kinetics analysis, it was found that addition of 40 wt% CNCs into PAN fibers reduces the activation energy of cyclization and crosslinking but has little effect on the activation energy of oxidation.

**CELL 419**

Polymer nanocomposites with cellulose nanocrystals: Effects of polymer grafting and processing methods on thermomechanical properties

Sandra Wolhuter1, Jens Natterodt2, Justin O. Zoppe3, justin.zoppe@unifr.ch, Christoph Weder1, Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland

Cellulose nanocrystals (CNCs) have emerged as an attractive reinforcing filler for a variety of polymer matrices as a result of their low density, high mechanical strength, stiffness and aspect ratio. CNCs further present added benefits of low environmental impact and origin from renewable resources, thus contributing toward reducing global dependence on petrochemicals. The high density of functional groups on the surface of CNCs allows various surface chemical modifications, such as surface-initiated polymerization SiP. This permits the transformation of relatively hydrophilic CNCs into hydrophobic particles, thereby enabling their use in hydrophobic matrices and one-component nanocomposites (OCNs). Here, we will present our recent efforts in surface-initiated polymerization of methacrylates from CNCs toward OCNs and new precursor methods that allow facile melt processing via compression and extrusion molding based on co-polymerization. Polymer grafting from CNCs was confirmed by FTIR spectroscopy and transmission electron microscopy (TEM). The thermomechanical properties of the subsequent nanocomposites were characterized by differential scanning calorimetry (DSC), thermomechanical analysis (TGA) and dynamic mechanical analysis (DMA). The final OCNs displayed superior to conventional two-component nanocomposites and the materials prepared by the co-precipitation method showed significantly improved properties compared to those processed by direct melt mixing.

**CELL 420**

Processing of chicken feathers using a deep eutectic solvent

Emmi Nuutinen1, emmi.nuutinen@vttech.vtt.fi, Anna-Stina Jäätiskäläinen1, Teknologian Aiempiikeskus2, VTT Technical Research Centre of Finland, Espoo, Finland

Poultry feathers are a remarkable side stream from food industry and currently there is no appropriate use for it. However, keratin extracted from poultry feather waste could replace fossil fuel derived polymers in selected material applications. In this work, feathers were dissolved in deep eutectic solvent (DES) and regenerated in anti-solvent to produce an uniform keratin feedstock. DESs are generally considered as cheap, gentle and environmental friendly solvents that are effective to dissolve protein. The used DES composed of urea and sodium acetate with low amount of water to improve the feather solubility. The processing conditions were optimized for the best keratin yield and molecular weight by varying temperature from 80°C to 100°C and reaction time from 2h to 48h. After the DES treatment, water was used as an anti-solvent to regenerate the dissolved keratin. The morphological features, chemical structure, thermal properties, as well as the hydrophobicity of the produced keratin were characterized. It was observed that both the chemical structure as well as the physicochemical properties of the feather keratin could be tailored by tuning the processing conditions. Furthermore, the obtained regenerated keratin could be further utilized in applications like composites and films.

**CELL 421**

Composites from natural resources: Hemp fiber reinforced composites from 3D orthogonal woven preforms and their potential applications in US

Anuradha Gupta1, agupta20@ncsu.edu, Textiles, North Carolina State University, Raleigh, North Carolina, United States

Natural fibers reinforcements are a prevalent option for applications in composite manufacturing. There is a significant ongoing research in the field of natural fiber reinforced composites, which mainly aims at reducing the overall carbon footprint. Natural fiber composites has a great potential...
as the focus of many industry is shifting from synthetic fibers that are commonly used in manufacturing composites today like glass, carbon and aramid to more sustainable natural fibers.

Some of the major issues with conventional synthetic fibers are high energy consumption during production and non-degradability. Similarly, polymer resins like epoxy and vinyl ester, which are most commonly used in high performance composites, are petroleum based. With the reserve of petroleum depleting, alternative sustainable fibers and resins are the substitute.

The application of natural fibers are growing in the field of engineering and technology due to its favorable properties like biodegradability, sustainability, high strength and corrosion resistance. Due to these benefits, synthetic fibers and resins from hazardous chemicals are being substituted with natural fibers and resins. These "Green biocomposites" or "biocomposites" have emerged, which is a blend of the intrinsic properties of fiber and matrix derived from natural resources.

Hemp fibers have been used as reinforcement in composites due to high specific strength and young’s modules. Moreover, hemp fibers possess a much higher vibration dampening capacity, higher fiber yields, pest resistant and drought resistance. All these properties make it an excellent candidate for composite reinforcement.

The objectives of this presentation is to explain the importance of composites from natural resources and showcasing hemp as a strong contender for composites, highlighting the potential application.

CELL 422

Two-step process for recovery of copper napthenate from end-of-life railroad ties

Holly L. Haber1,2, haber@pols.ueltk.edu, PyongChung Kim1,2, Stephen C. Chmaly1, Jeff Lloyd1, Yagya N. Regmi3,4,5, yagya.regmi@usu.edu, Nicole Labelle6,7, (1) Center for Renewable Carbon, University of Tennessee, Knoxville, Tennessee, United States (2) Forestry, Wildlife, and Fisheries, University of Tennessee, Knoxville, Tennessee, United States (3) Biosystems Engineering and Soil Science, University of Tennessee, Knoxville, Tennessee, United States (4) Center for Renewable Carbon, Knoxville, Tennessee, United States (5) Nusar Corp., Rockford, Tennessee, United States

Low cost of natural gas and strict boiler emissions standards discourage reusing preservation-treated railroad ties for heat and power generation after their primary service; increasing their landflling and encouraging environment impacting non-wood alternatives. Thermal desorption and inorganic extraction with biodegradable chelating agents aims to increase the economic viability of used treated wood as fuel through copper naphtenate (CN) removal; converting it into an upgraded thermalchemical conversion feedstock. Thermal desorption was tested at 225, 250, 275, and 300 °C for retention times of 30, 45, and 60 min to optimize organic CN components recovery, followed by inorganic removal with several different chelating agents. Extraction with 2,6-dicarboxylic acid after thermal desorption between 250 and 275 °C for 45 min had the highest efficiency; removing over 90% of the inorganics and lowering the biomass' ash content by 64%. Effective CN recovery promotes the continued use of the ties over nonrenewable fuel sources.

CELL 423

Economic analysis of integrated continuous process for colloidal lignin particle via aerosol flow method

Mariko Ago1, mariko.ago@aalto.fi, Camilla Abbatì da Assisi1, Luís Garcia Greca2, Ronaldis González1, Orlando Rojas1, (1) Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo, Finland (2) Department of Forest Biomaterials, College of Natural Resources, NC State University, College of Natural Resources, Raleigh, North Carolina, United States

Lignin colloidal particles (LP) are attracting increasing attention for novel biomaterials and multiphase systems. Recently, the synthesis of lignin particles with different techniques has been reported, including in situ as well as acid and anti-solvent precipitation. In this study, we introduce spherical lignin particles with sizes ranging from 30 nm to few microns synthesized in an aerosol flow reactor with in-situ fractionation. This method allowed high throughput and high yield production of dry lignin particles.1 By varying the lignin source and synthesis conditions, various types of nano- and micro-particle were obtained. The process involves a single step that continuously atomizes the lignin precursor solution, which forms an aerosol that then passes through a heating tube with the aid of a gas carrier. Dry lignin particles are then collected downstream in the system. The broad use of aerosol technologies stems from their distinct advantages over wet and solid-phase chemistry processes, namely, (1) absence of liquid by-products, (2) simple and less expensive particle collection, (3) few processing steps, (4) continuous operation and (5) high product yield. Moreover, transport phenomena, including diffusion in gases, afford more rigorous treatment, which facilitates process design towards products of high purity and non-equilibrium metastable phases.

The scalability of such synthesis platform for lignin colloidal particles is demonstrated together with improved product quality under decreased production costs. Here, we discuss the economic balance considering production costs and factoring constraints that are part of the scientific discussion to succeed in the expansion of the opportunities for valorization of lignin for a wide range of new products. According to the life cycle assessment of lignin extraction in Kraft pulping process2, utilization of extracted lignin is a key issue to reduce TRACI environmental impacts. This fact motivates related routes for the valorization of lignin. Overall, this study includes an estimation over the production costs of the lignin colloidal particles by the continuous process using mass allocation and provides guidance on process optimizations that can improve the economic performance of manufacturing process.

CELL 424

Synthesis of UV curable poly (ethylene glycol) diacrylate macromere based semi-IPN hydrogel with polysaccharides

Prutha Joshi, ppj0001@auburn.edu, Steven Beaux, Maria Aued. Auburn University, Auburn, Alabama, United States

Hydrogels are polymeric materials widely used in medicine due to their similarity with the biological components of the body. Hydrogels are hydrophilic hydrogel and biocompatible for cell proliferation and tissue support because of their hydrophilic nature, porous structure and elastic properties. The objective of this research is to obtain poly (ethylene glycol) diacrylate (PEGDA) based polysaccharide semi-interpenetrating networks (semi-IPNs). The mechanical and structural features of the PEGDA hydrogel was modulated by comprising polysaccharide networks, such as gelatin, chitosan, and nano-fibrillated cellulose (NFC).

Firstly, methylated gelatin and chitosan were synthesized with methacryly anhydride. Moreover, microwave synthesis of the PEGDA micromere was completed using linear poly (ethylene glycol) (PEG) and an excess of methacyryl anhydride. Secondly, the synthesized and freeze-dried powder of modified gelatin, modified chitosan, or NFC was completely dissolved in phosphate buffer saline and mixed with PEGDA aqueous solution. Finally, the completely dissolved mixture of both polymers was UV cured using a commercial photo-initiator, Irgacure 2959 (2-Hydroxy-1-(4-hydroxyethoxy) phenyl)(2-methyl-1-propanone). The mechanical properties and swelling characteristics of the cured hydrogels were investigated.

Altogether, the biomaterial hydrogel properties open the way for applications in the field of medicine. Mechanical properties of these hydrogels were demonstrated to be tunable for various biomedical applications through modification of the degree of methacrylization and the gel chemical composition. This suggests that the produced hydrogels could find applications in complex tissue engineering.

CELL 425

Incorporation of dialdehyde cellulose microfibrils within a biobased polyfurfuryl alcohol thermoset matrix: Structure and properties relations

Rime Ganfoud1, rime.ganfoud@gmail.com, Nathanial Guig2, Laurent Heux3, Nicolas Srinarrazu3, (1) CERMAV-CNRS, Grenoble Cedex09, France (2) Laboratory of Condensed Matter Physics, University Nice Sophia Antipolis, Nice Alpes Maritimes, France (3) Université Côte d’Azur, Nice, France

Furfuryl alcohol (FA) is a bio-based monomer directly obtained from furlough which is produced from hemisaccharic waste. Its polymerization is initiated with an acid catalyst to form a cross-linked poly(polyfurfuryl alcohol) (PFA) thermoset polymer. The high carbon content, chemical inertness and thermal stability of PFA have led to several applications e.g. in foundry molds, as fire resistant or corrosive resistant materials and for wood reinforcement. However, as brittleness is one of the most important weaknesses of PFA, its thermomechanical properties could be greatly improved by addition of cellulose microfibrils (MFC), as it can dissipate mechanical stresses. In order to create covalent bonding between PFA and cellulose to enable this dissolution, the MFC were first subjected to controlled periodate oxidation to form dialdehyde function. Then, the oxidized MFC were dispersed in FA prior to in situ polymerization. Different materials were prepared by varying either the MFC content or their degree of oxidation.

Morphological investigations were performed using transmission electron microscopy (TEM) to show the dispersion of the microfibrils within PFA. This technique also showed that MFC kept their fibrillated morphology. FT-IR and 13C solid state NMR measurements were performed to investigate the interactions between the furanic network and the oxidized MFC. The impact of oxidized MFC on both the PFA molecular mobility and glass transition behavior was evaluated with Dynamic Mechanical Analysis (DMA).

CELL 426

Fabrication of strong nanocomposite films with renewable forestry waste/montmorillonite/reduction of graphene oxide for fire retardant

Gegu Chen, cgg0207@163.com, Feng Peng, Chun-Li Yao, Runcang Sun. Beijing Forestry University, Beijing, China

It is desirable to develop products comprised of biodegradable components from green resources or renewable waste due to a shortage of fossil fuel. Large quantities of forestry waste are generated in the pulping process, one of which is wood auto-hydrolysates, which contains large amounts of hemicellulosic and some lignin. In this work, a green and facile route is proposed to convert wood auto-hydrolysate (WH) to value-added nanocomposite films. Wood auto-hydrolysate was combined with montmorillonite (MMT) as the basic components together with a small quantity of graphene oxide (GO) to produce a new ternary, bioinspired nanocomposite film with high strength and fire retardant properties. GO was initially used to fabricate the WH-MMT-GO ternary bioinspired nanocomposites, and the interfacial interaction between WH, MMT, and GO was enhanced by the synergistic effect of hydrogen and covalent bonds. The resulting nanocomposites WH-MMT-GO (FWSG+GO) with only 0.8 wt% rGO exhibited promising features, such as a good thermal stability (residual mass above 75% at 600 °C), and a high strength of 122 MPa, which was better than other hemicellulosic-based films or wood auto-hydrolysate based films. The films had excellent fire retardant properties. GO also reduced the weight fraction of the novel nanocomposites was reduced by more than 90% compared to the neat WH. Furthermore, when wood hemicellulose-based films are reported to be hydrophobic, the novel WH-MMT-GO nanocomposites proved to be hydrophobic due to the introducing of rGO. The proposed synthetic strategy could make the wood auto-hydrolysate useful for fabrication of fire-protective films, coatings, packaging, etc.
Cross-linkable hydrogels for 3D bioprinting

Nimna Alizadeh1,2, nza0037@auburn.edu, R. M. Broughton1,2, Maria Auad1,2, (1) Center for Polymers and Advanced Composites, Auburn university, Auburn, Alabama, United States (2) Chemical engineering, Auburn university, Auburn, Alabama, United States (3) Mechanical engineering, Auburn university, Auburn, Alabama, United States

3D printing is an additive manufacturing method that has advanced in biological applications in recent years. The challenges in 3D bioprinting are: a) to select the appropriate material and approaches, b) to make a reliable 3D model with all the details and c) to select the appropriate flow rate and speed of printing. In this research, 3D printer HYRELL 3UM with head CSD-30 which has 280 nm wavelength Ultraviolet (UV) lamp for photo-curing the material is used. Head CSD-30 can extrude viscous material by piston and UV lamp could cure the material immediately after coming out of the head. Two systems have been tested: i) Nanofibrillated cellulose/alginite mixtures and, ii) ultraviolet (UV) photo-cross-linkable interpenetrating hydrogels with Irgacure 2959 as an initiator. Rheological properties were used for checking the shear-thinning behavior of the material and strain sweep tests were performed for finding the maximum strain, which the material could tolerate without any permanent deformation. Moreover, rheological tests were used for determining the efficient flow rate and speed of the printing. 3D models were created by Ansys and Meshlab to remove excess faces in 3D structure.

Biobased Gels & Porous Materials

CELL 428

Thermal conductivity of bio-aerogels

Tatiana Budtova, Tatiana.Budtova@mines-paristech.fr. CEMEF/Mines ParisTech, Sophia Antipolis, France

Aerogels are ultra-light weight and highly porous nanostructured materials, with open pores and high specific surface area. They are synthesized via sol-gel route followed by solvent extraction with supercritical CO2. Classical aerogels are based on silica or synthetic polymers (for example, polyurethanes). At the beginning of the 21st century a new class of aerogels emerged, based on polysaccharides: bio-aerogels.

One of the extraordinary properties of some aerogels is their low thermal conductivity which can be lower than that of air (0.025 W/m.K), making them thermal super-insulating materials. Such materials prevent energy losses which is crucial in buildings, appliances and transport (refrigerated tracks) industrial sectors. Thermal super-insulation can be reached in mesoporous materials with low density. Does it work for bio-aerogels? Literature on this topic is rather scarce. In this presentation a review of the thermal properties of bio-aerogels will be made. Literature results will be compared with the new ones obtained recently in our laboratory. Problems, prospects and open questions will be discussed.

Approaches for development of cryogels scaling laws

Paulo V. Toledo, paulo.vinicius.toledo@usp.br, Denise Petri, dfp@usp.br. University of Sao Paulo, Sao Paulo, Brazil

The present study investigates the correlation between polysaccharide chemical structure and the properties of cryogels prepared with them. For this, chitosan, carboxymethylcellulose, hydroxypropyl methylcellulose, xanthan and diutan gum were chosen. Moreover, parameters such as polymers molar mass, concentration, and cross-linking conditions were evaluated. The synthesis of cryogels was performed through the slow stirring of polysaccharide in water, followed by melting, freezing at 285 K, freeze-drying, and dry cross-linking at 438 K over 7 or 25 minutes. The cryogels were analyzed by means of compression tests, contact angle measurements, scanning electron microscopy images and X-ray microtomography image reconstruction. Those methods allow creating empirical scaling laws concerning polysaccharides structure and aerogels properties. For instance, the compression modulus increased with the square of polymer concentration, the density increased linearly with the polymer concentration. Contact angle values were statistically independent on the polysaccharide structure. Micro CT analyses evidenced that the xanthan cryogels (Figure 1) have the largest surface area and the smallest pore size, indicating that the polysaccharide branching plays an important role on the aerogel structure.

High porosity cellulose-based foams by ice-templating

Carlo Antonini1, Otto Nylander2, Tomas Geiger1, thomas.geiger@empa.ch. (1) Applied Wood Materials, Swiss Federal Laboratories for Materials Science and Technology (Empa), Dübendorf, Switzerland (2) Fiber and Board Laboratory, Weidmann Electrical Technology AG, Rapperswil, Switzerland

Microfibrillated cellulose (MFC also known as nanofibrillated cellulose, NFC) is a cellulose-based, biodegradable, renewable, and intrinsically amphiphilic material, composed of high-aspect ratio fibrils, obtained through cellulose pulp disintegration. Cellulose fibrils possess outstanding mechanical properties, thanks to their high weight-to-strength ratio. In particular, MFC porous foams are attracting an increasing attention for their potential in a wide variety of applications, where low density and high surface areas are required, including filtration processes, gas adsorption and selective liquid absorption for remediation of polluted areas. One commonly used technique to fabricate MFC foams is based on ice templating, through the well-known freeze-drying process, in which an aqueous suspension of MFC fibres is frozen by liquid nitrogen and vacuum-dried, to obtain dry foams. However, the vacuum drying is a high energy-consuming step, and currently represents a bottle-neck for the process scale-up, needed for industrially relevant applications. As such, the current study approaches the issue of how to improve the ice templating strategy, avoiding the vacuum drying step, while achieving extremely high porosity.

To address the issue, we present a novel straightforward freeze-thawing-drying procedure, based on the use of urea as additive to the aqueous MFC suspension [1]. Such method allows the production of mechanically stable, lightweight MFC structures, avoiding foam collapse, upon facile freezing-drying steps.

For detailed foam structure characterization, results from high-resolution 3D X-ray tomography of the foams will be presented, to provide information on foam pore size and skeleton distribution, with μm-size resolution.

On the mechanism of freeze-induced crosslinking of aerogels made from periodate-oxidised cellulose nanofibrils

Torbjörn Pettersson1,2, torbj@kth.se, Johan Erlanson1, Per A. Larson1, Lars Wegberg1,2, (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) WWSC Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden

Aerogels made from nanocellulose have attracted great attention during recent years. One initial shortcoming of nanocellulose-based aerogels was their lack of mechanical integrity when exposed to liquid water, in which they easily disintegrate. This issue has been addressed by several researchers and several methods to chemically crosslink nanocellulose structures have been reported. A common crosslinking procedure involves addition of crosslinking agents to the nanocellulose before the fabrication of the dry material together with a curing step, although crosslinking has also been reported in the wet state by using, for example, aldehyde-containing nanocellulose and amine-containing crosslinkers. Another method to produce crosslinked cellulosic structures is to induce a significant amount of aldehydes in the cellulose backbone, for example by periodate oxidation, that induces inter-molecular and inter-fibrillar hemiacetals through a reaction with adjacent cellulose hydroxyls. Recently, a method was reported for producing wet-stable CNF aerogels by simply freezing and thawing dispersions of these modified nanofibrils, i.e. a method without energy and time consuming freeze-drying and thermal activation
of the crosslinker (J. Erlandsson et al., Applied Materials Today, 5, 2016, p246). However, in this initial investigation the focus was on presenting the new method and little attention was on the properties of the aldehyde-containing CNFs and the influence of their properties on the final properties of the aerogel. This also means that no dedicated experiments were performed to clarify the mechanism of formation of the structure, the crosslinking reaction or the influence of critical parameters of the aerogel preparation. This work aims to shed some light on the mechanism behind this freeze-induced crosslinking and the ability to form crosslinked networks in the form of aerogels. Besides characterisation of the aerogels formed, a large attention was on the use of colloidal probe AFM measurements to study the origin of the bonds involved in the cross-linking reaction between the cellulose fibrils.

Green synthesis of nanocellulose aerogels decorated with palladium nanoparticles and their application in water purification

Jin Gu1,2, qijun.pku@gmail.com, Anthony Dichage2, (1) Wood Science and Technology, South China Agricultural University, Guangzhou, Guangdong, China (2) School of Environmental and Forest Sciences, University of Washington, Seattle, Washington, United States

Synthesis of noble metal nanoparticles have attracted considerable interests due to their versatile catalytic properties for a wide range of chemical reactions. Specifically, palladium nanoparticle (Pd-NP) is one of the most widely used catalysts for cross-coupling, hydrogenation, dye reduction reactions etc. In this study, a regentless method was reported for synthesizing Pd-NPs supported on cellulose nanofibrils (CNFs). CNFs played a multiple role as a supporting matrix, capping and reducing agent. Stable Pd-NPs of 10–20 nm in diameter were successfully obtained by simply mixing the CNFs with an optimized concentration of the palladium precursor solution and heating the aqueous mixture to 90 °C for 1h. The CNF-Pd-NP hybrid materials could self-assemble to porous aerogel by a freeze-drying process. The resulting CNF-Pd-NP aerogels were further characterized by X-ray diffractions (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), inductively coupled plasma mass spectrometry (ICP-MS), and then tested to catalyze the degradation of Congo red (CR) and methylene blue (MB). The catalytic results indicate that within 20 min, CR and MB solutions with an initial concentration of 30 mg/L can be reduced to colorless forms. In addition, the CNF-Pd-NP aerogels showed reusability for multiple cycles without deterioration of catalytic activity, demonstrating great potential for applications in water purification and other catalytic systems.

Cellulose-reinforced and hybrid cellulose-based biofoams for structural and flame resistance applications

Pedro E. Fardim1,2, pfrdimm@abo.fi, Carl Lange1, Jasmina Obradovic1, (1) Abo Akademi University, Turku, Finland (2) Chemical Engineering, KU Leuven, Leuven, Belgium

Traditionally, polymers and macromolecular components used in the foam industry are mostly derived from petroleum. The current transition to a bio-economy creates demand for the use of more renewable feedstocks. Cellulose fibres have excellent potential for reinforcement or formation of biobased foams with engineering properties. In this work, we present two approaches for producing biofoams. First, acetylated epoxidized soybean oil and variable amounts of cellulose fibres were used in the production of bio-based foams and characterised by several techniques, including porosity measurements, nanointeraction testing, scanning electron microscopy, and thermogravimetric analysis. It was found that the introduction of cellulose fibres during the foaming process was necessary to create the three-dimensional polymer foams. The resulting foams possessed a porosity of approximately 56%, and the incorporation of cellulose fibres did not affect thermal behaviour. Scanning electron micrographs showed randomly oriented pores with irregular shapes and non-uniform pore size throughout the samples. In a second approach, we studied the flame propagation and combustion properties of a lightweight fibrous foam produced from a layered double hydroxides (LDH) modified thermostable pulp fibres. The in situ synthesis of Mg-Al LDH with pulp fibres was engineered to include both micron and nano-sized particles. The method allowed loading the fibres with LDH up to 34% (w/w). Observed pyrolytic effects included 65% reduction in CO2 production rate, and similar reductions in peak heat release rate (PHRR) and in amount of soot during the oxidative pyrolysis. The in situ synthesized LDH particles shielded the fibres from external heat by reducing the rate of oxidation and liberation of volatile gases. Effective charning was observed at the interphase of LDH nanoparticels and organic material.

Cellulose and cellulose composites for carbon dioxide sorption at low and elevated temperatures

Rohan Dassanyake, Chamilia Gunathilake, Arasha C. Dassanyake, Mietek Jaroniec, Noureddine Abidi1, noureddine.abidi@ttu.edu, (1) Chemistry and Biochemistry, Kent State University, Kent, Ohio, United States (2) Fiber Biopolymer Research Institute, Texas Tech University, Lubbock, Texas, United States

The current CO2 Capture, Storage, and Utilization technologies include absorption, adsorption, membrane and cryogenic processes. Among those, the adsorption processes on solid adsorbents have been regarded as the most attractive technique due to their high CO2 sorption capacity, low cost, low energy and reusability. In this regard, solid sorbents prepared from cellulose are promising because of their relative abundance, sustainability, biodegradability, non-toxicity, renewability, thermal stability and good sorption properties. Activated carbons possess high surface areas and low chemical reactivity, therefore, they have been widely used as adsorbents at low and ambient temperatures. On the other hand amidoximes have recently recognized as practical candidates for high temperature sorbents over typical amine-based solid sorbents. Here, we report the data for the CO2 capture by CO2-activated amine cellulose derived carbon monolith with enhanced microporosity and amidoxime-functionalized cellulose-based polymers at low (0°C) and elevated temperatures (120°C), respectively.

Low density foam-formed fibre structures with enhanced elasticity and strength

Katarina Torvinen, katarina.torvinen@vtt.fi, Tiina Pöhler, Lappalainen Timo, Jukka Ketoja. VTT, Jyvaskyla, Finland

In wet aqueous stable foams, air bubbles prevent fibre flocculation and sedimenting keeping the fibres separate even after drying of the material. In addition to the fibres, the foam can carry small, even nano-sized fibris in the foam vertices and interfaces ensuring their high retention in the final structure. This process, foam forming, opens up possibilities to use raw materials of different size range, from long regenerated or natural fibres up to cellulose nanofibris in a same material. The interactions between different-scale fibres and the foam provide tools to tailor both structural homogeneity and the micro-scale structure. In this work we investigated the effect of softwood cellulose and hemp fibres, water-soluble polymers, cellulose nanofibrils and new type of flaxinated wood fines on the strength formation of porous foam-formed fibre networks. The structure of these materials was studied by using x-ray micro-tomography and image analysis. The fibres material made of spruce wood and the cellulose nanofibrils significantly improved the compression and bending strength. Moreover, elasticity was enhanced by natural rubber accumulating at fibre joints and helping the network structure to expand back after compression. The future applications of the low density foamed structures include e.g. cushioning elements in packaging and acoustic materials in indoor construction. In the current applications, the properties and the production economics of cellulose-based products can be enhanced by the higher processing consistency in the manufacturing phase compared to the traditional water forming and the simultaneous use of longer fibres.