American Chemical Society
Division of Cellulose and Renewable Materials
Fall 2019 ACS National Meeting, San Diego, CA, August 25 - 29, 2019

W. Thielemans, Program Chair; G. Larkin, Program Chair

SUNDAY MORNING

Lignin Based Bioproducts
M. Nejad, Organizer; G. Beckham, Organizer; M. Paleologou, Organizer; E. L. Hegg, Organizer; D. Hodge, Organizer; J. Luterbacher, Organizer; D. Hodge, Presiding; N. A. Rorrer, Presiding
Papers 1-6

SUNDAY AFTERNOON

Lignin Based Bioproducts
M. Nejad, Organizer; G. Beckham, Organizer; D. Hodge, Organizer; M. Paleologou, Organizer; E. L. Hegg, Organizer; J. Luterbacher, Organizer; E. L. Hegg, Presiding; M. Paleologou, Presiding
Papers 7-12

SUNDAY EVENING

General Posters
G. M. Larkin, Organizer; Papers 13-30

MONDAY MORNING

Lignin Based Bioproducts
M. Nejad, Organizer; J. Luterbacher, Organizer; G. Beckham, Organizer; M. Paleologou, Organizer; E. L. Hegg, Organizer; D. Hodge, Organizer; G. Bauer, Presiding; M. Nejad, Presiding
Papers 31-36

MONDAY EVENING

Sci-Mix
W. Thielemans, Organizer; G. M. Larkin, Organizer; Papers 28, 25, 16, 26, 24, 20, 27, 22, 23, 29, 30

TUESDAY MORNING

Advances in Characterizing Modified & Degraded Wood
M. Aro, Organizer; G. M. Larkin, Organizer; M. Aro, Presiding; G. M. Larkin, Presiding
Papers 37-43

WEDNESDAY MORNING
Materials Advances in Nanocellulose Research for Engineered Functionality
H. Jameel, Organizer; L. A. Lucia, Organizer; L. Pal, Organizer; P. Sharma, Organizer; L. Pal, Presiding; P. Sharma, Presiding Papers 44-51

THURSDAY MORNING

Materials Advances in Nanocellulose Research for Engineered Functionality
H. Jameel, Organizer; L. A. Lucia, Organizer; L. Pal, Organizer; L. A. Lucia, Presiding Papers 52-59
CELL

DIVISION OF CELLULOSE AND RENEWABLE MATERIALS

W. Thielemans and G. Larkin, Program Chairs

SUNDAY MORNING

Section A

Marriott Marquis San Diego Marina
Rancho Santa Fe 1

Lignin Based Bioproducts

G. Beckham, E. L. Hegg, J. Luterbacher, M. Nejad, M. Paleologou, Organizers
D. Hodge, Organizer, Presiding
N. A. Rorrer, Presiding

8:30 Introductory Remarks.

8:35 1. Recent progress in the generation of lignin based water soluble polymers. P. Fatehi

9:00 2. Lignin-based thermoplastic blends: Biorefinery willow lignin and polylactic acid (PLA). M.J. Ovadias, B. Bujanovic


9:50 Intermission.


10:30 5. Radical polymerization of lignin materials. J. Jimenez, E. Ford

10:55 6. Recyclable and smart thermoset from lignin biophenols. M.M. Abu-Omar, S. Zhao, K. Hanson

SUNDAY AFTERNOON
Lignin Based Bioproducts

G. Beckham, D. Hodge, J. Luterbacher, M. Nejad, *Organizers*
E. L. Hegg, M. Paleologou, *Organizers, Presiding*

1:00 Introductory Remarks.

1:05 7. Characterization and catalytic upgrading of acetal-functionalized lignin. **J. Luterbacher**

1:30 8. Insights into the isolation and structural changes of lignin in inorganic ionic liquid. **X. Pan**


2:20 Intermission.

2:35 10. Lignin modification and/or selection for application in wood adhesives. **F. Monteil-Rivera**


3:25 12. Lignin as a polyol replacement in polyurethane applications. **M. Nejad**, M. Alinejad

**SUNDAY EVENING**

San Diego Convention Center
TBD

**General Posters**

G. M. Larkin, *Organizer*

7:00 - 9:00


15. Detoxification of sugarcane bagasse hydrolysate by atmospheric cold plasma to enhance bioethanol production. **T. Kuo, H. Wang, K. Cheng**

16. Production of bacterial cellulose by treating sugarcane bagasse hydrolysate with atmospheric cold plasma. **S. Huang, K. Cheng**

17. Preparation of chitin nanofiber-based composite/hollow particles by Pickering emulsion polymerization. **S. Noguchi, K. Yamamoto, J. Kadokawa**


21. Withdrawn

22. Improving the fouling resistance of nanocellulose membranes for ultrafiltration. **M. Yang, P. Hadi Myavagh, H. Ma, H. Walker, B.S. Hsiao**

23. Increased adsorption capacity for heavy metal ions via sequential oxidation of carboxycellulose nanofibers from raw wood. **M.C. Nolan**

24. Facile synthesis of vanillin from kraft lignin. **R. Zhang, T. Repo**


26. Dissolution of lignin-rich microfiber from organosolv assisted with catalysts and its regeneration. **H. Choi, J. Lee, T. Eom**

27. Sustainable pathways to increase lignin reactivity for resin applications. **M. Arefmanesh, E. Master, M. Nejad**

28. Lignin-derived carbon nanocomposites as sodium-ion battery anodes. **K. Jiang, X. Tan, Z. Li**

29. Withdrawn
30. Building wind turbines from renewable and recyclable composites. J.R. Dorgan, B. Tan, H. Bambhania, D. Cousins

MONDAY MORNING

Section A

Marriott Marquis San Diego Marina
Rancho Santa Fe 1

Lignin Based Bioproducts

G. Beckham, E. L. Hegg, D. Hodge, J. Luterbacher, M. Nejad, M. Paleologou, Organizers
G. Bauer, M. Nejad, Presiding

8:30 Introductory Remarks.

8:35 31. Redefining and redesigning lignin. J. Ralph, H. Kim

9:00 32. Alkaline enzymes for lignin valorization. A. Mialon


9:50 Intermission.

10:05 34. Evaluating the impacts of two-stage alkaline-oxidative pretreatment of hybrid poplar on lignin properties. S. Kumar Singh, A. Savoy, Z. Yuan, B. Bals, E.L. Hegg, D. Hodge

10:30 35. Chemical funneling of lignin derived monomers into aromatic chemicals. N. Yan


Future of Biomacromolecules at a Crossroads of Polymer Science & Biology

Synthetic Cells

Sponsored by POLY, Cosponsored by BIOL, CARB, CELL, COLL, ENVR, MEDI, PHYS and PMSE†
MONDAY AFTERNOON

Future of Biomacromolecules at a Crossroads of Polymer Science & Biology

Tissue Engineering

Sponsored by POLY, Cosponsored by BIOL, CARB, CELL, COLL, ENVR, MEDI, PHYS and PMSE

MONDAY EVENING

San Diego Convention Center
TBD

Sci-Mix

G. M. Larkin, W. Thielemans, Organizers

8:00 - 10:00

16, 20, 22, 23, 24, 25, 26, 27, 28, 29, 30. See Previous Listings.

TUESDAY MORNING

Marriott Marquis San Diego Marina
Rancho Santa Fe 1

Advances in Characterizing Modified & Degraded Wood

M. Aro, G. M. Larkin, Organizers, Presiding

8:00 Introductory Remarks.

8:05 37. Thermal conversion chemistry of wood: Consequences for quality control of heat treated wood products. W. Willems

8:55 39. Quantification of wood thermal treatment by electron paramagnetic resonance spectroscopy. J.A. McVay, S.M. Berry


9:45 Intermission.

10:00 41. Probing nanostructural changes in chemically modified wood cell walls with small angle neutron scattering. N. Plaza, J.E. Jakes, C.G. Hunt, S. Pingali, C.R. Frihart, D. Stone, L. Lorenz, D.J. Yelle

10:25 42. Beech wood thermal treatment level characterization by different treatment level markers. W. Willems, M. Altgen

10:50 43. Use of X-ray scattering to understand the mechanisms behind the moisture and decay resistance of epoxybutene modified wood. R.E. Ibach, N. Plaza

11:15 Discussion.

TUESDAY EVENING

Future of Biomacromolecules at a Crossroads of Polymer Science & Biology

Sponsored by POLY, Cosponsored by BIOL, CARB, CELL, COLL, ENVR, MEDI, PHYS and PMSE

WEDNESDAY MORNING

Section A

Marriott Marquis San Diego Marina
Marriott Grand Ballroom Section 8

Materials Advances in Nanocellulose Research for Engineered Functionality

Cosponsored by PMSE and POLY
H. Jameel, L. A. Lucia, Organizers
L. Pal, P. Sharma, Organizers, Presiding

8:00 Introductory Remarks.
8:05 44. Nitro-oxidized carboxycellulose nanofibers. P. Sharma, S.K. Sharma, B.S. Hsiao

8:30 45. Nitro-oxidized carboxy nanocellulose derived from agave for effective removal of lanthanides from water. S. Sharma, P. Sharma, B.S. Hsiao

8:55 46. Developing hydrophobic cellulosic membrane for membrane distillation. R. Joshi, T. Lindstrom, B.S. Hsiao

9:20 47. Designing cellulose nanocrystal films for superhydrofobicity without the use of fluorine-based chemicals. A. Cordova, R. Alimohammadzadeh, I. Sanhueza, A. Svedberg, A. Horvath

9:45 Intermission.

10:05 48. Carbonized nanocellulose as low-cost 1D carbon nanomaterials for energy storage. Z. Li, T. Thundat

10:30 49. Nanocellulose reinforced polymer composites as flexible mechanical energy harvesters. K. Shanmuganathan, F. Ram

10:55 50. Cellulose nanofibers biotemplated metal nanoparticles as a water dispersible SERS substrate. C. Rusin, Y. Boluk, M.T. McDermott


11:45 Concluding Remarks.

Future of Biomacromolecules at a Crossroads of Polymer Science & Biology

Delivery Systems

Sponsored by POLY, Cosponsored by BIOL, CARB, CELL, COLL, ENVR, MEDI, PHYS and PMSE

WEDNESDAY AFTERNOON

Future of Biomacromolecules at a Crossroads of Polymer Science & Biology

Biomaterials
Merriott Marquis San Diego Marina
Marriott Grand Ballroom Section 8

Materials Advances in Nanocellulose Research for Engineered Functionality

Cosponsored by PMSE and POLY
H. Jameel, L. Pal, Organizers
L. A. Lucia, Organizer, Presiding

8:00 Introductory Remarks.

8:05 52. Barrier performance of cellulose nanocrystal (CNC) films for high barrier packaging applications. M. Nuruddin, R. Chowdhury, J.P. Youngblood, J.A. Howarter

8:30 53. Spherical cellulose nanoparticles (CNPs) for magnetic resonance imaging (MRI) and X-ray computed tomography (CT). S. Chakravarty, F.J. Buchanan, J.M. Hix, E.M. Shapiro

8:55 54. Superabsorbent from cellulose nanofibers for oil and chemical spill responses. O. Laitinen, H. Liimatainen

9:20 55. Removal of chromium (VI) from aqueous solutions by cationic nanostructured cellulose. X. Huang, G. Dognani, P. Hadi Myavagh, B.S. Hsiao

9:45 Intermission.


10:50 58. Redispersible chitin nanocrystals extracted through electron beam irradiation followed by high pressure homogenization. H. Lee, J. Shin


11:40 Concluding Remarks.
Recent progress in the generation of lignin based water soluble polymers

Pedram Fatehi, pfatehi@lakeheadu.ca. Chemical Engineering, Lakehead University, Thunder Bay, Ontario, Canada

Lignin has been regarded as an under-utilized by-product of the chemical pulping and cellulosic ethanol industries. To improve the financial profit of these processes and prevent a major loss of resources, value-added products could be produced from lignin. Recently, different processes were developed for generating lignin at commercial scales in an effort to facilitate the production of value-added products from lignin. For example, the LignoBoost and LignoForce technologies are commercial processes for producing kraft lignin, while TMPBio technology is employed for producing hydrolysis lignin in a cellulosic enzymatic process. Due to the commercial availability of lignin, extensive research has been conducted on producing altered lignin based value-added products. However, efforts in producing value-added water-soluble lignin-based products including dispersants and flocculants are mainly limited to the research conducted by Dr. Fatehi in the past 7 years in Canada.

Dispersants and flocculants are water soluble chemicals with significant worldwide applications. Dispersants are widely used in the mining, oil, textile and construction industries. Flocculants are widely used in the mining industry for density control in thickeners, or as rheology modifiers in the concentrate thickeners, for instance. They are also used in municipal and industrial wastewater systems. However, the commercial dispersants and flocculants are mainly oil-based, ineffective, expensive and/or non-biodegradable.

Lignin can be tailored to have diverse charge densities, molecular weights and degrees of hydrophilicity, all of which are of significant importance for dispersants/flocculants. After chemical modification for dispersant and flocculant production, lignin-based polymers will inherent some unique features from lignin (e.g. hydrophobicity and three-dimensional structure) that are not available in the currently used commercial flocculants/dispersants. In this presentation, Dr. Fatehi will elucidate 1) recent development in the production of lignin-based water-soluble products following polymerization and grafting pathways, and 2) fundamental challenges and opportunities associated with the generation, characterization and use of such products.

Lignin-based thermoplastic blends: Biorefinery willow lignin and polylactic acid (PLA)

Mathew J. Ovadias, mjovadia@syr.edu, Biljana Bujanovic. Paper and Bioprocess Engineering, State University of New York College of Environmental Science and Forestry, Syracuse, New York, United States
The need to replace petroleum products in all aspects of society is as great as ever. Lignocellulosic biorefineries represent a great opportunity to do so while taking advantage of carbohydrates that do not affect the global food supply. Lignin valorization is an essential part of making future lignocellulosic biorefineries economical. This research will focus on derivatization and use of biorefinery lignin, specifically from willow (genus: Salix, family: Salicaceae), as a thermoplastic material in blends with biorenewable PLA. Since lignin has been shown to have antioxidants and UV absorbing properties, the goal of this research is to produce thermoplastic blends that have expanded functionality while maintaining or improving the thermal and mechanical properties of PLA. Willow chips made from a blend of commercial willow cultivars were subjected to hot-water extraction (autohydrolysis), a biorefinery pretreatment to remove most hemicelluloses. Lignin is a byproduct of this pretreatment and was recovered from the hydrolysate.

Lignin recovered from a process based on autohydrolysis has relatively high hydrophilicity. Inherently, it is incompatible with commercial plastics, including PLA. Therefore, lignin was esterified with acetic anhydride (C$_2$) and lauroyl chloride (long chain-fatty acid, C$_{12}$). Following C$_{12}$ esterification, the free fatty acid remained in the lignin derivative. In this study, hexane extraction was proposed to remove the free fatty acid. Structural and thermal properties of recovered and esterified lignins were evaluated prior to blending with PLA at various concentrations (1-20% w/w) via lab-scale melt extrusion. Filaments at 1% (w/w) lignin content were analyzed by light microscopy to examine the extent of lignin aggregation. All filaments were tested for mechanical and thermal properties.

### Polymers from biphenyl-linked lignin dimers

Nicholas A. Rorrer$^1$, nicholas.rorrer@nrel.gov, Jared Anderson$^1$, Joel Miscall$^1$, Mariel Price$^2$, Gregg Beckham$^1$. (1) National Bioenergy Center, National Renewable Energy Laboratory, Golden, Colorado, United States (2) Department of Chemistry, Colorado State University, Fort Collins, Colorado, United States

The catalytic depolymerization of lignin almost invariably results in a wide variety of reaction products due to the heterogeneous nature of the substrate. Lignin-derived monomers from multiple depolymerization processes can be readily upgraded to useful molecules for implementation into fuels, chemicals, or materials. Conversely, dimers of lignin typically exhibit C-C linkages and are quite difficult to selectively valorize. A common, highly recalcitrant linkage in lignin is the biphenyl dimer (5-5’ linkage), which does not typically find use or implementation in materials. To that end, here 5-5’ dimers are implemented into polycarbonates, polyurethanes, and epoxy resins. Material properties are studied as a function of side chain functionality. For comparison to incumbent materials wherein bisphenol A is employed, endocrine disruption potential is also investigated via displacement of estradiol. Additionally, bio-based lactones are implemented to introduce recyclable moieties in the backbones of these polymers (e.g. polycarbonates and epoxy resins). Overall, materials synthesized from the 5-5’ dimers...
possess properties that are competitive with or exceed the analogous polymers obtained from bisphenol-A.

CELL 4

From trees to plastics: High-performance polymers from lignin-rich feedstocks

**Thomas H. Epps, thepps@udel.edu. Chemical Engineering, University of Delaware, Newark, Delaware, United States**

We demonstrate that materials with reproducible thermal and mechanical characteristics can be synthesized in a controlled and predictable manner from batches of monomers with complex and somewhat variable compositions, such as minimally processed bio-oils obtained from depolymerized lignin. We used this approach in the fabrication of high-performance pressure sensitive adhesives (PSAs) from chemicals directly obtained from raw biomass deconstruction. A particularly unique and translatable aspect of this work was the use of a monomer obtained from real biomass, as opposed to a model compound or lignin-mimic, to generate well-defined and nanostructure-forming polymers. In one example, poplar wood depolymerization followed by minimal purification steps produced two aromatic compounds, 4-propylsyringol and 4-propylguaiacol, with high purity and yield. Efficient functionalization of those aromatic compounds with either acrylate or methacrylate groups generated monomers that could be easily polymerized by a scalable reversible addition-fragmentation chain-transfer (RAFT) process to yield polymeric materials with high glass transition temperatures and robust thermal stabilities, especially relative to other potentially biobased alternatives. These lignin-derived compounds were used as the major component in low dispersity triblock polymers comprised of 4-propylsyringyl acrylate and n-butyl acrylate (also can be biobased). The resulting PSAs exhibited excellent adhesion to stainless steel without the addition of any tackifier or plasticizer. The 180° peel forces were up to 4 N cm⁻¹ and tack forces were up to 2.5 N cm⁻¹, competitive with commercial Fisherbrand™ Labeling Tape and Scotch® Magic™ Tape, demonstrating the practical significance of our biomass-derived materials. Also, we investigated systems of model and ‘real’ lignin-derived monomers to gain greater understanding of the kinetic parameters for the multicomponent RAFT polymerizations that can be predicted using kinetic data from corresponding homopolymerizations, reactivity ratios, and feed compositions. The glass transition and thermal degradation temperatures of the resulting polymers also were shown to be predictable and adjustable prior to polymerization.
Radical polymerization of lignin materials

Javier Jimenez, jjimene@ncsu.edu, Ericka Ford. North Carolina State University, Raleigh, North Carolina, United States

Lignin has been mass produced in the paper and pulp industry with about 50 million tons produced in 2013. However, of the 50 million tons, only 2% was further refined for commercial use whereas the remaining 98% was burned as low-value fuel. Ultimately, this untapped biomaterial can be used in polymeric blends with petroleum-derived synthetics to decrease costs and increase the environmental sustainability of the finished products. However, within the use of lignin, there have been notable problems in its processibility, which are attributed to its low molecular weight and structural irregularities.

Depending on the process of extraction, lignin types can have different chemical structures. These differences can affect the build-up of molecular weight and their rheology post polymerization. Both Kraft lignin and acid-hydrolyzed lignin were used to investigate the effect of =ene group (C=C) concentration on the polymerization of each lignin type. Solution viscosities of Kraft lignin dissolved in dimethyl sulfoxide (DMSO) increased as the weight percentage of free radical initiator reached 20% of lignin. An elastic, DMSO insoluble polymer formed once initiator concentration reached 50% of lignin. Further viscosity did not increase with initiator concentration for reactions involving acid-hydrolyzed lignin. NMR analysis showed distinct variation on specific peak ranges as noted in literature indicating structural changes.

Recyclable and smart thermoset from lignin biophenols
Recent research advances have shown that lignin can be upgraded first via RCF (Reductive Catalytic Fractionation) directly from lignocellulosic biomass into biophenols. Alternatively lignin can be fractionated using protective group chemistry and subsequently upgraded over a metal catalyst into biophenols. In this presentation we will discuss several chemical approaches that utilize lignin based biophenols to make thermoset polymers that surpass petroleum based materials in their mechanical properties. Additionally novel features can be incorporated into our polymers enabling recycling, healing and memory shape in response to stimuli.

CELL 7

Characterization and catalytic upgrading of acetal-functionalized lignin

Jeremy Luterbacher, nathalie.matthey@epfl.ch. Biological Environmental engineering, Cornell University, Ithaca, New York, United States

The production of various chemicals from lignin usually involves its initial depolymerization into aromatic monomers. During depolymerization, the biggest challenge is usually not achieving the desired reaction, but rather avoiding being outcompeted by other, detrimental reactions. Specifically, ether bond cleavage reactions, which control lignin extraction and depolymerization are often outpaced by condensation reaction that make extracted lignin very difficult to upgrade. We have shown that acetal formation during lignin extraction can reversibly “trap” stabilized intermediate molecules, reducing degradation and increasing product yields. Lignin can be extracted during pretreatment as stabilized oligomers and still retain its ability to be upgraded at near-theoretical yields. Because, this lignin can be isolated quantitatively in a soluble form and have its original structure retained by the stabilization chemistry, it offers a number of unique characterization and catalytic upgrading opportunities. Using nuclear magnetic resonance (NMR) techniques, we can precisely analyze structure-conversion relationships and develop models to very accurately predict (<3% error) upgrading yields based on NMR spectra. We have used this isolated soluble lignin to study support and solvent effects during catalytic upgrading without interference of other biomass components as well as to demonstrate continuous lignin upgrading in flow over supported metal catalysts.

CELL 8

Insights into the isolation and structural changes of lignin in inorganic ionic liquid

Xuejun Pan, xpan@wisc.edu. Biological Systems Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States
Our studies demonstrated that lignin could be quantitatively isolated as a solid fraction from lignocellulose when cellulose and hemicellulose were hydrolyzed into monosugars in an inorganic ionic liquid (acidic lithium bromide trihydrate (ALBTH) system) under mild conditions (40 mM HCl at 110 °C), and the isolated ALBTH lignin had great potential for downstream valorization because of high purity, low molecular weight, and non-condensed nature. Based on the observations, a facile and fast method was developed for the quantitation of lignin in biomass, which gave comparable results with the existing Klason (sulfuric acid) method. The characterization of the isolated lignin indicated that the lignin was extensively depolymerized to low molecular weight (MW = 2,000 ~ 4,000) in solid state without solubilization, and the isolated lignin had abundant uncondensed moieties (i.e., Hibbert's ketones and benzodioxanes), which had not been identified and detected in other isolated lignins before. Study using lignin model compounds verified that the lignin depolymerization was catalyzed by LiBr and acid synergistically in the ALBTH system via α-benzyl carbocation intermediate. The cleavage of the β-O-4-aryl ether bond led to the Hibbert’s ketone, while the ring formation between the α-benzyl carbocation and the methoxyl group on the adjacent benzene ring resulted in the benzodioxane structures. Condensation occurred when lignin model compounds were treated in ALBTH system, but the condensation of the real lignin in biomass was very limited in the ALBTH, because the mobility and accessibility of both the α-benzyl carbocation intermediates and the lignin fragments with electron-rich aromatic sites were limited or blocked in solid state, which prevented them from condensation.

**CELL 9**

**Oxidative deconstruction of lignin for the production of renewable chemicals and products**

Justin K. Mobley¹, Justin.mobley@uky.edu, Mark Meier¹, Zhen Fang¹, Mark Crocker¹,³, Yang Song²,³, Ashley Morris³, Matthew Weisenberger³, Stephanie Sorensen¹,³. (1) Chemistry, University of Kentucky, Lexington, Kentucky, United States (2) Chemistry, University of Kentucky, Lexington, Kentucky, United States (3) Univ. of KY CAER, Lexington, Kentucky, United States

While significant progress has been made over the past decade in the field lignin depolymerization, lignin remains one of the grand challenges to the bio-economy. Indeed, the utilization of lignin continues to be the main barrier to the implementation of cellulosic ethanol. This is, in part, due to the heterogeneity of structures in lignin and the relatively few processes that can break lignin down to monomers efficiently. Moreover, a variety of lignins are produced, which can have wildly different properties in terms of structure, solubility, and molecular weight. To combat this, we have examined a variety of lignins with our newly developed lignin depolymerization catalyst, Au/Li-Al LDH. This reaction system involves a heterogenous Au/Li-Al LDH catalyst in combination with O₂, followed by base hydrolysis in 0.1 M NaOH. Additionally, we tested a variety of lignin depolymerization techniques on two promising lignins in order to give an experimental review of the literature. It was found that the Au/Li-Al LDH catalyst/O₂ system in
combination with base hydrolysis efficiently depolymerizes a variety of lignins to small aromatic acids and aldehydes more effectively than the other processes tested. While the monomers may be used as renewable chemicals and feedstocks in their own right, we have examined their use, as well as the residual lignin, to make a variety of lignin products such as epoxy resins, carbon fibers, and activated carbons.

**CELL 10**

**Lignin modification and/or selection for application in wood adhesives**

**Fanny Monteil-Rivera**, fanny.monteil@cnrc-nrc.gc.ca. *Aquatic and Crop Resource Development, National Research Council Canada, Montreal, Quebec, Canada*

For decades, there has been a worldwide interest in developing new applications for lignin. Given the abundance of phenolic groups in lignin, a logical application for lignin consists in the replacement of phenol in wood adhesives like, for instance, in phenol-formaldehyde (PF) resins. Currently, levels of phenol replacement up to about 30% are considered reachable for plywood, without affecting the strength properties of the resulting wood composite, whereas similar levels are hard to reach for OSB. In order to increase the level of incorporation while maintaining viable process conditions, approaches including pre-activation and modification have been proposed. Despite these efforts, a lack of understanding resides on what a good lignin should look like for application in PF resins. In this study, two Kraft softwood lignins were selected and subjected to various green chemical reactions in order to modify their content and nature of phenolic groups. All unmodified and modified lignins were analyzed using \(^{31}\)P NMR, FT-IR, and size exclusion chromatography (SEC) and modification parameters were correlated with the structure and size of the resulting lignins. Selected samples were used as ingredient in the synthesis of lignin-PF resins and the ensuing resins were tested for dry bonding strength towards wood by the use of an Automatic Bond Evaluation System (ABES). Correlating lignin detailed structure with its performances as wood adhesive allowed the identification of lignin critical parameters for application in PF resins.

**CELL 11**

**Polyurethanes from unmodified technical lignin fractionated by sequential precipitation**

**Yun-Yan Wang**, ywang226@utk.edu, Priya Sengupta\(^2\), Yunqiao Pu\(^3\), Charles E. Wyman\(^2,4\), Charles M. Cai\(^2,4\), Arthur J. Ragauskas\(^1,3,4\). (1) Department of Forestry, Wildlife, and Fisheries, Center for Renewable Carbon, University of Tennessee Institute of Agriculture, Knoxville, Tennessee, United States (2) Center for Environmental Research and Technology (CE-CERT), Bourns College of Engineering, University of California Riverside, Riverside, California, United States (3) Joint Institute for Biological Science, Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee,
The quest for the valorization of technical lignins has been a keen interest for lignin chemists in the past 40 years. Owing to its multifunctionality, one of the promising strategies is to employ lignin as low-cost replacement of petro-based polyols in the production of polyurethanes. The structural heterogeneity and purity of technical lignins impeded effective incorporation of lignin in polymeric materials. Here, high-, medium- and low-molecular-weight fractions of an industrial softwood Kraft lignin preparation were prepared by sequential precipitation using a co-solvent system. A series of secondary polyols were applied in the lignin-polyurethane synthesis to improve lignin miscibility in the crosslinked network, and consequently enhanced the stiffness of the polymeric materials. In recent years, the development of lignocellulose biorefineries has provided new growth spots of technical lignins in addition to those generated as co-products in the pulp and paper industry. A hardwood solvolysis lignin was extracted by acidic aqueous tetrahydrofuran in a novel pretreatment called cosolvent enhanced lignocellulosic fractionation (CELF). Different formulations of polyurethanes synthesized with CELF lignin has been explored. The effects of lignin molecular characteristics and their intermolecular interactions with secondary polyols and isocyanates on mechanical and thermal properties of the lignin-based polyurethanes were investigated by tensile tests, DMA, SEM, and TGA.

**CELL 12**

**Lignin as a polyol replacement in polyurethane applications**

*Mojgan Nejad, nejad@msu.edu, Mona Alinejad. Forestry, Michigan State University, East Lansing, Michigan, United States*

The first step in defining the suitability of lignin as a polyol replacement is to measure its reactivity toward isocyanate. In this study, the properties of more than ten different lignin samples were measured using phosphorus nuclear magnetic resonance spectroscopy ($^{31}$PNMR) to determine hydroxyl content and gel permeation chromatography (GPC) for molar mass distribution analysis. Additionally, C, H, N, S, Na and K content of lignins were measured using elemental analyzer and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Subsequently, the degree of reactivity of these lignin samples was measured with four different isocyanates: methylene diphenyl disocyanate (MDI), toluene disocyanate (TDI), phenyl isocyanate (mono NCO), and polymeric methylene diphenyl disocyanate (pMDI). In each case, lignin was mixed with an isocyanate(NCO) based on 1:1 equivalent weight and the percentage of unreacted NCO were analyzed using titration (ASTM D5155), quantitative Fourier transform infrared spectroscopy (FTIR). Also, the reaction kinetics between lignin and NCO was studied using differential scanning calorimetric (DSC). The FTIR and DSC data were analyzed using MATLAB software. Finally, the correlation between lignin properties and their reactivity toward isocyanates were modeled using partial least square regression (PLSR) modeling with Umetric software. Our preliminary results indicate lignins display
a higher reactivity toward MDI and pMDI than TDI, and the aliphatic hydroxyl content of the lignin has the most significant effect on the reactivity of lignins toward isocyanate.

**CELL 13**

**Chemoenzymatic synthesis of carboxy-terminated maltooligosaccharides as cross-linking agent**

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Carboxy-terminated maltooligosaccharides are expected as cross-linking agent for condensation reaction with other biopolymers. As enzymatic glycosylation progresses regio- and stereoselectively, it is useful for synthesis of functional saccharide materials with well-defined structure. Phosphorylase catalyzes glucosylation of α-D-glucose 1-phosphate (Glc-1-P) and maltooligosaccharide as a glycosyl donor and glycosyl acceptor, respectively. As this enzyme shows weak specificity for the recognition of the substrate structures, we already reported that thermostable phosphorylase (from *Aquifex aeolicus* VF5)-catalyzed glucuronolysis using α-D-glucuronic acid 1-phosphate (GlcA-1-P) as a glycosyl donor. In this study, we synthesized carboxy-terminated maltooligosaccharide (GlcA-Glc-GlCOONa) by chemoenzymatic approach including the glucuronolysis. Oxidation of the reducing end of maltoheptaose was first performed using hypoiodous acid. Introduction of a glucuronic acid residue at the non-reducing end of the oxidized maltooligosaccharide (Glc₆-GlCOONa) was then performed by the phosphorylase-catalyzed glucuronolysis using GlcA-1-P. The MALDI-TOF MS of the product indicated that the enzymatic glucuronolysis took place accompanied with the enzymatic disproportionation of Glc₆-GlcCOONa to give GlcA-Glcₙ-GlCOONa with varying degrees of polymerization.
Synthesis of carboxy-terminated maltooligosaccharide (GlcA-Glcₙ-GlcCOONa).

CELL 14

Synthesis of 2-deoxyamyloses by phosphorylase-catalyzed enzymatic polymerization

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Phosphorylase catalyzes enzymatic polymerization of α-D-glucose 1-phosphate (Glc-1-P) as a monomer using a maltooligosaccharide primer to produce α(1→4)-glucan (amylose). Because of loose specificity for the recognition of substrates, phosphorylase recognizes several analogue substrates of Glc-1-P to give non-natural oligosaccharides. In this study, the synthesis of 2-deoxyamyloses was investigated by thermostable phosphorylase (from Aquifex aeolicus VF 5)-catalyzed enzymatic polymerization of D-glucal via the in-situ production of α-2-deoxy-D-glucose 1-phosphate (2dGlc-1-P). The enzymatic copolymerization of D-glucal with Glc-1-P was also carried out. The ¹H NMR spectrum of the isolated product by the enzymatic polymerization of D-glucal supported the structure of 2-deoxyamylose. The XRD profile of the product showed a different pattern from that of amylose, suggesting its intrinsic crystalline structure. Furthermore, the ¹H NMR spectra of the products, which were obtained by the enzymatic copolymerization of D-glucal and Glc-1-P, indicated that the compositional ratios of the two units were almost depending on the feed ratios, suggesting comparable reactivities of D-glucal and Glc-1-P. The XRD measurement of the products with the comparable unit ratios showed a broad diffraction pattern compared with those of amylose and 2-deoxyamylose. It suggested that the products had amorphous structure owing to random sequence of 2-deoxyglucose units and glucose units. In addition, the product with 4: 6 unit ratio could form a film by casting the DMSO solution and drying.
Thermostable phosphorylase-catalyzed enzymatic polymerization of D-Glucal via in-situ formation of 2dGlc-1-P.

CELL 15

Detoxification of sugarcane bagasse hydrolysate by atmospheric cold plasma to enhance bioethanol production

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Bioethanol offers a sustainable solution for transition from fossil-based fuels to renewable alternatives. The one produced from agricultural and forest residues, which is called lignocellulosic bioethanol, shows less conflicts with the food supply compared to the one made from food crops. Since the recalcitrant structure of lignocellulosic material, the process of pretreatment and hydrolysis should be done prior to fermentation. However, toxic compounds that inhibit fermentation were also produced during the process, which reduce the productivity of bioethanol. Here we show that the technique of atmospheric cold plasma contributed to the degradation of those inhibitory compounds. In this study, sugarcane bagasse was chosen as lignocellulosic material and was pretreated and hydrolyzed by H₂SO₄ before fermentation. After the process, inhibitory compounds such as formic acid, acetic acid, furfural and hydroxymethylfurfural (HMF) were detected in the sugarcane bagasse hydrolysate at the concentration of 1.3, 2.5, 1.5, 0.5 g/L, respectively. The effect of inhibitors degradation by atmospheric cold plasma showed that at 120W treatment for 25 minutes could decreased formic acid, acetic acid, HMF and furfural by 19.6, 2.0, 57.4, 100%, respectively. Our results demonstrate that atmospheric cold plasma could effectively degrade the inhibitors within hydrolysate, therefore enhance the productivity of bioethanol. We anticipate the great potential of the technique in the field of renewable energy.

CELL 16

Production of bacterial cellulose by treating sugarcane bagasse hydrolysate with atmospheric cold plasma

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Bacterial cellulose (BC), a biopolymer produced by various groups of microorganism, especially acetic acid bacteria, is a high-value material. Due to its unique physicochemical properties including high water absorption capacity, tensile strength, permeability, crystallinity and biocompatibility, BC has been applied in multiple fields,
particularly in the aspect of cosmetics such as facial mask, wound dressing and skin tissue engineering. In fact, poor yields and the high cost of using chemical culture medium limit the large scale production of BC. Thus, we aim to use the inexpensive sugarcane bagasse as a raw material for culture medium to produce BC. The chemical process, pretreatment and acid hydrolysis with sulfuric acid, is the most commonly used method to obtain fermentable sugars from sugarcane bagasse, so we would pretreat and hydrolyze it with 1.25% and 2% sulfuric acid, respectively, before fermentation. However, toxic substances such as formic acid and furan derivatives including furfural and 5-hydroxymethylfurfural (HMF), resulting from pretreatment and hydrolysis will inhibit the growth of microorganisms. A novel technology, atmospheric cold plasma, is employed in this study to degrade toxic compounds in the sugarcane bagasse hydrolysate and a treatment with 120W for 25 minutes was found to decrease formic acid, furfural and HMF by 20%, 100% and 57%, respectively. Extra nitrogen source concentration, pH value and nitrogen to carbon ratio would be used as the factors of response surface methodology (RSM) to evaluate the optimum conditions for high production BC. By this work, atmospheric cold plasma treated sugarcane bagasse could be expected as a potential raw material to make BC more widely available in the cosmetic industry.

CELL 17

Preparation of chitin nanofiber-based composite/hollow particles by Pickering emulsion polymerization

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Because chitin is an abundant natural polysaccharide composed of N-acetyl-D-glucosamine units linked by β(1→4)-glycoside bonds, its effective utilization as the biomass resource has attracted much attention to obtain new bio-based materials. However, chitin is poor in processability and solubility because of strong crystallinity due to numerous inter- and intramolecular hydrogen bonds. Previously, we reported that the regeneration from a chitin/1-allyl-3-methylimidazolium bromide ion gel using methanol fabricated self-assembled chitin nanofibers. On the other hand, Pickering emulsion is emulsion, in which solid materials are used as an emulsion stabilizer in place of surfactants. This presentation reports Pickering emulsion polymerization of styrene using self-assembled chitin nanofibers as an emulsion stabilizer to prepare composite and hollow particles.

Styrene was first added to the maleylated anionic chitin nanofibers / aqueous ammonia dispersion, followed by ultrasonication to obtain an emulsion, where styrene droplets were surrounded by the nanofibers. Radical polymerization was then conducted in the presence of K2S2O8 as an initiator to form the composite particles. Particle sizes became smaller as the amounts of emulsion stabilizers increased. We then attempted the conversion of the composite particles into hollow particles by dissolving out inner polystyrene using toluene. The SEM images confirmed hollow morphology.
Figure 1. Pickering emulsion polymerization of styrene using maleylated chitin nanofibers to produce composite particles and conversion into hollow particles

CELL 18

Synthesis of mixed chitin esters in ionic liquid

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Chitin is a natural polysaccharide abundantly present in nature, and thus, very important biomass resource. However, since chitin has strong crystallinity by intermolecular hydrogen bonding between acetamido groups, it is poor in solubility and processability, leading to mostly unutilization. We have already found that an ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr), dissolves chitin at most in 4.8 wt %. We also found that chitin acylates (chitin esters) with high degree of substitution (DS) were obtained by acylation of chitin using acyl chlorides in AMIMBr. However, processability of the product was not largely improved, probably due to the remaining hydrogen bonds between acetamido groups. In this study, we synthesized a mixed chitin ester having adamantoyl and stearoyl groups in AMIMBr, in which the hydrogen bonds would be weaken by introducing such bulky and long alkyl groups on the chitin chain (Scheme1). The IR and $^1$H NMR spectra of the product indicated that chitin adamantate stearate with high DS was obtained. In the XRD profile, the diffraction peaks assignable to chitin crystalline structure greatly decreased, and a diffraction peak ascribable to end-to-end packing of stearoyl groups was shown at $2\theta = 3.0^\circ$. The DSC pattern showed an
endothermic peak due to enthalpy relaxation of the packing structure at 7 °C. These results have suggested that the processability of the product is potentially expressed. Indeed, as the product was dissolved in chloroform, the solution could be thinly casted to obtain a flexible film.

Scheme 1. Synthesis of chitin adamantate stearate in AMIMBr

CELL 19

Dissolution and functionalization of chitin using deep eutectic solvents

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Chitin is a natural polysaccharide abundantly present on the earth, and thus, a very important biomass resource. However, because it has high crystallinity due to strong intra- and intermolecular hydrogen bonding, its solubility and processability are poor, leading to hardly utilization. We have already reported that an ionic liquid (IL), 1-allyl-3-methylimidazolium bromide, dissolves chitin in concentrations up to 4.8 wt%, but the color of the solution is blacked, owing to the presence of bromide. Deep eutectic solvents (DESs), analogs of IL, have recently been found to act as good solvents for polysaccharides. DESs are systems formed from eutectic mixtures of hydrogen bond accepters and donors. In this study, we found that DESs composed of various imidazolium ILS and thiourea as hydrogen bond accepters and donor, respectively, dissolved chitin in 2~5 wt%. The DESs were first prepared by heating mixtures of the ILS and thiourea at 100 °C for 30 min with stirring. A predetermined amounts of chitin were then added to the DESs and the mixtures were kept at room temperature for 24 h, followed by heating at 100 °C for 24 h (Scheme 1). The dissolution state was observed by a CCD camera view. Furthermore, we found that 1-butyl-3-vinylimidazolium bromide
/ thiourea (1: 0.2) DES swelled 20 wt% of chitin. Functionalization of chitin using the DESs are now in progress, which will be reported in this presentation.

Scheme 1. Dissolution of chitin in DESs composed of ionic liquids with thiourea.

CELL 20

Removal of water toxins via ligand-functionalized cellulose-based membranes

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Safe drinking water is still a vital necessity in many countries around the world. The purification of water from available sources requires the removal of many toxic metals and metalloids. A bio-accessible membrane/adsorbent system offers a potentially economical and environmentally friendly purification process. The objective of this work is to functionalize cellulose-based membranes that can also selectively remove lead, arsenic, and other toxins from drinking water. Dried jute ground to micro-sized fibers was bleached using sodium hypochlorite and oxidized using sodium periodate to introduce aldehyde functionality. The aldehyde groups provide a site for attachment of appropriately functionalized metal binding moieties. Metal coordinating picolinate and thiol-containing ligands have been developed using computational design methods to selectively coordinate the desired toxins in the presence of common hard metals found in water. Progress in the design and synthesis of these novel chelating agents incorporating groups for covalent attachment to oxidized cellulose, incorporation into cellulose-based membranes with adsorption capability, and applications in water purification will be reported.

CELL 21

Precipitated ferric hydroxide on carboxylated nanocellulose for remediation of nitrate
Nitrate pollution is common among municipal waste water streams, ranging from 1 – 10 ppm in the United States. When this nitrate rich solution enters oceans, lakes, and sounds, the algae blooms and subsequent eutrophication create an environment which is no longer hospitable for domestic species and recreational use. Our study reports the use of precipitated ferric hydroxide on carboxylated nanocellulose for the remediation of nitrate from solutions of water. Cellulose was obtained from underutilized sources of cellulose based biomass for the purpose of upcycling into functional nanomaterials. The biomass was carboxylated by nitro-oxidation, reported in previous work, and further homogenized to produce dispersed nanofibers. Ferric chloride and sodium hydroxide were used for the precipitation of ferric hydroxide. The composite was then characterized and tested for nitrate adsorption capacity.

CELL 22

Improving the fouling resistance of nanocellulose membranes for ultrafiltration

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Membrane fouling is a common and serious issue in ultrafiltration (UF), caused by clogging and aggregation of proteins and other biomolecules in the feed stream. The irreversible fouling would result in the reduction of filtration efficiency, especially in polymeric membranes, and require higher energy for filtration. Many approaches have been demonstrated that can mitigate the membrane fouling problem. These approaches include the increase in surface hydrophilicity, enhanced electrostatic repulsion between the foulants and membrane, and tailored surface roughness and pore size. In this study, we investigated if nanocellulose-based membranes could reduce the fouling tendency for ultrafiltration of wasted water with negatively charged contaminants. This is because nanocellulose particles have both hydrophilic and hydrophobic components and negative surface charges. In specific, we examined the factors of surface charge density, roughness, hydrophilicity, membrane pore size, and supporting substrates on the fouling tendency. The chosen membranes were prepared by coating of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) oxidized cellulose nanofibers (CNF) on three substrates: highly negatively charged electrospun polyacrylonitrile (PAN) substrate, slightly negatively charged cellulose acetate (CA) substrates, and non-charged cellulose filter papers. All membranes exhibited high permeation flux (33 LMH - 61 LMH) under low pressure (0.1 psi) with high rejection rate (90% - 99%) in the cross-flow filtration tests, using bovine serum albumin (BSA) as a model protein. The fouling results indicate that the combined effect of negative charge and hydrophilicity on the CNF surface has significantly reduced the fouling tendency of the membranes, while the
membrane pore size, roughness and supporting substrates have less impact on the fouling property but they greatly influence the permeation flux and rejection ratio.

CELL 23

**Increased adsorption capacity for heavy metal ions via sequential oxidation of carboxy cellulose nanofibers from raw wood**

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The aim of the present study is to investigate the possibility of increasing the carboxylate concentration of caborxycellulose nanofibers (CNF). The oxidation procedures used in this study were nitric acid, sodium periodate, and sodium chlorite. Nitric acid oxidation was conducted on raw wood biomass in order to produce 6-carboxy cellulose (6CC) nanofibers, and then further oxidized to produce 2,3,6-tricarboxycellulose (TCC) nanofibers with higher carboxylate content. Furthermore, we look to analyze the effects of increased carboxylate content on the adsorptivity capabilities of the oxidized cellulosates when introduced into solutions containing heavy metal ions (this study will utilize Pb^{2+} ions). The sequential oxidation reactions conducted in this study produced 6CC nanofibers with a carboxylate concentration of 1.1 mmol/g and TCC nanofibers with 1.4 mmol/g. After Pb^{2+} remediation experiments, a gelation effect was seen to occur in vials containing the 6CC samples, while in the vials containing the TCC samples, white flocculants can be seen to collect at the bottom of the vials. ICP-MS data was collected from both sets of remediation experiments; 6CC nanofibers has an adsorption efficiency between 63-93%, while TCC nanofibers has an adsorption efficiency between 78-99%.

CELL 24

**Facile synthesis of vanillin from kraft lignin**

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Enormous amount of kraft lignin as a side product from paper industry is mainly burned for energy rather than used in synthesis of added-value products. Lignin-to-vanillin is one of the most promising processes in terms of renewability and sustainability. In this study we report a facile synthesis of vanillin utilizing technical kraft lignin by combining fractionation and catalytic oxidation. The molecular distribution, structure, inner linkages and functional groups of soluble fractions derived from alcohols were characterized. Then the soluble fractions were subjected to oxidize to produce vanillin. After a 60 min reaction, amount of vanillin produced was 10.7 wt%, which is up to 71% from the theoretical maximum. The method proposed herein showed a promising possibility for producing value-added vanillin from commercially technical lignin in terms of the high yield obtained and low-cost of chemicals used.
Analyzing the degree of branching in lignins: Theoretical and experimental results

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Lignin is a heterogeneous aromatic polymer found in woody biomasses, accounting for a significant percentage of all renewable carbon. The primary means by which lignin can be utilized for the synthesis of higher value products is through thermochemical conversion schemes that can include pyrolysis, liquefaction and gasification. One of the most important first steps in thermochemical conversion of lignins is in understanding their structure on a molecular level. Recently, it has been shown that this structure can be computationally modeled using four characteristics: 1) the monomer composition (p-hydroxyphenyl, guaiacyl, and syringyl content); 2) the bond-type composition; 3) the molecular weight characteristics; and 4) the degree of branching in the polymer. While the first three characteristics have been well-studied in numerous previous publications, to date there is comparatively less in-depth study describing how to measure or calculate the degree of branching. In this poster we will present some results, along with their underlying theoretical basis, on the branching coefficient for a range of contrasting lignins. The branching coefficient is defined as the probability that one given aromatic monomer unit in a lignin polymer is bonded to three or more other units.

Using earlier published work, it is possible to show that based on the molecular weight characteristics of lignin (number-averaged and weight-averaged), the branching coefficient can be calculated and that it must be within the range of 0.00 to 0.33. We calculate the branching coefficients using experimental molecular weight data for two kraft lignins from pine and eucalyptus woods (0.18 and 0.03, respectively), one soda lignin from wheat straw (0.01) and one organosolv lignin from wheat straw (0.00).

Continuing work will include the analysis of molecular weight for milled-wood lignins from corn stover, Douglas fir and hybrid poplar woods. Additionally, we will explore the nature of the differences in branching between hardwoods, softwoods and grass-type biomasses, and investigate possible correlations between branching determined by molecular weight with important lignin characteristics that can be measured through other analytical methods, including carbon-13 NMR and FTIR spectroscopy.

Dissolution of lignin-rich microfiber from organosolv assisted with catalysts and its regeneration

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Studies on dissolution and regeneration of lignin-containing fiber to value-added new materials have been expanded due to increased environmental awareness. In this study, pine organosolv microfibers treated by a high boiling point solvent assisted with two different types of catalysts were prepared and then subjected to a NaOH/urea dissolution process to investigate the underlying mechanisms of solubilization in terms of lignin content, cellulose DP, hemicellulose content and its composition, and aspect ratio of microfibers. In addition, the dissolved solutions were regenerated in a coagulant bath to verify the structure-property relationship of the resultant lignocellulose film. This study showed that the dissolution behavior of lignin-rich microfiber in the NaOH/urea solution was in a complex way, affecting the mechanical properties of the lignocellulose film fabricated.

**CELL 27**

**Sustainable pathways to increase lignin reactivity for resin applications**

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Lignin is the most abundant natural aromatic polymer and contains both aliphatic and aromatic hydroxyl groups with excellent potential to replace polyol in formulations of polyurethane resins. However, inaccessibility of hydroxyl functional groups embedded in the lignin structure is a major limiting factor to broaden its application as polyol. Thus, lignin modification is necessary to increase the number of hydroxyl groups, or make them more accessible to react with isocyanate. In this study, ionic liquids (ILs) as a green recyclable solvent was used to increase the hydroxyl content of Organosolv lignin samples isolated from both hardwoods and softwoods. Modified lignin with bromide based ionic liquid has been analyzed by size exclusion chromatography (GPC), quantitative phosphorus nuclear magnetic resonance spectroscopy (\(^{31}\)P NMR), quantitative 2D (heteronuclear single quantum coherence) HSQC NMR and XPS (X-ray photoelectron Spectroscopy). Increase in both aliphatic and aromatic hydroxyl functional group, decrease in molecular weight, particle size and B-O-4 linkages in lignin samples was observed after the treatment. Lignin’s reactivity towards isocyanates was improved after ionic liquid treatment compared to untreated samples. We have also further investigated this reaction by studying chemical structures of lignin model compounds (vanillin, coniferyl alcohol, guaiacylglycerol-beta-guaiacyl ether) before and after ionic liquid treatment, using advanced analytical techniques such as: proton, carbon and phosphorus NMR, FTIR (Fourier transform infrared spectroscopy), LC-MS (liquid chromatography-mass spectroscopy). The results showed the breakage of B-O-4 linkage in the lignin model compounds. Lignin modification with ionic liquid can be an efficient and environmental friendly technique to increase lignin reactivity as a biobased polyol in polyurethane resin synthesis applications.

**CELL 28**
Lignin-derived carbon nanocomposites as sodium-ion battery anodes

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The eager demand for sustainable and efficient energy storage systems emerges research of novel electrode materials. Carbon-based material is one of the most studied class of anode materials for every storage systems. However, carbon electrode materials in today’s energy storage devices are manufactured predominantly from non-renewable resources, by mining and refining graphite or by pyrolysis of hydrocarbons derived from petroleum. Lignin, as the most dominant aromatic biopolymer on earth, has been extensively explored for value-added applications in the past decade. It is one of the most ideal carbon precursors due to its coal-like molecular structure, which leads to the resulting carbon suitable for intercalation of large atoms.

We aim to prepare lignin-derived carbon nanocomposite material as anode material for sodium ion batteries (SIBs). By integrating the unique aromatic-rich molecular structures with reduced graphene oxide (RGO) via a “one-pot” hydrothermal synthesis approach, the carbon nanocomposite materials are composed of three-dimensional (3D) porous structure with layered graphene-like carbon building blocks. The carbon nanocomposite anode shows a significant capacity of 300 mAh g\(^{-1}\) at low charging current. The anode retained 90% of the initial capacity even after 100 test cycles. Comparing with the pure lignin derived carbon anode, the carbon nanocomposite showed a significant increase in capacity at high charging rate, which attributes to the 3D structure and the porous nature of the composite. The 3D architecture of lignin-based nanocomposites is a group of promising sustainable anode material for SIBs and leads to multiple eco-friendly and value-added applications.
Porous carbons derived from renewable biomass as high performance supercapacitor with high mass loading

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With increased interest in energy and environment issues, high-performance energy storage is needed for renewable energy. Supercapacitors (SCs), also called electrochemical electrical double-layer capacitors, have been of great attention as one of the most attractive energy storage devices for sustainable energy storage devices due to their high power capability, fast charge/discharge rates, ultra-long cycling life and low maintenance cost. The breakthroughs in the design of nanostructured carbon materials lies at the heart of developing advanced SCs. Naturally abundant biomass is a green, alternative carbon sources and they can be easily converted into porous carbons with many desired properties via simple, low cost and environmentally friendly methods. In this study, we have developed porous carbon based electrodes from waste coffee grounds for SCs. The resulting electrodes for SCs exhibited excellent electrochemical performances with a high mass loading of active materials. These properties are attributed to the synergistic combination of the high surface area of ACs and reduced graphene oxides that provide a multi-functional binder between ACs. This combination can also improve the wettability of electrode, which is beneficial for enhanced contact between the electrode material and electrolyte. Symmetric two electrode system
exhibits outstanding charge storage capacity, reaching a high specific capacitance and excellent rate capability in both aqueous electrolyte and non-aqueous electrolyte.

**CELL 30**

**Building wind turbines from renewable and recyclable composites**

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For the first time ever, a styrene-free, biobased formulation suitable for infusion processing of thermoplastic composites is reported. Biobased polylactide (PLA) is soluble in methyl methacrylate (MMA) and this new styrene free system is suitable for fabricating composite parts. Extensive rheological and physicochemical characterization of PLA dissolved in MMA is reported. The Flory interaction parameter is described by $\chi = 0.40 \pm 0.04$, the Mark–Houwink relationship at 30 °C as $[\eta] = 0.017M_0^{0.73}$, and the expansion factor is $\alpha = 1.45 \pm 0.25$. The values of $a$, $\chi$, and $\alpha$ indicate that MMA is a good solvent for PLA. Both thermoplastic and thermosetting biobased resin systems have been developed. Mechanical properties on unidirectional fiberglass panels made via vacuum infusion are equivalent to commercial epoxy systems; tensile moduli of 40 GPa are achieved. Several end of life recycling options are discussed and it is experimentally demonstrated that glass, monomers, and polymers can be reclaimed and reused for several applications including recasting of new composite parts.
Redefining and redesigning lignin

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As lignin is a polymer formed from its phenolic monomer radicals by purely chemical radical coupling reactions, the breadth of options for ‘designing’ the composition and structure of lignins is unparalleled. New phenolic monomers can be introduced into the polymer, and new ‘natural’ lignin monomers are constantly being discovered; we predict that there will be at least one new class of monomers discovered before this ACS meeting! Inspired by Nature’s incorporation of the non-lignin-pathway flavonoid, tricin, into monocot lignins, and hydroxystilbenes into palm endocarp lignins, researchers can now also contemplate plants in which the lignins incorporate valuable components that can be subsequently retrieved from ‘waste’ streams. Caffeoyl alcohol-derived lignin polymers represent a class of ‘ideal lignins’ for conversion to monomeric phenolic commodity chemicals in high yield. Moreover, lignins have now been successfully ‘redesigned’ to contain readily chemically cleavable ester bonds in the polymer backbone, facilitating improved industrial processing – for example, chemical pulping, or pretreatment options for the saccharification of wall polysaccharides to sugars for liquid biofuels production. In addition to the apparent necessity to modify our stance on just what defines a plant lignin, and to speculate on the limits to what constitutes a lignin monomer, we appear to be entering a reinvigoration period for lignin research aimed at its manipulation for improved utilization and value.

Alkaline enzymes for lignin valorization

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Industrial lignocellulosic biomass processing generates high volumes of diverse lignin streams. Valorization of these streams is challenging due their heterogeneous chemical composition, recalcitrance, and poor solubility. Efficient fractionation, depolymerization and activation of lignin will lead to the formation of new value chains in Biorefinery sector with the production of bio-based products such as coatings, binding agents, fillers, special chemicals, etc. Current lignin depolymerization methods often include harmful chemicals or/and require harsh conditions which promote unwanted reactions or degraded reaction products. Therefore, the development of scalable and sustainable strategies for industrial lignin valorization will lead towards the success of biorefineries. A Finnish biotechnology company, MetGen Oy, pioneer in the design and development
of industrial enzymes for biomass conversion, has brought to the market several lignin oxidizing enzymes, including MetZyme® PURECO™, an extremely thermostable laccase obtained by bacterial genetic engineering. Although laccases have long been considered as a potentially promising tool in lignin depolymerization, their applications were limited to ambient pH, where lignin is poorly soluble in water. MetZyme® PURECO™, because of its unique properties, unlocks these limitations by addressing lignin at its soluble state: in alkaline pH (up to 11) and at elevated temperatures (up to 85 °C) in solvent-free aqueous solution. For industrial applications, lignin in solvent-free aqueous conditions allows the utilization of robust membrane separation technologies yielding in an effective fragmentation of the enzymatically modified lignin. Depending on the fractions generated and the functionalization of these lignin fragments, multiple industrial applications such as polyurethane, epoxy for coating, adhesives and foams can be developed. This will open new opportunities for biorefinery lignin valorization thus paving the way for sustainable and more cost-efficient biorefinery business model.

CELL 33

Biomimetic cleavage of β-O-4 bonds using small organic thiols

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The replacement of petrochemicals with lignin is challenging due, in part, to the expensive inputs and caustic depolymerization techniques typically required. Nature, however, provides an example of lignin depolymerization under relatively mild conditions. In the β-aryl ether cleavage pathway of wood degrading bacteria, the cleavage of β-O-4 bonds occurs in a three-step process: 1) oxidation of the α-carbon hydroxyl group, 2) glutathione nucleophilic attack on the β-carbon, displacing the phenoxyde, and 3) reduction of the above-formed glutathione ether’s S-C bond with a second glutathione, releasing the second lignin fragment and the glutathione disulfide. This work focuses on replicating the nucleophilic and reductive cleavage of the β-O-4 bond using only small organic thiols, without the aid of proteins or metals. Oxidized lignin dimer models treated with β-mercaptoethanol and related thiols undergo cleavage with yields ranging from 30% to 100% depending on the specific reaction conditions. The sensitivity of this cleavage to lignin-relevant functional groups was probed to determine the scope of the reaction. As in the enzymatic pathway, oxidation of the α-carbon hydroxyl group is required for reductive cleavage by the thiols. Primary and secondary beta aryl ether bonds were cleaved while tertiary sites were unreactive as expected for a nucleophilic substitution reaction. Lastly, the reaction tolerates a variety of functional groups on both the phenolic and keto aromatic rings (e.g., authentic S-S and G-G dimers). Having mechanistically analyzed the reactions in well-defined model dimers, we applied this process to real lignin, achieving approximately 68% molecular weight reduction. This work exemplifies a reductive biomimetic approach to lignin
depolymerization by mimicking the nucleophilic thiol-mediated ether cleavage found in the enzymatic β-aryl ether cleavage pathway.

CELL 34

Evaluating the impacts of two-stage alkaline-oxidative pretreatment of hybrid poplar on lignin properties

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We have recently developed a two-stage pretreatment comprising an alkaline pre-extraction followed by a Cu-catalyzed alkaline hydrogen peroxide (Cu-AHP) treatment that is effective at pretreating hardwoods at relatively mild reaction conditions. We previously demonstrated that this process is capable of achieving high yields of sugars from enzymatic hydrolysis and high yields of aromatic monomers from the catalytic depolymerization of lignin. In this work, we focus on characterizing how biomass source and reaction conditions used during the alkaline pre-extraction impact the subsequent processing stages as well as lignin yields and properties. Specifically, five hybrid poplars were subjected to alkaline pre-extraction under various conditions including differences in time (15-300 min), temperature (90-155 °C), alkali loadings (0.1-0.2 g/g biomass), and solid to liquid ratios (10-20% wt/v) and the impact on lignin recovery and purity was determined. Empirical models were developed to relate lignin extraction and recovery during the pre-extraction stage to reaction severity. For select conditions, lignin properties are assessed and include β-O-4 content determined by ^13C NMR, molecular mass distributions as determined by gel permeation chromatography, and susceptibility to depolymerization to aromatic monomers using thioacidolysis and formic acid-catalyzed depolymerization and these properties are demonstrated to be a function of pre-extraction conditions. Finally, the pre-extracted biomass from select conditions is assessed for its response to the subsequent Cu-AHP treatment and enzymatic hydrolysis and the overall impact of processing conditions on process economics are determined through a technoeconomic analysis.

CELL 35

Chemical funneling of lignin derived monomers into aromatic chemicals

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Despite the rapid advances in lignin depolymerisation, two issues remain. First, lignin is composed of three types of substituted phenols connected by a number of C–O and C–C bonds, forming a three-dimensional amorphous, irregular polymer. Second, lignin
polymers may undergo non-selective fragmentation and rearrangement during depolymerisation, further complicating the product stream.

One solution to the problem is to produce lignin with a simpler structure via generic engineering. For instance, overexpression of the ferulate 5-hydroxylase gene in poplar (Populus spp.) affords lignin with almost pure syringyl units and close to 90% β-O-4 linkages. Nevertheless, this technique is currently not widely applied and its economic viability remains to be seen. Another solution is to develop strategies that are able to converge complex monomers derived from lignin into a single stream. An elegant biological funnelling strategy was proposed and developed, in which a lignin liquor stream was converted to polyhydroxyl acid, forming the foundation of various end uses. As far as we are aware, one-step chemical transformation that convert, or conceptually that are able to convert, lignin derived monomer mixtures such as 2-methoxy-4-propylphenol and 2,6-dimethoxy-4-propylphenol into a single value-added product is rare.

In this presentation, we communicate two recent approaches developed in our lab to produce aromatic compounds from lignin derived mixtures. Despite the complexity of decomposed lignin, the structures of the products are not without patterns. A common feature for the monomers obtained from lignin under neutral or reductive conditions is that they are substituted phenols bearing zero to two methoxyl groups in the ortho-position and an alkyl group in the para-position. In the first route, we developed selective de-methoxyl and de-alkyl chemistry to convert a mixture of substituted phenols to be converted into a single-compound phenol. In the second route, a mixture of lignin derived oil is upgraded into terephthalic acid via sequential demethoxylation, carbonylation, and oxidation steps.

**CELL 36**

**Exploiting the phase behavior of lignin with renewable aqueous solvents: Enabling higher-value applications**

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By exploiting the novel liquid–liquid equilibrium that exists between lignin and hot, one-phase solutions of aqueous renewable solvents, crude bulk lignins can be simultaneously fractionated, cleaned, and solvated for conversion to high-value, high-quality bioproducts. This unusual phase behavior forms the basis for the ALPHA (Aqueous Lignin Purification with Hot Agents) process. With ALPHA, control of the purity, molecular weight, and chemical functionality of lignin becomes possible. In particular, lower molecular weight (MW) lignins and impurities are extracted into the solvent-rich phase, and higher MW lignins are solvated and purified of impurities in the polymer-rich phase. Phase-transition temperatures from solid–liquid to the desired liquid–liquid equilibrium have been measured for mixtures of Kraft lignins with aqueous solutions of methanol, ethanol, isopropanol, acetic acid, and acetone. Furthermore, the
global phase behavior exhibited by these systems has been measured for selected (pseudo-)ternaries, including the lignin–acetone–water and lignin–acetic acid–water systems. Two examples of how the LLE region exhibited by these systems facilitates materials applications will be presented: (1) By using the solvated, polymer-rich phase, the continuous dry-spinning of high MW lignin fractions into micron-sized fibers is made possible. These fibers were subsequently converted into low-cost carbon fibers almost 40% stronger than any lignin-based carbon fiber reported to date. (2) Low MW lignins were isolated by a two-stage process that first uses the solvent-rich phase to isolate a low MW lignin fraction; that fraction is then purified by transferring it to the polymer-rich phase. The resultant lignin was subsequently used to create dispersions for coating applications.

CELL 37

Thermal conversion chemistry of wood: Consequences for quality control of heat treated wood products

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The air-free thermal conversion of wood is remarkably universal, despite of the notable differences between carbohydrate and lignin chemistry of hard- and softwoods. Many thermally modified physical and chemical properties can be characterised by a single (chemical) marker, independent of the wood species. This is explained by the universal evolution of the CHO elemental composition of thermally modified wood, containing information on the polarity and redox potential changes in the lignocellulose matrix. However, the effects of heat treatment on the mechanical properties and some complex properties (such as the biodegradation resistance) require an additional marker characterizing the cohesive strength of the lignocellulose matrix. Based on this background, the merits and limitations of selected quality control methods for thermally modified wood are discussed.
Evolution of CHO composition of wood by thermal conversion and changes in polarity and average carbon oxidation state.

**CELL 38**

**Integrating multi-scale studies of chemically modified wood**

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Advanced experimental tools are needed to study modified wood across the cellular and subcellular length scales. We recently developed tools to study wood and the effects of cell wall modification by PF resin and moisture at these small size scales. In this talk, the utility of these tools will be demonstrated by studying model bondlines in wood made using a phenol formaldehyde adhesive. The wood-adhesive bondline is extraordinarily difficult to study given the porosity of wood and the multiple length scales over which many potential interactions can occur between the wood and adhesive to enhance or degrade the bond performance. Synchrotron-based micro X-ray fluorescence microscopy (µXFM) and micro X-ray computed tomography (µXCT) are used to map the penetration of adhesive into the wood anatomical structure. Nanoindentation has been developed into a tool capable of assessing the effects of moisture and adhesive infiltration on wood cell wall mechanical properties. Using custom-built in situ humidity chambers with µXCT and small angle neutron scattering (SANS), the moisture-induced swelling in wood was studied across the cellular and subcellular length scales in bondlines spanning from the millimeters to nanometers. The new insights these tools provide towards understanding moisture-durability in wood.
adhesive bondlines will be discussed. Finally, a new model to aid in the discussion of chemical modifications at the wood nanostructure will be presented.

CELL 39

Quantification of wood thermal treatment by electron paramagnetic resonance spectroscopy

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The process of heat treating wood has been utilized to improve its properties, such as moisture resistance, dimensional stability, resistance to fungal decay, and aesthetically appealing color. These properties may be achieved without added chemicals and could therefore be considered more environmentally friendly. They also allow for the potential broader applications of indigenous softwoods, instead of relying on the often slower growing hardwoods. However, the extent of heat treatment and its correlation to these desirable properties is difficult to measure. Others have shown correlations between free radical content and the temperature of heat treatment. Here we present our work measuring the radical content by electron paramagnetic resonance (EPR) spectroscopy. We examined samples treated in a pilot-scale kiln (an industrially relevant process), as well as samples treated in a highly controlled and quantifiable manner by thermogravimetric analysis (TGA) instrumentation. From these data we have attempted to correlate the effects of moisture content and heat treatment extent with the free radical signal. We aim to provide the thermally treated wood industry with reliable methods for quantifying heat treatment.

CELL 40

Formulated feedstocks for biorefining: Monitoring key biomass chemical characteristics

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With a diverse portfolio of biomass sources that includes agricultural and forest residue, municipal solid waste, and purpose-grown energy crops (herbaceous and woody), the southeastern U.S. is projected to provide more than 60 percent of the Nation’s supply of alternative renewable fuel. To meet this expectation, the concept of a centralized preprocessing depot capable of handling different biomass types has been advocated. Housing operations for size reduction, drying, densification and related pretreatment methods, the depot will: 1) introduce supply chain efficiencies to lower feedstock cost, 2) eliminate dependence on a single biomass source, 3) allow construction of larger-scale biorefineries to improve economics, and 4) improve quality and consistency of delivered feedstock for specific platforms. Several technological advances are needed
to realize this vision, including improved real-time access to information on the chemical composition and physical property changes that are induced by multiple preprocessing steps. Recent work has generated new data on the variation in carbon content, moisture content, and ash content and composition (alkali and alkali earth metals) of several high-impact biomass sources, including switchgrass and pine residue. Multivariate statistical analysis of near infrared spectroscopic data was used to model (Projection to Latent Structures) these important properties. This presentation will discuss quality of the different models while highlighting related progress in the development of online sensors to monitor biomass properties that directly impact downstream conversion to fuels. As a result of this effort, a valuable new tool is emerging to directly evaluate the impact of biomass properties on preprocessing operations, and provide new insight into aspects of the feedstock-conversion interface.

CELL 41

Probing nanostructural changes in chemically modified wood cell walls with small angle neutron scattering

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While wood products are esthetically pleasing, their hygroscopicity leads to dimensional changes induced by environmental variations in humidity and/or temperature. Their dimensional instability has made it difficult to provide durable coatings, adhesives and/or sealants. Research in wood-water interactions at the macro level has improved our understanding of the wood-water relationships, but research at the subcellular level (from 1 to 100 nm) is lacking. However, techniques able to probe the wood cell wall nanostructure often need labeling, harsh surface preparation or must be performed under vacuum. Advanced neutron scattering techniques are ideally suited to probe changes in wood nanostructure because neutrons provide increased contrast due to their isotope sensitivity and allow for in situ humidity control. Small angle neutron scattering (SANS) studies have successfully measured the moisture-induced swelling of wood nanostructure from 1 to 100nm. These SANS studies revealed that moisture-induced swelling at the cellulose elementary fibril level is a major contributor of transverse swelling in the S2 cell wall layer and, therefore, must be addressed by treatments meant to impart durability. Likewise, contrast variation studies capable of measuring the effects of chemical modifications, such as acetylation or phenol-formaldehyde infiltration, on the wood nanostructure and its induced swelling revealed that these modifications can minimize swelling at the elementary fibril level, even though they modify the wood nanostructure differently.

CELL 42
Beech wood thermal treatment level characterization by different treatment level markers

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Beech wood was heat-treated in a pressure reactor at twenty different settings of temperature, steam pressure and duration. The temperature and pressure were chosen to ensure either dry, moist or wet conditions during the thermal conversion of the beech wood samples. The treated beech samples were characterized by four different physical/chemical markers: dry mass loss (due to hemicellulose degradation), equilibrium moisture content at 20°C/65%RH (showing loss of hygroscopicity), the electron paramagnetic signal (lignin radical content) and the O/C-elemental composition ratio. All markers appeared to be mutually linked, provided that the samples were thoroughly leached in water before testing to facilitate the relaxation of matrix polymers and removing trapped degradation products in the matrix. The O/C-marker has the valuable and unique property of providing an absolute metric for the thermal treatment level by standardized analytical procedures, correlating with many physicochemical properties of the material. This result is relevant for the quality assessment of randomly picked thermally modified wood samples, independent of the raw material and processing data from the manufacturer.

CELL 43

Use of X-ray scattering to understand the mechanisms behind the moisture and decay resistance of epoxybutene modified wood

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Chemical modification of the hydroxyl groups of wood can improve the properties of wood by providing moisture and biological resistance, as well as dimensional stability. Southern pine solid wood was chemically modified to various weight percentage gains (WPG) with epoxybutene (EpB, 8%-38% WPG). After modification, specimens were extracted with a toluene: ethanol (2:1) solution for 2 hours or water leached for 2 weeks. The equilibrium moisture content (EMC) at 30%, 65% and 90% relative humidity (RH) and 27 °C was determined on all specimens. Laboratory soil block decay evaluations against the brown-rot fungus Gloeophyllum trabeum was performed and weight loss calculated by mass loss.

Biological efficacy was found, and the biological resistance correlated with the lowering of the equilibrium moisture content, suggesting that the mechanism of efficacy was due to moisture exclusion. To assist in understanding the mechanism of effectiveness, small angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) were both
performed. Preliminary WAXS results showed that the modification did not significantly change the cellulose crystalline lattice parameters. Preliminary SAXS results showed that epoxide addition led to an increased polydispersity in the microfibril alignment and broader microfibril angle distributions, thus, suggesting that modification may target regions outside the microfibrils. Further experimentation is underway to confirm these results.

CELL 44

Nitro-oxidized carboxycellulose nanofibers

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A sustainable nitro-oxidation method has been used to extract carboxycellulose nanofibers directly from untreated (raw) agricultural residues such as Bean stalk, Sorghum stalk and Maize stalk. The use of nitric acid-sodium nitrite during nitro-oxidation has effectively removed the lignin and hemicellulose, and securely generated the carboxycellulose fibers. The slurry of carboxycellulose fibers then passed to homogenizer at low pressure of 250 bar for 1 cycle to produce nanofibers. The nanofibers generated from bean stalk, sorghum stalk and maize stalk have possessed carboxylate content in the range of 0.57-0.67 mmol/g. The structural characterization of these nanofibers was carried out using FTIR, WAXD, ¹³C CPMAS NMR and TGA/DTG analysis. In addition, the morphological characterization using TEM and AFM measurements have shown the length of these nanofibers were less than 1000 nm and width was in between 4-6 nm. Analysis of effluent after neutralization with base has shown the presence of high concentration of nitrate (244.3 mg N/L), nitrite (3.02 mg N/L), perfectly fit as a nitrogen rich fertilizer for plants. The effluent was also found as a rich source of organic carbon having total organic carbon (TOC) was 113 mg C/L and total nitrogen (TN) content observed was 241 mg N/L.

CELL 45

Nitro-oxidized carboxy nanocellulose derived from agave for effective removal of lanthanides from water

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**Abstract**

Water shortage is a global concern of growing population. Worldwide, over 1.1 billion people lack access to clean drinking water due to various contaminations including Fluoride, heavy metal ions, Arsenic or other organic pollutants. In this study, we demonstrate a new way to remove high concentration Lanthanide ions from water using renewable and sustainable nanocellulose materials. In specific, we have developed
Carboxycellulose nanofibers (NOCNF) from untreated (raw) Agave biomass using a simple and cost-effective nitro-oxidation approach. The resulting NOCNF, having an average width of 4.3 nm and an average length of 800-1000 nm, possessed 1.02 mmol/g carboxylate content, high surface charge (−65 mV), and hydrophilicity (static contact angle 39°). The resulting nanofibers (NOCNF) were found to be an effective medium to remove Ln³⁺ ions from water. For example, a low concentration of NOCNF suspension (0.20 wt %) could remove Ln³⁺ ions over a large concentration range (50–5000 ppm) in a relatively short time period (≤4 min) at various conditions (pH 4 to 9). Furthermore, NOCNF characterized by NMR, WAXD, FTIR, SEM, TEM, BET, AFM, TGA, XPS, elementals analysis and ICP MS techniques. This study demonstrated a viable, economic and sustainable solution for removal of Lanthanide ion impurities from water, without risk of cross contaminations.

CELL 46

Developing hydrophobic cellulosic membrane for membrane distillation

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Water scarcity affects 40% of the global population and is one of the biggest challenges of the modern world. Membrane distillation (MD) is an emerging water purification technique capable of purifying highly saline or contaminated water, which can help to alleviate water stress especially for the off-grid community. MD is a thermally driven separation process, in which only vapor molecules can pass through a porous “hydrophobic” membrane. Polymeric membranes that are currently employed in water filtration techniques have a large carbon footprint. There is need to employ sustainable, low-cost and environmentally friendly options to reduce the carbon footprint without compromising performance. Our aim is to develop a composite porous hydrophobic/hydrophilic membrane prepared by ‘cellulosic’ micro/nano fibers obtained entirely from under-utilized biomass, which also have the advantage of being biodegradable and biocompatible. The hydrophobic top layer should be a thin barrier layer to stop liquid penetration followed by a thick hydrophilic supporting substrate. The porosity of the entire membrane should be in the range of 30-85%. To achieve this goal, carboxylated cellulosic nanofibers (obtained from wood and non-wood plant such as jute) were crosslinked with wet strength additives to improve their mechanical properties and water swelling. Micro-scale roughness necessary for hydrophobic surface was obtained by adding fillers like precipitated calcium carbonate. The hydrophobic treatment of the barrier layer was achieved by sizing with alkyl ketene dimer to obtain a high contact angle to stop liquid penetration. Different characterization techniques like infra-red spectroscopy, solid-state NMR, scanning electron microscopy, transmission electron microscopy, and contact angle were used to study the structure-property-
processing relationship of this sustainable cellulose-based membranes for MD applications.

CELL 47

Designing cellulose nanocrystal films for superhydrofobicity without the use of fluorine-based chemicals

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Cellulose nanocrystal (CNC) films were designed in a way for accomplishing superhydrophobicity by combining eco-friendly engineering and metal-free catalysis. The resulting CNC films exhibited high contact angles (>150 degrees) and excellent water-stability. The method is versatile and different functional groups were attached to the CNC surface.

CELL 48

Carbonized nanocellulose as low-cost 1D carbon nanomaterials for energy storage

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The ever-growing energy storage requirements have stimulated the intensive investigation of electrochemical energy storage technologies. A quick literatures search reveals that one of the driving forces is the innovations in nanoscale carbon materials. More specifically, it is the carbon nanotubes (CNTs) and graphene which bring the revolution in energy storage. However, these carbons never came with low price tag, which greatly limited the industrial application. With impressive mechanical properties and excellent flexibility, nanocellulose is one of the most promising innovations in the modern forest industry. Depending on the processing, nanocellulose can be generally catalogued into 2 groups: cellulose nanofibrils (CNF) and nanocrystals (CNC). CNF are manufactured by mechanically delaminating or bacteria-assisted digesting cellulose rich biomass. They share similar geometric dimensions with CNTs, typically few micrometers in length and 10-50 nanometers in diameter. In the contrast, CNC, processed through acid digestion, is much shorter (~ 100 nm) and thinner (typically around 10 nm). Is it possible to carbonize and use them as low-cost 1D carbon nanomaterials?

In our research supported by Alberta Innovates, carbonized cellulose nanofibrils (CNF) have been employed to improve the rate performance of traditional activated carbon
(AC) in supercapacitors. Benefiting from the large amount of surface functionalities, CNF form strongly interconnected composite with AC, which turns into a free-standing carbon nanofibers/AC film after carbonization. In the obtained film, carbon nanofibers are ‘welded’ on AC particles and integrate them into one piece of carbon. When tested as supercapacitor electrode at commercial level mass loading, the composite film exhibits 2 times slower capacitance fading at high current and 3 times higher maximum power density than the bare AC.

Conductive atomic force microscope (C-AFM) analysis reveals that the network of carbonized CNF possesses markedly better electron transport efficiency than the AC particles.

**CELL 49**

**Nanocellulose reinforced polymer composites as flexible mechanical energy harvesters**

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Bio-derived polymer composites have gained tremendous attention in recent years. Cellulose, a natural polysaccharide is one of the most widely used biopolymers owing to its physical and chemical properties, biodegradability etc. The ability to convert cellulosic materials from waste biomass to nanometer sized fibrils has led to new properties and applications. Nanocellulose refers to two different types of nanomaterials: short, low aspect ratio cellulose nanocrystals or cellulose nanowhiskers (CNC or CNW) and long, high aspect ratio cellulose nanofibrils (CNF). This talk will be focused on the morphology and surface of nanocellulose and how they can be used to induce polar ferroelectric crystal phases in polymers. We also demonstrate the enhanced piezoelectric performance of these polymer nanocomposites as flexible mechanical energy harvesters. Device made up of electrically poled PVDF/fluorinated nanocellulose composite films yielded orders of magnitude higher voltage output than neat PVDF in vibrational energy harvesting. PVDF/FNC nanocomposites exhibit a strain at break of 10-15% and can charge a capacitor in few seconds, which suggests
potential use of these nanocomposites as flexible energy harvesting materials at large strain conditions.

CELL 50

Cellulose nanofibers biotemplated metal nanoparticles as a water dispersible SERS substrate

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Cellulose nanofibers (CNF) are a renewable material used in many applications such as electronics, hydrogels and polymers. Many applications of CNF are driven by its’ native surface chemistry or by tailoring the surface chemistry. A common surface modification of CNF is TEMPO-oxidization, where surface primary hydroxyls are converted to surface carboxylate groups.

Our research aims to develop a water dispersible surface-enhance Raman scattering (SERS) substrate using noble metal decorated CNF. Generally, SERS analysis is performed using a solid-based substrate, where the analyte of interest is applied via a drop of solution, or by dipping the substrate in a contaminated solution. The main drawback of these substrates is the poor precision and slow analysis times. By using a solution-based substrate, we can mitigate poor analysis precision via excellent solution homogeneity and obtain faster analysis times through solution mixing. In the development of our substrate, we use highly oxidized CNF as a biotemplate for the synthesis of nanoparticles. The nanofibers have two important roles in the development of a water dispersible substrate: 1) carboxylated CNF are easily dispersed in water and 2) CNF act as a nucleation site for nanoparticle growth. In our work, metal nanoparticles have been grown in close proximity to each other on the nanofibers and used as a stable solution-based substrate.

The use of CNF as a biotemplate for the synthesis of metal nanoparticles and water dispersible SERS substrate is a value-added application for the forestry and pulp industry. Our substrate also shows potential as a field deployable substrate for rapid on-location analyses.

CELL 51

High performance of PET coated with bionanomaterials in oxygen barrier and optical properties in digital age

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Nanomaterials from biomass become trendy in recent years as an alternative for fossil-fuel originated materials. Last decade, cellulose, and chitin, the two most abundant biomaterials from nature have achieved great steps in fibrillation at the nanoscale, for instance, TEMPO-mediated oxidation cellulose nanofiber and chitin whisker. Both biomaterials become more popular in a wide range of applications, from nanocomposite in the polymeric field to functional materials in the biomedical sphere. Among practical applications, the contribution of cellulose and chitin nanomaterials in food packaging sector also need to be concerned because of their bio-origin, stability, biocompatibility, antibacterial ability, and high transparency. All of the superior properties from cellulose and chitin stated above were united by layer-by-layer spraying process in this research. We focus on improving oxygen barrier ability of PET substrate by coating cellulose and chitin nanomaterials simultaneously. A considerable decrease in oxygen transmittance rate at 0.5 mLm$^{-2}$day$^{-1}$ on commercial PET film has been made with regard to a tight combination between layers of nanomaterials. Furthermore, optical characteristics were also improved in term of haziness while a little decrease in transparency was observed, and coating layers also suppressed the growth of bacteria effectively. Practical interferences between coated PET with RFID and QR code were investigated. Our research has highlighted potential applications of bionanomaterials in food packaging field with numerous properties matching well with demanding criteria for smart materials in age of the Internet of Things.

Schematic of coating nanochitin and nanocellulose on PET substrate by LbL sparying process

**CELL 52**

*Barrier performance of cellulose nanocrystal (CNC) films for high barrier packaging applications*
Cellulose Nanocrystals (CNCs) are promising materials for the packaging industry due to their non-toxicity, abundance in nature and biodegradability. In packaging applications, CNC coatings can improve the gas barrier performance of traditional low barrier polymer films because of their high crystallinity. Due to their brittleness, obtaining sufficient quality CNC coated polymer films is challenging. In this study, CNC-based pure and composite films were coated on polypropylene film by shear coating to investigate the barrier performance of the coated films. The study suggests that controlling the alignment of the CNCs can control the free volume of the system, which enhances the barrier performance. Furthermore, the addition of polymer into CNC suspension can significantly improve the barrier performance of the CNC films.

Different parameters of the Nanocellulose films with corresponding crystalline domains arrangement

CELL 53

**Spherical cellulose nanoparticles (CNPs) for magnetic resonance imaging (MRI) and X-ray computed tomography (CT)**

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Cellulose is a naturally occurring polymer of glucose. Cellulose based nanofibers and nanoparticles (CNPs) are characterized by their large surface area, high aspect ratio, and high Young's modulus, leading to potential applications in packaging, sensing, electronics. Further, a major attraction of CNPs for biomedicine is that they biodegrade to glucose, whereas traditionally used polymers such as PLGA degrade to inflammatory acidic components. Conventionally, CNPs have been produced by acid hydrolysis, enzyme treatment or chemical oxidation of natural product cellulose, with inefficient and cumbersome protocols. Here, we demonstrate the synthesis of spherical CNPs using a facile oil in water (o/w) emulsification technique, starting with cellulose triacetate. This unique strategy can be used to encapsulate hydrophobic superparamagnetic and/or X-ray dense nanocrystals (NCs) for MRI and X-ray CT applications. In this work, we first fabricated spherical cellulose triacetate nanoparticles (CTNPs). Next, these CTNPs were subjected to alkaline saponification to re-generate spherical CNPs. An optimized process (base concentration, reaction time) provides a major improvement over previous reports pertaining to the size and structural integrity of final CNPs. All NPs produced were extensively characterized using a variety of techniques; DLS, SEM, TEM, IR and ICP-OES. Further, this strategy was used to encapsulate superparamagnetic iron oxide NCs within CTNPs and CNPs. The resulting iron oxide CTNPs (IO-CTNPs) exhibit high in vitro cell viability. Subsequently, in this work we report the base-catalyzed regeneration of IO-CNPs from the IO-CTNPs, their detailed characterization, extensive in vitro biocompatibility and in vivo MRI. In addition, co-encapsulation of X-ray dense TaOx NCs within the CNPs together with CT evaluation of the resulting TaOx-CNPs is demonstrated.
Figure 1: a) Synthetic scheme for empty Cellulose Triacetate NPs (CTNPs); b) Scanning Electron Microscopy (SEM) images for empty CTNPs with Transmission Electron Microscopy (TEM) images in the inset; c) synthetic scheme for regeneration of cellulose by alkaline saponification; consequent generation of empty cellulose NPs (CNPs) from CTNPs; d) SEM images depicting the change in NP morphology due to alkaline saponification of CTNPs (top panel) to form CNPs (bottom panel); the scale bar is for 200 nm; e) reaction progress monitored by FT-IR spectroscopy; the disappearance of C=O stretch at 1750 cm⁻¹, consequent with the removal of triacetate groups to generate CNPs from CTNPs; f) synthetic scheme for encapsulation of iron oxide nanocrystals in cellulose triacetate to form iron-oxide cellulose triacetate NPs (IO-CTNPs); g) SEM images for IO-CTNPs with TEM images in the inset; h) Table showing NP characterization.

Synthesis and Characterization of Cellulose NPs

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Superabsorbent from cellulose nanofibers for oil and chemical spill responses

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Superabsorbents are highly appealing materials for use in cleaning up of oil and chemical spills. Especially, the development of low cost and highly efficient green superabsorbents is highly desired. Aerogels, as ultra-light three-dimensional (3D) and highly porous materials, demonstrate great superiority in oil and organic pollutants clean-up. Notably, biomass aerogels have also attracted widely interest due to the advantages of wide availability, low cost, renewability and nontoxicity to ecology. This research demonstrates a straightforward method of producing a cellulose nanofiber absorbent that is low-cost, environmentally friendly, ultralight, highly porous, hydrophobic, and reusable. Hydrophobic modification (silylation) and freeze-drying of cellulose nanofiber hydrogels resulted in sponges with ultralow density (0.003 g/cm\(^3\)) and high porosity (up to 99.8%). The sponges exhibited excellent oil/water absorption selectivity and ultra-high oil (marine diesel oil, kerosene, gasoline, motor oil, castor oil, or linseed oil) and organic solvent (dimethyl sulfoxide, chloroform, n-hexane, toluene, acetone, or ethanol) absorption capacity. In particular, the nanofiber absorbent showed selectivity in absorbing marine diesel oil from an oil-water mixture and possessed ultra-high absorption capacities of up to 143 g/g, much higher than those of the commercial absorbent materials (i.e., polypropylene based material inside oil boom) (8–25 g/g) that were used as references. Additionally the absorbed oil could be readily recovered by means of simple mechanical squeezing, and the superabsorbent could be reused at least 30 cycles. The above-mentioned advantages make nanocellulose superabsorbents s promising material for cleaning oil and chemical spills.

**CELL 55**

**Removal of chromium (VI) from aqueous solutions by cationic nanostructured cellulose**

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Nowadays, with the rapid population growth as well as technological advancement, the use of heavy metals has been remarkably accelerated. Among all the heavy metals, chromium is widely-used in textile, metal finishing, tanning, nutrition, electroplating, wood preservative, etc. The uncontrolled release of trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)) into water sources and soils have caused significant environmental problems, as Cr (VI) is highly carcinogenic with negative impacts on human health. In this study, a low-cost and high-efficiency cationic nanostructured cellulose bio-adsorbent was prepared by oxidizing cellulose microscale fibers (extracted from sugar cane) with sodium periodate followed by modification with Girard’s reagent T. The resulting cationic dialdehyde cellulosics (c-DAC) having different degrees of substitution were tested for the Cr (VI) adsorption, where effects of the chromium concentration, contact time and pH value were investigated. The cationization modification also generated a great deal of internal surface through partial defibrillation
within the microfibers. The maximum adsorption capacity of the c-DAC against Cr (VI) was found to be 80.5 mg g\(^{-1}\) at an initial concentration of 300 mg L\(^{-1}\). The chosen isotherm model for the analysis of equilibrium adsorption was the Langmuir Model, while the kinetic study showed that the adsorption mechanism could also be fitted by the pseudo-second-order model. c-DAC samples exhibited reasonable and stable adsorption capacity under a wide pH range, as the cationic charge on c-DAC’s surface remains positive. The results suggest that the adsorption mechanism is dominated by the electrostatic interactions between the positively charged cellulose surface and the negatively charged chromate ions.

**CELL 56**

**Bioactive nanocellulose for bacterial capture and anti-adhesion**

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Nanocellulose offers many interesting physicochemical properties that have generated exciting visions of future biological applications. Naturally derived cellulose nanofibrils (CNFs), a renewable, biocompatible and easily modified nanomaterial, were rendered bioactive via one-step functionalization with mannopyranoside (CNFs-mannose) for control of bacterial pathogenesis. The recognition affinity of the bioactive surfaces towards type 1-fimbriated _Escherichia coli_ (E. coli) was assessed using genetically engineered strains as well as wild-type bacteria. Bacterial binding to the nanofibrils was attributed to the specific interactions between FimH proteins on fimbriated _E. coli_ and prevalent mannose groups on the nanofibrils. Impregnation of porous substrates with CNFs-mannose furnished the substrates with capability of capturing fimbriated _E. coli_ from aqueous media. Adhesions of pathogenic _E. coli_ strains to infected host cells are primarily mediated through carbohydrate–protein interactions. Interestingly, CNFs-mannose efficiently inhibited adhesion of fimbriated _E. coli_ to mannosylated surfaces resulting in 100-fold reduction of bacterial adhesion. These findings highlight the potential of cellulose nanofibrils as a broadly applicable multivalent platform and exemplify sugar grafted nanofibrils as effective tools in control of bacterial pathogenesis, bacterial removal as well as in many other applications.

**CELL 57**

**Improved dispersion and interfacial bonding between nanocellulose and poly(lactic acid) using solvent infiltration and ball milling methods**

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The dispersion and distribution of the nanocellulose reinforcing phase are the key factors that determine the interfacial adhesion of nanocellulose in polymeric matrices, and ultimately dictate the structure and properties of the cellulose nanocomposites. In this study, we have used two new compounding methods to make cellulose nanofibrils (CNFs)-poly(lactic acid) (PLA) composites: (1) solvent-assisted PLA infiltration to CNF foams and (2) ball milled CNF followed by melt-blended with PLA. These two methods were compared with direct mixing of crushed freeze-dried CNF in PLA and the covalent surface functionalization of CNF using 3-aminopropyltriethoxysilane (APTS). The compounded CNF-PLA mixture was used to generate CNF-PLA composite specimens. The mechanical strengths, morphological properties, chemical structures, and thermal stability of the composites were characterized using numerous methods. The results of the different manufacturing techniques are discussed and compared. This study demonstrated size reduction and solvent-assisted infiltration as alternative methods to improve the dispersion and interfacial bonding of nanocellulose in a matrix for the manufacture of green composites.

**CELL 58**

**Redispersible chitin nanocrystals extracted through electron beam irradiation followed by high pressure homogenization**

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A green strategy for extracting chitin nanocrystals (ChNCs) was conducted by a facile two-step process to combine electron-beam irradiation (EBI) of chitin pulp in dry state and subsequent disintegration using high pressure homogenization (HPH), when compared to the conventional production by strong acid hydrolysis. The EBI-treatment proved a significant reduction in the degree of polymerization, whereas the carboxylate content was meaningfully increased by the oxidation of the primary alcohol in effective dosage ranges. The resulting ChNCs had the uniform width of 10–20 nm and the controllable length of 261–757 nm, respectively, indicating a rod-like shape, preserved crystallinity indices (CrI = 84–94%), anionic surface charge (absolute amounts of 32.0–36.7 mV), and comparable thermal stability ($T_{d\text{ onset}} = 180–230 ^\circ C$ and $T_{d\text{ max}} = 300–330 ^\circ C$), similar to those of conventional ChNCs. To prove redispersibility after drying the EBI-treated ChNCs for storage and transport, the irradiated chitin pulp was counterionized with alkaline solution, disintegrated through HPH, neutralized with CO$_2$, and spray-dried to obtain free-flowing and flour-like powder, which could be redispersed in water by simple stirring (24h), showing no irreversible particle aggregation. This
simple and innovative approach offers a promising production process of ChNCs for
green and sustainable characteristics.

Figure 1. TEM images of (a) ChNCs obtained by HCl hydrolysis, (b) ChNCs fabricated from
chitin pulp dissociated by electron-beam irradiation (EBI), and (c) Redispersed ChNCs extracted
by EBI, after spray drying.

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Fabrication of high-strength antimicrobial chitosan-nanocellulose composite coatings

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The increasing rate of acute global bacterial infections is precipitating an effort to
develop effective and sustainable hygienic products. The present work targets a
significant innovation in biodefense through the design of a sustainable, biodegradable,
and high strength antimicrobial plasma-enhanced chitosan/nanocellulose-based
biocomposite (hand towels, tissue wipes, and related products) that combats hand-
borne bacterial transmission. Chitosan, a naturally occurring polymer, has been studied
for its antimicrobial properties against a vast array of bacteria (Gram-positive and Gram-
negative) as well as fungi, but mostly in association with strong antimicrobial coupling
agents. To improve the antimicrobial activity of chitosan, a biocomposite of chitosan and
nanocellulose was incorporated into tissue from recycled fibers, which were treated with
environmentally friendly atmospheric oxygen plasma to activate surface antimicrobial
properties. The release properties of the chitosan-nanocrystals biocomposite of
differently treated tissue paper was studied with respect to effectiveness against
bacteria. This composite delivered a 99% reduction in bacterial growth in addition to
significant improvements in hydrophilicity and water absorption properties.