

WORKING TO CREATE A SUSTAINABLE FUTURE

# 27<sup>th</sup> Bio-Environmental Polymer Society Meeting





# June 23-25, 2021 Hosted by Rowan University

### **Current BEPS Officers 2021**

#### President

Joe Stanzione, III Associate Professor of Chemical Engineering Founding Director, Advanced Materials & Manufacturing Institute (AMMI) Rowan University, USA

#### **Vice President**

Cecily Ryan Associate Professor

Mechanical & Industrial Engineering Department

Montana State University, USA

#### Treasurer

Nandika D'Souza Professor Associate Dean for Undergraduate Studies University of North Texas, USA

#### Counselors

Greg Glenn Bioproduct Research Unit

US Department of Agriculture

Pacific West Area, USA

A.B. Kousaalya Postdoctoral Research Fellow Chemical Engineering Department Rowan University, USA

Amar Mohanty Professor Director, Bioproducts Discovery & Development Center (BDDC) University of Guelph, Canada Richard Gross Constellation Chair Center for Biotechnology and Interdisciplinary Studies Rensselaer Polytechnic Institute (RPI), USA

> Manjusri Misra Professor Biological Engineering Department University of Guelph, Canada

Srikanth Pilla Robert Patrick Jenkins Endowed Professor Founding Director, Clemson Composites Center Clemson University, USA

Jinwen Zhang Professor School of Mechanical & Materials Engineering Washington State University, USA

## **Message from the BEPS President**



Dear Attendees:

It is my pleasure and honor to welcome you all to the Bio-Environmental Polymer Society (<u>BEPS</u>) 2021 27<sup>th</sup> Meeting. The 27<sup>th</sup> Meeting has been put together by the BEPS Executive Committee and dedicated folks within the <u>Henry M. Rowan</u> <u>College of Engineering</u> and the Advanced Materials & Manufacturing Institute (<u>AMMI</u>) at <u>Rowan University</u> (Glassboro, NJ, USA). As President of BEPS, I could not have created such a packed and impactful 3-day meeting without their tireless efforts and support. I cannot thank them enough. The meeting is entirely virtual; however, I am extremely excited about the program and I truly believe that

knowledge will be exchanged, ideas will be created and discussed, and networking will still occur, despite us all not being physically present.

The BEPS meetings aim at bringing scientists and researchers from across the globe to present and exchange breakthrough ideas related to biobased and sustainable materials and technologies. This year's meeting theme is "Bridging Sustainability Gaps via Reshaped Polymers and Mindsets." Reshaped is utilized to describe redesigning all facets of plastics, from raw materials to processing to in-use and end-use properties to societal impacts to education. Over the next three days, more than 80 speakers will present their research related to the meeting's theme with topics divided into 6 tracks: (1) Biodegradability & Sustainability; (2) Synthesis of Bio-based Polymers; (3) Applications of Bio-based Materials; (4) Advances in Polymer Manufacturing; (5) Progress in Lignin Valorization; and (6) Bio-based Composites & Components. Each of these talks tackle critical challenges associated with their respective domain(s). I am sure that each one of you will identify subjects of his/her interest and will benefit from many fruitful and enriching discussions.

I would like to thank you for attending this year's meeting. I would like to also thank all the presenters, both confirmed invited speakers and open submitters, for putting together such wonderful abstracts. We could not have put together such an exciting meeting without your support and willingness to contribute. We are looking forward to your presentations and the conversations that result from them. Furthermore, I would like to congratulate this year's BEPS Award winners, all of whom are presenting and information about them and their respective awards highlighted in this program booklet. Additionally, I would like to thank Composites Part C: Open Access (JCOMC) for their support of this year's meeting through the creation of a Special Issue dedicated to BEPS. Information about this Special Issue, including the opportunity to contribute to it free of charge, can be found in this program booklet and on the BEPS and JCOMC websites. I encourage you to consider contributing to this Special Issue, which could not have been made possible without the support of Profs. Amar Mohanty and Manju Misra (University of Guelph, Canada). Thank you both! Lastly, I congratulate you all for your commitment and active participation, and wish you to stay healthy, safe, and positive!

I hope to see you in-person soon!

Sincerely,

Joe Stanzione, III, Ph.D. Associate Professor of Chemical Engineering Founding Director, Advanced Materials & Manufacturing Institute (AMMI) Rowan University Glassboro, NJ, USA

## **About BEPS**

**Mission & Scope:** Biomass is the most readily implementable solution to manufacture sustainable materials, including polymers, to meet the increasing demand for global populace while tackling the growing risks of climate change. In this context, BEPS is a non-profit society that seeks to: (1) Advance fundamental knowledge of design, chemical/biochemical synthesis, processing, analyses & applications of polymers derived from readily renewable carbon; (2) Feature new technology and commercial successes presented by businesses; (3) Welcome biorefinery-related research that aims to develop and integrate individual biomass process streams with primary biomass components; and (4) Promote basic research, training and education, and facilitate exchange of information among researchers in areas of biology, chemistry, materials science, life-cycle analysis, agriculture, forestry, environmental policy and waste management.

**History:** The Bio-Environmental Polymer Society was founded in 1992. Those involved in the formative stages included Richard Gross, Sam Huang, Dave Kaplan, Steve McCarthy, and Denise Rutherford. A critical meeting was organized in 1991, titled "*Symposium on Environmentally Degradable Polymers: Technical*, *Business and Public Perspectives*", involving  $\sim$  140 scientists from major corporations, government laboratories and universities. This meeting ultimately resulted in the formation of a new society: Bio/Environmentally Degradable Polymer Society (BEDPS). Later, this name was modified to Bio-Environmental Polymer Society (BEPS) to reflect interest in synthetic, renewable (bio-based) and degradable polymers.

**BEPS Activities:** The primary mechanism of information exchange is through the BEPS website and participation at our Annual/Semi-Annual Meetings. These meetings are typically in June, August, or September and consist of scientific, marketing, and informational presentations over several days. A broad range of topics is presented at the meeting through both oral and poster presentations. Key topics included in the BEPS Meetings include:

- Progress on commercialization efforts of bio-based monomers, polymers, and corresponding materials;
- Green routes for polymer chemical or enzymatic recycling;
- Polymers used for application in foods, nutrition, and agriculture;
- Innovations in chemical and biocatalytic routes to monomers and polymers;
- Innovative chemical processes for conversion of lignocellulose to value-added products;
- Biopolyesters;
- Green chemical catalysts for bio-based monomer and polymer synthesis;
- Protein-based materials and carbohydrate-based materials;
- Biocatalytics routes to natural polymers;
- Modification of natural polymers to tune physical and biological properties;
- Metabolic and protein engineering to develop catalysts for green polymer chemistry;
- Bio-based composites, coatings, and structural materials;
- Biofibers;
- Life-cycle analysis of bio-based processes;
- Studies of polymer biodegradability (soil, marine, compost, anaerobic digestion) and other end-oflife options; and
- Process developments (*e.g.*, continuous bioprocesses, downstream aspects).

## **BEPS Lifetime Achievement Award Recipient**



The 2021 BEPS Lifetime Achievement Award is given to **Dr. Manjusri (Manju) Misra** for her outstanding life-long contributions in the field of bio-based polymers and materials.

Dr. Manju Misra is a professor and Tier 1 Canada Research Chair (CRC) in Sustainable Biocomposites in the School of Engineering and holds a joint appointment in the Department of Plant Agriculture at the University of Guelph. As well, she is the Research Program Director of the Bioeconomy Panel for the Ontario Agri-Food Innovation Alliance, a program between the Ontario Ministry of Agriculture and Rural Affairs (OMAFRA) and the University of Guelph. She has authored more than 800

publications, including 405 peer-reviewed journal papers, 21 book chapters, and 53 patents. She is a Fellow of the Royal Society of Chemistry (UK), the American Institute of Chemical Engineers (AIChE), and the Society of Plastic Engineers (SPE). In 2012, Dr. Misra received the prestigious "Jim Hammar Memorial Award" from the BioEnvironmental Polymer Society. In 2017, Dr. Misra also received the Andrew Chase Division Award in Chemical Engineering from the Forest Bioproducts Division of AIChE. In 2020, she was selected as one of Canada's Most Powerful Women: Top 100 Award Winner in the Manulife Science and Technology from the Women Executive Network.

**About the Award:** The BEPS Lifetime Achievement Award is a prestigious award, and is given to BEPS members who have made outstanding contributions that have advanced the scientific field and/or technological development of biopolymers, bio-based materials, or bioplastic/materials related to bioenergy. The nominee is recognized as a leader in their field and must have held the position of full professor or equivalent (*i.e.*, GS15, senior scientists, and/or engineers) for two years or longer.

## **BEPS Outstanding Young Scientist Award Co-Recipient**



The 2021 BEPS Outstanding Young Scientist Award is given to **Dr. Cecily Ryan** for her outstanding contributions in the field of bio-based polymers and materials over a very short span of time.

Cecily Ryan is an Assistant Professor at Montana State University in Mechanical Engineering. She received her undergraduate degree in Materials Science and Engineering from MIT and an M.S. in Applied Physics from Caltech where she did research in materials for optoelectrical devices. She earned a Ph.D. in Civil and Environmental Engineering from Stanford University, working with Drs. Sarah Billington and Craig Criddle to understand the end-of-life degradation mechanisms

of sustainable biopolymer composites. Prior to her doctoral studies, she was on the research and development team for two Silicon Valley startups focused on sustainable cement and concrete. Sustainability remains a focal point of her research, including material processing, structure, property relationships for biobased and biodegradable composites and incorporation of biobased functional fillers into composites.

**About the Award:** The BEPS Outstanding Young Scientist Award is given to individuals who have made significant scientific contributions and have demonstrated outstanding ability and scholarly accomplishments in scientific research in the fields of biopolymers, bio-based materials, or bioplastic/materials related to bioenergy. The nominee must hold a tenure-track position at the assistant/associate/full professor level or the equivalent in government research or industry (*i.e.*, GS11-GS14, scientists, and/or engineers). This individual will be under the age of 40 by December 31<sup>st</sup> of the current year of the BEPS meeting.

## **BEPS Outstanding Young Scientist Award Co-Recipient**



The 2021 BEPS Outstanding Young Scientist Award is given to **Dr. Wil V. Srubar, III** for his outstanding contributions in the field of bio-based polymers and materials over a very short span of time.

Dr. Wil Srubar is an associate professor of civil and architectural engineering and materials science at the University of Colorado Boulder, where he leads the Living Materials Laboratory. Dr. Srubar holds a Ph.D. from Stanford University, as well as B.S. and M.S. degrees from Texas A&M University and the University of Texas at Austin, respectively. His research integrates biology, polymer

science, and cement chemistry to create low-carbon, biomimetic, and living material technologies for the built environment. He has authored > 85 technical journal articles, book chapters, and conference proceedings, and his work has been highlighted in *The Washington Post, National Public Radio*, and *The New York Times*.

**About the Award:** The BEPS Outstanding Young Scientist Award is given to individuals who have made significant scientific contributions and have demonstrated outstanding ability and scholarly accomplishments in scientific research in the fields of biopolymers, bio-based materials, or bioplastic/materials related to bioenergy. The nominee must hold a tenure-track position at the assistant/associate/full professor level or the equivalent in government research or industry (*i.e.*, GS11-GS14, scientists, and/or engineers). This individual will be under the age of 40 by December 31<sup>st</sup> of the current year of the BEPS meeting.

## James Hammar Memorial Service Award Recipient



The 2021 BEPS James Hammar Memorial Service Award is given to **Dr. Jinwen Zhang** for his outstanding service and dedication to the Bio-Environmental Polymer Society (BEPS).

Jinwen Zhang is a professor at the school of Mechanical and Materials Engineering, Washington State University. He received his bachelor's degree in textile chemistry in 1984 and master's degree in dye chemistry in 1991, and in 1996 he received his Ph.D. degree in polymer science from University of Massachusetts Lowell. For more than 20 years, Dr. Zhang has been working on sustainability related polymer research, which ranges from synthesis, processing and application development of polymer

materials. Dr. Zhang has published more than 120 journal papers, 11 book chapters and 1 book. In addition, he has also been awarded 7 U.S. patents.

**About the Award:** The James Hammar Memorial Service Award was created in 2000 in honor of W. James Hammar who worked tirelessly for eight years in helping to establish the Bio-Environmental Polymer Society (formerly Bio/Environmentally Degradable Polymer Society) before his untimely death in 1999. Jim was a Division Scientist at 3M with a long, distinguished research career and a strong passion for scientific excellence. Jim's devotion to the Society was inspirational and the standards of service and excellence he set were instrumental to the success of the Society during the early years. The Jim Hammar Memorial Service Award is presented to a member of the Bio-Environmental Polymer Society who best exemplifies the qualities of service and dedication inspired by Jim Hammar. The James Hammar Memorial Service Award is presented to BEPS members who have been involved with the Society for at least three years.

## Composites Part C: Open Access (JCOMC)

### Special Issue: Bioenvinromental Polymers Society (BEPS): Bridging Sustainability Gaps via Reshaped Polymers and Mindsets

In collaboration with Composites Part C: Open Access (JCOMC), we are pleased to announce the creation of a Special Issue entitled, "*Bio-Environmental Polymers Society (BEPS): Bridging Sustainability Gaps via Reshaped Polymers and Mindsets.*" This Special Issue is in association with their Sustainable Composites Editor-in-Chief, Amar Mohanty (University of Guelph). Srikanth Pilla (Clemson University), Cecil Ryan (Montana State University), and Joe Stanzione (Rowan University) will be serving as co-guest editors of the Special Issue. Participants of the BEPS 2021 27<sup>th</sup> Meeting, and others who conduct similar research, will have the opportunity to contribute free of charge, as long as the manuscript is received by September 30, 2021. Topics of great import to the composites industry and to the wider materials community, from biodegradability and sustainability to synthesis of bio-based polymers and composites to advances in polymer manufacturing, will be of great interest. We will begin to accept manuscript submissions on June 1, 2021. For details about JCOMC, please visit their website, link below.

Composites Part C: Open Access

# 27<sup>th</sup> BEPS – Meeting Schedule

Day 1: 23 June 2021 (Wednesday)

June 23, 2021	Bioenvironmental Polymers Society (BEPS) 2021 27th Meeting (ALL TIMES Eastern Time)							
9:00-9:10 am	Welcome Remarks							
	Plenary Session P1 (BEPS Outstanding Young Scientist Award Co-recipient Winner)							
9:10-9:50 am	P1.1 - Electrically Conductive Biobased Fillers and Composites							
	Cecily Ryan							
	Montana State University, USA							
9:50-10:00 am	Coffee Break							
10:00 am - 12:30 nm	Concurrer	S2 - Synthesis of Bio-based Polymers						
	Session Chair: John Chea	Session Chair: Tristan Bacha						
	S1.1 - Data-driven Approach to Understanding Polymer	S2.1 - From Eugenal to Biobased Polymers: A Platform Approach						
10:00-10:20 am	Degradation in the Ocean							
	Invited Speaker: Robert Mathers	Invited Speaker: Sylvain Caillol						
	S1.2 - Techno-Economic Analysis and Life Cycle Assessment of	Institut charles Gernardt Montpellier, France						
	Lignin Fractionation and Valorization Via the Alpha Process:	S2.2 - Renewability is Not Enough: Sustainable Synthesis of						
10:25-10:45 am	Upgrading to Value-Added Products	Biomass-derived Monomers and Polymers						
	Invited Speaker: David Shonnard	Invited Speaker: Michael Meier						
	Michigan Technological University, USA	Karlsruhe Institute of Technology, Germany						
	With The Environment	S2.3 - Ocean Digestible Bioplastics						
10:50-11:10 am	Invited Speaker: Richard Venditti	Invited Speaker: Stephen Miller						
	North Carolina State University, USA	University of Florida, USA						
	S1.4 - Potential Microparticles Entering the Air and Water	S2.4 - Engineering Non-Isocyanate Polyurethanes to be 100%						
11.1E 11.2E am	Environment from Nonwoven Products: Methodology	Biobased and Recyclable by Design						
11.15-11.55 dill	Sooiin Kwon	Invited Spekaer: Srikanth Pilla						
	North Carolina State University, USA	Clemson University, USA						
	S1.5 - Degradable and thermally Stable Spiro Polycycloacetals from	\$2.5 - Developing Betulin-Based Polyesters from Birch Bark						
11:40-noon	Renewable Resources	52.5 - Developing betain based i olyesters from biren bark						
	Yanchun Tang	Invited Speaker: Melissa Gordon						
	S1.6 - Oxo-Biodegradable LLDPE Films Subjected to Gamma	S2.6 - Biodiversification of Natural Rubber by Metabolic						
	Irradiation and Accelerated Weathering	Engineering						
12:05-12:25	Tomas Madera-Santana	Invited Speaker: Katrina Cornish						
	Resesarch Center in Food & Development, México	Ohio State University, USA						
12:30-2:00 pm	Lunch Break	+ Faccions						
2:00-4:30 pm	S1 - Biodegradability & Sustainability	S2 - Synthesis of Bio-based Polymers						
	Session Chair: Alexandra Chong	Session Chair: Jasmin Vasquez						
	S1.7 - Poly(ethyleneterephthalate) (PET) Recycling: Current	S2.7 - Progress in Sustainable Long-Chain Aliphatic Polyethylene						
2:00-2:20 pm	Strategies, Shortcomings, and Reinforced Composites	Mimics						
	Michael Snowdon	Invited Speaker: Chuanbing Tang						
	S1.8 - Sustainability Assessment, Process Development, and Life	S2.8 - Glycerol Ketals as Building Blocks for a New Class of						
2.25.2.45.45	Cycle Analysis	Biobased (Meth) Acrylate Polymers						
2:25-2:45 pm	Invited Speaker: Gerardo Ruiz-Mercado	Shailja Goyal						
	US Environmental Protection Agency, USA	Iowa State University, USA						
	51.9 - Effect of Gliding Arc Plasma Treatment on Soil Degradation	S2.9 - Chemoenzymatic Polymerization of L-Serine Ethyl ester						
2:50-3:10 pm	Invited Speaker: Christopher Lewis	Takumi Watanabe						
	Rochester Institute of Technology, USA	Kyoto University, Japan						
	S1.10 - Biodegradable Plastic Detected in Soil Two Years After	S2.10 - A Green and Sustainable Platform for Biopolymers						
3:15-3:35 pm	Incorporation of Agricultural Plastic Mulch	Production using a Marine Photosynthetic Purple Bacterium						
	Alexis Gillmore	Choon Pin Foong						
		S2.11 - Genome-Engineered Pseudomonas Alloputida for						
3:40-4:00 pm	S1.11 - Pathways for Isoflavone Extraction from Soybean Meal	Conversion of Lactose to mcl-PHA						
	Invited Speaker: Kirti Yenkie	Invited Speaker: Trevor Charles						
	Rowan University, USA	University of Waterloo, Canada						
4:05-4:25 pm	S1.12 - Effects of COVID-19 Pandemic on the Municipal Solid	S2.12 - Self-catalytic Preparation of Epoxy vitrimers: Mechanical						
	Waste Management	Performance, Adaptivity, and Recyclability						
	University of Guelph, Canada	Washington State University, USA						
4:30-5:00 pm	Q&A Session, Presentation of the James Hammar Me	morial Service Award Recipient, and Closing Remarks						

# 27<sup>th</sup> BEPS – Meeting Schedule

#### Day 2: 24 June 2021 (Thursday)

June 24, 2021	Bioenvironmental Polymers Society (BEPS) 2021 27th Meeting (ALL TIMES Eastern Time)						
9:00-9:10 am	Welcome Remarks						
	Plenary Session P2 (BEPS Lifetime Achievement Award Winner)						
	Session Chair: Joe Stanzione						
9:10-9:50 am	P2.1 - Single-use Plastics:	Challenges & Alternatives					
	Manjusri Misra						
9:50 10:00 am	University of Guelph, Canada						
9.50-10.00 am	Concurren	nt Sessions					
10:00 am - 12:30 pm	S4 - Advances in Polymer Manufacturing	S5 - Progress in Lignin Valorization					
	Session Chair: Alexandra Chong	Session Chair: John Chea					
	S4.1 - Applications of Biodegradable Polymers for Fused	S5.1 - Carbon Fibers Derived from Lignin-based Productors					
10:00-10:20 am	Deposition Modeling 3D Printing	Soli carbon ribers benved nom Eighn based ricearsors					
10100 10120 0111	Invited Speaker: Adriána Kovalčík	Invited Speaker: Amod Ogale					
	Brno University of Technology, Czech Republic	Clemson University, USA					
	and Application	1 June faction of Lignin					
10:25-10:45 am	Invited Speaker: Greg Glenn	Invited Speaker: Charles Mullen					
	USDA ARS Pacific West Area, USA	USDA ARS ERRC, USA					
	S4.2 Understanding Storeotypical Implications in DLA Polymors	S5.3 - Fractionating and Purifying Hybrid Poplar Lignins with					
	for Manufacturing Performance and Processability	Aqueous Renewable Solvents for Higher-value Applications: Fibers,					
10:50-11:10 am	for managed angle en of managed and recessation (	Foams, and Carbons					
	Invited Speaker: Ramani Narayan	Invited Speaker: Mark Thies					
	Michigan State University, USA	Clemson University, USA					
	Covalent Bonds Enable Sustainable Chemical Recycling of	S5.4 - Resolving the Discrepancies in the True Molecular Weight of					
11:15-11:35 am	Traditional Non-Recyclable Polymers and Composites	Lignins with the Assistance of the ALPHA Process					
	Invited Speaker: John Torkelson	Zachariah Pittman					
	Northwestern University, USA	Clemson University, USA					
	S4.5 - Thermosetting Bio-Derived and Environmentally Friendly	S5.5 - Exploiting the Liquid-Liquid Phase Behavior of Hybrid Poplar					
	Polymers for Additive Manufacturing	Lignin in Ethanol-Water Solutions to Produce Precursors for Value-					
11:40-noon	Invited Speaker: John La Scala	Added Applications Graham Tindall					
	IIS Army Research Laboratory						
	S4.6 - Modifying Polyethylene Terephthalate through Reactive	S5.6 - Life cycle Assessment of Lignin-containing Cellulose					
12:05-12:25	Twin Screw Extrusion to Improve Enzymatic Degradation	Nanocrystais (LCNCs) isolation using Deep Eutectic Solvents (DES)					
	Akanksha Patel	Shiva Zargar					
	University of Massachusetts Lowell, USA	University of British Columbia, Canada					
12:30-2:00 pm	Lunch Break and BEPS Executive Committee Board Meeting (12:45-	1:45 pm)					
2.00-4.30 nm	S3 - Applications of Bio-based Materials	S2 - Synthesis of Bio-based Polymers					
2.00-4.50 pm	Session Chair: Matthew Schwenger	Session Chair: Tristan Bacha					
		S2.13 - Enhancing Properties in Fatty Acid-Derived Thermoplastic					
	S3.1 - Developing Highly Effective Polysaccharide Flocculants	Elastomers by Incorporating a Transient Network					
2:00-2:20 pm	Invited Speaker: Wim Thielemans	Invited Speaker: Megan Robertson					
	KU Leuven, Belgium	University of Houston, USA					
	S3.2 - Biobased Coating for the Rejuvenation of Old Asphalt	S2.14 - Performance Advantages for Bioproducts in Manufacturing,					
2:25-2:45 pm	Shingles	Performance, and End-of-Life					
	Invited Speaker: Nacu Hernandez						
	S3.3 - Advances in Biopolymers for Environmental and Biomedical	S2.15 - High Performance Epoxy-AmineThermosets Based on Furan					
	Applications	Building Blocks					
2:50-3:10 pm	Invited Speaker: Xiuzhi (Susan) Sun	Invited Speaker: Giuseppe Palmese					
	Kansas State University, USA	Drexel University, USA					
	S3.4 - The Adhesion and Thermal Properties of Hot Melt Adhesive-	S2 16 - High Strength Thermosets from High Functionality Bio-					
	based Nature Rosin and Poly(butylene adipate-co-terephthalate)	based Resins					
3:15-3:35 pm	for Packaging	In ited Greeker Deer Webster					
	Seoul National University, South Korea	North Dakota State University USA					
3:40-4:00 pm	Secon Hacional Oniversity, South Korea	Hortin Bakota State Oniversity, USA					
	S3.5 - Adhesion Property of PBS Hot-Melt Adhesives by Rosin Type	S2.17 - Recent Advances in Cashew Nutshell Liquid Technology					
	Kwang-Hyun Ryu	Invited Speaker: Joseph Mauck					
	Seoul National University, South Korea	Cardolite Corporation, USA					
4:05-4:25 pm	S3.6 - Shelf Life Extension of Postharvested Climacteric Fruits by	S2.18 - Polyester Technology for Greener Cosmetic Ingredients: Re-					
	Using Edible Coatings	envisioning Classic Chemistry for Enhanced Performance and					
	Neelima Tripathi	Invited Speaker: Mike Fevola					
	IIT Kanpur, India	Inolex, USA					
4:30-5:00 pm	Q&A Session and Closing Remarks for the Day						

# 27<sup>th</sup> BEPS – Meeting Schedule

#### **Day 3: 25 June 2021 (Friday)**

June 25, 2021	Bioenvironmental Polymers Society (BEPS) 2021 27th Meeting (ALL TIMES Eastern Time)							
9:00-9:10 am	Welcome Remarks							
	Plenary Session P3 (BEPS Outstanding Yo	ung Scientist Award Co-recipient Winner)						
	Session Chair: Joe Stanzione							
9:10-9:50 am	P3.1 - Novel Biopolymer and Biomineral Material Technologies for the Built Environment							
	Wil Srubar, III							
9·50-10·00 am	University of Colorado, USA							
5.50-10.00 am	Concurrent Sessions							
10:00 am - 12:30 pm	S4 - Advances in Polymer Manufacturing	S6 - Bio-based Composites & Components						
	Session Chair: Tristan Bacha	Session Chair: Alexandra Chong						
	S4.7 - Challenges in Formulating and Processing Charged Fiber-	S6.1 - High Cycle Fatigue Strength of Flax Fiber and Flax/Carbon						
10:00-10:20 am	Based Materials	Fiber Reinforced Thermoset Composites						
	Invited Speaker: Blair Brettman	Invited Speaker: Chad Ulven						
	Georgia Institute of Technology, USA	North Dakota State University, USA						
	54.8 - Highly Compostable High OleicSoy-Based Impact-Modifiers	S6.1 - Addressing Decreased Thermal Stability of Biodegradable						
10:25-10:45 am	Via Reactive Extrusion with Polyesters	Plastics with the Addition of Biochar and Biomass Filler Materials						
		Montana State University USA						
	S4.9 - Multicomponent Adsorption and Membrane Separations to	S6.3 - Strategic Assembly of Bio-Based Resins with Recycled						
	Enable New and More Efficient Biopolymer Production Processes	Carbon Fibers: New Advances in Green Composites						
10:50-11:10 am	Invited Speaker: Sankar Nair	Jasmin Vasquez						
	Georgia Institute of Technology, USA	Rowan University, USA						
	C4.10 Description Compounding of Displastics via Twin Futureign for	S6.4 - Property Enhanced Biobased Packaging from Polybutylene						
	34.10 - Precision Compounding of Bioplastics via Twin Extrusion for	Succinate and Nanocellulose Composites as a Sustainable						
11:15-11:35 am	SD Flidhlents	Biodegradable Alternative						
	Invited Speaker: Charlie Martin	Anuradhi Liyanapathiranage						
	Leistritz Extrusion, USA	University of Georgia, USA						
		S6.5 - Production and Physicochemical Characterization of Value-						
	S4.11 - Bio-Based Resins for Additive Manufacturing	added Biocarbon Produced from Slow Pyrolysis of Waste Mixed						
11:40-noon		Bio-Oil						
	Invited Speaker: Alexander Bassett	Kanjeet Mishra						
	SA 12 - EDM 3D Printed Sustainable Biocomposites from Recycled	S6.6 - Physicochemical Characterization of Bio-Carbon Produced						
	Ocean Plastics and Soy Hull-based Biocarbon	from the Slow Pyrolysis of Pine Nut Shells and Walnut Shells						
12:05-12:25	Benjamin Maldonado-Garcia	Kikaoseh Agweh						
	University of Guelph, Canada	University of Guelph, Canada						
12:30-2:00 pm	Lunch Break	•						
	Concurrent Sessions							
2:00-3:40 pm	S1 - Biodegradability & Sustainability	S6 - Bio-based Composites & Components						
	Session Chair: John Chea	Session Chair: Jasmin Vasquez						
	S1.13 - Micro-Nano Plastics in the Environment: Challenges and	S6.7 - Natural and Waste Fillers in Biodegradable Polymeric						
2:00-2:20 pm	Solution Pathways	Composites and Foams						
	Poritosh Koy	Charferd University UCA						
	S1 14 - Biodegradable Blends of Poly(3-bydroxybutyrate-co-3-	Station Oniversity, USA						
	hydroxyvalerate) and Poly(s-caprolactone) by in situ, Reactive	Composites from Polyphthalamide (PPA) and with Polyamide 4.10						
2·25-2·45 nm	Compatibilization)	Blends						
2120 2110 pin	Peter Zvtner	Mateo Gonzalez de Gortari						
	University of Guelph, Canada	University of Guelph, Canada						
	S1.15 - The Aquatic Biodegradation of Wood-based Bathroom							
	Tissue, Cotton Microfibers, and Flushable Wipes in Wastewater	56.9 - Effects of Biochar Amendment in an in-pot Experiment for						
2:50-3:10 pm	Treatment Plant Sludge	the Purposes of Growing Glycine Max.						
	Madilynn Smith	Tara Allohverdi						
	North Carolina State University, USA	University of Guelph, Canada						
3:15-3:35 pm	S1.16 - Effects of Environmental Weathering on Particle	S6.10 - Poly(3-hydroxybutyrate-co-3-						
	Morphology Probed from Engineered Biodegradable Micro-and	hydroxyvalerate)/Polypropylene Carbonate Based Green						
	Nanoplastic Materials Used for Environmental Studies	Composites with Distillers Dried Grains with Solubles (DDGS)						
	Anton Astner	Akhilesh Pal						
	University of Tennessee Knoxville, USA	University of Guelph, Canada						
3.40-4.00 nm	O&A Session and Confe	arence Closing Remarks						

## 27th BEPS – Speaker Abstracts

Day 1: 23 June 2021 (Wednesday)

Plenary Session P1.1: 9:10-9:50 am (Eastern Time) (Invited Speaker)

#### **Electrically Conductive Biobased Fillers and Composites**

#### Cecily Ryan

Department of Mechanical & Industrial Engineering, Montana State University, Bozeman, MT, USA

Biobased and biodegradable components for electronics have exciting potential to reduce e-waste and be utilized in disposable sensors and devices. For this work, we focus on biobased electrically conductive fillers from lignin-derived biochar (biocarbon) particularly suited to 3D printing and rapid prototyping applications. This work seeks to understand and tailor the electrical conductivity and processability of the biochar when used as a filler material in biopolymer composites. We used a statistical approach to examine factors such as pyrolysis temperature, composition, moisture content, surface area and particle size to evaluate key contributing factors in the conductivity and thermal decomposition temperature when processed in two of the common biopolymers: PHBV and PLA. Decreases in oxygen content and changes in particle size are associated with increases in electrical conductivity of the lignin-derived filer. Residual inorganics from the processing and biomass were found to be key factors in the commonly observed phenomenon that biochar can reduce the thermal decomposition temperature of the biopolymer when processed into composite materials. With these insights, we were able to produce an electrically conductive biochar, from lignin isolated in a collaborator's lab at Montana State University that can also be stably incorporated into biopolymer composites.

#### **Concurrent Session S1 – Biodegradability & Sustainability:** 10:00 am – 12:30 pm (Eastern Time)

Session Chair: John Chea (Rowan University)

S1.1: 10:00 – 10:20 am (Eastern Time) (**Invited Speaker**)

#### Data-driven Approach to Understanding Polymer Degradation in the Ocean

Kyungjun Min, Joseph D. Cuiffi, Robert T. Mathers

Department of Chemistry, Pennsylvania State University, New Kensington, PA, USA

Although concepts such as "green polymer chemistry" and "sustainable materials" encompass a wide variety of strategies, the 12 principles of green chemistry usually serve as a compass to assist design of experiments. As such, combining ideas like "waste reduction", the "use of renewable feedstocks" and "design for degradation" has great potential for producing sustainable materials. Recent reports in the literature (Angew. Chem. Int. Ed. 2019, 58, 50–62) suggest that terms like "degradable" and "biodegradable" depend on environmental condition. In this regard, ocean conditions greatly differ from soil or compost conditions. As a result, many bio-based polymers, like PLA, degrade much more slowly in the ocean than expected. This presentation will discuss a data-driven approach to understand how physical properties and structural features on a molecular level control degradation in an ocean environment.



#### Techno-Economic Analysis and Life Cycle Assessment of Lignin Fractionation and Valorization Via the Alpha Process: Upgrading to Value-Added Products

#### Daniel Kulas<sup>1</sup>, Mark Thies<sup>2</sup>, David Shonnard<sup>1</sup>

#### 1. Department of Chemical Engineering, Michigan Technological University, 1400 Townsend Dr, Houghton, MI, USA

#### 2. Department of Chemical and Biomolecular Engineering, 206 S. Palmetto Blvd, Clemson University, Clemson, SC, USA

This study investigated the environmental and economic sustainability of the Aqueous Lignin Purification with Hot Agents (ALPHA) process. The ALPHA process has been recently investigated for the fractionation and purification of raw, bulk lignins recovered from cellulosic ethanol biorefineries or Kraft pulp mills. The ALPHA process exploits the novel liquid-liquid equilibrium that exists between lignin and hot, one-phase solutions of aqueous renewable solvents to simultaneously purify and fractionate raw bulk lignin. In particular, both the purity and molecular weight (MW) of a given lignin fraction can be controlled. Here, ALPHA is proposed for the isolation of lignin from a corn stover-to-ethanol plant into purified low, medium, and high MW fractions for producing polyurethane foam, activated carbon, and carbon fiber, respectively. Two aqueous renewable solvents were analyzed: acetic acid and ethanol.

Our analysis shows positive economic and environmental results for producing lignins of controlled molecular weight and purity via ALPHA. Solvent choice was found to have a significant impact on production of fractionated lignin using ALPHA, with a minimum selling price of \$838/tonne for using acetic acid vs. \$463/tonne with ethanol. Converting lignins processed with ethanol–water solutions into high-value products such as activated carbon, carbon fibers, and polyurethane foam yields \$151 million/year in profit, which over 30 years results in a total net present value (NPV) of \$533 million using a discounted cash flow analysis. The NPV is most sensitive to lignin yield, solvent choice, and the lignin substitution percentage for polyol in PU foam. A life cycle assessment was conducted to determine the "gate-to-gate" greenhouse gas emissions and energy consumption of the lignin-based products compared to fossil-based equivalents using SimaPro. A value allocation scenario was conducted and determined that products generated using the ALPHA process with ethanol have similar or lower greenhouse gas emissions than the same products from fossil feedstocks.



#### S1.3: 10:50 – 11:10 am (Eastern Time) (Invited Speaker)

#### Microfibers Shed During Laundering and Their Interactions With The Environment

<u>Richard A. Venditti<sup>1</sup></u>, Marielis C. Zambrano, Soojin Kwon, Joel J. Pawlak, Mary Ankeny, Jesse S. Daystar, Harry Frost, Carlos C. Goller, Karen Leonas

<sup>1</sup>Presenter, Elis & Signe Olsson Professor, Department of Forest Biomaterials, North Carolina State University, 3036E Biltmore Hall, Raleigh, NC, USA

The presence of persistent synthetic microparticles (< 5 mm) in our waterways and oceans is an emerging issue of which long term consequences are not known. Textile microfibers released during home laundering, use and disposal can be a significant contributor to microplastic pollution and is an important environmental issue.

Over the past five years, our interdisciplinary research group at NCSU has studied the generation of shed microparticles, their aquatic biodegradation and interaction with the microbiome, and possible solutions to the issue. This presentation will highlight some of the key findings.

Initially, we explored polyester, cotton, and rayon fabrics and found that they shed during washing in the range of (2,000 to 16,000 microfibers / g fabric). In general, cellulose-based fabrics released around 80% more microfibers than polyester during washing and drying. The aerobic biodegradation of these shed fibers was evaluated under the action of microbes found in lake water, seawater, and activated sludge at a low concentration from a wastewater treatment plant. Under these conditions, the biodegradation potential was the same: Cotton > Rayon > Polyester/Cotton >> Polyester. Polyester did not appreciably degrade in any of the systems. Distinct microbial communities were developed during the biodegradation process according to the material inoculated. Bacterial diversity analyses in the different biodegradation inoculums show that there are distinct bacterial communities related to the assimilation and mineralization of complex carbohydrates that were promoted with cellulosic samples different than the polyester sample.

Further research showed that common textile finishes on cotton fabrics influenced the generation of microfibers during laundering and their biodegradation rate. Fabrics with higher abrasion resistance, higher yarn breaking strength, higher frictional coefficients, and less softness (less fuzz or hairiness) are correlated with the number of microfibers shed during laundering. The effect of recycled cotton and polyester materials with the same fabric constructions had on shedding during laundering was also evaluated. Unexpected results showed that fabrics with recycled materials did not shed more than fabrics with virgin materials, suggesting that factors such as yarn twist, thread count, interlacing/interlooping pattern, and points of friction within the textile are more important.

Ongoing research is underway to evaluate new biopolymers that show an adequate balance of performance and environmental biodegradability at practical manufacturing costs and scale. These findings will help the textile industry to find a balance between sustainability, performance, and appearance during the design and selection of materials and treatments for the reduction of synthetic or natural microfiber shedding from textiles.

#### Potential Microparticles Entering the Air and Water Environment from Nonwoven Products: Methodology Development and Initial Findings

# Soojin Kwon, Marielis C. Zambrano, Joel J. Pawlak, Ryan Fraizer, Franklin Zambrano, Ronalds W. Gonzalez, Richard Venditti

Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, NC, USA

Nonwovens are a class of materials that are formed when fibers and filaments are laid in a web in a random fashion. They are greatly valued for their physical properties and inexpensive nature, which is why they are often used in single use applications, such as medical garments, wipes, and personal care products such as diapers and the like. Many studies on microparticles have been performed on textile materials, but much less attention has been paid on microfiber generation of nonwovens. Air-born microparticles can be produced when the nonwoven experiences mechanical impacts, shear and rubbing, or when air or gas flows through and across its surface. Water-born microparticles from nonwovens can be generated when liquids flow through and along the surface (for example a filter) or when the nonwovens end up as litter in the environment, experience mechanical actions and are exposed to water. In this study, microparticle generation was examined with fifteen nonwoven commercial products and a series of meltblown polypropylene nonwoven structures all manufactured on the same pilot plant machine each with a carefully controlled set of production conditions. Water-born microparticles were assessed by subjecting nonwovens to a tumbling container holding water and steel balls (Launder Ometer). The amount of microparticles generated ranged from 1 to 65 mg per gram of nonwoven. In general, wetlaid nonwovens showed higher generation of microparticles. Air-born microparticles were assessed by subjecting nonwovens to a dusting measurement device that shook sheets with a controlled shaking action (120 stroke per minute). The microparticle sizes emitted were determined using a Fiber Quality Analyzer, which could measure tens of thousands of fibers in a rapid manner. Microparticle dimensions were 0.15 mm to 0.55 mm in length and 15 µm to 30 µm in width for the water based experiments. For the air-based experiment, the 0.5 - 4.0 mg of microfibers were released per gram material, while 1 - 65 mg / gram material of microfibers were released from the water based experiment. Nonwovens generated different amounts of microparticles depending on their raw materials and bonding, such as web formation and bonding. Meltblown nonwovens emitted less microparticles than other nonwoven materials, including spunbond nonwovens or carded and The physical properties of the nonwoven material imparted by the hydroentangled nonwovens. manufacturing process and raw materials were important factors in microparticle generation. The present study has significance in that microparticle generation from nonwovens was confirmed and quantified for a given, limited set of conditions. The results indicate that nonwoven materials can be engineered as to minimize microparticle generation during use or end of life. Research is ongoing in our labs to understand more details of the microparticle production process in nonwovens and to understand how alternative biodegradable polymers can be used for nonwoven applications, so that when microparticles are shed from the nonwovens they biodegrade in the environment.

#### S1.5: 11:40 - noon (Eastern Time)

#### Degradable and thermally Stable Spiro Polycycloacetals from Renewable Resources

<u>Yanchun Tang</u>,<sup>a</sup> Fahimeh Khakzad,<sup>a</sup> Srikanth Vijjamarri <sup>a</sup> Hongda Cao,<sup>a</sup> Minjie Shen,<sup>a</sup> Karla Solis,<sup>a</sup> and Megan L. Robertson<sup>a</sup>

> <sup>a</sup> William A. Brookshire Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX, USA

A series of partially bio-based spiro polycycloacetals were synthesized using bio-renewable feedstocks, such as vanillin and its derivative syringaldehyde, along with pentaerythritol and commercially available co-monomers including 4,4'-difluorobenzophenone and bis(4-fluorophenyl) sulfone. These spiro polycycloacetals displayed high thermal stabilities (degradation temperatures in the range of 343 - 370 °C, as quantified by 5% mass loss) and glass transition temperatures (in the range of 179 - 243 °C). Importantly, these polymers were effectively degraded to small molecules under acid-catalyzed hydrolytic conditions in less than 7 h. The kinetics of hydrolytic degradation was quantified through *in situ* NMR analyses.

S1.6: 12:05 – 12:25 pm (Eastern Time)

#### Oxo-Biodegradable LLDPE Films Subjected to Gamma Irradiation and Accelerated Weathering

Luis A. Val-Félix and Tomás J. Madera-Santana<sup>1</sup>

<sup>1</sup>Centro de Investigación en Alimentación y Desarrollo, A.C. Carr. Gustavo E. Astiazarán Rosas No. 46. 83304 Hermosillo, Son México.

Linear low density polyethylene (LLDPE) is widely used as a packaging material for different purposes, mainly in food packaging. The accumulation of this material in the environment contributes to plastic pollution, which generates environmental problems and harmful effects on biodiversity. To reduce the durability of LLDPE in the environment, oxo-biodegradation is a solution to this problem, since the increase in abiotic oxidation, the decrease in molecular weight, and the presence of biodegradable materials allows the biodegradation of this plastic [1].

In this work, four films were processed by blown film extrusion (LLDPE, LLDPE+1PA, LLDPE+50TPS, and LLDPE+50TPS+1PA). These films were subjected to gamma irradiation at a dose of 30 kGy (Gammacell 220 Excel, Nordion), and subjected to accelerated weathering for 0, 15, 25, 50, and 100 h using a QUV weathering tester model QUV<sup>®</sup>/se<sup>3</sup>. The laboratory exposure conditions were cycles 8 h of UV light (UVA-340 lamps operated at 83 W/m<sup>2</sup>/nm @ 340 nm) at 70 °C, and 4 h of condensation at 50 °C. The tests to evaluate the degradation of the samples were mechanical (tensile strength, % of elongation at break, and tensile modulus), color (luminosity and color difference), structural analysis by FTIR, thermal (DSC and TGA), and morphological (OM and SEM). The biodegradation of selected samples was assessed under aerobic conditions, based on respirometric measurements [2].



Figure 1. SEM micrograph and biodegradation (%) of SF (LLDPE+50TPS+1PA) irradiated (30 kGy) and subjected to accelerated weathering (25 h), with (+) cellulose and (-) LLDPE controls.

Roy PK, Sureka P, Rajagopal C, Chatterejee SN, Choudhary V. (2006) Polym Degrad Stab 91:1791.
Corti A, Sudhakar M, Chiellini E. (2012) J Polymer Environ 20:1007.

#### Concurrent Session S2 – Synthesis of Bio-based Polymers: 10:00 am – 12:30 pm (Eastern Time)

Session Chair: Tristan Bacha (Rowan University)

#### S2.1: 10:00 – 10:20 am (Eastern Time) (**Invited Speaker**)

#### From Eugenol to Biobased Polymers: A Platform Approach

#### Sylvain Caillol<sup>1</sup>

#### <sup>1</sup>ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Recent years have witnessed an increasing demand on renewable resource-derived polymers owing to increasing environmental concern and restricted availability of petrochemical re-sources. Thus, a great deal of attention was paid to renewable resources-derived polymers and to thermosetting materials especially, since they are crosslinked polymers and thus cannot be recycled. Also, most of thermosetting materials contain aromatic monomers, able to confer high mechanical and thermal properties to the network. Therefore, the access to biobased, non-harmful, and available aromatic monomers is one of the main challenges of the years to come. Starting from phenols available in large volumes from renewable resources, our team designed platforms of chemicals usable for the synthesis of various polymers. Hence, we have previously studied, tanins, lignin-derived vanillin or cardanol. Recently, we studied an interesting natural phenol, eugenol (4-allyl-2-methoxyphenol), which is a major component of clove oil or could be obtained from lignin. It is an aromatic renewable resource with potential to replace some petroleum-based aromatic monomers. We interestingly synthesized a new platform of eugenol-derived monomers and developed a series of various polymers therefrom.

Various aromatic building blocks bearing polymerizable functions were synthesized: epoxy, amine, acid, carbonate, alcohol, (meth)acrylates... (Figure 1). These bio-based aromatic monomers can potentially lead to numerous polymers. The substitution of bisphenol A was studied in epoxy thermosets. Materials were prepared from the biobased epoxy monomers obtained from eugenol. Their thermo-mechanical properties were investigated and the effect of the monomer structure was discussed. High Tg phenol-free phenolic thermosets have been synthesized. Phenol and formaldehyde free phenolic thermosets were also prepared with high thermal stability. We also interestingly synthesized a new platform of eugenol-derived methacrylates and studied for the first time their reactivity in radical aqueous emulsion (and miniemulsion) polymerization.



Fig. 1: From eugenol to a platform approach of monomers for polymers

S2.2: 10:25 – 10:45 am (Eastern Time) (Invited Speaker)

#### Renewability is Not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers

#### Michael A. R. Meier<sup>1</sup>

 <sup>1</sup>Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC) & Institute of Biological and Chemical Systems
– Functional Molecular Systems (IBCS-FMS), Straße am Forum 7, 76131 Karlsruhe, Germany.

In order to develop truly 'green' polymeric materials, using renewable resources is insufficient.[1] The renewable feedstocks rather have to be used in a sustainable fashion by combining as many of the principles of green chemistry as possible and by applying quantitative methods of sustainability evaluation.

Within this contribution, the focus will be on new approaches for the synthesis of polymeric materials from carbohydrates. Sustainable functionalization strategies of cellulose, including new solubilisation and catalysis concepts[2] as well as the use of multicomponent reactions,[3] will be discussed. Most recently, we could demonstrate the preparation of regenerated celluse fibres from a new switchable solvent system (Figure 1).[4] Furthermore, the more sustainable preparation and characterization of well established materials, such as cellulose acetate, will be disclosed.



Figure 1: Optical investigation of regenerated cellulose fibres.

#### **References**

[1] A. Llevot, P.-K. Dannecker, M. von Czapiewski, L.C. Over, Z. Söyler, M.A.R. Meier, *Chem. Eur. J.* 2016, 22, 11510. [2] a) K.N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M.A.R. Meier, *ACS Sustainable Chem. Eng.* 2019, 7, 1826; b) K.N. Onwukamike, T. Tassaing, S. Grelier, E. Grau, H. Cramail, M.A.R. Meier, *ACS Sustainable Chem. Eng.* 2018, 6, 1496. [3] a) Z. Söyler, K.N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M.A.R. Meier, *Biomacromolecules* 2021, 22, 586. [4] A. Kirchberg, M.A.R. Meier, *Macromol. Chem. Phys.* 2021, 2000433.

#### **Ocean Digestible Bioplastics**

Stephen A. Miller<sup>1</sup>

<sup>1</sup>The George and Josephine Butler Laboratory for Polymer Research Department of Chemistry University of Florida, Gainesville, Florida 32611-7200, USA

The degradation of polymers in the environment is an important topic, given the increased understanding of commercial plastic persistence on land and—perhaps more visibly—in the oceans. The slow step of polymer degradation is usually the breakdown of high molecular weight polymers to oligomers and monomers. Thereafter, microbial metabolic conversion to carbon dioxide is considerably faster. This presentation will describe various strategies for installing hydrolyzable *weak links* into polymer chains—while not sacrificing important properties, such as glass transition temperature. This weak link strategy can facilitate the initial hydrolysis of polymers into oligomers and monomers under oceanic (near neutral) conditions. Specific functional groups that serve as weak links include acetals, pyrrolidinone-esters, and aliphatic esters.



Figure 1. Environmental degradation of polymers is accelerated when they possess segments that are both hydrophilic and hydrolyzable.

#### References

P. Qi, H.-L. Chen, H. T. H. Nguyen, C.-C. Lin, S. A. Miller "Synthesis of biorenewable and waterdegradable polylactam esters from itaconic acid" *Green Chem.* **2016**, *18*, 4170–4175. http://dx.doi.org/10.1039/c6gc01081d

2 O. Nsengiyumva, S. A. Miller "Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid" *Green Chem.* **2019**, *21*, 973–978. http://dx.doi.org/10.1039/c8gc03990a

#### S2.4: 11:15 – 11:35 am (Eastern Time) (Invited Speaker)

#### Engineering Non-Isocyanate Polyurethanes to be 100% Biobased and Recyclable by Design

James Sternberg and Srikanth Pilla<sup>1</sup>

<sup>1</sup>Clemson Composites Center Clemson University, Clemson, SC, USA

Polyurethanes rank among the 6<sup>th</sup> most produced plastic globally and carry significant risks to health and safety due to the use of isocyanates in the polymer composition. In addition, polyurethanes are some of the least recycled materials due to their crosslinked nature precluding typical thermal processing techniques. To address these issues and enable a sustainable and circular design to polyure than esynthesis, a biobased and non-isocyanate route has been innovated that introduces labile chemical linkages capable of dissociation post-synthesis for chemical recycling. Kraft lignin was utilized as a highly abundant industrial by-product from the paper pulping industry to create reactive cyclocarbonated precursors using glycerol and dimethyl carbonate as benign reagents. Curing with renewable diamines enabled a 100% biobased non-isocyanate polyurethane (NIPU) verified by radiocarbon analysis. The NIPU foams met mechanical standards for rigid foam insulation envisioning their use in automotive applications, construction and packaging. To chemically recycle the foam post-synthesis a high-pressure hydrolysis technique was used to solubilize and depolymerize the foam and allow lignin and diamine extraction. Aware of the degradation that often occurs to lignin when it is used in chemical reactions, a detailed study of its structural alteration was completed, and a chemical stabilization technique was used to recycle lignin with added functionality and solubility. NIPU foams were able to be synthesized with 100% recycled lignin showing similar properties to first generation foams. These studies have led to additional efforts toward the synthesis of 100% biobased NIPU foams using algae oil as well as work centered on enabling room-temperature curing for foam-in-place applications. The synthetic sequence proposed here in tandem with a highly efficient chemical recycling step has demonstrated the ability to create a closed loop polyurethane lifecycle using biobased and benign techniques.

#### 100% Biobased Lignin-NIPU Foam



#### S2.5: 11:40 – noon (Eastern Time) (**Invited Speaker**)

#### **Developing Betulin-Based Polyesters from Birch Bark**

Melissa B. Gordon,<sup>a</sup> Silvio Curia,<sup>b</sup> Lindsay Soh,<sup>a</sup> Alexandra M. Chong,<sup>b</sup> and Joseph F. Stanzione, III<sup>b</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, Lafayette College, Easton, PA, USA <sup>b</sup>Department of Chemical Engineering, Rowan University, Glassboro, NJ, USA

The development of polymers from renewable resources is driven by increasing concern over environmental impact and diminishing fossil fuel reserves. With enhanced interest in biobased polymer development, investigation of plastics derived from natural precursors that offer similar properties to petroleum-derived polymers is needed. In this work, we investigated the use of betulin, a naturallyoccurring diol that can be extracted from birch bark in high yields, as a building block for the formation of bio-based polyester thermoplastics and thermosets. We showed that these polymers can be synthesized directly from betulin with biobased diacids through metal-catalyzed melt polyesterification reactions, and systematically assessed structure-property relationships by altering the diacid co-monomer. Thermoplastics ranged in weight average molecular weight from 7,500 g mol<sup>-1</sup> to 60,300 g mol<sup>-1</sup> and exhibited glass transition temperatures ( $T_{s}$ s) between 48 °C to 214 °C. By incorporating glycerol as a crosslinker, thermosets were fabricated, which exhibited storage moduli at 25 °C ranging from 2.0 to 790 MPa and  $T_{gs}$  that are tunable over a 100 °C range depending upon the diacid selected. Moreover, all samples exhibited thermal stabilities above 300 °C in both nitrogen and air. Overall, our results indicate that betulin is a promising building block in the preparation of biobased polyester thermoplastics and thermosets. Further, this approach may be used to systematically investigate promising yet unexplored natural building blocks for the preparation of high-performance biobased polymers.



S2.6: 12:05 – 12:25 pm (Eastern Time) (Invited Speaker)

#### **Biodiversification of Natural Rubber by Metabolic Engineering**

<u>Katrina Cornish</u><sup>1,2</sup>, Joshua J. Blakeslee<sup>1</sup>, Seema Nath<sup>1</sup>, Nikita Amstutz<sup>1</sup>, Kristof Molnar<sup>2</sup>, Carin A. Helfer<sup>2</sup> and Judit E. Puskas<sup>2</sup>

Departments of <sup>1</sup>Horticulture and Crop Science, and <sup>2</sup>Food, Agricultural and Biological Engineering, Ohio Agricultural Research and Development Center, College of Food, Agricultural and Environmental Science, The Ohio State University, 1680 Madison Avenue, Wooster, OH, USA

Natural rubber (*cis*-1,4-polyisoprene) is produced by about 2,500 plant species. Natural rubber (NR) molecular weight, polydispersity and gel content, rubber particle composition and size distribution vary among species but were thought to be consistent in mature plants within a single species. Thus, rubber tree (*Hevea brasiliensis*) NR, the sole commercially available source today is used in about 50,000 products because of its material consistency and product reproducibility.

In this presentation, we show, for the first time, that intrinsic rubber properties of guayule (Fig.1) can be changed by manipulation of the genes encoding enzymes that produce the monomer (isopentenyl pyrophosphate), and initiator (allylic pyrophosphate) for rubber biosynthesis. This research opens the door to on-purpose biodiversification and natural rubber in crop plants, opening new market opportunities.



Figure 1. A field of guayule crop.

Genotype	NR fold increase	Mol wt (kg/mol)	Polydi- spersity	Gel %	Oligomer %	Viscosity (mL/g)
Wild type	1	1,300	1.33	0	13	491
Wild type	1	1,150	1.19	0	25	436
Transgenic	2.15	1,218	2.32	68	22	361
Transgenic	2.32	506	3.96	0	18	201
Transgenic	2.18	88	4.78	45	23	206
Transgenic	1.70	88	6.63	17	26	49

**Table 1.** Changes in rubber properties caused by transgene insertion.

Concurrent Session S1 – Biodegradability & Sustainability: 02:00 pm – 04:30 pm (Eastern Time)

Session Chair: Alexandra Chong (Rowan University)

S1.7: 02:00 – 02:20 pm (Eastern Time)

#### Poly(ethyleneterephthalate) (PET) Recycling: Current Strategies, Shortcomings, and Reinforced Composites

Michael Snowdon<sup>1,2</sup>, Manjusri Misra<sup>1,2\*</sup>, Amar K. Mohanty<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Road East, Guelph, Canada.<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Road East, Guelph, Canada

As single-use plastics are being scrutinized worldwide, the need to address disposal concerns and alternatives is growing. However, plastic bottles are still being manufactured with the polymer PET and made up more than 8% of the world plastic production in 2018, totaling 30,000,000 tons. As such, recycling of post-consumer PET is the most prominent option for avoiding its plastic waste. PET recycling is well established over most other polymers, but there exists a large discrepancy in terms of the global PET reclamation with a recycling rate of less than 50% on average. Various factors including the quality, cleanliness, collection, sorting, types, color, purity, structure composition, additives, etc. all play a role in whether this recyclate can be recovered or suitable for secondary use in various applications. Even with several recycling options available, the most common is the mechanical recycling method. These processes provide recycled PET (rPET) that are predominantly used in textile fibres and other non-food applications. Yet, rPET tends to show lower mechanical performance over the competing virgin PET and requires reinforcement or other additives to offset its drawbacks in other applications, further reducing the environmental impact of the blends. These new composite variations and further optimization of the recycling stream are imperative to meeting sustainability in the future and meeting new regulations with greater recycled content in products.

#### Acknowledgements:

This research was financially supported by: (i) the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph – Bioeconomy for Industrial Uses Research Program (Project Nos. 030486 and 030578); (ii) the Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants Project No. 400320; (iii) the Agriculture and Agri-Food Canada (AAFC) and Competitive Green Technologies, Canada through AgSci Cluster Program (Project No. 054712).

#### S1.8: 02:25 – 02:45 pm (Eastern Time) (Invited Speaker)

#### Sustainability Assessment, Process Development, and Life Cycle Analysis

#### Gerardo J. Ruiz-Mercado, Ph.D.

Office of Research & Development, U.S. Environmental Protection Agency, Cincinnati, OH, 45268, USA

Current environmental, social, and economic challenges have raised consciousness and led to incorporating the concept of sustainability and sustainable development into process design and optimization, such as pollution prevention and control, sustainable process design, sustainability assessment, and life cycle analysis. Therefore, this presentation provides compressive definitions regarding sustainable development, sustainability assessment and design, life cycle analysis, and their application in manufacturing more environmentally friendly chemicals with lesser occupational releases and exposure. Moreover, this talk explains the concepts of life cycle assessment (LCA), life cycle inventory (LCI), bottom-up approaches for estimating LCIs, and releases allocation for a chemical of concern. Also, this talk will describe a strategic implementation of an integrated framework with a process modeling/simulation environment, pollution control units (PCU), LCI generation, and sustainability assessment that can inform the environmental performance of a particular chemical manufacturing system. The developed framework is applied to a relevant case study for the manufacturing of a chemical of interest. The application results show process improvements in terms of sustainability performance represented by GREENSCOPE<sup>1</sup> sustainability indicators and LCI generation after implementing the appropriate PCUs for waste stream treatment. The case study demonstrates the effectiveness of the proposed framework for integrating chemical process simulation, PCU, LCI generation, and GREENSCOPE for improving the sustainability performance of chemicals during their manufacturing life cycle stages.

The views expressed in this abstract are those of the author and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency (EPA). Any mention of trade names, products, or services does not imply an endorsement by the U.S. Government or the EPA. The EPA does not endorse any commercial products, services, or enterprises.

<sup>&</sup>lt;sup>1</sup> https://www.epa.gov/chemical-research/assessing-chemical-process-sustainability-greenscope

#### Effect of Gliding Arc Plasma Treatment on Soil Degradation of Biodegradable Plastic Mulch Films

Swapnil Bhattacharya, Harshal J Kansara, Celina Alvarado, Carlos A. Diaz, Jeffrey Lodge and Christopher L. Lewis

#### Rochester Institute of Technology, Rochester NY, USA

Polymer mulch films are traditionally made from non-biodegradable polymers such as polyethylene. These films are utilized to improve crop yields by promoting soil moisture and temperature retention, preventing weed growth and minimizing erosion in areas of heavy rain. Because they are non-degradable, traditional mulch films must be removed from the soil and disposed of at the end of the season. This imposes monetary costs to the farmer and presents potentially undesirable end-of-life scenarios including landfilling or incineration. Biodegradable polymer mulches are commercially available with the potential to circumvent these drawbacks. However, slow degradation rate is one reason preventing their widespread adoption. In this study we explore a surface activation strategy as a means to enhance the rate of biodegradation of mulch films in soil. We hypothesize that surface treatment will accelerate microbial adhesion thereby reducing the time prior to the onset of degradation. To test this hypothesis two commercially available, PBAT based agricultural mulch films are treated using a laboratory scale gliding arc plasma process. Treatment conditions are varied and the samples are subsequently buried in soil. Preliminary results concerning the effect of plasma treatment on surface and bulk properties before and after aging in soil for several months will be presented.

#### Biodegradable Plastic Detected in Soil Two Years After Incorporation of Agricultural Plastic Mulch

#### Alexis B. Gillmore, Anton F. Astner, Douglas G. Hayes, Sean M. Schaeffer

#### University of Tennessee Knoxville, Knoxville, TN, USA

Biodegradable polymers are a promising alternative to conventional ones like polyethylene in agricultural plastic mulches because after use the biodegradable mulches are mineralized into carbon dioxide and microbial biomass in soil or in compost instead of being landfilled. Our objective is to determine the average residence time of biodegradable plastic fragments in soil. We have retrieved plastic fragments from soil two years after the use and incorporation of biodegradable plastics, and we are developing methods to chemically identify and quantify biodegradable plastics through proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR). Accumulation or vertical transport of plastic in soils could decrease soil health.

**Approach** – In fall 2020, we sampled East Tennessee research fields where two biodegradable plastic mulch films made from two different polyesters – polybutylene adipate terephthalate (PBAT) and polylactic acid (PLA) were used in a vegetable production system for four seasons (2015 to 2018). The original field experiment used a randomized complete block design with four blocks providing replicates of each polymer type. We collected soil samples from three cores randomly spaced near the center of each plot to avoid edge effects, then homogenized the three cores. Samples were collected at 0-20, 20-40, and 40-60 cm depths. Microplastic fragments 250-2000  $\mu$ m in length were identified by a density-based extraction in colloidal silica then visual inspection with a stereomicroscope. <sup>1</sup>H NMR was used to qualitatively identify PLA and PBAT recovered through a chloroform-methanol extraction of bulk soil.

**Hypotheses** – We hypothesized that plastic fragments would still be present after two years and that some would be found below tillage depth. Biodegradable mulches may degrade differently in the field than what is observed in laboratory testing under ideal conditions. Plastic fragments, like other material in soil, can move downward along with percolating water. We expected PLA plots to contain more plastic than PBAT plots because PLA is more resistant to biodegradation at ambient temperatures. Both polymer treatments were expected to contain more plastic fragments than the no-mulch control plots.

**Results** – For microplastics in the 250-2000  $\mu$ m size range, statistical analysis was performed with the SAS Design and Analysis macro collection version 2.11 curated by Arnold Saxton at the University of Tennessee Knoxville. Analysis suggests the depth x polymer treatment interaction may be a significant predictor of plastic recovered by surface area (mixed model ANOVA p=0.094<0.1). Surface PLA plots contained more microplastic than any other group (Tukey HSD, p<0.05). The other levels of the depth x polymer interaction were not significantly different from each other. NMR analysis demonstrated that plastic was present in all surface treatment plots including the no-mulch control plots – likely due to tillage mixing after the field trial ended. Plastic was not identified in untilled margin soil near the field. Subsurface samples await NMR analysis.

**Implications** – These results suggest that microplastics >250  $\mu$ m in length are not traveling vertically in soil during mulch degradation. Plastic is present in the soil as fragments too small to be observed visually; that plastic was detected through NMR spectroscopy. Further investigation is needed because accumulation of plastic fragments in the soil could have negative consequences for soil hydraulic conductivity by clogging soil pores. Colloidal plastic fragments could be transported deeper into soil and groundwater; consequences of micro and nano-plastic contamination in water sources are not yet well understood. Vertical transport could also be influential in plastic degradation because degradation depends on microbial activity, which is greatest at the soil surface. Fast vertical transport could increase plastic accumulation. To monitor for accumulation, we need robust methods to measure plastic particles too small to be identified visually which will include developing quantitative NMR methods.

#### S1.11: 03:40 – 04:00 pm (Eastern Time) (Invited Speaker)

#### Pathways for Isoflavone Extraction from Soybean Meal

John D. Chea<sup>1</sup>, Joseph F. Stanzione, III<sup>1</sup>, and Kirti M. Yenkie<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Henry M. Rowan College of Engineering, Rowan University, NJ - 08028, USA

The United States produces over 125 million metric tons of soybeans annually for animal feed, export, and human consumption. Soybeans are rich in nutrients such as amino acids, proteins, and carbohydrates<sup>1</sup>. Particularly of interest within soybean meal is phytochemicals, called isoflavones, which are abundant at 0.15 wt% on average and can prove beneficial in the health and nutraceutical sector due to their anti-inflammatory and cancer inhibition properties<sup>2,3</sup>. Recent research progress has shown that isoflavones can be used to synthesize high-performance materials with high thermal stabilities<sup>4</sup>.

Currently, isoflavones are synthesized from non-renewable, non-sustainable chemical sources through a series of substitution reactions with low conversion efficiencies. The use of natural and renewable resources, such as soybean meal, is a more promising and sustainable route to extract isoflavones. The lab-scale studies have shown that large quantities of solvents are required for isoflavone extraction from soybean meal and some of them can be hazardous<sup>5</sup>. Thus, there is a significant need for commercially scalable, economical, and sustainable strategies for extracting isoflavones from soybean meal.

To this end, we have developed a superstructure-based optimization framework for analyzing multi-scale isoflavone extraction pathways from soybean meal, including evaluating their potential for commercialization through technoeconomics and sustainability assessment. This framework is applied to soybean meal with a target isoflavone recovery goal and includes mathematical models for various extraction technologies. This method simultaneously compares the alternative extraction and purification technologies to assess the most economically viable pathway by developing the superstructure-based optimization as a mixed-integer nonlinear programming problem in General Algebraic Modeling Systems (GAMS) Modeling Language. Each technology model comprises material and energy balances, utilities, design options, industrial constraints, product purity constraints, and economics<sup>6,7</sup>. By analyzing alternative options simultaneously, this study can systematically assess the viability of the extractions processes at multiple scales, from lab to pilot to industrial. If the extraction pathway is proven economically viable at a larger scale, then the price of these naturally-derived isoflavones can be improved, effectively making their commercialization more attractive than synthetically derived isoflavones from petroleum sources.

#### References

- (1) Lee, T.; Tran, A.; Hansen, J.; Ash, M. 2019. USDA ERS
- (2) Higdon, J.; Drake, V.; Delage, B. 2019. Soy Isoflavones
- (3) Joy, S.; Siow, R. C. M.; Rowlands, D. J. et.al. J. Biol. Chem. 2006, 281 (37), 27335–27345.
- (4) Hernandez, E. D.; Stanzione, J. F. et. al. ACS Sustain. Chem. Eng. 2016, 4 (8), 4328–4339.
- (5) Yoshiara, L. Y.; Madeira, T. B. et. al. Int. J. Food Sci. Nutr. 2012, 63 (8), 978–986.
- (6) Chea, J. D.; Yenkie, K. M. et. al. Ind. Eng. Chem. Res. 2020, 59 (13), 5931–5944.
- (7) Wu, W.; Yenkie, K. M.; Maravelias, C. T. *Comput. Chem. Eng.* 2017, *96*, 1–17.

#### Effects of COVID-19 Pandemic on the Municipal Solid Waste Management

Poritosh Roy<sup>1,2</sup>, Amar K. Mohanty<sup>1,2</sup>, Alexis Wagner<sup>3</sup>, Shayan Sharif<sup>4</sup>, Hamdy Khalil<sup>5</sup>, Manjusri Misra<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Ontario, N1G 2W1, Canada

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Ontario, N1G 2W1, Canada

<sup>3</sup>Innovation, Science and Economic Development Canada, 235 Queen St, Ottawa, ON, K1A 0H5 Canada

<sup>4</sup>Ontario Veterinary College, University of Guelph, 50 Stone Road E., Guelph, ON, N1G 2W1 Canada, <sup>5</sup>Woodbridge Foam Corporation, 4240 Sherwoodtowne Boulevard, Mississauga, ON, L4Z 2G6, Canada

Municipalities provide waste management services for their residents to meet one of their essential needs, being the safe and timely collection of waste. This vital service, including municipal solid waste (MSW) management, has recently been interrupted by the outbreaks of the novel coronavirus (COVID-19). Various changes made to waste collection and management systems, because of COVID-19, has affected waste segregation and recycling processes. Different sectors such as food, waste management, and healthcare rely on single-use plastics to prevent transmission of COVID-19. However, an environmentally friendly alternative to widely used single-use plastics will be beneficial in easing waste management problems described. Various initiatives are underway to manage growing volumes of MSW, while simultaneously controlling the spread of infectious diseases. One such strategy is using movable grate incineration technology coupled with adequate disinfection processes as a potential solution to managing COVID-19 waste or any other future outbreaks. This option scheme will be discussed and explored as it would mitigate the risk of spread and improve the sustainability of MSW management systems.

#### Acknowledgments

This study was financially supported by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) – University of Guelph, the Bioeconomy Industrial Uses Research Program Theme (Project # 030486, 030578); the Ontario Ministry of Economic Development, Job Creation and Trade ORF-RE09-078 (Project #053970, 054345); the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) program Project No. 460788; and the Agriculture and Agri-Food Canada (AAFC), Maple Leaf Foods, Canada and the Bank of Montreal (BMO), Canada through Bioindustrial Innovation Canada (BIC) Bioproducts AgSci Cluster Program (Project Nos. 054015, 054449 and 800148).

#### Concurrent Session S2 – Synthesis of Bio-based Polymers: 02:00 pm – 04:30 pm (Eastern Time)

Session Chair: Jasmin Vasquez (Rowan University)

S2.7: 02:00 – 02:20 pm (Eastern Time) (**Invited Speaker**)

#### Progress in Sustainable Long-Chain Aliphatic Polyethylene Mimics

#### Chuanbing Tang

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, USA

Polyethylene (PE) is not only one of the most manufactured plastics, but also among the most challenging polymers toward enhanced sustainability. The highly inert C-C bonds in PE are difficult to degrade. There are many strategies on processing of PE for upcycling or recycling. On the other hand, long-chain aliphatic condensation polymers contain a low portion of hetero atoms (e.g., O, N), which can otherwise resemble PE. This kind of polymers are thus called PE mimics, which provide a different avenue for a sustainable alternative of PE. The presence of hetero atoms enables new potentials for this class of polymers. This presentation will discuss recent efforts toward design and synthesis of various long-chain aliphatic PE mimics that bear low density active bonds such as ester and amide. Particularly, a class of sustainable ultrastrong elastomers from biomass-derived long-chain polyamides will be detailed. The supramolecular interactions, crystallization as well as unidirectional stretching allow the achievement of silk-mimicking properties with tensile strength over 300 MPa while maintaining elasticity at relatively low strain. The structure-property relationships will be discussed.



#### **References:**

 Stempfle, F., Ortmann, P., and Mecking, S. Long-Chain Aliphatic Polymers To Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. *Chem. Rev.* 2016, 116, 4597-4641.
Song, L., Zhu, T., Yuan, L., Zhou, J., Zhang, Y., Wang, Z., and Tang, C. Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures. *Nat. Commun.* 2019, 10, 1315.

#### Glycerol Ketals as Building Blocks for a New Class of Biobased (Meth) Acrylate Polymers

Shailja Goyal,<sup>1</sup> Fang-Yi Lin,<sup>1</sup> Michael Forrester,<sup>1</sup> William Henrichsen,<sup>1</sup> Grace Murphy,<sup>2</sup> Liyang Shen,<sup>1</sup> Tung-ping Wang,<sup>1</sup> and Eric Cochran<sup>1</sup>

<sup>1</sup> Chemical and Biological Engineering Department, Iowa State university, Ames, IA, 50011, USA <sup>2</sup> Department of Chemistry, Iowa State University, Ames, Iowa, 50011, USA

Biodiesel is produced from various vegetable or animal fats and has emerged as a potential substitute for diesel fuel. Life cycle analyses suggest that biodiesel is carbon-neutral, and is compatible with existing diesel engine design. According to the 2018 National Diesel Board Report, biodiesel production goal for the US is about 4 billion gallons by 2022. Each ton of biodiesel production generates about 10 wt % glycerol, or about 4 million gallons of crude glycerol in the market. While there are many factors that affect the cost of biodiesel (such as feedstock and plant operation), the current lack in the value of glycerol by-product has a major impact. Thus, the glut of glycerol created in the market calls for its alternate use for new applications to make biodiesel production more cost-effective.

This work explores the synthesis of glycerol based thermoplastic polymers. We synthesized glycerol ketals by the reaction of glycerol and various ketones such as acetone, butanone and cyclopentanone. The acrylic and methacrylic derivatives of these glycerol ketals were synthesized using enzymatic transesterification to yield monofunctional monomers. Radical Addition Fragmentation Chain Transfer (RAFT) technique was used to synthesize linear, low PDI polymers. The molecular weight of the polymers was determined using SEC and thermal properties were studied using Differential Scanning Calorimetry (DSC). Rheology was done to understand the flow characteristics and entanglement behavior. In further studies, these polymers will be studied for various applications such adhesives and biomedicine. Also, these polymers will be used to study the effect of different pendant chain groups in polymer solutions and morphology for acrylic diblock polymers.



# Chemoenzymatic Polymerization of L-Serine Ethyl ester without Side-Chain Protection of Monomer

Takumi Watanabe,<sup>1</sup> Kousuke Tsuchiya,<sup>1\*</sup> Keiji Numata<sup>1,2\*</sup>

<sup>1</sup> Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

<sup>2</sup> Biomacromolecules Research Team, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Poly(L-serine) (polySer) has tremendous potential in applications of polypeptide-based materials due to the versatile uses of hydroxy groups in their side-chain. PolySer has typically been prepared by ring-opening polymerization of  $\alpha$ -amino acid *N*-carboxyanhydride derivative [1]. However, the synthesis of polySer from Ser monomer without a protecting group on the hydroxy group is not achieved to date. In this study, chemoenzymatic polymerization (CEP) of L-serine ethyl ester (Ser-OEt) was performed in order to realize the synthesis of polySer without its side-chain protection (**Figure 1a**). Since the CEP proceeds in a high regio- and stereoselective manner due to the substrate specificity of enzymes, side-chain protection is not required even when the monomer has a reactive functional group [2].

When the CEP of Ser-OEt was carried out, a precipitate formed during the polymerization at a basic pH of around 8.5. The precipitate was MALDI-TOF characterized by MS spectrometry. and a series of peaks corresponding to the polySer with a degree of polymerization (DP) ranging from 5 to 22 were confirmed (Figure 1b). The formation of oligo(L-serine) with DP from 2 to 4 was confirmed in the water-soluble part of the resultant solution. These results indicate that the polySer with DP larger than 5 was precipitated during the CEP of Ser-OEt. Moreover, the structural characterization of the precipitated polySer using circular dichroism, infrared spectroscopy, and the synchrotron wide-angle X-ray diffraction measurements indicated that the resultant polySer formed β-strand/sheet structure in both solid and solution states.



**Figure 1**. (a) Scheme of the CEP of Ser-OEt. (b) MALDI-TOF MS spectrum of the precipitate formed during the CEP of Ser-OEt conducted at pH 8.5.

**Reference**: [1] Yang, Z.; Mao, Z.; Ling, J., *Polym. Chem.* **2016**, *7*, 519-522. [2] Tsuchiya, K.; Numata, K. *Polym. Chem.* **2020**, *11*, 560-567.

#### A Green and Sustainable Platform for Biopolymers Production using a Marine Photosynthetic Purple Bacterium

Choon Pin Foong<sup>1</sup>, Mieko Higuchi-Takeuchi<sup>2</sup>, and Keiji Numata<sup>1,2</sup>

<sup>1</sup> Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8246, Japan

<sup>2</sup> Biomacromolecules Research Team, Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Climate change, depletion of natural resources, and food and water insecurity are emerging crises that have been alerted human to adopt sustainable development and lifestyles. Numerous efforts have been made to promote biobased and biodegradable polymers as alternative materials to replace widely used fossil-based and non-biodegradable polymers. However, bioprocess reformation, which is also part of the life-cycle assessment (LCA), is receiving less attention. Thus, we have been developing a marine photosynthetic purple bacterium, *Rhodovulum sulfidophilum*, as a green and sustainable platform for polyhydroxyalkanoate (PHA) and spider silk protein production. This bacterium confers advantages from both photosynthetic and halophilic organisms. *R. sulfidophilum* produces PHA or bioplastic in a growth-associated manner, which is suitable for continuous PHA production (chemostat). Wild type strain could accumulate PHA up to 35 wt% of cell dry mass, while our engineered mutant strains grew 1.6-fold faster and accumulate 1.4-fold higher PHA content. On the other hand, recombinant *R. sulfidophilum* that carried major ampullate spidroin (*MaSp*) gene from spider *Trichonephila clavipes*, was able to produce up to 4 mg/L (7% of total proteins) spider silk protein in artificial seawater medium under phototrophic growth condition.



#### S2.11: 03:40 – 04:00 pm (Eastern Time) (**Invited Speaker**)

#### Genome-Engineered Pseudomonas Alloputida for Conversion of Lactose to mcl-PHA

#### Aranksha Thakor, Trevor C. Charles

#### Department of Biology, University of Waterloo, Waterloo, Ontario, Canada

The dairy industry generates large amounts of waste lactose, which is potentially a valuable feedstock for PHA production. Much of this waste material is currently disposed of, at great cost. The use of such low value waste material would substantially improve the economics of PHA production, while also solving waste disposal. Many *Pseudomonas* strains can produce mcl-PHA, a polymer with a broad range of properties and uses, but they are unable to use lactose or galactose as carbon source. As a first step to convert lactose to mcl-PHA, we have engineered *Pseudomonas* alloputida strain KT2440 using the *lac* operon from *E. coli* and the DeLey-Doudoroff pathway genes for galactose metabolism from other *Pseudomonas* strains. These genes were inserted into the genome adjacent to the PHA synthesis genes in an operon arrangement, and successfully expressed. The genome-engineered strains were able to grow on lactose or galactose as sole carbon source and produce mcl-PHA copolymers. Using these strain constructs, we have demonstrated the successful conversion of lactose to mcl-PHA materials as an integral component of our *Circular Bioeconomy* framework.
S2.12: 04:05 – 04:25 pm (Eastern Time) (**Invited Speaker**)

# Self-catalytic Preparation of Epoxy vitrimers: Mechanical Performance, Adaptivity, and Recyclability

# Jinwen Zhang

School of Mechanical and Materials Engineering Composite Materials and Engineering Center Washington State University, Pullman, WA 99164, USA

Dynamic covalent network polymers are considered alternatives to current thermosetting polymers and have received extensive investigation. Vitrimers can undergo associative dynamic bond-interchange reactions at elevated temperature to display a certain degree of adaptivity but behave like thermosets at service temperature. Epoxy vitrimers that work via the dynamic transesterification (DTER) mechanism have received the most study. Many of the early epoxy vitrimer works are purposely kept stoichiometrically imbalanced and use high catalyst concentration to ensure adaptable and malleable properties.

Our group has made a great effort on developing catalyst-free or internally catalyzed epoxy vitrimers. *Our approach* is to introduce self-catalysis into the reaction system, so both the curing of vitrimer preparation and subsequent DTER in the crosslinked polymer at elevated temperature can take place without external catalysts. It is critical to maintain sufficient hydroxyls and ester linkages in the system to enable adequately fast DTER and hence decent adaptivity. In addition, we have also investigated the simple and eco-friendly recycling of the epoxy vitrimers via hydrolysis or alcoholysis.

# **Day 2: 24 June 2021 (Thursday)**

# Plenary Session P2.1: 9:10-9:50 am (Eastern Time) (Invited Speaker)

## **Single-use Plastics: Challenges & Alternatives**

#### Manjusri Misra

#### School of Engineering and Bioproducts Discovery & Development Centre, Department of Plant Agriculture, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

Plastic has become an integral part of society, ranging from a variety of applications such as everyday goods (food packaging) to high-end products (medical and transportation). The rampant use and reliance on plastic has become a paramount environmental issue for the world. The main culprit for this negative impact on the environment comes from the poor management practices of plastic waste disposal. The current production of plastic is forecasted to grow, reaching one billion tons per year by 2050, which is more than double the present capacity. Most of the plastic produced is used for packaging, where 50% of the plastic production is allocated for single-use purposes. Considering the short lifetime of single-use plastics (days to less than six months), the management of plastic waste disposal is crucial. When plastic is left in the environment, they pose major concerns as the plastic will breakdown into smaller particles resulting in microplastics which is known to have a devastating impact on the ecosystem and has growing impact on human health.

According to the Ellen MacArthur Foundation, they have enacted a New Plastic Economy Initiative that has outlined targets of reaching "100% reusable, recyclable or compostable plastic packaging by 2025". The topic of this presentation will focus on the challenges that the three main categories of packaging structures pose, and the innovative solutions needed to combat their environmental issues. Category one: mixed material packaging (plastic, paper, and metal); category two: difficult to recycle multi-layer films that cannot be separated easily, often entering the waste stream; and category three: mono-material items that are impractical to recycle (disposable products such as cutlery, straws, and takeout containers). Plastic has become an essential part of our everyday lives. Banning single-use plastics will create a gap/opportunity in the market for viable sustainable alternatives. Biodegradable and compostable plastic demonstrates a promising alternative to the single-use plastic, without a waste problem. For an effective widespread adoption of these changes in the market, an integrated approach needs to include regulatory policies and incentives, options for proper end-of-life, and other creative ways to address the complex journey of developing and implementing sustainable materials. Ultimately, a successful integration of these sustainable materials.

Acknowledgements: (i) The Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) – University of Guelph, the Bioeconomy Industrial Uses Research Program Theme (Project Nos. 030486 and 030578); (ii) OMAFRA-University of Guelph Gryphon's Leading to the Accelerated Adoption of Innovative Research (LAAIR) Program (Project No. 030416); (iii) the Ontario Research Fund, Research Excellence Program; Round-9 (ORF-RE09) from the Ontario Ministry of Economic Development, Job Creation and Trade, Canada (Project No. 053970); and (iv) the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) program Project No. 460788.

# Concurrent Session S4 – Advances in Polymer Manufacturing: 10:00 am – 12:30 pm (Eastern Time)

Session Chair: Alexandra Chong (Rowan University)

# S4.1: 10:00 – 10:20 am (Eastern Time) (**Invited Speaker**)

# Applications of Biodegradable Polymers for Fused Deposition Modeling 3D Printing

# Adriana Kovalcik

# Institute of Food Chemistry and Technology, Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic

Over the last several years additive manufacturing technologies, specially fused deposition modelling (FFM) has gained popularity in several industries including aerospace and defence, healthcare, automotive, electrical and electronics and even in households. It was estimated that the global 3D printing filament market generated revenue of USD 739 million in 2020. It is supposed that the outbreak of COVID-19 also contributed to diverse applications of 3D printed materials in the medical segment. One of the priorities of the 21st century is to develop and use such technologies and products that would systematically contribute to the improvement of the health of our planet and people. The principle of FDM is an extrusion of the molten filament and gradual deposition of layers and their solidification resulting in a 3D object. In order to meet the criteria for a green deal strategy, it is necessary to develop biobased and biodegradable filaments with physical properties required by individual industrial sectors. Our study aims in the biotechnological conversion of food waste into biodegradable polymers and biocomposites with applicability as a matrix material for filaments production. This work summarizes the applicability of polyhydroxyalkanoates (PHA) and poly(lactic acid) (PLA) as thermoplastics for FFM with respect to their thermal, rheological and mechanical properties. The fabrication of 3D models on the base of PLA is common but the use of PHAs is limited to the specific copolymers or blending with PLA [1]. The focus of our research is on the development and implementations of biodegradable and biocompatible filaments in the pharmaceutical and medical fields [2].

## Acknowledgement

This work was funded by the Internal Brno University of Technology project FCH-S-21-7483.

## References

[1]. A. Kovalcik, Recent Advances in 3D Printing of Polyhydroxyalkanoates: A Review, The EuroBiotech Journal 5(1) (2021) 48-55. <u>https://doi.org/10.2478/ebtj-2021-0008</u>.

[2]. A. Kovalcik, L. Sangroniz, M. Kalina, K. Skopalova, P. Humpolíček, M. Omastova, N. Mundigler, A.J. Müller, Properties of scaffolds prepared by fused deposition modeling of poly (hydroxyalkanoates), International Journal of Biological Macromolecules 161 (2020) 364-376. https://doi.org/10.1016/j.ijbiomac.2020.06.022. S4.2: 10:25 – 10:45 am (Eastern Time) (Invited Speaker)

# Solution Blow Spinning of Polymer Solutions: Technology and Application

Eliton Medeiros<sup>1</sup>, Artur Klamczynski<sup>2</sup>, Bor-sen Chiou<sup>2</sup>, William Orts<sup>2</sup>, William Hart-Cooper<sup>2</sup>, <u>Gregory</u> <u>Glenn<sup>2</sup></u>

<sup>1</sup>Materials and Biosystems Laboratory (LAMAB), DEMAT, UFPB, 58051-900 João Pessoa, Brazil <sup>2</sup>Bioproduct Research Unit, WRRC, USDA-ARS, Albany, CA 94710

Solution blow spinning (SBS) is a technique that was developed as an alternative to electrospinning for making non-woven webs of micro- and nanofibers from polymer solutions. SBS has a fiber production rate many times higher than electrospinning and can produce fibers with diameters ranging from 40 nm for poly(lactic acid) to several micrometers for poly(methyl methacrylate). The original apparatus designed for SBS consisted of a syringe pump that delivered a polymer solution through an inner nozzle (see graphic). A concentric outer nozzle delivered a high-pressure stream of air that impinged on the polymer solution as it exited the inner nozzle. Further analysis showed that the pressure difference and shear at the gas/solution interface was effective in drawing multiple strands of polymer solution that were then carried by the flow of air towards a collector. During flight, the solvent component of the strands rapidly evaporates forming a web of micro and nanofibers. Fibers made by SBS can be easily formed into yarns of micro- and nanofibers or non-woven films that could be applied directly onto biological tissue or collected in sheets on a rotating drum.



SBS can be used on a wider array of polymer solutions than electrospinning and can be scaled-up easier and at a lower cost. SBS was demonstrated on a wide array of polymer solutions including PLA, PGA, PVA, gelatin, and fillers including carbon nanotubes. Our studies have demonstrated applications for this technology in the area of sensors, medical treatments, cosmetics, and ceramic fibers. Porous nanofibers were shown effective in controlled-release studies. Nanocomposite fibers were also made using cellulose nanowhiskers isolated from unique plant sources including eucalyptus and mandacaru.

# Understanding Stereotypical Implications in PLA Polymers for Manufacturing Performance and Processability

# Moh Alhaj & Ramani Narayan

## Biobased Materials Research Group, Michigan State University, East Lansing MI, USA

Polylactide (PLA) polymers are the world's foremost 100% biobased resin with both composting and recycling end-of-life options in harmony with Ellen MacArthur Foundation "Circularity Model". It is commercially manufactured by converting lactic acid to lactide, which is then polymerized to PLA. These molecules present unique and intriguing stereochemistry that dictate manufacturing, performance properties, and processability. However, it is seldom discussed and not well understood in the role it can play and impact product performance and use.

Lactic acid is a molecule with one chiral center, and so it exists in two enantiomeric forms, the R-(or D-) enantiomer and the S-(or L-) enantiomer. Most microorganisms used in industrial fermentation produce optically pure S (L) lactic acid enantiomer, which is converted to the lactide monomer. The process involves forming a low molecular weight poly(lactic acid), and then depolymerizing the low molecular weight poly(lactic acid) to the lactide monomer. The elevated temperatures used during the conversion process results in racemization of some S (L) lactic acid enantiomer to the R (D) enantiomer. The predominant stereoisomer formed is the S,S-(L,L) lactide. The next stereoisomer formed is the meso (R,S)-lactide, as each of the R-lactic units is most likely to become paired with an S-lactic unit rather than another R-lactic unit. Some R,R-lactide can be formed but is typically very small (negligible) due to the small concentration of R-lactic units in the system.

The amount of meso lactide impacts % crystallinity and tacticity of the resultant PLA product. Its presence at levels greater than 10% results in a totally amorphous polymer that cannot be crystallized. In this lecture we present the use of proton NMR and polarimetry to analyze the stereochemistry of the lactide and the resultant PLA molecule. We will critically review and discuss the stereochemical implications for PLA through studies on different PLA compositions of L, meso, and D-content synthesized in out laboratory.

# S4.4: 11:15 – 11:35 am (Eastern Time) (Invited Speaker)

# Transforming Thermosets into Thermoplastics: Dynamic Covalent Bonds Enable Sustainable Chemical Recycling of Traditional Non-Recyclable Polymers and Composites

<u>John M. Torkelson</u><sup>1,2</sup> Kailong Jin,<sup>1</sup> Lingqiao Li,<sup>1</sup> Xi Chen,<sup>1</sup> Sumeng Hu,<sup>1</sup> and Mohammed Bin Rusayyis<sup>2</sup>

> <sup>1</sup>Department of Chemical and Biological Engineering <sup>2</sup>Department of Materials Science and Engineering Northwestern University, Evanston, IL 60208, USA

The production of conventional crosslinked polymer networks and their composites, i.e., thermosets and thermoset composites, was estimated to consume more than 40 billion kg of polymer in the year 2020. Unfortunately, thermosets cannot be melt-reprocessed into moderate- to high-value products because permanent crosslinks prevent melt flow. Two of many examples include rubber tires, disposed at a rate approaching 300 million per year in the United States alone, and polyurethane (PU) foam, with major economic and sustainability losses resulting because the spent materials are commonly landfilled or burned for energy. Here, we will report on research demonstrating the ability to employ simple one-step or twostep reactions to produce networks and network composites with dynamic covalent crosslinks that are robust at use conditions but allow for melt-state reprocessing at high temperature. Unique to our research group, we have developed two approaches that allow for melt-state reprocessing of addition-type polymer networks and network composites. These include polymers synthesized directly from monomers containing carbon-carbon double bonds, which are often used in coatings and flooring, and those synthesized from combined polymer and monomer with both containing carbon-carbon double bonds, similar to materials used in tire production. Both approaches allow for full crosslink density recovery after multiple reprocessing steps. We also demonstrated for the first time the reprocessability with full crosslink density recovery of PU and PU-like networks, the latter made from polyhydroxyurethane and polythiourethane. An "Achilles heel" has been identified with regard to the application of dynamic covalent networks, i.e., such networks are subject to creep at elevated or sometimes even room temperature, which is often highly undesirable. We have addressed this limitation in two ways. In one case, we add a fraction of permanent crosslinks to dynamic covalent networks, suppressing creep. In a second class of systems, we employ dynamic chemistry with a sufficiently high activation energy, e.g., ~100-120 kJ/mol, to allow for reprocessability at 130-160 °C but with the dynamic chemistry essentially fully arrested at 70-80 °C. Finally, we note that biomass-derivable molecules can be employed to produce many dynamic covalent polymer networks, and we will provide a brief discussion of examples of such monomers and pre-polymers that can be used to good effect for these materials. Additionally, we will also describe an example of how recovery of monomer or pre-polymers from spent networks may be achieved, thereby allowing for the synthesis of new materials from spent polymer.



S4.5: 11:40 – noon (Eastern Time) (**Invited Speaker**)

## Thermosetting Bio-Derived and Environmentally Friendly Polymers for Additive Manufacturing

John J. La Scala, Anthony Clay, Joshua Mitchell, David VanOosten, Ian McAninch

Manufacturing Science and Technology Branch, DEVCOM Army Research Laboratory, FCDD-RLW-MD, Aberdeen Proving Ground, MD, 21005 USA

DEVCOM Army Research Laboratory is developing polymer additive manufacturing (AM) technologies for a variety of applications, including replacement parts for Army weapons, platforms, and support equipment that have long lead-times, structural parts, body panels, armor, and replacements for metal parts for light-weighting. We have investigated a number of bio-derived and environmentally friendly formulations for additive manufacturing, including bio-derived polymers based on isosorbide and hesperetin and environmentally friendly aza-Michael addition formulas as an alternative to polyureas. Isosorbide methacrylate, which is derived from sorbitol, has been formulated into stereolithography (SLA) polymer resin for 3D printing. Using isobornyl acrylate or 4-acryloylmorpholine as reactive diluents, we were able to reduce the brittleness of the isosorbide-based polymers and retain high glass transition temperatures ( $T_g$ ) of up to 231°C. Addition of oligomeric urethane (meth)acrylate crosslinkers further improved the mechanical properties of the polymers, whereby the strength approximately doubled to 55 MPa at 25°C, while maintaining high thermal properties,  $T_g > 190°C$ , and low viscosities, < 140 cP, that are desirable for photoinduced AM applications.

Hesperetin is a bio-derived flavanone that contains a high level of aromaticity and conjoined rings that should enable production of high performance resins. We produced hespertin resins with a one, two, and three methacrylates per molecules, the latter, being completely methacrylated and blended these with reactive diluents, including 4-acryloylmorpholine. Although formulations were produced with  $T_g$  greater than 200°C, the properties were generally lower than that of isosorbide formulations. It is likely that the heterocylic ring degrades or de-cyclizes resulting in reduced properties. Formulations based on naringenin, another flavanone are also being developed, but the solubility of naringen methacrylate is considerably lower than hesperetin analogs due to the absence of the methoxy functionality on naringenin. Future formulations will investigate partially alkoxylation as a strategy to solubilize naringen methacrylates in other monomers.

Lastly, aza-Michael addition chemistries were explored in direct write ambient reactive extrusion 3D printing as an alternative to polyureas that use isocyanate monomers. To increase reactivity and reduce gel time, piperazine-terminated monomers were synthesized using an aza-Michael pre-step polymerization of piperazine and acrylates to build oligomers, or pre-polymers. By formulating a blend of piperazine-based amines and curing them with acrylates, we successfully printed cylindrical geometries currently as high as 6 inches without slumping via ambient reactive extrusion. The printed material had a measured  $T_g$  of -5°C and a storage modulus of 2,300 at -40°C. To the authors' knowledge, this marks the first reporting of an aza-Michael polymer for 3-D printing. We are able to produce materials with a range of properties from glassy to elastomeric by adjusting the structures of the starting monomers.

# Modifying Polyethylene Terephthalate through Reactive Twin Screw Extrusion to Improve Enzymatic Degradation

# Akanksha Patel, Allen C. Chang, Margaret J. Sobkowicz

Department of Plastics Engineering, University of Massachusetts, Lowell, MA, USA

Polyethylene terephthalate (PET) is a ubiquitous material known for its unique properties (e.g., high strength to weight ratio, transparency, chemical resistance, electrical insulator properties and gas barrier properties) that is used in applications including bottles, fabrics, solar panels, automotive industry, etc. Increasing demand for PET has precipitated a need for improved recycling technology, especially for single use PET waste. So far, enzymatic degradation has shown promise as an environmentally responsible alternative for PET chemical recycling that yields economically useful products (e.g., terephthalic acid, adipic acid). However, due to low conversion rates, it is challenging to scale up the degradation system. In our work, PET waste is pre-treated using reactive extrusion with multifunctional polyols like ethylene glycol (EG) in an ultra-high twin screw extruder (TSE) system. The reactive extrusion process introduces a cost and energy efficient method to modify material properties (e.g., crystallinity, glass transition temperature, surface area) which may improve enzyme efficiency. The effect of varying EG weight percentage (0.7 wt.%-12.3 wt.%) at different extruder throughput and screw speeds was evaluated. Intrinsic viscosity (IV), Molecular weight (M<sub>n</sub>) and thermal properties of extruded samples were investigated and compared with the post-consumer PET waste. There was a decrease in IV and Mn of PET with change in loading percentage of EG. PET extruded with EG has reduced glass transition temperature (Tg) and increased crystallinity (%). These reactive extrusion runs have lowered the Mn from 24500 g/mol to 3000-4000 g/mol and Tg from 82 °C to 66-68 °C. A mechanical grinder was used to increase the surface area of EG mixed PET samples, while a particle size analyzer and sieve analysis were used to calculate the resultant surface area and particle size distribution. There was an increase in yield during enzymatic degradation with higher surface area of extruded samples. The pretreatments investigated here could provide a significantly faster, energy efficient enzymatic process for recovery of high value products from waste PET.



Figure 1: Reactive Extrusion of Polyethylene terephthalate (PET) using Ethylene glycol.

# Concurrent Session S5 – Progress in Lignin Valorization: 10:00 am – 12:30 pm (Eastern Time)

Session Chair: John Chea (Rowan University)

S5.1: 10:00 – 10:20 am (Eastern Time) (**Invited Speaker**)

# **Carbon Fibers Derived from Lignin-based Precursors**

Sagar Kanhere, Elijah Taylor, Graham Tindall, Prof. Mark C. Thies, and Prof. Amod A. Ogale

Dow Chemical Professor of Chemical Engineering Director, Center for Advanced Engineering Fibers and Films Clemson University, Clemson, SC 29634, USA

Currently, a vast majority of carbon fibers (over 90%) are produced from polyacrylonitrile (PAN) precursor that is synthesized from a toxic monomer, acrylonitrile, an organic cyanide. Also, during carbonization of PAN fibers, toxic byproducts such as HCN are produced. Therefore, production of carbon fibers from environmentally responsible and bio-renewable precursors has been of growing industrial interest. Prior literature studies, including ours, have addressed the use of softwood kraft lignin. In this study, we report on hybrid poplar (HP) derived lignin because HP is one of the fast-growing trees that can be grown and cut at a sustainable rate.

Lignin obtained from HP pulp was cleaned and fractionated using an ALPHA process developed by Thies and co-workers. HP-derived lignin fractions existing as solutions in ethanol-water mixtures were converted to lignin fibers using a dry-spinning process developed by Ogale and co-workers. The precursors consisted of two grades of fractionated HP lignin with molecular weights ( $M_w$ ) of about 12,000 and 16,000 Da. Various combinations of spinning conditions were employed to obtain a draw-down ratio (DDR) as high as 8. The precursor fibers were successfully crosslinked by thermo-oxidative stabilization and carbonized at 1000°C. CFs possessing a nominal diameter of 10 µm were produced. Raman spectroscopy conducted on CFs revealed a disordered carbon peak (D-peak) at 1310 cm<sup>-1</sup> and a graphitic crystalline peak (G-peak) at 1580 cm<sup>-1</sup>. Ratio of G-to-D peak area was only about 0.3, indicating a predominance of disordered carbon structure, similar to that observed for softwood kraft lignin-derived CFs. Consistent with this microstructure, the tensile strength of CFs was about 0.6 to 1.0 GPa and a modulus of about 35 to 50 GPa. Although not comparable to properties of CFs obtained from high-cost PAN precursors, these properties are among best reported for carbon fibers derived from hybrid poplar-based lignin. Ongoing studies are investigating different process conditions to minimize defects to enhance properties of the resulting carbon fibers.



SEM micrographs showing carbon fibers possessing a kidney-bean shaped cross-section generated due to out-diffusion of solvent during dry-spinning of lignin precursor fibers that is retained after carbonization

## S5.2: 10:25 – 10:45 am (Eastern Time) (Invited Speaker)

## Production and Characterization of Bio-oils from Solvent Liquefaction of Lignin

#### Charles A. Mullen and Gary D. Strahan

USDA-ARS Eastern Regional Research Center, 600 E. Mermaid Ln., Wyndmoor, PA 19038, USA

The development of the emergent bio renewable economy to reduce the extraction and consumption of fossil fuels has resulted in the development of many new technologies to convert portions of lignocellulosic material to biofuels, alternatives to high volume petrochemicals, and new biomaterials. However, lignin which accounts for about 20% of biomass derived carbon is often left underutilized. Finding high value uses for lignin by-products is critical to the economic viability of biorefineries. There have been many recent developments in homogeneous catalysis for breaking C-O bond types present in lignin structures in model compounds, but these approaches have been less successful when applied to native lignins. Higher temperature thermochemical processes are less chemically selective than lower temperature catalytic approaches, but their efficiency in producing liquid products makes them attractive for biorefinery operations.

In this presentation we will discuss the depolymerization of lignin via the solvent liquefaction process comparing, among other variables, the use of high boiling solvents versus low boiling solvents. High boiling solvents have the advantage of reducing the overall pressure requirement but are more difficult to separate from the lignin products for reuse. We will compare the results obtained with the more traditional solvolysis reagents such as ethanol or water/ethanol mixtures over a range of process temperatures ( $200 - 400 \,^{\circ}$ C) and residence times. We will also present the results when various solvents are used in combination with catalysts and hydrogen donor additives (e.g. formic acid). In addition to typical characterization methods (e.g. GPC, fractionation), in this presentation, detailed characterization of any higher molecular weight portions of lignin depolymerization products will also be presented via diffusion orientated NMR spectroscopy (Figure). The latter will be used to distinguish functional groups distribution over MW ranges. We will also discuss possible applications for lignin depolymerization products in renewable polymers and materials.



# Fractionating and Purifying Hybrid Poplar Lignins with Aqueous Renewable Solvents for Highervalue Applications: Fibers, Foams, and Carbons

Graham Tindall,<sup>1</sup> Villo Becsy-Jakab,<sup>2</sup> David Hodge,<sup>2</sup> Zachariah Pittman,<sup>1</sup> Christopher Kitchens,<sup>1</sup> Amod Ogale,<sup>1</sup> Sagar Kanhere,<sup>1</sup> Mojgan Nejad,<sup>3</sup> Christian Henry,<sup>3</sup> Mark Roberts,<sup>1</sup> Chengjun Wu,<sup>1</sup> and <u>Mark C.</u> Thies<sup>1</sup>

<sup>1</sup>Clemson University, Chemical and Biomolecular Engineering, Clemson, SC, USA <sup>2</sup>Montana State University, Chemical and Biological Engineering, Bozeman, MT, USA <sup>3</sup>Michigan State University, Forestry and Chemical Engineering & Material Science, East Lansing, MI, USA

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 a fractionation process that we refer to as Aqueous Lignin Purification with Hot Agents, or ALPHA. With this technology, control of both the purity and molecular weight of lignin becomes possible. Furthermore, ALPHA has been developed for continuous operation, so it can be commercially scaled up. Finally, ALPHA has the added advantage of using renewable solvents that are or could be produced within the biorefinery, including aqueous solutions of acetic acid or ethanol.

Lignin is like any other polymer in that the molecular weight can have a dramatic impact on its suitability for a given application. Furthermore, polymer purity can be an equally important factor if the desired materials properties are to be achieved. Three large and growing markets have been identified for "ALPHA" lignin use: (1) high-performance carbon fibers for automotive applications, (2) rigid polyurethane foams for spray insulation for buildings, and (3) activated carbon for food and pharmaceutical use. For such higher-value applications, we hypothesize that today's commercially available bulk lignins have too broad a molecular weight (MW) distribution and are too low in purity to give acceptable performance.

Recent advances in the use of ALPHA-processed, hybrid poplar lignins, encompassing a wide range of molecular weights and purities, for the above applications will be discussed.



# Resolving the Discrepancies in the True Molecular Weight of Lignins with the Assistance of the ALPHA Process

Zachariah Pittman<sup>1</sup>, Graham Tindall<sup>1</sup>, Mark Thies<sup>1</sup>, and Christopher Kitchens<sup>1</sup>

<sup>1</sup>Clemson University, Clemson, SC, USA

Lignin constitutes nearly 30% of all renewable carbons in the biosphere and hold tremendous potential value as a source material for a wide breadth of downstream applications. However, the complexity and heterogeneity of lignin streams, as a result of the delignification process and natural variety in source materials, make it exceptionally difficult to develop. Advancement of lignin technologies hinges on the ability to clean and purify technical lignins into well-defined and fractionated streams. Here we employ a patented process titled "Aqueous Lignin Purification with Hot Agents" (ALPHA). The characterization of complex polymers is a bottleneck for sustainable material development, with lignin being no exception. Currently, there are enormous discrepancies in literature regarding the true molecular weights of lignin and presents a notable obstacle for improving purification, fractionation, and material models. One promising technique for calculating the absolute molecular weight and distribution of lignins is size-exclusion chromatography (SEC) coupled with multi-angle light scattering equipped with an infrared laser (MALS<sub>IR</sub>) and bandwidth filters. This approach both suppresses and blocks fluorescence, respectively, which has led to overestimation of molecular weight of previous MALS experiments. We demonstrate how SEC-MALS<sub>IR</sub> can be used to accurately calculate the molecular weight distributions of a variety of lignin sources and ALPHA-processed fractions. A universal lignin elution curve derived from MALS<sub>IR</sub> is applied to compensate for lingering non-SEC interactions, fluorescent, and absorption related phenomena that cause erroneous and poorly reproducible measurements. In doing so, we decouple discrepancies discovered between mobile phases, lignin fractions and the individual contributions of non-ideal behavior during liquid chromatography and light scattering. Additionally, we can more directly and accurately compare molecular weights, distributions and polydispersity's across a wide variety of technical lignins and their derivatives. Moving forward, this work presents an improved methodology of using a SEC-MAL<sub>IR</sub> technique to help bridge the characterization gap that inhibits meaningful lignin development across the field.



# Exploiting the Liquid-Liquid Phase Behavior of Hybrid Poplar Lignin in Ethanol-Water Solutions to Produce Precursors for Value-Added Applications

<u>Graham Tindall</u><sup>1</sup>, Villo Becsy-Jakab<sup>2</sup>, David Hodge<sup>2</sup>, Zachariah Pittman<sup>1</sup>, Christopher Kitchens<sup>1</sup>, Amod Ogale<sup>1</sup>, Sagar Kanhere<sup>1</sup>, Mojgan Nejad<sup>3</sup>, Christian Henry<sup>3</sup>, Mark Roberts<sup>1</sup>, Chengjun Wu<sup>1</sup>, and Mark C. Thies<sup>1</sup>

<sup>1</sup>Clemson University, Chemical and Biomolecular Engineering, Clemson, SC, USA <sup>2</sup>Montana State University, Chemical and Biological Engineering, Bozeman, MT, USA <sup>3</sup>Michigan State University, Forestry and Chemical Engineering & Material Science, East Lansing, MI, USA

Lignin is an abundant biopolymer with unique functionality that is a commonly produced byproduct from cellulose enrichment processes such as papermills. This aromatic polymer is synthesized by plants to add structural support to woody biomass. Conventionally, papermills burn lignin for its heating value in order to cover the energy demands of the mill while reclaiming catalytic salts for the pulping process. While these mills are well established, bioethanol refineries are generally recognized as unprofitable, even if they could potentially produce fuels with a lower environmental impact. If the coproduct lignin could be recovered, purified, and leveraged as a revenue source, the value proposition of bioethanol refineries would be fundamentally improved. On top of supporting these refineries, finding economically feasible and renewable means of purifying/upgrading lignin opens up this currently under-utilized resource as a new feedstock for material and chemical applications. Previous work with Kraft lignins has shown that ethanolwater solvents (with specific composition, temperature, and solvent-to-lignin ratio) produce liquid-liquid phase equilibria. Labeled as the ALPHA (Aqueous Lignin Purification with Hot Agents) Process, this technology has been applied to lignin sources isolated from Hybrid Poplar (HP) trees via alkaline pulping. Ethanol-water solutions have proven to be effective at simultaneously fractionating HP lignin by molecular weight and removing impurities that are harmful to downstream, value-added applications. In this work we examine the impacts of fractionation and purification on the ability for HP lignin to serve as a precursor for applications such as carbon fibers, polyurethane foams, and activated carbon.

# Life cycle Assessment of Lignin-containing Cellulose Nanocrystals (LCNCs) Isolation using Deep Eutectic Solvents (DES)

Shiva Zargar<sup>1</sup>, Jungang Jiang<sup>1,2</sup>, Feng Jiang<sup>1</sup>, Qingshi Tu<sup>1</sup>

1. Department of Wood Science, The University of British Columbia, 2424 Main Mall, Vancouver, British Columbia, V6T 1Z4, Canada

2. Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083. China

Recently, deep eutectic solvent (DES) attracted great interest in isolating nanocellulose owing to its distinct advantages of biodegradability, low toxicity, and recyclability. Lignin-containing cellulose nanocrystals (LCNCs) obtained using DES pretreatment showed an improvement in the performance of nanomaterials production. The environmental assessment of innovative processes is critical to improving the efficiency and sustainability at the design stage. Hence, this study evaluates and compares the environmental impacts of LCNCs production from the thermomechanical pulp (TMP) following acidic DES pretreatment (binary system of "choline chloride - oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid dihydrate" or ternary system of "choline chloride – oxalic acid 3. The evaluation was conducted through a cradle-to-gate life cycle assessment adopting TRACI [v2.1, February 2014] for evaluating global warming potential (GWP) and acidification potential (AP) impact categories, and the Cumulative Energy Demand [v1.0.1, January 2015] LCIA method for energy use (MJ). The average GWP, AP, and energy use were 34 kg CO<sub>2</sub>-eq, 0.15 kg SO<sub>2</sub>-eq, and 919 MJ per kg LCNCs, respectively. The sensitivity analysis showed that different degrees of reduction in environmental impacts could be achieved by varying the input volume and/or reuse frequency of DES solutions. The largest reduction in GWP, AP, and energy use was achieved by reducing the input volume of DES solutions to 20% of its default value.



Concurrent Session S3 – Applications of Bio-based Materials: 02:00 pm – 04:30 pm (Eastern Time)

Session Chair: Matthew Schwenger (Rowan University)

S3.1: 02:00 – 02:20 pm (Eastern Time) (**Invited Speaker**)

# **Developing Highly Effective Polysaccharide Flocculants**

Blockx J.<sup>a,b</sup>, Verfaillie A.<sup>a,b</sup>, Muylaert K.<sup>a</sup>, Thielemans W.<sup>b</sup>

<sup>*a*</sup> Aquatic Biology, Department of Biology, KU Leuven, Belgium <sup>*b*</sup> Sustainable Materials Lab, Department of Chemical Engineering, KU Leuven, Belgium

Cellulose nanocrystals (CNCs), extracted from cotton via a standard  $H_2SO_4$  acid hydrolysis, were chemically modified with methyl-imidazolium (MIM) and pyridinium (PYR) grafts at various degrees of substitutions (DS). The extent of grafting was determined by elemental analysis and FTIR and XPS spectroscopy, while retention of crystallinity and morphology were confirmed by WAXS and AFM respectively.  $\backslash$ 

When testing *Chlorella Vulgaris* (freshwater microalgae) flocculation, it was found that the flocculation efficiency did not vary significantly with surface graft or with DS. However, the required dose varied virtually linearly with DS and remained independent of graft type (Fig 1(a)). Applying these flocculants to marine microalgae *Nannochloropsis oculata*, flocculation remained effective and flocs could readily be removed using a large pore filter (Fig 1 (b)).



Fig.1 (a) Minimum dose to induce flocculation of *Chlorella vulgaris* for cationically-modified CNCs, and (b) Harvesting efficiency by filtering flocs created by flocculation of *Nannochloropsis oculata with* cationically-modified CNC.

Adhesion force histograms and rupture distance measurements by securing (1) a microalgal cell on the AFM tip and probing a film of modified CNCs or (2) modified CNCs on the AFM tip and probing microalgal cells in solution, both showed that the interaction is governed by electrostatic interactions. This explains the linear relation between DS and required dose for flocculation. The interaction force for PYR-CNCs with *Chlorella vulgaris* was only a third of that for MIM-CNCs but that did not seem to affect its flocculation efficacy. Therefore, the strength of interaction does not seem to be a very important parameter so that our results show that increasing DS is more important than optimizing the type of cationic charge. Our work shows that CNCs offer great potential as biobased flocculants, even in high-ionic strength conditions. Extending this work to the removal of particulate matter in waste water is currently in progress and shows similar excellent flocculation performance, showing the wide applicability of cationic CNCs as flocculants.

# S3.2: 02:25 – 02:45 pm (Eastern Time) (Invited Speaker)

# **Biobased Coating for the Rejuvenation of Old Asphalt Shingles**

Nacu Hernandez,<sup>a</sup> Robert Downs,<sup>a</sup> Michael Forrester,<sup>a</sup> Andrew Becker,<sup>a</sup> and Eric Cochran.<sup>a</sup>

<sup>a</sup> Iowa State University, Department of Chemical and Biological Engineering, Ames, IA, USA

According to a new report by Reports and Data, the global asphalt shingles market is forecasted to reach USD 9.8 billion by 2027. Asphalt shingles are a type of waterproof roofing material that has a long lifespan and is relatively inexpensive; in addition to their numerous colors and styles, makes them the most popular type of roofing material in North America. However, more than 11 million tons of asphalt shingle waste is generated in the US alone each year. In this study, we explored the use of a biobased emulsion, composed of a partially epoxidized soybean oil with a biobased surfactant, to produce a spray that served as a rejuvenator of aged shingles. As asphalt shingles age, they become brittle, becoming less resistant to wind and hail. The application of the biobased spray to aged asphalt shingles restored their flexibility and dramatically improved their granule retention. This improvement makes for much longer-lasting asphalt shingles capable of standing extreme weather conditions for increased periods and thus decreasing the number of shingles that end up in landfills.



# S3.3: 02:50 – 03:10 pm (Eastern Time) (Invited Speaker)

# Advances in Biopolymers for Environmental and Biomedical Applications

#### Xiuzhi Susan Sun

Department of Grain Science and Industry and Department of Biological and Agricultural Engineering Kanas State University, Manhattan, KS 66506, USA

Sustainability is a constant driving factor for the development of cost-effective durable applicable biobased materials for various applications, particularly for environmental and biomedical uses. Utilization of those abundant biobased agriculture feedstocks for value-added bioproducts is important. This seminar will focus on advanced technologies of biobased chemicals and biopolymers for adhesives, coatings and hydrogels. Examples will be given to highlight: 1) biobased resins for environmental safe adhesives and coatings; 2) peptide based hydrogels for biomedical applications.

S3.4: 03:15 – 03:35 pm (Eastern Time)

# The Adhesion and Thermal Properties of Hot Melt Adhesive-based Nature Rosin and Poly(butylene adipate-co-terephthalate) for Packaging

JiHyun Cho, HyunJoong Kim

Lab. of Adhesion & Bio-Composite Seoul National University, Institute of Agriculture and Life Sciences, Seoul, Republic of Korea

**1. Introduction:** Currently, the use of disposable products is increasing rapidly due to the effects of packaging, delivery and courier because of COVID-19. As a result, a large amount of household waste is generated. As interest in the environment increases, materials used for packaging are also being replaced with materials that have a low environmental load when discarded.

In this study, bio-degradable hot melt adhesive (HMA) was prepared from PBAT Poly(butylene adipateco-terephthalate) which is well-known biodegradable polyester, and natural rosin for packaging [1-2]. To examine the adhesion properties of natural rosin as a tackifier in the biodegradable polymer, the thermal properties were measured using Thermogravimetric Analysis (TGA), Rheometer and shear strength of the HMA were tested using Universal Testing Machine (UTM).

**2. Experimental:** PBAT/Rosin composites were prepared by using twin-screw extruder (BAUTEK Co., Ltd, Korea). Various contents of the PBAT/Rosin were prepared via a melt blending technique. The Extrusion temperatures were from at 80 °C to 160 °C and the pelletized using pelletizer (BAUTEK Co., Ltd, Korea). The composition of the rosin was varied to 0, 10, 20, 30 and 40 wt %, respectively.

**3. Results and Discussion:** Figure 1. (a) present the blends were prepared by adding rosin to increases for the adhesive properties. The composition ratio of the rosin increased, and the measured shear strength of the blends were peak at 7:3 sample and then decreased again when the rosin composition over the 40 wt%. Figure 1. (b) and (C) shows complex viscosity and storage modulus, respectively. And its blend as a function of temperature from  $100^{\circ}$  C to  $180^{\circ}$  C. The complex viscosity and storage modulus of all samples have typical tendency to decrease with increasing rosin contents. Figure 1. (d) and (e) curves show that thermal decomposition properties and DTG of PBAT/Rosin blends. This finding indicates that the addition of rosin decreasing the thermal decomposition temperature.

**4. Conclusions:** The results of this study showed that the natural rosin decreases the viscosity, it increases wettability and consequently shows improved adhesion performance.

**5. References:** [1] Y. Fu, G. Wu, X. Bian, J. Zeng and Y. Weng, 2020, 25, 3946; [2] S. K. Vineeth, R. V. Gadhave, 2020, 10, 49-65



Figure 1. (a) shear strength, (b) storage modulus, (c) complex viscosity, (d) TGA curve (e) DTG curve of PBAT/Rosin blends.

# Adhesion Property of PBS Hot-Melt Adhesives by Rosin Type

Kwang-Hyun Ryu<sup>a</sup>, Ji-Hyun Cho<sup>a</sup>, Hyun-Joong Kim<sup>a</sup>

<sup>a</sup>Lab. of Adhesion & Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul, Republic of Korea

As the environmental pollution caused by the indiscriminate use and disposal of non-degradable plastics has become an internationally-surged problem, the urging needs of biodegradable materials also arise in the adhesive field. In particular, the main component of HMA used in packaging are non-degradable polymers such as PO(polyolefin) and EVA(ethylene vinyl acetate), which can negatively affect the environment. In this study, HMA was prepared through melt compounding using PBS(polybutylene succinate) such as biodegradable polymer with rosins, and adhesion property on the LDPE(low density polyethylene) film was evaluated and investigated on the cause of the results.

Solvent extraction rosin (Rosin), dehydrogenated rosin (Rosin-DH), and dehydrogenated rosin ester (Rosin-DHE) were selected to confirm the change in adhesion performance according to modification and content of rosin. The mixing ratio was 5, 10, 20, 30 wt% with respect to PBS. To quantify the adhesion performance of HMA, the peel strength on the corona treated LDPE film is measured. As a result, the most significant results were shown in HMA added Rosin in PBS, neat PBS did not adhere at all on LDPE film. In contrast to the Rosin series, adhesion of Rosin-DHE series in which the carboxylic group was removed through esterification was hardly revealed on LDPE film. The causes of the phenomenon were described in this study through changes in compatibility, rheological properties and crystal morphology of prepared HMA.



Figure 1. a) Peel strength for PBS HMA on LDPE film by rosin type, b) Complex viscosity for PBS HMA at angular frequency of 1 rad/sec, c) GPC(Gel Permeation Chromatography) results for Rosins, d) POM(Polarized Optical Microscopy) image of PBS HMA, e) The crystallization temperature from DSC (Differnetial Scanning Calorimetry) by rosin type, content.

#### S3.6: 04:05 – 04:25 pm (Eastern Time)

#### Shelf Life Extension of Postharvested Climacteric Fruits by Using Edible Coatings

Neelima Tripathi<sup>1</sup>, Jayita Dutta<sup>2</sup>, Beena Rai<sup>2</sup> and Sri Sivakumar<sup>1†‡§</sup>

<sup>1</sup>Department of Chemical Engineering, <sup>†</sup>Material Science Programme, <sup>\*</sup>Centre for Environment Science and Engineering, <sup>§</sup>Centre for Nanosciences,

<sup>1</sup>Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh – 208 016, India

<sup>2</sup>TCS Research, Tata Research Development and Design Centre, 54B, Hadapsar Industrial Estate, Pune – 411 013. India

In this study, the film-forming ability was initially checked for the prepared coating solution for enhancing the shelf life of postharvested fruits. The optimized solution casted film was characterized for structural, thermal and surface analyses. The coating solution was prepared that can retain the postharvest quality of fruits which was observed by the aesthetical appeal of the coated fruits. The precursors selected for the formulation of the coating were Food and Drug Administration (FDA) approved which retained the aesthetical appeal for more days than that of uncoated fruits. The enhancement in the shelf life of the coated fruits was observed by percentage weight loss and ripening rate. On the seventh day, coated fruits showed a decrease in 24% weight loss than uncoated fruits. The production of O<sub>2</sub>, CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> gases of uncoated and coated fruits were obtained and compared. Further, rheological and UV absorption analyses determined the characteristic properties of the coating solution. The coated fruits showed a delay in ripening peak, and 37% reduction of ethylene gas was compared to uncoated fruits.

#### Acknowledgment

The authors acknowledge the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), Government of India for providing the funding under the National Post-Doctoral Fellowship Scheme (project number SERB/CHE/2017217).

Concurrent Session S2 – Synthesis of Bio-based Polymers: 02:00 pm – 04:30 pm (Eastern Time)

Session Chair: Tristan Bacha (Rowan University)

S2.13: 02:00 – 02:20 pm (Eastern Time) (Invited Speaker)

# Enhancing Properties in Fatty Acid-Derived Thermoplastic Elastomers by Incorporating a Transient Network

Megan L. Robertson, Wenyue Ding, Josiah Hanson

University of Houston, Houston, TX, USA

Thermoplastic elastomers (TPEs) are widely used in electronics, clothing, adhesives and automotive components due to their high processability and flexibility. ABA triblock copolymers, in which A represents glassy endblocks and B the rubbery midblock, are commercially available TPEs. The most commonly used triblock copolymer TPEs contain glassy polystyrene endblocks and rubbery polydiene midblocks. However, commercial TPEs are derived from petroleum. The manufacturing and disposal of petroleum-derived products have undesired environmental impacts, which promotes development of TPEs from sustainable sources. Vegetable oils and their fatty acid derivatives are attractive alternatives to petroleum due to their abundancy and low cost. Our group has previously reported replacing polydienes in commercial TPEs with sustainable polyacrylates derived from fatty acids. However, polymers with bulky constituents, such as the long alkyl side-chains of fatty acid-derived polymers, typically exhibit poor mechanical performance due to lack of entanglements in the rubbery matrix. To improve the mechanical properties, a transient network was incorporated into the fatty-acid derived midblock through hydrogen bonding. Specifically, triblock copolymers containing polystyrene endblocks and a midblock composed of a random copolymer of poly(lauryl acrylate) (derived from lauric acid) and acrylamide (which undergoes hydrogen bonding) were synthesized. Quantitative FTIR analysis confirmed the formation of a transient network. The polymers exhibits disordered spherical morphologies, desirable for application as TPEs. Rheological measurement revealed the order-disorder transition temperature reduced with increasing acrylamide content, beneficial for high temperature melting process. Importantly, triblock copolymers with hydrogen bonding in the matrix exhibited significantly higher modulus, strain at break, and tensile strength as compared to comparable polymers in the absence of hydrogen bonding.

Transient crosslinker



Unentangled



Dynamically crosslinked

# S2.14: 02:25 – 02:45 pm (Eastern Time) (Invited Speaker)

## Performance Advantages for Bioproducts in Manufacturing, Performance, and End-of-Life

# Nicholas A. Rorrer, Gregg T. Beckham, Caroline Hoyt, Scott R. Nicholson, Avantika Singh, Alberta Carpenter, Chen Wang

#### National Renewable Energy Laboratory, Golden, CO, USA

The unique functionality afforded to biomass possess the opportunity to re-design today's chemicals and materials to have enhanced performance. In general, this enhanced performance can manifest as advantages in manufacturing (e.g. use of less toxic intermediates, faster reaction times), life time performance (e.g. better thermomechanical performance), or at the end-of-life. Importantly, rigorous calculations of the current industrial practices must be performed to assess performance advantages, especially in manufacturing. In the current work, we will present our recent baseline data for all polymers produced at a scale of > 1 MMT and point to how these results motivate future work into the 're-design' of tomorrow's plastics. Additionally, using the same framework we will present results from our recent investigations into epoxy-based thermosets (with both amines and anhydrides as the hardeners) to elucidate the benefit of heteroatoms from biomass. Results from this work demonstrate the promise of leveraging performance advantaged bioproducts for multiple applications beyond just material performance. Future work will continue to explore how heteroatoms from biomass enable the manufacturing benefits discussed here.

## S2.15: 02:50 – 03:10 pm (Eastern Time) (Invited Speaker)

#### High Performance Epoxy-AmineThermosets Based on Furan Building Blocks

Xi Chu, Jian Gao, John J. La Scala\*, Giuseppe R. Palmese

Department of Chemical and Biological Engineering, Drexel University Philadelphia PA, 19104, USA

\* Manufacturing Science and Technology Branch, DEVCOM Army Research Laboratory, FCDD-RLW-MD, Aberdeen Proving Ground, MD, 21005 USA

A family of furan-based epoxy-amine thermosets will be discussed. Furfuryl amine (FA) was coupled using a series of aldehydes to form di-furan di-amine (DFDA) containing a variety of bridge carbon substituents and a tetra-amine (TFTA) having four furan rings. FA and DFDA were epoxidized with epichlorohydrin to form di-functional (FDE) and tetra-functional (TGDFDA) epoxies respectively. These glycidyl amine epoxy resins are self-catalyzed and undergo anionic polymerization at temperatures greater than 100°C to form cross-linked networks with Tg in the range of 100°C. FDE and TGDFDA can also be cured using amine hardeners. DFDA was used to cure FDE and TGDFDA to create fully furan-based thermosets with T<sub>g</sub> as high as 200°C (tan delta). Mechanical testing in compression revealed that the new systems have high Young's modulus (up to 5.5 GPa), high yield strength (up to 180 MPa), and high strains to failure (up to 90%). The unique nature of these biobased materials lies in the unprecedented combination of high modulus, high vield strength, and high failure strain relative to incumbent systems. This behavior is attributed to the presence and interactions of the furan rings within the network structure. Additionally, the furan-based systems exhibit remarkable char yields (~50%), far exceeding values of petroleum-based counterparts. The superior property characteristics of the furan-based epoxies can potentially enhance the performance of adhesives, coatings, and composites used in the transportation, construction, and aerospace industries.

#### S2.16: 03:15 – 03:35 pm (Eastern Time) (Invited Speaker)

#### High Strength Thermosets from High Functionality Bio-based Resins

Dean C. Webster

Coatings and Polymeric Materials North Dakota State University Fargo, ND USA

A challenge faced with transitioning from polymer materials derived from petrochemical sources to biobased sources is in designing materials having the performance properties required for today's applications. High performance thermoset polymers are used in applications such as coatings, composites, and adhesives and are made in-situ from the crosslinking reactions of functional low molecular weight resins or functional oligomers. While vegetable oils are readily available and amenable to functionalization to be used in thermosets, their long aliphatic hydrocarbon chains tend to result in materials that are soft and flexible. However, we have found that by creating multifunctional resins from vegetable oil fatty acids and a highly functional rigid polyol, thermosets can be formed that have the strength and stiffness for use in high performance coatings and composites. For example, epoxidized sucrose esters of vegetable oil fatty acids, such as epoxidized sucrose soyate (ESS) crosslinked with cyclic anhydrides yield thermosets having high modulus, solvent resistance, and hardness. Methacrylated epoxidized sucrose esters can be used to form high performance resins that can be cured with free radicals and used in composites using either glass or natural fibers. It has also been discovered that 100% bio-based thermosets can be made from the watercatalyzed crosslinking of epoxidized sucrose soyate with naturally-occurring acids such as citric or tartaric acids. Conversion of the epoxy groups into cyclic carbonate groups leads to highly functional resins that can be cured using multifunctional amines to yield polyurethanes without using isocyanates. Methacrylated and acrylated resins can also be cured using UV light for use in 3D printing. In all of these examples, the thermosets formed have properties far superior to their triglyceride oil counterparts and equivalent or superior to current petrochemical resins. A similar approach is also applied to lignin, where a green process for direct functionalization of lignin has been discovered. Thermosets from functionalized lignin can be made which are strong and tough.



# S2.17: 03:40 – 04:00 pm (Eastern Time) (Invited Speaker)

# **Recent Advances in Cashew Nutshell Liquid Technology**

Joe Mauck<sup>†</sup>, Anbu Natesh<sup>†</sup>, Chetan Tambe<sup>†</sup>, Fernanda Tavares<sup>†</sup>, Emre Kinaci<sup>‡</sup>, Hong Xu<sup>†</sup>

<sup>†</sup>Cardolite Corporation, Bristol, PA, USA <sup>‡</sup>Drexel University, Philadelphia, PA, USA

Materials derived from cashew nutshell liquid (CNSL), an olfenic phenolic compound mixture contained in the outer shell of the cashew nut have been used for decades in the manufacture of friction resins, adhesives, sealants, elastomers, and heavy-duty industrial and anticorrosive coatings. Growing environmental concerns across industries have helped expand the use of CNSL derivatives into new applications such as non-ionic surfactants, polyurethane foams, composite resins, and isocyanate blocking agents. Additionally, CNSL-based materials are now being explored as building blocks and additives in bioplastic polymer formulations and as biobased replacements for traditionally petrochemical-derived materials.



S2.18: 04:05 – 04:25 pm (Eastern Time) (Invited Speaker)

# Polyester Technology for Greener Cosmetic Ingredients: Re-envisioning Classic Chemistry for Enhanced Performance and Sustainability Improvement

Michael J. Fevola

Vice President, Head of Research & Development INOLEX, Inc., 2101 S. Swanson St., Philadelphia, PA, 19148 USA

Polyesters are an important class of ingredients used in skin care, sun care, hair care, and color cosmetics, where they can function as film formers, fixatives, emollients, and conditioning agents. Of all the synthetic polymers employed in personal care and cosmetics, polyesters are perhaps the most strongly aligned with the principles of green chemistry and sustainable design. Aliphatic polyesters employ inherently safer, nontoxic chemistry and environmentally friendly manufacturing processes, and they tend to be readily biodegradable due to the enzymatically-labile ester bonds comprising the polymer backbone. Combinations of synthetic strategies, such as end-capping with monofunctional reactants and incorporating polyfunctional monomers for branching and crosslinking, enable polyester structures to be tailored to deliver the properties required for the sophisticated performance required in product formulations. Recent advances in polyesters for cosmetics include the use of 100% renewable biobased starting materials, which further improves the sustainability of these ingredients. Polyesters such as Capryloyl Glycerin/Sebacic Acid Copolymer demonstrate excellent versatility and serve as platforms for ingredient design, whereby one chemistry can yield a diverse range of functional ingredients via structural optimization to achieve application-specific performance benefits.



# **Day 3: 25 June 2021 (Friday)**

# Plenary Session P3.1: 9:10-9:50 am (Eastern Time) (Invited Speaker)

# Novel Biopolymer and Biomineral Material Technologies for the Built Environment

## Wil V. Srubar, III

# University of Colorado Boulder, Boulder, CO, USA

Recent advances in biological engineering have enabled autonomous, high-fidelity biomanufacturing of useful biochemical, biomineral, and biopolymer building blocks that can be leveraged in the design and fabrication of construction material biotechnologies and living architectures at the human scale.

This presentation will highlight research that integrates the fields of synthetic biology, microbiology, materials science, and structural engineering to design and fabricate biomimetic and living biopolymeric materials for the built environment. In one study, we take inspiration from antifreeze proteins to design and fabricate biomimetic ice-binding molecules that prevent freeze-thaw damage in concrete without the use of air-entraining admixtures. We also show how photosynthetic microorganisms can be leveraged in the design of biopolymer and biomineral-based living building materials that display both biological (i.e., living, regenerative self-healing) and structural (i.e., load-bearing) function.

Finally, this talk will highlight the challenges that emerge working across length scales and disciplines, as well as the grand opportunity that exists for biologists and materials scientists to work together to create never-before-imagined biological material solutions for critical societal problems in energy, water, and the built environment.

# **Concurrent Session S4 – Advances in Polymer Manufacturing:** 10:00 am – 12:30 pm (Eastern Time)

Session Chair: Tristan Bacha (Rowan University)

# S4.7: 10:00 – 10:20 am (Eastern Time) (Invited Speaker)

# **Challenges in Formulating and Processing Charged Fiber-Based Materials**

Nasreen Khan<sup>1</sup>, Manali Banerjee<sup>1</sup>, <u>Blair Brettmann<sup>1,2</sup></u>

1) Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA

2) Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA

Natural fibers such as cellulose are attractive to improve sustainability of commercial plastics. Cellulose nanomaterials have a high surface area covered with hydroxyl groups, which makes them attractive for tailored molecular interactions, such as hydrogen bonding and electrostatic, as well as for further chemical modification. However, materials derived from natural sources present greater heterogeneities compared to traditional synthesized particles and the strong interactions cellulose is capable of lead to challenges in processing. We specifically examine the variability in cellulose nanomaterials and how charged cellulose nanomaterials interact with polymers to lead to dense aggregated phases. We have studied oppositely charged polyelectrolyte systems for the regimes where they form precipitate, coacervate, or soluble phases in the presence of negatively charged cellulose nanofibrils (CNFs). The adsorption, aggregation and effect on water retention in the nanofibrils is shown to depend on a number of polymer properties, including hydrophobicity, molecular weight and complex phase. Understanding how these different formulation aspects impact the interactions with CNFs points to the fundamental mechanisms of the stability and water retention, which can lead to improved design of polymers for cellulose-containing products. We also discuss emerging approaches to formulation development and how these might be applied to cellulose-containing composite materials.



# Highly Compostable High OleicSoy-Based Impact-Modifiers via Reactive Extrusion with Polyesters

Eric W. Cochran, Baker W. Keuhl, Michael J. Forrester, Austin D. Hohmann

Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, USA

In this talk I share recent progress we have made with the application of poly(acrylated epoxidized high oleic soybean oil) (PAEHOSO) as a biobased and biodegradable impact modifier for polyesters. With proper modification, polyesters like poly(L-lactic acid) (PLLA) and poly(butylene terephthalate) (PBT) can serve as high performance engineering thermoplastics. To date, the most effective impact modifiers have been rubber-filled core-shell particles. While composites bearing these particles have excellent performance, the cost and sustainability are drawbacks, especially in materials like PLLA that are often chosen for their renewable carbon and biodegradability. PAEHOSO and related copolymers comprise a family of biobased and highly compostable thermoplastic rubbers from high oleic soybean oil. These polymers contain a rich variety of residual functionality—epoxy, vinyl, ester, and alcohol—that can be exploited in the extruder barrel to yield interface-stabilizing graft copolymers with a chemically complementary matrix component. By tuning the PAEHOSO architecture and compounding parameters, we can design extrudates with rubbery PAEHOSO micelles encapsulated by a robust interfacial region. These micelles effectively blunt crack propagation and dissipate energy through cavitation, increasing the impact strength by up to two orders of magnitude with minimal deterioration in modulus.



S4.9: 10:50 – 11:10 am (Eastern Time) (**Invited Speaker**)

# Multicomponent Adsorption and Membrane Separations to Enable New and More Efficient Biopolymer Production Processes

## <u>Sankar Nair</u>

## School of Chemical & Biomolecular Engineering Georgia Institute of Technology, Atlanta, GA, 30332-0100, USA

This talk will discuss our progress on developing materials-based separation processes for biorefinery applications. The discussion will be centered on the kraft process, which is a high-volume biorefining process that yields biopolymer (cellulose), biobased chemical (tall oil), and bioenergy (steam and electricity) products. The key role of advanced separation processes in increasing the energy efficiency of the kraft process and enabling valorization of stream components, will be highlighted in the context of three interconnected issues. First, we will illustrate the importance of imagining biorefineries as an interconnected network of conversion and separation processes, and the possibility for materials-based separations to enable new ways of valorizing stream components. Second, we will illustrate the differing separation challenges encountered in stream fractionation versus product purification, both of which are critical for biorefineries. Third, we will explore the development and identification of versatile and inexpensive separation materials that can operate in harsh conditions of temperature, pH, and multicomponent conditions. The twin issues of stream dilution and complexity are considered throughout this discussion.

# S4.10: 11:15 – 11:35 am (Eastern Time) (**Invited Speaker**)

## **Precision Compounding of Bioplastics via Twin Extrusion for 3D Filaments**

#### Charles Martin

#### Leistritz Extrusion, Branchburg, NJ, USA

Twin screw extruders (TSEs) are used to mix bio-based polymers, additives, particulates and active ingredients to impart targeted and unique properties into the final product. Pellets are often produced that are then processed on a single screw extruder mated to a downstream system to make a 3D filament which is then converted into a unique 3D part. The same downstream system can be integrated with a twin screw extruder to extrude a filament in one-step, or even directly with the 3D printing device, which drastically reduces the formulation's heat and shear history experience. A comparison of the different manufacturing methodologies, with the benefits of each, will presented and explained.

# S4.11: 11:40 – noon (Eastern Time) (Invited Speaker)

## **Bio-Based Resins for Additive Manufacturing**

<u>Alexander W. Bassett</u><sup>1,2</sup>, Amy E. Honnig<sup>1</sup>, Claire M. Breyta<sup>1</sup>, Ian Dunn<sup>1</sup>, John J. La Scala<sup>2</sup>, Joseph F. Stanzione III<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Rowan University, Glassboro, NJ 08028, USA <sup>2</sup>U.S. Army DEVCOM Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

Vinyl ester resins (VERs) are used to produce polymeric materials for a variety of commercial and military applications due to their relatively high strengths, moduli, thermal stabilities, and chemical resistances. Most commercially available VERs are petroleum-based and are typically cured into polymeric materials via traditional manufacturing techniques, such as resin transfer molding, compression molding, and thermal curing. Renewable, bio-based sources have been identified as more environmentally sustainable solutions to popular platform chemicals derived from petroleum. In an effort to design sustainable materials, biobased feedstocks have become major sources of interest for the development of polymers and composites. To achieve similar properties to industrial VERs, bio-based resins need to possess some aromatic content to impart favorable thermal, viscoelastic, and mechanical properties. Lignin is an abundant natural source of aromaticity and, among the many lignin derived compounds, vanillin has been shown to be a viable platform chemical for the development of VERs. Additionally, additive manufacturing, more commonly known as 3D printing, has gained significant traction as a promising manufacturing technique over traditional methods due to the ability to create customizable parts with complex geometries on demand. One method of additive manufacturing, stereolithography (SLA), is a 3D printing method that utilizes photopolymerization to create a customizable part layer by layer. A resin must have a low viscosity and the ability to be cured via light in order to be viable for SLA.

In this study, a low viscosity, vanillin-based VER was prepared via a solventless, one-pot, 100 % atom efficient reaction. Photorheology, along with the measured photocure parameters, were utilized to determine the feasibility of the resin to be additively manufactured using SLA. The vanillin-based resin was subsequently printed via SLA to determine polymer performance. Extent of cure analysis demonstrated that the printed resin, after a mild post cure, achieved favorable extents of cure. Viscoelastic, thermogravimetric, and mechanical testing was performed to investigate the properties of the resin cured via SLA. This study shows the prepared, bio-based VER was successfully applied to additive manufacturing and that the resin has the potential to be used as a standalone high-strength material for SLA. Furthermore, the resin system also has potential as a formulation base for tunable SLA resin and printed polymer properties while retaining significant bio-based content.

# FDM 3D Printed Sustainable Biocomposites from Recycled Ocean Plastics and Soy Hull-based Biocarbon

Benjamin Maldonado-Garcia<sup>1,2</sup>, Akhilesh K. Pal<sup>1</sup>, Amar K. Mohanty<sup>1,2</sup> and Manjusri Misra<sup>1,2</sup>

<sup>1</sup>School of Engineering, Thornbrough Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, Canada

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, Canada

Around 7.8 million metric tonnes of plastics have been produced since 1950, of which around 100,000 tonnes have leaked into the ocean and endangered marine life. Efforts to clean the ocean are increasing as well as utilizing the recycled plastics as feedstock material for developing upcycled products. Since the collection of plastics from the ocean and its separation require too much effort, ocean plastics can be used as an alternative feedstock material to petroleum-based virgin thermoplastics. Thus, leveraging its easy processing transformation and abundance in the environment. For this research, a mixture of plastics collected from the ocean, such as high density polyethylene (HDPE) and polypropylene(PP), were used to develop alternative materials that can be profitable for the use of 3D printing. 3D printing is the cuttingedge technology of this century due to its versatility in building intricate objects layer-by-layer at a short period of time. Among 3D printing technologies, fused deposition modelling (FDM) is the most common technique used to fabricate complex shaped objects. To avoid failure under axial and flexure loads, the build-up of the object can be modified using various parameters. The main goal of this research is to perform a comparative study between injection molded and FDM-based 3D printed samples, using a blend of recycled HDPE and PP (70:30) and its composites after incorporating soy hull biocarbon (20 wt%). In detail, a design of experiments was conducted using Minitab software method (Taguchi -L9) to find the most significant parameters that affect the mechanical properties of the 3D printed samples. The results suggest that the injection molded samples showed better mechanical properties as compared to 3D printed samples. However, an improvement (34%) in Young's modulus of 3D printed HDPE/PP (70/30) blend was observed compared to its injection molded counterparts. Overall, the 3D printed HDPE/PP/Biocarbon composite showed an improvement  $\sim 11$  and  $\sim 15\%$  in Young modulus and flex modulus.

## Acknowledgements

The authors are thankful to: (i) Ontario Ministry of Economic Development, Job Creation and Trade ORF-RE09-078 (Project Nos # 053970 and 054345); (ii) Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), University of Guelph, Bioeconomy Industrial Uses Research Program Theme Project Nos # 030252 and 030485; and (iii) Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants Project No # 400320 for their financial support.

#### Concurrent Session S6 – Bio-based Composites & Components: 10:00 am – 12:30 pm (Eastern Time)

Session Chair: Alexandra Chong (Rowan University)

S6.1: 10:00 – 10:20 am (Eastern Time) (Invited Speaker)

# High Cycle Fatigue Strength of Flax Fiber and Flax/Carbon Fiber Reinforced Thermoset Composites

Md. Zahirul Islam, Ali Amiri, Chad A. Ulven

Mechanical Engineering Department North Dakota State University Fargo, ND 58102, USA

In order to explore the long-term reliability of flax fiber and flax/carbon fiber hybrid reinforced thermoset composites under fluctuating loads, fatigue tests were conducted at different percentages of load associated with ultimate tensile strength (UTS) of each composite type and with different loading frequencies. The high cycle fatigue strength (HCFS) of the composites was investigated using both stabilized sample surface temperature based thermographic and dissipated energy per cycle-based approaches. For the thermographic based approach, the change in temperature of the samples during cyclic loading was captured using an infrared camera. Stabilized temperature and dissipated energy per cycle were compared with applied stress and different loading frequencies applied. Both analysis exhibited a bilinear behavior and the intersection point of the two curves was used to determine HCFS. HCFS for unidirectional flax fiber reinforced composites was found to decrease slightly with increasing loading frequency. Unlike fatigue life, stabilized temperature and dissipated energy-based models are convenient to define HCFS as they are timesaving and have little variation from sample to sample. Finally, it was determined that a strategic flax and carbon fiber hybridization can produce composites that are as strong as synthetic fiber composites while containing a high bio-based content of natural fibers.

# Addressing Decreased Thermal Stability of Biodegradable Plastics with the Addition of Biochar and Biomass Filler Materials

# Seth Kane<sup>1</sup>, Rachel Ulrich<sup>2</sup>, Cecily Ryan<sup>1</sup>

<sup>1</sup>Dept. of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT, USA <sup>2</sup>Dept. of Mathematical Sciences, Montana State University, Bozeman, MT, USA

Carbon filler materials (e.g., carbon black) are commonly used as filler materials to improve the electrical conductivity of polymers. However, carbon black is petroleum-based and does not biodegrade, making its application in biodegradable plastics undesirable. One promising alternative to carbon black is biochar, a carbon powder produced by pyrolysis of biomass. Of particular interest are lignin-derived biochars, which with the optimal feedstock and pyrolysis conditions show higher electrical conductivity than common carbon blacks. Despite this promise, many studies examining the addition of biochar to the common biodegradable plastics poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polylactic acid (PLA) show a decrease in thermal degradation temperature and crystallinity of the polymer when biochar is added. This decrease in thermal stability results in a material that is challenging to process and low in strength. In this study, we examine the mechanisms behind these observed decreases in thermal properties with the addition of biochar. To this end, we examined ten biochars produced from a variety of feedstocks and characterized their impact on PHBV and PLA thermal degradation temperature and crystallinity. Preliminary results indicate that alkali metals in biochar are responsible for the observed decrease in thermal degradation temperature in both PHBV and PLA. We then develop methods to remove alkali metals from biochars. These results demonstrate a path to improving the thermomechanical properties of biochar-filled PHBV and PLA. Further, common biomass fillers (e.g., lignin and wheat stems) have high concentrations of alkali metals and are shown to decrease the thermomechanical properties of PLA and PHBV. Therefore, these results have wide-reaching implications for biomass-filled composites and demonstrate a method to improve the viability of fully biodegradable composite materials.

# Strategic Assembly of Bio-Based Resins with Recycled Carbon Fibers: New Advances in Green Composites

Jasmin Z. Vasquez<sup>a</sup>, Laura Mazzocchetti<sup>b,c</sup>, Emanuele DÁngelo<sup>b,c</sup>, Joseph F. Stanzione, III<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, Rowan University, Glassboro, NJ 08028, USA <sup>b</sup> Department of Industrial Chemistry "Toso Montanari", University of Bologna, V.le del Risorgimento 4, 40136 Bologna, Italy

<sup>c</sup> Interdepartmental Center for Industrial Research on Advanced Applications in Mechanical Engineering and Materials Technology, CIRI-MAM, University of Bologna, V.le del Risorgimento 2, 40136 Bologna, Italy

Carbon fiber reinforced polymers (CFRPs) are often claimed to help save energy and improve the efficiency of systems in which they are used due to their extraordinary specific performance properties. However, at present, CFRPs cannot be classified as sustainable materials due to the energy-intensive processes involved in their manufacturing and their fossil origin, both for the polymer matrix, which is normally an epoxy resin, and for the carbon fibers. Due to the growing worldwide demand for CFs, there is a critical need to bridge the sustainability gap that exists in the CFRPs industry. Herein, we present our development of short CFRPs (SCFRPs) that were fabricated via a compression molding technique. Recycled carbon fibers reclaimed by the pyro-gasification of CFRP scraps were characterized and utilized as reinforcements for epoxy resins, including a cardanol-based epoxy resin, and directly compared with SCFRPs containing as received and chemically treated commercial carbon fibers. Spectroscopic, thermomechanical, thermogravimetric, and mechanical measurements were performed to fundamentally understand the processing-structure-property relationships of our assembled SCFRPs. For the SCFPRs that exhibited glassy behavior at 25 °C, results demonstrate that the recycled carbon fibers are viable reinforcing agents to produce lightweight composites for non-structural applications. As for the SCFPRs that exhibited rubbery-like behavior at 25 °C, results demonstrate that the recycled carbon fibers coupled with a cardanolbased epoxy matrix could be promising systems for anti-vibration components applications. As a result of our work, we are generating a valuable library of new bio-based polymeric composites containing recycled carbon fiber that are potentially greener, low-cost, lightweight composites with promising and desirable performance properties.
# Property Enhanced Biobased Packaging from Polybutylene Succinate and Nanocellulose Composites as a Sustainable Biodegradable Alternative

## Anuradhi Liyanapathiranage†, and Sergiy Minko†

†Nanostructured Materials Lab, University of Georgia, Athens, Georgia 30602, USA

Over the decades, excessive use of petrochemical polymers has led to land pollution, to which single-use plastics are responsible to a greater degree. In the spectrum of widely commercialized commodity plastics, primary packaging consumes single-use plastics in large volumes resulting in more than 31% of annual solid waste accumulation in the USA. Packaging defines critical aspects of a product, quality, safety, processing, technology, engineering, marketing, and branding. However, single-use plastics from packaging materials have limitations in reusing and recycling processes at the end of their lifecycles. Once single-use plastics ended up in landfills, they generate microplastics, polluting the geosphere in critical aquatic and marine ecosystems. Hence, biodegradable green alternatives for the packaging industry from biobased materials are a timely approach. With the emerging concerns on sustainability, there is a persisting necessity for altering technologies and reshaping our lifestyles to generate a greener footprint.

Our project has focused on developing sustainable and biodegradable solutions for primary packaging using biobased materials. Polybutylene succinate (PBS) is a biodegradable aliphatic polyester that inherits promising characteristics as a feasible replacement for polypropylene. PBS is favorable for commercial-scale production and has a steady supply chain. However, some performance attributes of PBS, such as thermo-mechanical and barrier properties, required to be improved for packaging. This research highlights our progress in enhancing mechanical and barrier properties of PBS using reinforcing modified cellulose nanofibrils (NFC). NFC are one-dimensional nanomaterial extract from plant biomass. Surface modified NFC were used in this research to improve interactions between the polymer matrix and reinforcing fillers (Figure 1a, b). Furthermore, thermal, mechanical, physicochemical, morphological, and structural differences of PBS-NFC (surface modified vs. unmodified) composites have been assessed to evaluate processing feasibility and investigate property enhancements.



Figure 1. PBS-NFC composites with variations of modified and unmodified NFC contents. a. tensile modules; b. complex viscosity (m=modified NFC and Un= unmodified NFC).

# Production and Physicochemical Characterization of Value-added Biocarbon Produced from Slow Pyrolysis of Waste Mixed Bio-oil

Ranjeet K. Mishra<sup>2</sup>, Amar K. Mohanty<sup>1,2</sup>, and Manjusri Misra<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada

The rapid growth of the world's population, scarcity of energy resources, and combined effects of global warming have emphasised a necessity for cleaner energy production. Bio-oil proves to be a vital component in diminishing the dependence on petroleum resources and provides a unique, profitable, sustainable, and environmentally-safe alternative for waste management and reducing greenhouse gas emissions. This study provides a fundamental foundation for the generation of functionalized biocarbon from waste mixed biooil (WMB) through the slow pyrolysis technique. WMB was pyrolyzed in a fixed bed horizontal tube reactor at a temperature of 600°C and 900°C, with a heating rate of 10°C min<sup>-1</sup>, and a 30 min holding time under non-oxidizing ambient (nitrogen) conditions. Experimentally, the operating temperature was determined to have the most influence on the yield and properties of the biocarbon. Specifically, a pyrolysis temperature of 600°C produced a higher yield of biocarbon with 14% as opposed to 900°C with 11%. Energy dispersive spectroscopy (EDS) established that the carbon content derived at 900°C is higher than the carbon content obtained at 600°C. Furthermore, the increased carbon content improved the electrical conductivity (EC) and thermal conductivity (TC) for WMB-based biocarbon. Additionally, scanning electron microscopy (SEM) confirmed that the biocarbon produced at 900°C has larger and harder particles with a smooth surface in comparison to biocarbon produced at 600°C. In conclusion, biocarbon obtained from a higher pyrolysis temperature is more promising for material applications.

### Acknowledgements:

The present work is carried out with the financial support of: i) The Agriculture and Agri-Food Canada (AAFC) and Competitive Green Technologies, Canada through the AgSci Cluster Program (Project # 054712); (ii) the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph – Bioeconomy for Industrial Uses Research Program (Project # 030332); and (iii) the Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants (Project # 401111).

# Physicochemical Characterization of Bio-Carbon Produced from the Slow Pyrolysis of Pine Nut Shells and Walnut Shells

<u>Kikaoseh Agweh<sup>1,2</sup></u>, Ranjeet Mishra<sup>1,2</sup>, Michael Snowdon<sup>1,2</sup>, Guowei Chen<sup>1,2</sup>, Amar K. Mohanty<sup>1,2</sup>, and Manjusri Misra<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Road East, Guelph, Canada

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Road East, Guelph, Canada

Developing biobased substitutes to more traditional sources of carbon in the form of biocarbon is salient in considerations of environmental and health. As collective effort continues within the scientific community to discover and develop new sources of bio-carbon, tree nuts provide a unique, sustainable, profitable, and environmentally friendly alternative. With the annual production of pine nuts and walnuts being in the tens of thousands and million tons range, respectively, pine nut shells (PNS) and walnut shells (WNS) proffer a sustainable alternative source of bio-carbon with minimal negative environmental impact. PNS and WNS were pyrolyzed at 500°C and 900°C in a fixed bed horizontal reactor. The obtained bio-carbon was characterized for its thermal stability, ash content, elemental content, graphitic content, functionality, surface morphology and electrical conductivity. The pyrolysis results showed the leading impact on the vield and properties of the bio-carbons. PNS and WNS provide 32.4% and 27.8% vield at 500°C contrasted with 28.1% and 24.5% at 900°C. The elemental study of PNS and WNS bio-carbon confirmed that the carbon content obtained at 900°C was higher than the carbon content obtained at 500°C. The morphology analysis showed PNS and WNS bio-carbon to be enhanced at 900°C compared to 500°C bio-carbon. The bio-carbon obtained at 900°C was found to have superior purity due to the elimination of more impurities. Furthermore, the electrical conductivity of PNS and WNS bio-carbon acquired at 900°C was significantly higher than the bio-carbon obtained at 500°C. Based on the data, it can be surmised that bio-carbon gained at higher temperature is preferable for material applications.

### Acknowledgements:

This research was financially supported by: i) The Agriculture and Agri-Food Canada (AAFC) and Competitive Green Technologies, Canada through AgSci Cluster Program (Project No. 054712); (ii) the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), Canada/University of Guelph – Bioeconomy for Industrial Uses Research Program (Project # 030332); and (iii) the Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants Project #401111.

## **Concurrent Session S1 – Biodegradability & Sustainability:** 02:00 am – 03:40 pm (Eastern Time)

Session Chair: John Chea (Rowan University)

S1.13: 02:00 – 02:20 pm (Eastern Time)

## Micro-Nano Plastics in the Environment: Challenges and Solution Pathways

Poritosh Roy<sup>1,2</sup>, Manjusri Misra<sup>1,2</sup>, and Amar K. Mohanty<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Ontario, N1G 2W1, Canada <sup>2</sup>Department of Plant Agriculture, University of Guelph, Ontario, N1G 2W1, Canada

Plastics have become an integral aspect of everyday human activity and are becoming ubiquitous in all facets of the economy. Waste or leaked plastics degrade into microplastics (MPs) or even nanoplastics (NPs). The leaked plastics and plastic-containing products used in agriculture, various polymer fabrics, and cosmetic products are the major sources of MP pollution in our ecosystems. They are abundant, environmentally persistent, and complex. MPs are pervasive in all channels of human interaction (in soil, water, and the atmosphere) and are hazardous for biota in all ecosystems. As a result, MPs are contaminating food systems and inevitably affecting human health. MPs migrate from one sector to another, its last destination seems to commonly be the oceans. The growing concern for the severity of plastic pollution has attracted multiple stakeholders to look for potential remedies. Although numerous efforts are underway to evaluate the effects of MPs on terrestrial and aquatic ecosystems, their detrimental impacts on the environment and human health.

### Acknowledgments

This study was financially supported by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) – University of Guelph, the Bioeconomy Industrial Uses Research Program Theme (Project # 030486, 030578); the Ontario Ministry of Economic Development, Job Creation and Trade ORF-RE09-078 (Project #053970, 054345); the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) program Project No. 460788; and the NSERC, Canada Discovery Grants Project # 400320 and 401111.

# Biodegradable Blends of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and Poly(ε-caprolactone) by in situ Reactive Compatibilization)

Peter Zytner<sup>1,2</sup>, Feng Wu<sup>1,2</sup>, Amar K. Mohanty<sup>1,2</sup>, and Manjusri Misra<sup>1,2</sup>

<sup>1</sup>School of Engineering, University of Guelph, Thornbrough Building, 50 Stone Road East, Guelph, Canada

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, 50 Stone Road East, Guelph, Canada

As the use of single-use plastics continues to increase, the need for a sustainable alternative is extremely high. By creating a biodegradable option to replace petroleum-based plastics, the environmental impact of these products can be significantly reduced. Selecting the right polymers can result in a sustainable alternative which meets all the necessary criteria for various applications. The reactive extrusion of poly(3hydroxybutyrate-co-3-hydroxyvalerate)/poly(ɛ-caprolactone) (PHBV/PCL) blends was conducted with the assistance of cross-linker 1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TAIC) and peroxide. It was found that the compatibility of the two polymers only improved when the peroxide and TAIC were used together. This was demonstrated by the reduction in PCL particle size and reduced interfacial gap between the PHBV and PCL. The mechanical, thermal, morphological, and rheological properties of the compatibilized blends were determined and subsequently compared against the blends without TAIC and peroxide. The ideal TAIC content was found to be 1 phr, where the elongation at break of the blends was 380% greater than that of the PHBV/PCL blend lacking any additives and a 700% improvement over neat PHBV. The improved interfacial compatibility, reduced PCL particle size, and improved uniformity of the PHBV crystals are all characteristics which improve the toughness of the blend. Fourier transform infrared (FTIR) and rheological studies are used to explore the reaction mechanism between the compounds involved. This work shows that PHBV and PCL are cross-linked by TAIC, which results in the formation of a PHBV-PCL co-polymer. This subsequently improves the compatibility of the blend along with its mechanical, thermal, and morphological properties. The biodegradable polymer blends prepared during this study have significantly improved toughness and high crystallinity, and as such are recommended for use in sustainable packaging applications or other similar fields.

**Acknowledgements:** This research was financially supported by the Ontario Ministry of Agri-culture, Food and Rural Affairs (OMAFRA)/University of Guelph -Bioeconomy for Industrial Uses Research Program (Project # 030255, 030486); OMAFRA-University of Guelph Gryphon's LAAIR Program (Project # 298635); the Ontario Research Fund, Research Excellence Program Round-9 (ORF-RE09) from the Ontario Ministry of Economic Development, Job Creation and Trade (Project # 053970 and 054345); and the Natural Sciences and Engineering Research Council of Canada(NSERC), Canada Discovery Grants (Project # 400320).

## The Aquatic Biodegradation of Wood-based Bathroom Tissue, Cotton Microfibers, and Flushable Wipes in Wastewater Treatment Plant Sludge

# <u>Dr. Madilynn M Smith</u><sup>1</sup>, Dr. Marielis Zambrano<sup>1</sup>, Dr. Richard Venditti<sup>1</sup>, Dr. Joel Pawlak<sup>1</sup>, Dr. Jesse Daystar<sup>2</sup>, MSc. Mary Ankeny<sup>2</sup>

<sup>1</sup>Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA <sup>2</sup>Cotton Incorporated

Fibers from textile products have been observed in significant quantities in wastewater treatment plants (WWTP) as a result of effluents from washing machines and from airborne microfibers that deposit on the ground and transfer to the sewer system. Microfibers are also generated and released into aquatic environments through the flushing of textile materials. Most wipes and paper products recommended for flushing are primarily cellulosic and, although cellulose is known to disperse to a safe size for travel through home plumbing, some nonwoven materials primarily non-biodegradable wet wipes, directly enter waterways and create pipe clogs along with sewage overflow issues. This research aims to further analyze their fate in wastewater treatment plants and examine their biodegradability in WWTP sludge. The biodegradation of commonly flushed materials was assessed using an ECHO respirometer over a course of 110 days. Materials tested included wood-based bathroom tissue, cotton fibers, flushable wipes, and polypropylene-based wipes. Materials (3.5g) along with 800 ml of test media (WWTP sludge + nutrients + water) were combined in a reaction vessel and placed in the ECHO



respirometer. The ECHO respirometer was used to track the production and concentration of gases (O<sub>2</sub> and CO<sub>2</sub>) using near-infrared (NIR) sensors and flowmeters to monitor the gas concentration and flow. Biodegradation was calculated by comparing the CO<sub>2</sub> produced relative to the theoretical CO<sub>2</sub> based on the overall carbon content. The cotton was observed to degrade faster and to a higher extent than the other materials. The Reference Material (Microcrystalline Cellulose) reached  $64.32 \pm 1.90$  % of biodegradation in the 110 days. The cotton fibers reached the highest percent biodegradation of  $88.16 \pm 1.65$  %. The tissue paper reached a percent biodegradation of  $78.61 \pm 0.74$  % whereas flushable wipes reached a degradation of  $75.88 \pm 11.22$  %. The polypropylene-based wipes did degrade by  $18.23 \pm 0.47$  %, due to its partial cellulose content. These results provide a robust and complete picture of the biodegradation of cotton materials, bathroom tissue, and wipes in aquatic environments and can serve as a valuable information for creating more sustainable wipe materials.

# Effects of Environmental Weathering on Particle Morphology Probed from Engineered Biodegradable Micro-and Nanoplastic Materials Used for Environmental Studies

Anton F. Astner<sup>1</sup>, Douglas G. Hayes<sup>1\*</sup>, Hugh M. O'Neill<sup>2</sup>, Barbara R. Evans<sup>2</sup>, Sai Venkatesh Pingali<sup>2</sup>, Volker S. Urban<sup>2</sup>, Timothy M. Young<sup>3</sup>, David P. Harper<sup>3</sup>

<sup>1</sup>The University of Tennessee, Biosystems Engineering and Soil Science, 2506 E J. Chapman Dr, Knoxville, TN 37996, USA

<sup>2</sup>Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37831, USA <sup>3</sup>The University of Tennessee, Center for Renewable Carbon, 2506 Jacob Dr, Knoxville, TN 37996, USA

On agricultural farmland, environmentally dispersed microplastics (MPs) and nanoplastics (NPs) from degraded mulch films and other plastic materials pose a severe ecotoxicity threat to terrestrial soilorganisms and ecosystems. Terrestrial NPs can aggregate, adsorb chemicals, and potentially serve as vectors to carry pesticides into the food web or absorb them into the plant. Most current fundamental studies investigating the fate and transport of plastic particulates in terrestrial environments use unrealistic MP and NP surrogates, such as monodisperse polystyrene spheres. In contrast, this study aimed to prepare realistic MPs and NPs from agricultural weathered (W) and unweathered (but cryogenically treated) (U) films through milling, grinding, and to characterize the physicochemical and dimensional properties. The first objective was to compare cryogenic cooling versus environmental weathering as pretreatments on the MPs (106 µm) and NPs (~120 nm) using two biodegradable plastic feedstocks (U), frequently used for agricultural specialty crop growth. The MPs and NPs formation occurred from biodegradable mulch films composed of polybutyrate adipate-co-terephthalate (PBAT) and a polylactic acid/polyhydroxybutyrate (PLA/PHA) blend. The second objective evaluated the influence of polymer type on the morphological changes during mechanical MPs and NPs formation, essential for environmental studies. The impact of weathering increased MPs' particle circularity while the aspect ratio and surface roughness decreased, suggesting the formation of more geometrically uniform particles. The NPs dimensions of U-PBAT were irregularly shaped and possessed an average surface roughness of  $12 \pm 1.0$  nm. The stepwise transformation of MPs to NPs was characterized through a time series (60 counts) of wet grinding runs applied to W- and U-MPs. Environmental weathered materials produced slightly smaller NPs for PBAT (dp of 122 nm and 132 nm for W- and U-, respectively). In comparison, cryogenic treatment of U-PLA/PHA yielded smaller NPs (115 nm); however, significant larger particles for W-PLA/PHA (266 nm). The latter observation reflects the presence of cross-linkages between the PLA and the filler material (CaCO<sub>3</sub>) formed through photodegradation, suggesting that W-PLA/PHA are more resistant to comminution. This study successfully demonstrated a robust formation method for MPs and NPs from biodegradable plastics through mechanical impact as it would occur during the tillage into the soil. The finding of dimensionally larger NPs from W-PLA/PHA after mechanical formation indicates that these agricultural W-NPs may be more recalcitrant to biodegradation than NPs from W-PBAT and may reside longer in agricultural ecosystems.

## **Concurrent Session S6 – Bio-based Composites & Components:** 02:00 am – 03:40 pm (Eastern Time)

Session Chair: Jasmin Vasquez (Rowan University)

S6.7: 02:00 – 02:20 pm (Eastern Time) (**Invited Speaker**)

#### Natural and Waste Fillers in Biodegradable Polymeric Composites and Foams

Sarah L. Billington<sup>1</sup>, Emma S. Bowers<sup>1</sup>, Andrew H. Kim<sup>1</sup>, Sabbie A. Miller<sup>2</sup>, Hai Haham<sup>3</sup>, Curtis W. Frank<sup>1</sup>

<sup>1</sup>Stanford University, <sup>2</sup>Kinestral Technologies, <sup>3</sup>U.C. Davis, USA

Wood, plastics, and drywall make up a significant portion of construction and demolition waste. These materials are often used for short durations, are resistant to degradation in landfills, and are energy intensive to separate and recycle. Many of these materials can potentially be replaced by rapidly renewable and biodegradable (when out of service) materials. Biobased composites and rigid insulating material for buildings that contribute to energy-efficient building operations have been investigated for in-service properties, environmental impact, and biodegradation at end of life. Specifically, biodegradable polyesters, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(lactic acid) (PLA) are combined with natural fiber fabrics to form composites and with nanocrystalline cellulose and biochar to form foams. The main drawbacks that prevent more widespread use of these materials are their high cost, low melt strength, and susceptibility to thermal degradation. This presentation will give an overview of a large research program on the development of PHBV and PLA composites and foams with the inclusion of various natural fibers and fillers from recycled and waste materials for eventual use in the building industry. Example studies that will be presented include the use of biochar to assist in PLA foaming to achieve PLA foams with similar or higher cell densities as expanded polystyrene foams. Biochar was found to be an effective class of nucleating agents that can increase PLA cell density up to four orders of magnitude with an almost ten-fold decrease in mean pore size.[1] An initial cradle-to-gate environmental impact assessment of PLA foams with microcellulose fibers developed by collaborators [2] has been conducted. Energy and material flows for the constituent materials as well as for the laboratory production were considered. Anaerobic biodegradation experiments are underway to expand the environmental impact assessment to be cradle-tograve. The potential for both biobased composites and biobased foams to be combined in structural insulated panels for improved energy efficiency in buildings will also be discussed.

# Statistical Design of Biocarbon Reinforced Sustainable Composites from Polyphthalamide (PPA) and with Polyamide 4,10 Blends

Mateo Gonzalez de Gortari<sup>1,2</sup>, Guowei Chen<sup>2</sup>, Arturo Rodriguez-Uribe<sup>2</sup>, Fantahun M. Defersha<sup>1</sup>, Stefano Gregori<sup>1</sup>, Manjusri Misra<sup>1,2</sup>, Amar K. Mohanty<sup>1,2</sup>

<sup>1</sup>School of Engineering, Thornbrough Building, University of Guelph, Guelph, N1G 2W1, Ontario, Canada. <sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science

<sup>2</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1, Ontario, Canada

To evaluate the novel material space of composites made out of polyphthalamide (PPA), polyamide 4,10 (PA4,10), biocarbon (BioC), and a chain extender (Joncryl®), a full factorial design of two levels and four factors was used, employing a total of 16 composite formulations. To optimize the material space, the following factors were considered: 10-20 wt.% of biocarbon, a pyrolysis temperature of 500-900 °C, the presence or absence of the chain extender, and the ratio of PPA:PA4,10 (25:75 to 75:25) as the polymer matrix. A linear regression model was utilized to estimate the effect of each factor on the characteristics of the composites. It was discovered that the main influence on the mechanical properties was the content of PPA and the wt.% of the biocarbon, while the other two parameters had a lesser role.

Acknowledgements: The authors are thankful for the financial support to carry out this research from the following agencies: (i) the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph – Bioeconomy for Industrial Uses Research Program (Project # 030332); (ii) the Natural Sciences and Engineering Research Council (NSERC) of Canada – Discovery Grants (Project # 400320); (iii) the NSERC - Collaborative Research and Development Grants (CRD) (Project # 401637) with the partner industries Prism Farms Limited and Competitive Green Technologies, Leamington, Ontario, Canada.

## Effects of Biochar Amendment in an In-pot Experiment for the Purposes of Growing Glycine Max.

<u>Tara Allohverd</u>i<sup>1</sup>, Amar K. Mohanty<sup>1,2</sup>, Istvan Rajcan<sup>1</sup>, K. Peter Pauls<sup>1</sup>, Clarence Swanton<sup>1</sup>, Manjusri Misra<sup>1,2</sup>

<sup>1</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Ontario, N1G 2W1, Canada

<sup>2</sup>School of Engineering, Thornbrough Building, University of Guelph, Ontario, N1G 2W1, Canada

Considering the affects of climate change on precipitation rates and the significant challenges with fertilization leaching across the globe, biochar (or biocarbon) as a soil amendment may hold the solution to accomplish sustainable agricultural initiatives. Biochar, created via pyrolysis of biomass, provides plants with essential nutrients, sequesters carbon in soil, and holds water for plant uptake. There is evidence to show how biochar, as a soil amendment, benefits the growth of *Glycine max* (Soybean plant) through its various properties. These properties include surface functionality, surface area, pore volume, pore size distribution, cation exchange capacity (CEC) and more. It is hypothesized that the use of biochar will increase above ground biomass depending on the concentration of amendment along with feedstock type. A comparison of Switchgrass and Coconut shell feedstock types on the growth of soybean plants in a greenhouse experiment has been carried out, along with assessing the physical and chemical properties of each biochar type. In this experiment, 10% dry weight was compared to 20% dry weight amendment in pots. Furthermore, there will be a discussion on field relevance and agricultural applications.

**Acknowledgments:** This study was financially supported by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) – University of Guelph, the Bioeconomy Industrial Uses Research Program Theme (Project # 030486, 030578); the Ontario Ministry of Economic Development, Job Creation and Trade ORF-RE09-078 (Project #053970, 054345); the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) program Project No. 460788; and the Agriculture and Agri-Food Canada (AAFC), Maple Leaf Foods, Canada and the Bank of Montreal (BMO), Canada through Bioindustrial Innovation Canada (BIC) Bioproducts AgSci Cluster Program (Project Nos. 054015, 054449 and 800148).

# Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/Polypropylene Carbonate Based Green Composites with Distillers Dried Grains with Solubles (DDGS)

Akhilesh K. Pal<sup>1\$</sup>, Kjeld W. Meereboer<sup>1,2</sup>, Manjusri Misra<sup>1,2</sup> and Amar K. Mohanty<sup>1,2</sup>

 <sup>1</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada
<sup>2</sup>School of Engineering, Thornbrough Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada

This research is focused on the fabrication of injection molded poly(3-hydroxybutyrate-co-3hydroxyvalerate) (PHBV)/poly(propylene carbonate) (PPC) blends (60/40) and (40/60) and their composites by incorporating water-washed distillers dried grains with solubles (DDGS) (15 and 25 wt.%) in the presence/absence of peroxide (0.5 phr). Various analytical properties such as mechanical, thermal, and surface morphology have been investigated to observe the effect of DDGS and peroxide on the blend's properties. The inclusion of peroxide increased the glass transition temperature ( $T_{e}$ ) ~9.6 °C of the PHBV/PPC (60/40) blend, indicating a strong linkage between the PHBV and PPC polymers. It was also supported by SEM analysis as no phase separation between PHBV and PPC was observed. A slight reduction in the thermal stability of PHBV/PPC blends and composites was detected as compared with PHBV due to the reduced crystallinity as the amorphous segments were increased after adding PPC. The addition of DDGS (25 wt.%) improved the tensile modulus of PHBV/PPC (60/40) and PHBV/PPC (40/60) blends with peroxide by ~40.7 and 1.5%, respectively, due to its fibrous flaky structure. Significant improvement of ~19 and 91 % for the elongation at break of the PHBV/PPC (60/40) blend matrix was detected without and with adding peroxide, respectively, as compared to pristine PHBV which is brittle. The notched Izod impact strength of the PHBV/PPC (60/40)-based composite was improved by ~15 and ~22.6% as compared with pristine PHBV and PHBV/PPC (60/40) blend, respectively.

### Acknowledgements

The authors would like to thank the following for their financial support: Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph-Bioeconomy for Industrial Uses Research Program (Project # 030177 and 030255); Ontario Ministry of Economic Development, Job Creation and Trade ORF-RE09-078 (Project # 053970 and 054345); and Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants (Project # 401111 and 400320).