PROPOSED
Center for Bioplastics and Biocomposites

INDUSTRY ADVISORY BOARD
KICKOFF EVENT

NOVEMBER 10-12, 2014
IOWA STATE UNIVERSITY, AMES, IA
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Welcome to the kickoff event for the proposed National Science Foundation (NSF) Industry & University Cooperative Research Center (I/UCRC) for Bioplastics and Biocomposites (CB²). CB² will be the premier research center dedicated to biobased plastics and composites, covering the complex and diverse aspects of establishing and promoting the use of renewable materials including feedstock logistics, material synthesis and compounding, product design and customer acceptance, life cycle assessment, and end-of-life treatment. It is funded through industry support as well as the NSF.

Within Iowa State University, 26 faculty members and their teams of scientists and graduate students focus on bioplastics. They have established large-scale feedstock facilities, equipment for chemical and thermal analysis, polymer processing machines, fermentation laboratories (from bench- to pilot-scale), carbon dating equipment, and facilities for testing commercial composting. Seventeen faculty and staff members at Washington State University are part of CB², many of whom are part of the longstanding Composite Materials and Engineering Center, which has developed new polymer and composite building materials from a range of recycled and virgin resources, resulting in numerous patents and inventions.

Over the next day and a half we will introduce you to this proposed collaborative center and its key personnel, bringing together innovation-driven research from industry and academia focused on bioplastics and biocomposites. The three primary goals of this meeting are to introduce our vision of research in this field, listen to your feedback on our proposed center, and select projects for funding. Faculty and staff members will be available to address your questions and provide additional information; so, you will be able to evaluate the potential impact of the center’s research efforts on your company and its short- and long-term goals. Fourteen research proposals will be presented for your review and feedback over the course of this meeting. There will be ample time for reviewing posters, networking, touring laboratories, and, of course, having dinner together.

Representatives from the State of Iowa and Iowa State’s administration will detail their support for the proposed center, and the National Science Foundation directors overseeing the center will provide input on the NSF’s vision for this I/UCRC and their role in ensuring transparency and successful knowledge development and transfer.
Over the next few days we want you to make yourself at home at Iowa State, a public land-grant research university. Iowa State has 1,800 faculty members and over 34,000 students from all 50 states and 100 foreign countries. It is a leading research institution, with research expenditures over $171 million. Future meetings will also be hosted at Washington State, which is also one of the nation’s top land grant universities, conducting transformational research and providing world-class education to more than 26,000 undergraduate, graduate, and professional students.

The collaboration between the two institutions is geographically and technologically strategic and is critical to the center’s success.

Thank you for your participation and we look forward to a productive and successful meeting.

Best regards,

David Grewell
Director
Center for Bioplastics and Biocomposites
Iowa State University

Michael Kessler
Site Director
Center for Bioplastics and Biocomposites
Washington State University
The proposed Center for Bioplastics and Biocomposites (CB²), pending approval from the Iowa Board of Regents, is a National Science Foundation Industry & University Cooperative Research Center (I/UCRC) that will focus on developing high-value biobased products from agricultural feedstocks.

CB² is a collaborative effort by the Biopolymers & Biocomposites Research Team at Iowa State University, the Composite Materials and Engineering Center at Washington State University, and industry members to conduct commercially relevant research.

Iowa State and Washington State are in a unique position to successfully develop and operate a bioplastics center. Iowa State is an established leader in the area of biobased products and Washington State has a strong history of research and inventions in natural fiber polymer composites. By bringing together their expertise, the center will be able to successfully transfer their ideas, results, and technology to the U.S. plastics industry.

**GOALS**

The goals of this center are threefold: (1) to improve the basic understanding of the synthesis, processing, properties, and compounding of bioplastic and biocomposite materials; (2) to develop reliable material characteristics data for industrial partners; and (3) to support large-scale implementation of renewable materials. In order to achieve these goals, the activities will be:

- Collaboration with industry to develop fundamental knowledge of bioplastics and biocomposites
- Dissemination of this knowledge through publications, workshops, and tradeshows
- Education of future researchers, engineers, and scientists

**CB² VISION**

The vision of the center is to develop the knowledge that will allow the production of an array of high-value products, including plastics, coatings, adhesives, and composites, from agricultural and forestry feedstocks that are compatible with current industrial manufacturing systems and thereby promoting rural development.
RESEARCH THRUST AREAS

The proposed CB² will focus on six research thrust areas that will promote industry-wide acceptance of bioplastics and increase the use of sustainable materials. Each thrust area is listed below.

SYNTHESIS AND COMPOUNDING
This thrust area will develop fundamental understanding of bioplastic synthesis and compounding, including fermentation and polymerization. This includes renewable oil-based plastics, biobased waxes, monomers, elastomers, poly(ester-amides), sustainable approaches to advanced functional materials and polymer additives, and feedstock production.

PROCESSING
This thrust will focus on the specific requirements of biobased polymers and composites during vital processing operations. This will include melt processing, extrusion, and molding as well as secondary operations such as cutting, welding, and coating.

BIOCOMPOSITES
Knowledge of biocomposites, including fiber synthesis, biobased resin systems, and biobased fiber systems, will be developed in this thrust. These areas include self-healing composites, fiber production from lignin, nano-technologies as well as biobased composites.

BIOBASED PRODUCTS
This thrust will focus on commercialization of bioplastic products. Commercialization includes, but is not limited to, composting, product labeling, and economic analysis. Some of the groups already existing system is an interactive life cycle assessment web-based software that allows users to easily analysis their current and future products.

MEDICAL APPLICATIONS
Biomedical uses of polymers will be a thrust. Because many of these materials are biodegradable and non-toxic, they have been intensively investigated for use in medical devices. Research in this area will capture the large sector of the polymers industry that has interest in this area.

MODELING
This thrust will study energy and mass transfer for employed processing techniques such as extrusion and injection molding. The long-term goal is to develop models based on fundamental principles that can be used across a wide range of sciences.

ORGANIZATION
Iowa State is the lead institution and responsible for the overall operation of the center. Each institution has a site director who will be responsible for administration of all research, budget, outreach, and related activities at their institution. There is an independent center evaluator who meets all NSF requirements. Intellectual property and contract related issues are administered by each institution respectively, but there is a general agreement with the center to resolve differences. The center activities are supported by industrial memberships in accordance with NSF eligibility requirements for a multi-university I/UCRC.
INDUSTRY MEMBERS

3M Company
Archer Daniels Midland Company
Berry Plastics Corporation
Bioplastics Magazine
The Boeing Company
Branson Ultrasonics Corporation, a business of Emerson Electric Co.
CC Lubricants
Dixie Chemical Company, Inc.
Dukane Corporation
Eco-Products, Inc.
Ford Motor Company
Hyundai America Technical Center, Inc.
Inland Label
Laurel BioComposite, LLC
M-Base Engineering + Software GmbH
Minnesota Corn Research & Promotion Council
Newell Rubbermaid
The Powder Coating Research Group
RheTech, Inc.
Siegwerk USA Co.
SuGanit Systems, Inc.
Taylor Technologies, Inc
USDA-ARS National Center for Agricultural Utilization Research
We would like to acknowledge and thank the following centers, colleges, and departments for their participation in the CB² Industry Advisory Board Kickoff Event. They have provided generous support throughout the development of this event.

**Center for Biorenewable Chemicals**  
Iowa State University

**Center for Crops Utilization Research**  
Administrative unit for CB²  
Iowa State University

**College of Agriculture and Life Sciences**  
Iowa State University

**College of Engineering**  
Iowa State University

**Composite Materials and Engineering Center**  
Washington State University

**Department of Agricultural and Biosystems Engineering**  
Iowa State University

**Leading the Bioeconomy Initiative**  
Iowa State University

**National Science Foundation**

**School of Mechanical and Materials Engineering**  
Washington State University

**Voiland College of Engineering and Architecture**  
Washington State University
Center for Crops Utilization Research – Second Floor Atrium in the Food Sciences Building

6:00 P.M. RECEPTION

Appetizers, beverages, and a cash bar will be available.

7:00 P.M. WELCOME ADDRESS

LAWRENCE JOHNSON
Director, Center for Crops Utilization Research

BILL NORTHEY
Iowa Secretary of Agriculture

BRENT WILLETT
Executive Director, Cultivation Corridor

Tour the Center for Crops Utilization Research facilities.

8:00 P.M. ADJOURN
All meeting activities are located in J.B. Davidson Conference Room – 1306 Elings Hall, unless noted otherwise.

7:30 A.M.  REGISTRATION
Continental breakfast will be available.

8:00 A.M.  OPENING REMARKS
MICHAEL CRUM  
Vice President, Economic Development and Business Engagement
WENDY WINTERSTEEN  
Dean, College of Agriculture and Life Sciences
SARAH RAJALA  
Dean, College of Engineering

8:30 A.M.  MEETING GOALS, VISION, AND CAPABILITIES
DAVID GREWELL  
Director, Center for Bioplastics and Biocomposites
MICHAEL KESSLER  
Site Director, Center for Bioplastics and Biocomposites

8:40 A.M.  MEETING ORGANIZATION
DAVID GREWELL  
Director, Center for Bioplastics and Biocomposites
8:45 A.M.  NATIONAL SCIENCE FOUNDATION
            I/UCRC PRESENTATION

            SHASHANK PRIYA
            Program Director, Fundamental Research Program for
            Industry & University Cooperative Research Centers,
            National Science Foundation

            MACK SHELLY
            National Science Foundation Center Evaluator

9:45 A.M.  BREAK

            Refreshments will be available.

10:00 A.M.  PROJECT PRESENTATIONS

            There will be seven 15-minute research project presentations:
            eight minutes for the presentation, five minutes for questions and
            answers, and two minutes to complete the L.I.F.E. form.

1.1 – Tackifiers from Sugars
        JASON CHEN

1.2 – Towards Biobased Polyethylene Terephthalate (PET)
        JASON CHEN

1.3 – Development of Biorenewable Thermoplastic Elastomers
        ERIC COCHRAN

2.1 – Production of Low-cost Carbon Fiber from Heavy Fraction of Fast Pyrolysis Bio-oil
        XIAONGLAN BAI

2.2 – Producing Low-cost Lignin Feedstock for Carbon Fiber Production
        ANNETTE SORENSEN

2.3 – Sustainable Hydrophilic/Hydrophobic Nanocomposites from Electrospun Poly(lactic acid) Nanofibers, Bacterial Cellulose, and Nanocrystalline Cellulose
        CHUNHUI Xiang

5.1 – Interfacial Healing of Biopolymers
        DAVID GREWELL

11:45 A.M.  LUNCH

            Sukup Atrium
1:00 P.M.  PROJECT PRESENTATIONS

There will be seven 15-minute research project presentations: eight minutes for the presentation, five minutes for questions and answers, and two minutes to complete the L.I.F.E. form.

4.1 – Mechanochemically Activated and/or Functionalized Cellulose Powders and Their Reinforced Plastic Compounds for More Demanding Applications
   MICHAEL WOLCOTT

4.2 – Pyrolytic Lignin-polyester-based Hot-melt Adhesives and Sealants
   ARMANDO MCDONALD

   SAMY MADBOULY

4.4 – Development of a Life Cycle Assessment Tool for Screening of Trade-offs Among Processing Costs, Environmental Impacts, and End-of-life Options
   KURT ROSENTRATER

4.5 – Understanding Consumer and Industry Perceptions of and Willingness to Pay for Bioplastic Products
   JOHN BEGHIN

4.6 – Development of Biobased VOC-free Powder Coating Resin Systems
   JINWEN ZHANG

4.7 – Improving Thermoplastic Properties of Starch for Food and Non-food Packaging Applications
   BUDDHI LAMSAL

2:45 A.M.  BREAK

Refreshments will be available.

3:00 P.M.  POSTER PRESENTATIONS

There will be 13 two-minute research poster presentations: two-minutes for the presentation and no questions and answers.

A complete list of poster presentations can be found on page 89.
3:30 P.M. **POSTER REVIEWS**
Sukup Atrium
The Industry Advisory Board will have 30 minutes to review and rank the posters.

*Refreshments will be available.*

4:00 P.M. **INDUSTRY ADVISORY BOARD ORGANIZATIONAL MEETING AND FORMATIVE DISCUSSION**
Industry Advisory Board members and National Science Foundation only.

5:15 P.M. **ELINGS HALL AND SUKUP HALL TOURS**
Tour the two newest buildings of the Biorenewables Complex at Iowa State University.

6:15 P.M. **NETWORKING TIME**
Sukup Atrium
*Beverages and a cash bar will be available.*

7:00 P.M. **TECHNICAL FORUM, SOCIAL, AND DINNER**
Sukup Atrium
**BRENT SHANKS**
Director, Center for Biorenewable Chemicals

9:00 P.M. **ADJOURN**
AGENDA

Day 3/November 12

J.B. Davidson Conference Room – 1306 Elings Hall

7:30 A.M.   CONTINENTAL BREAKFAST AND NETWORKING

8:00 A.M.   L.I.F.E. FORM REVIEW AND DISCUSSION

9:30 A.M.   INDUSTRY ADVISORY BOARD ORGANIZATIONAL MEETING AND FORMATIVE DISCUSSION

   Industry Advisory Board members and National Science Foundation only.

11:30 A.M.  ANNOUNCE GRANTS, ACTION ITEMS, AND PLANS FOR NEXT SEMI-ANNUAL MEETING

11:50 A.M.  SUMMARY AND CLOSING REMARKS

Noon       ADJOURN

   Box lunches will be available.
## THRUST AREA: SYNTHESIS AND COMPOUNDING

1.1 – Tackifiers from Sugars
10:00 A.M. – JASON CHEN

1.2 – Towards Biobased Polyethylene Terephthalate (PET)
10:15 A.M. – JASON CHEN

1.3 – Development of Biorenewable Thermoplastic Elastomers
10:30 A.M. – ERIC COCHRAN

## THRUST AREA: BIOCOMPOSITES

2.1 – Production of Low-cost Carbon Fiber from Heavy Fraction of Fast Pyrolysis Bio-oil
10:45 A.M. – XIANGLAN BAI

2.2 – Producing Low-cost Lignin Feedstock for Carbon Fiber Production
11:00 A.M. – ANNETTE SORENSEN

2.3 – Sustainable Hydrophilic/Hydrophobic Nanocomposites from Electrospun
Poly(lactic acid) Nanofibers, Bacterial Cellulose, and Nanocrystalline Cellulose
11:15 A.M. – CHUNHUI XIANG

## THRUST AREA: BIOBASED PRODUCTS

4.1 – Mechanochemically Activated and/or Functionalized Cellulose Powders
and Their Reinforced Plastic Compounds for More Demanding Applications
1:00 P.M. – MICHAEL WOLCOTT

4.2 – Pyrolytic Lignin-polyester-based Hot-melt Adhesives and Sealants
1:15 P.M. – ARMANDO MCDONALD

1:30 P.M. – SAMY MADBOULY

4.4 – Development of a Life Cycle Assessment Tool for Screening of Trade-offs
Among Processing Costs, Environmental Impacts, and End-of-Life Options
1:45 P.M. – KURT ROSENTRATER

4.5 – Understanding Consumer and Industry Perceptions of and
Willingness to Pay for Bioplastic Products
2:00 P.M. – JOHN BEGHIN

4.6 – Development of Biobased VOC-free Powder Coating Resin Systems
2:15 P.M. – JINWEN ZHANG

4.7 – Improving Thermoplastic Properties of Starch for Food and
Non-food Packaging Applications
2:30 P.M. – BUDDHI LAMSAL

## THRUST AREA: MODELING

5.1 – Interfacial Healing of Biopolymers
11:30 A.M. – DAVID GREWELL
THRUST AREA: SYNTHESIS AND COMPOUNDING

1.1 — Tackifiers from Sugars

Principal Investigator(s): Jason Chen* and Michael Kessler
Site: Iowa State University and Washington State University

Project Objectives. The proposed research aims to develop (1) high-temperature tackifiers derived from isosorbide and (2) curing technologies that transform selected isosorbide-based tackifiers into hybrids of tackifiers and adhesives.

Industrial Relevance, Need, and Appropriateness for the Center. Tackifiers are monomers or oligomers that provide an instantaneous non-covalent bond to a surface. Once bound to a surface, tackifiers resist separation from the surface by becoming stiffer under strain. These glassy semi-solids are major components (by cost and weight) of pressure-sensitive adhesives and also find use as oil additives.

The broad utility of tackifiers renders the proposed work relevant to many member companies. Biobased tackifiers are commonly used, but the proposed materials promise higher performance at a cost competitive with that of common tackifiers such as abietic acid. Additionally, tackifier hybrids will incorporate structural features that confer reversible or irreversible changes to materials properties in response to well-defined environmental cues. Such tunable properties may find use in a broad range of smart materials.

Experiment Plan. Aqueous suspensions of starch are used as low-grade tackifiers, but sugar water has unstable properties; the water evaporates to yield a sticky residue that does not stay tacky indefinitely. As shown in figure 1, we unexpectedly identified a promising tackifier1 while synthesizing a designed isosorbide-based diisocyanate.2 This tackifier is readily prepared on kilogram scale in a single solvent-free reaction. The pure material is approximately five times more tacky than abietic acid, and its mechanical properties are indefinitely stable. Characterization of a family of closely-related monomeric tackifiers revealed that slight changes to structure altered the useful temperature range without impacting the extent of maximum tack (see figure 2). These tackifiers have promising tack and thermal stability, and they cover a broad range of viscosity. However, despite attempts to identify high-temperature tackifiers, none of the members of the current family are optimized for high temperatures.

![Figure 1. Unexpected discovery of an isosorbide-based tackifier.](image1)

![Figure 2. Tack versus temperature for selected monomeric tackifiers.](image2)
We predict that oligomeric tackifiers related to the monomeric materials characterized to date will have superior high-temperature properties. Fisher esterification of isosorbide with simple diacids should yield oligomeric tackifiers. We have demonstrated the viability of this approach by characterizing a single oligomeric mixture. As shown in figure 3, the oligomeric material is a little less tacky, but high tack is available over a wider temperature range peaking at 80-100°C. The wider temperature range and slight reduction in tack is presumably because the mixture contains multiple components that are maximally tacky at different temperatures. Depending on the stoichiometry of the isosorbide and diacid components, the oligomeric tackifier can be tuned so as to be of higher or lower weight; higher weight is expected to lead to a higher glass transition temperature and a higher temperature at which maximum tack is observed. We aim to optimize our oligomeric tackifiers to cover the temperature range 50-120°C.

Because these tackifiers are molecularly well-defined, they are amenable to the design of hybrid materials that can change properties in response to pre-defined environmental cues such as heat, UV light, radical initiator, transition metal catalyst, pH change, or redox change. Potential properties that might change as a result of curing include the glass transition temperature, tack, and viscosity. As an example of a potential application, this technology may give rise to a liquid that can be filled into cracks or applied between two surfaces and then cured to form a permanent bond. Tacky monomeric uncured materials would help hold the system together, and curing under well-defined conditions would convert the tackifiers into polymeric adhesives. In a proof-of-concept demonstration, an alkene-containing smart tackifier was thermally cured into a non-tacky, highly-crosslinked thermoset that was a hard solid even above 200°C (see figure 4). Depending on the choice of curing chemistry, reversible changes to thermo-mechanical properties may also be envisioned. We propose to investigate a variety of other potential hybrid materials with the aim of identifying promising curing chemistries, both permanent and reversible.

**Proposed Deliverables.** The following deliverables are expected: (1) optimized tackifiers covering the temperature range 50-120°C and (2) first-generation tackifier hybrids.

**Research Facilities.** Organic synthesis space and thermo-mechanical characterization instruments (e.g., DSC, TGA, load frame, rheometer) are available to the project. No equipment purchases are needed.

![Figure 3. Oligomerization raises the maximum tack temperature.](image1)

![Figure 4. Proof-of-concept example of a tackifier hybrid.](image2)
Timeline and Budget. The work will be performed by a graduate student research assistant. The projected timeline for this one-year project is shown below. A budget of $50,000 is proposed:

Graduate student stipend, tuition, and benefits: $40,000
Chemicals, consumables, and instrument time: $10,000

<table>
<thead>
<tr>
<th>Task and Deliverables</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
</tr>
</thead>
</table>
| Develop high-temperature tackifiers  
  • Optimized tackifiers | X  | X  | X  | X  |
| Design tackifier hybrids  
  • First-generation hybrid materials | X  | X  | X  | X  |

1 ISU Research Foundation disclosure #04118, PCT filed.
2 ISU Research Foundation disclosure #04032, PCT filed.
Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 1.1 – Tackifiers from Sugars

**Principal Investigator(s):** Jason Chen* and Michael Kessler

**Site:** Iowa State University and Washington State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

**Level of Interest**

- [ ] Very Interested
- [ ] Interested
- [ ] Interested with Change
- [ ] Not Interested

- [ ] Abstain (Outside my group’s ability to evaluate)

**Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.**

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: _______________________________________________________________________

Your Organization: _______________________________________________________________________


1.2 — Towards Biobased Polyethylene Terephthalate (PET)

Principal Investigator(s): Jason Chen  
Site: Iowa State University

Project Objectives. The objective of the proposed research is a catalytic, solvent-free synthesis of dimethyl succinyl succinate (DMSS). A limited project scope is proposed because there is significant uncertainty in the proposed research; however, success in this research would lead to a highly-practical synthesis of DMSS and would justify follow-up research towards the efficient conversion of DMSS into dimethyl terephthalate (DMT).

Industrial Relevance, Need, and Appropriateness for the Center. Terephthalic acid (TPA) and its dimethyl ester (DMT) are synthesized primarily for the production of PET, a widely-used thermoplastic in the food industry. TPA and DMT may be used interchangeably in PET production. Some methods to synthesize biobased TPA or DMT have been described, but to date none of the methods are mature; alternative approaches might ultimately prove environmentally and/or economically superior.

DMSS is a dimethyl succinate dimerization product that finds use as a precursor to quinacridone pigments. Although in principle the addition of one equivalent of hydrogen gas and a double dehydration should allow DMSS to be converted into DMT, a SciFinder search for related approaches returns no chemical literature (inclusive of patents) describing the conversion of DMSS into DMT (or into TPA). Dimethyl succinate is an appealing starting point for biobased materials because the corresponding diacid (succinic acid) is available at lower cost through fermentation than from petroleum feedstock. Nonetheless, DMSS is currently too expensive to be a commercially-viable precursor to DMT in large part because of the requirement for stoichiometric strong acids and bases.

Experiment Plan. DMSS is currently prepared through a sodium methoxide-mediated dimerization of dimethyl succinate. The initially formed sodium salt of DMSS is extracted into water, and then DMSS is isolated after acidification of the aqueous mixture. This process is high-yielding, but the base cannot be made into a catalyst due to the strong acidity of DMSS as compared with dimethyl succinate; the sodium salt of DMSS is incapable of deprotonating dimethyl succinate. Although several patents have been issued for this process, all of the methods use the same base-mediated chemistry. We propose to develop an acid-promoted synthesis of DMSS. Unlike the base-mediated reaction, the acid-promoted process may be envisioned as a catalytic reaction. Furthermore, since strong acids more readily dissolve in organic molecules than strong bases, the reaction likely could be performed in the absence of solvent.

Brønsted acids (e.g., sulfuric acid) are appealing candidates for this process because of their exceptionally low cost. On the other hand, Lewis acids (e.g., titanium or aluminum salts) offer a broader range of reactivity due to the availability of different metals and oxidation states. This reactivity range may be further tuned through ligand selection. For example, porphyrin-based ligands may be used to generate Lewis acid complexes that are incapable of chelating to the ketoester functionality of DMSS; such Lewis acid complexes may have superior
catalyst turnover kinetics. We will screen both Brønsted and Lewis acids for their ability to catalyze DMSS synthesis under solvent-free conditions.

Once we have identified a suitable catalyst class, we will optimize the reaction conditions such as temperature and catalyst loading. As appropriate, we will also optimize the catalyst structure. As appropriate, we may also investigate using an acid catalyst that has been immobilized onto a solid support in order to run the reaction under heterogeneous conditions; doing so might simplify (or even completely eliminate) any post-reaction processing needed to remove or neutralize the acid.

The proposed research appears straightforward, but lacks literature precedent. It is possible that all prior attempts to develop an acid-catalyzed synthesis of DMSS were unsuccessful. It is also possible that the research has been successfully performed, but the results remain a trade secret. In view of these uncertainties, we are limiting the scope of the proposed research to just the synthesis of DMSS in order to minimize the project cost. However, we hope to later investigate the synthesis of DMT from DMSS. Ketone reduction and subsequent dehydration should yield a cyclic diene. This cyclic diene should readily undergo an aerobic oxidation to yield DMT. Alternatively, if aromatization can be effected under the transfer hydrogenation conditions then DMT might be prepared directly from DMSS. If successful, this would not only shorten the synthetic sequence, but also reduce reductant consumption by 50%.

**Proposed Deliverables.** The following deliverable is expected: an acid-catalyzed, solvent-free synthesis of DMSS from dimethyl succinate.

**Research Facilities.** Organic synthesis space is available to the project. No equipment purchases are needed.

**Timeline and Budget.** The work will be performed by a graduate student research assistant under the guidance of Chen. The projected timeline for this one-year project is shown below. A budget of $48,000 is proposed:

- Graduate student stipend, tuition, and benefits: $40,000
- Chemicals, consumables, and instrument time: $8,000

<table>
<thead>
<tr>
<th>Task and Deliverables</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
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<tbody>
<tr>
<td>Identify preferred catalyst family</td>
<td>X</td>
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<td>X</td>
<td></td>
</tr>
<tr>
<td>Optimize reaction conditions</td>
<td></td>
<td>X</td>
<td>X</td>
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<tr>
<td>Deliverable: reaction conditions</td>
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<td>X</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 1.2 – Towards Biobased Polyethylene Terephthalate (PET)
Principal Investigator(s): Jason Chen
Site: Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested
☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: ____________________________________
1.3 — Development of Biorenewable Thermoplastic Elastomers

Principal Investigator(s): Eric W. Cochran* and R. Chris Williams
Site: Iowa State University

Project Objectives. To date, the Cochran-Williams team has investigated only applications for asphalt modification. The application space of rubbery polymers and copolymers thereof is far more diverse than this, and the primary objective of the present proposal is to further develop the technology towards a material formulation of interest to the Industry Advisory Board (IAB). Example applications include, but are not limited to, adhesives, films, packaging materials, sealants, additives, and/or rubbers. Success will be measured not only through the ability of the developed materials to meet or exceed preexisting specifications, but also the economics of full or partial replacement. The first phase of the project will

- characterize the melt and solid-state requirements for the targeted applications based on preexisting specifications and currently used materials, and the appropriate performance benchmarks will be identified. Physical and chemical requirements will inform the choice of triglyceride composition, level of monomer functionality, comonomer(s), and chain sequence (e.g., statistical copolymer versus block copolymer);
- synthesize a library of candidate biobased materials, with subsequent identification of which formulations are most promising; and
- conduct a techno-economic analysis of the most promising materials.

Industrial Relevance, Need, and Appropriateness for the Center. Societal Level: The proposed research will eventually replace millions of tons of petroleum-based products with biorenewables. New jobs will be created as the technology continues to be transferred to the industry.

Figure 1. Comparison of spot prices for vegetable oils with contract pricing for butadiene, a crucial component of the rubber/elastomer industries. This project will bring to market renewable thermoplastic elastomers that are cost competitive with their petrochemical-based alternatives.
Industrial Level: Industries that apply the Cochran-Williams technologies will benefit economically through lower cost materials and the positive public image from “going green.”

K-12 Outreach: Cochran is PI on a recently awarded (ENG-1406296) RET Site titled, “RET Site in Engineering and Computer Science: Energy and Sustainability—To Develop the Green Collar Workforce for the 21st Century,” that will provide hands-on internships to 13 engineering and pre-engineering teachers each summer. Each summer a number of these teachers will be a part of this and other CB² projects through their internship.

As disclosed in Thermoplastic elastomers via atom transfer radical polymerization of plant oil. U.S. Patent Application 20130184383 A1,¹ Cochran and Williams have developed technology based on controlled free radical polymerization that allows the polymerization of the multifunctional monomers provided by nature into thermoplastic rubbers, which can also be co-polymerized with hard segments such as styrene to form statistical or block copolymers, yielding a thermoplastic elastomer. These materials have similar performance to their petrochemical analogues, but are highly competitive from an economic perspective due to the severe cost escalations of rubbery-industry-critical monomers such as butadiene and isoprene (see figure 1). For this reason, the CB² membership is excited for the opportunity to access this technology and to be able to direct its development to suit their end-use applications.

Experimental Plan. The research team will actively collaborate with member companies to apply our recently developed technologies for converting vegetable oils and other biomass-derived feedstocks to thermoplastic elastomers to serve a product line of interest to member companies. Prior to the initiation of the project, the team, through consultation with the IAB, will select a target application, for example, a particular pressure-sensitive adhesive. The team will gather published data, conduct rheological measurements, adhesion studies, and other work to develop a set of benchmarks the triglyceride-based alternative must meet or exceed. Based on these data, the team will select a triglyceride composition (pure species oil or custom-designed interesterified oil) with a linolenic/oleic/saturate profile with the appropriate level of functionality. The oil will be epoxidized and acrylated to form the soft segment monomer. Three such candidate monomers will be produced. The hard segment monomer will also be fixed early on in the project (e.g., styrene, methyl methacrylate). Each monomer/comonomer will be polymerized into a series, with varying for example the hard segment content and molecular weight. The materials will be evaluated and compared to the application-specific benchmarks. In the last month of the project, the economics of the most favorable formulations will be evaluated, and the data and go-no-go recommendations will be incorporated into the primary deliverable, the final report.

Proposed Deliverables. A final report will include (1) a description of the materials designed for the project and any characterization data thereof, (2) techno-economical evaluation of the most promising biomaterials compared to the current state-of-the-art, and (3) a go-or-no-go recommendation for further commercialization activities. Publications will be withheld until patent filings, if such protection is desired by the CB² membership.

Research Facilities. Cochran and Williams manage a combined 3,000 ft² laboratory space equipped with over 30 feet of hood space for bench-scale chemistry. A 10-L reactor is available for scale-up to kilogram quantities of material as needed, and a 1-L reaction calorimeter may be used for reaction engineering. A full complement of polymer characterization equipment is available including GPC and access to world-class NMR facilities. Thermal characterization (DSC, DTA/TGA), mechanical characterization (rheology: DMA/DSR, Instron), access to a full suite of polymer processing equipment, and structural characterization (electron microscopy, X-ray scattering) are available to the research team in on-campus facilities.
**Timeline and Budget.** The $50,000 budget includes approximately $5,000 for materials and supplies, $15,000 for faculty commitment (approximately 0.75 summer months), and $25,000 for graduate tuition, fringe benefits, and stipend (approximately 6.0 student months), and $5,000 for indirect costs.

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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 1.3 – Development of Biorenewable Thermoplastic Elastomers
Principal Investigator(s): Eric W. Cochran* and R. Chris Williams
Site: Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested
☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Your Name: ____________________________________________________________

Your Organization: _____________________________________________________
THRUST AREA: BIOCOMPOSITES

2.1 — Production of Low-cost Carbon Fiber from Heavy Fraction of Fast Pyrolysis Bio-oil

Principal Investigator(s): Xianglan Bai*, Melissa Montalbo-Lomboy, Robert Brown, Marjorie Rover, and Patrick Johnston

Site: Iowa State University

Project Objectives. In this project, we propose to investigate the possibility of producing low-cost carbon fiber using the heavy fraction of bio-oil from fast pyrolysis of biomass. This provides a cost effective raw-material source for carbon fiber production. If successful, the outcome of the proposed research will provide valuable insights in producing low-cost carbon fiber from renewable resources.

Industrial Relevance, Need, and Appropriateness for the Center. Carbon fiber (CF) is a light-weight material that has superior tensile strength. Because of its unique characteristics advantages, it is popular in many applications. However, its application is currently limited because of its high production cost associated with the price of polyacrylonitrile (PAN), the main precursor of CF. Lignin extracted from biomass feedstock (pulp and cellulosic ethanol industries) could be a renewable alternative of PAN for low-cost CF. Usually this is achieved by mixing large amounts of PAN and/or plasticizer with the lignin to achieve a functional CF precursor but the result is a significantly inferior CF compared to those produced from PAN. These problems are mainly attributed to three-dimensional molecular structure of lignin, which makes it intractable in its unmodified state, and impurities carried over from lignin extraction processes.

Alternatively, fast pyrolysis, a robust and cost effective process that depolymerizes biomass in the absence of oxygen and at moderate temperatures, can be used to generate lignin-derived CF precursors. Fast pyrolysis yields a liquid mixture of sugars, acids, aldehydes, ketones, furans, aromatics, and phenolic monomers known as bio-oil that can be upgraded to biofuels and other biobased products. Bio-oil also contains 20-30 wt% of phenolic oligomers, also called pyrolytic lignin, as products of lignin depolymerization. These viscous, non-volatile molecules are difficult to upgrade to fuels and often cause problems if they are not separated from the other constituents in bio-oil prior to bio-oil upgrading. We have developed technology to separate pyrolytic lignin from other bio-oil constituents as a bio-oil heavy fraction (HF). Our work suggests that HF bio-oil has superior properties to lignin for use as a CF precursor. For example, it has a lower softening point than lignin, facilitating the spinning process of the precursor material during CF production. HF bio-oil also has higher carbon content than lignin, which could be important to improving the yield of CF. Moreover, it contains much lower metal and sulfur content than lignin, an important requirement in high quality CF production. More importantly, it may be possible to convert the phenolic oligomers in HF bio-oil into polymers with the high degree of linearity required to meet the mechanical properties of CF. We hypothesize that using HF bio-oil as a CF precursor will produce better quality and higher yield of CF than is possible with lignin.

Experimental Plan. Task 1. Conduct preliminary test to produce CF from existing HF bio-oil HF bio-oil sample(s) previously produced in our lab from hardwood will be used as raw material to make CF for testing the concept.

Task 2. Produce HF bio-oil from different feedstock at different temperatures Three different biomass feedstocks (for example, red oak, cornstover, switchgrass) will be selected and fast pyrolyzed in a bench scale fluidized bed, with pyrolysis temperatures of 450°C, 500°C, and 550°C, respectively. Bio-oil will be collected
in 3-5 fractions maintained at different temperatures. Only the fractions containing the pyrolytic lignin will be utilized for this project. The HF bio-oil from the pertinent collected fractions of produced bio-oil will be further extracted if needed. HF bio-oil will be characterized using GPC, TGA, FTIR, NMR, CHN, Karl-fisher and ICP for overall molecular weight distribution, volatility, glass transition temperature, the extent of structural alignment, carbon content, moisture content and inorganic impurities. The existing bio-oil will be tested utilizing the same characterization protocol and compared to the newly produced oils.

**Task 3.** Produce CF from HF bio-oil and compare the qualities of final products HF bio-oil samples will be used to produce CF. The performance of the HF bio-oil materials in the three steps of CF processing (spinning, thermostabilization and carbonization) and the qualities of final products will be compared.

**Task 4.** Modify and HF bio-oil and characterize its properties HF bio-oil samples will be modified thermally or chemically prior to CF production and its properties will be characterized.

**Task 5.** Assess the quality of CF produced from modified HF bio-oil The quality of CF produced from modified HF bio-oil will be assessed.

**Task 6.** Conduct techno-economic analysis to assess the cost of CF based on fast pyrolysis Conduct an elementary techno-economic analysis based on the experimental results to determine the production cost.

**Potential risk and mitigation.** The quality of CF from HF bio-oil is unknown, and could be inferior to CF from PAN; in the case, we will mix HF bio-oil with different fractions of acrylonitrile to produce CF.

**Proposed Deliverables.** (1) Existing HF bio-oil is tested for CF production, (2) New HF Bio-oils from different types of biomass and temperatures are tested for CF production, (3) Quality of CF from different HF bio-oil is compared, (4) Structure of HF bio-oil is modified, (5) Quality of CF produced from optimized HF bio-oil is evaluated, and (6) Production cost of CF based on HF bio-oil is determined.

**Research Facilities.** The Biorenewables Research Laboratory has pyrolysis reactors that can produce fractionated bio-oil and a state-of-the-art analytical laboratory. Extruders are available in the bioplastics and biopolymers labs in the Center for Crops Utilization Research.

**Timeline and Budget.** The total proposed budget is $179,156 over three years, $59,934 in the first year. A PhD student in Mechanical Engineering will receive a ½ time appointment each year.

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<td>Structure of HF bio-oil optimized for CF</td>
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<td>Quality of CF from HF bio-oil evaluated</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 2.1 – Production of Low-cost Carbon Fiber from Heavy Fraction of Fast Pyrolysis Bio-oil

**Principal Investigator(s):** Xianglan Bai*, Melissa Montalbo-Lomboy, Robert Brown, Marjorie Rover, and Patrick Johnston

**Site:** Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

**Level of Interest**

- [ ] Very Interested
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Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: _____________________________________
2.2 — Producing Low-cost Lignin Feedstock for Carbon Fiber Production

Principal Investigator(s): Birgitte Ahring* and Samy Madbouly
Site: Iowa State University and Washington State University

Overview. Carbon fibers are currently manufactured from polyacrylonitrile precursors and pitches which are fossil fuel-based. The carbon fibers are used as specialty products in aerospace, automobiles, wind turbines, and other industrial applications. In the transportation sector, these fossil-fuel based carbon fibers have shown to reduce vehicle weight by around 60% while having the disadvantage of significantly higher costs controlled by the current oil economy.1 Biomass lignin has been studied by a number of federal agencies including DOE as a low-cost carbon fiber feedstock. However, these studies have indicated that the unavailability of suitable lignins and high processing costs still significantly plagued the industry. Typical lignin sources such as pulping industries and current cellulosic ethanol production which uses a dilute acid treatment of biomass produces modified or sulfonated lignins which are brittle and unsuitable for carbon fiber production without considerable modification and processing.2 Studies have shown that the primary disadvantage of adding chemicals during the biomass pretreatment process is that lignins after pretreatment and on cooling will redistribute, re-Condense, and form droplets that will adhere to cellulose.3

Project Objectives. In this project, we would like to investigate biomass lignin produced through a novel Wet explosion pretreatment (WEx) process developed by Birgitte Ahring (PI) as low-cost carbon fiber feedstock. This process has been examined in pilot scale and is currently being scaled to demonstration scale for producing low-cost cellulosic sugars. In this process, oxygen is added to the hydrated biomass after heating to set temperatures (150-200°C) followed by flashing of the mixture to atmospheric conditions after the reaction. Initial NMR analysis of wet-exploded biomass lignin have indicated that there was a significant shift in the lignin structure which prevented redistribution and re-polymerization of lignin on cooling after the pretreatment process.4 Scanning electron microscopic measurements of wet-exploded wheat straw also showed a number of small fragments with a loose structure indicating that a more porous structure with an increased surface area was obtained after wet explosion pretreatment5 while hydrothermal pretreatment of wheat straw resulted in a more intact fibrous structure. In the proposed project, carbon fibers will be produced from the wet-exploded corn stover lignin using established protocol at the Department of Materials Science and Engineering at Iowa State University. The wet-exploded lignin as carbon fiber source will be compared with lignin produced from dilute acid pretreatment of the same raw material (corn stover) that is going to be a common lignin type due to the implementation of cellulosic ethanol occurring right now.

Industrial Relevance, Need, and Appropriateness for the Center. During carbon fiber production, lignin (after significant separation and purification) will be reacted with an acid anhydride to produce modified lignin followed by co-polymerization before electro-spinning in order to obtain suitable carbon fiber for the automotive industry (requires tensile strength of 1.72GPa and modulus of 172 GPa). However, the best lignin-based carbon fiber produced to date from biomass lignin has an average strength of 1.07 GPa and modulus of 82.7 GPa with extensibilities of 2.03%. We hypothesize that wet-exploded biomass lignin can outperform existing standards due to its high porosity and surface area compared to technical lignin and would also decrease process costs through reduction in separation and purification operations required to clean technical lignin. The lignin would further be a by-product of sugar production for production of cellulosic ethanol. Washington State University (WSU) has worked closely with CleanVantage, LLC (which holds patents for WEx process) on effective biomass pretreatment to allow easy access to cellulose microfibrils for effective sugar breakdown into second-generation biofuels. The current biorefinery platform
developed by WSU also involves an innovative process that can effectively and economically convert biomass sugars to carboxylic acids such as lactic acid and butyric acid which can be used to modify lignin or can be polymerized and blended with lignin used in carbon fiber production. At Iowa State University, Samy Madbouly has already developed manufacturing standards and protocols for producing carbon fiber from biomass lignin using novel electro-spinning and melt-spinning techniques. The primary goal of the proposed project would be to decrease feedstock cost which amounts to about 51% of the total manufacturing cost of carbon fiber.

**Experimental Plan.** In this process, WEx pretreatment of biomass (corn stover) will be done at temperatures between 170 and 200°C and oxygen loadings between 5 and 7.5%. The biomass lignin obtained will be separated after enzymatic hydrolysis and used for carbon fiber production. Previous studies have indicated that wet explosion pretreatment of many cellulosic biomasses at optimal conditions resulted in a yield of over 90% cellulose conversion to glucose and nearly 100% conversion of hemicellulose to xylose. After enzymatic hydrolysis of the pretreated biomass such as corn stover, the solid fraction will contain up to 90% insoluble lignin. Separation of lignin will be done using alkali treatment. The separated lignin will then be esterified using butyric or acetic acid anhydride to produce modified lignin. This lignin esterification is usually done to increase the miscibility of the lignin with thermoplastic aliphatic ester, reduces its brittleness and increases its flexibility to be made into fibers. The glass transition temperature of the wet-exploded biomass lignin along with its surface methodology will be studied both before and after modifications. Small amount of biobased polymer binders, such as poly(lactic acid) (PLA) or polyamide (PA, tall oil-based resin) (up to 15 wt%) will be melt-mixed with lignin to form carbon fiber mats for further improvement in the fiber stretching and to control the fiber diameter prior to pyrolysis into carbon fiber. Our novel proposed surface modification process will significantly enhance the mechanical properties and improve the processability of lignin-based precursor. Electro-spinning of our modified lignin with a small amount of polyacrylonitrile (PAN) will be also considered in this proposal to reduce the diameter of lignin fibers from microfiber size (melt-spinning) to nanometer scale (electro-spinning), and transform the nano-fibers into flexible carbon fiber mats to be used in carbon fiber reinforced polymer matrix composites (CFRP). The wet-exploded lignin as carbon fiber source will be chemically (surface morphology) and mechanically (tensile strength) compared with lignin produced from dilute acid pretreatment.

**Proposed Deliverables.** Final report including (1) study of wet explosion conditions to obtain optimal lignin structure from lignocellulosic biomass; (2) esterification and blending of lignin to produce carbon fiber precursors; (3) production of carbon fiber mats with high lignin concentration and outstanding mechanical properties; and (4) finally, lignin based carbon fiber will be used to prepare CFRP with an emphasis on understanding their structure-property relationship.

**Research Facilities.** The Washington State University at Tri-Cities operates the Bioproducts, Sciences and Engineering Laboratory fully equipped with biomass research labs, high pressure catalytic reactor rooms, bioprocessing labs fitted with fermentation bioreactors and analytical characterization with capabilities including HPLC, GC-MS and ICS. The WSU-Tricities also operates an off-campus pilot facility along with CleanVantage, LLC which has all necessary equipment for large scale wet-explosion and fermentation of lignocellulosic biomass. The Biopolymers & Biocomposites Research Team at Iowa State University houses various carbon fiber production and testing equipments including twin-screw micro-compounder, fiber spin line, compression molding, universal testing, modulated DSC, dynamic mechanical analyzer, thermogravimetric analyzer, thermo-mechanical analyzer, controlled stress rheometer, and high voltage electro-spinning equipment.
Timeline and Budget. This is a two-year project. The budget is $60,000 per year ($30,000 for WSU and $30,000 for ISU) to pay for graduate student and cover the cost of materials and supplies, testing, and time of the PIs.

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**Level of Interest Feedback Evaluation (L.I.F.E.) Form**

**Project Name**: 2.2 – Producing Low-cost Lignin Feedstock for Carbon Fiber Production  
**Principal Investigator(s)**: Birgitte Ahring* and Samy Madbouly  
**Site**: Iowa State University and Washington State University

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Note: This information will not be divulged during the review.

Your Name: ____________________________

Your Organization: ______________________
2.3 — Sustainable Hydrophilic/Hydrophobic Nanocomposites from Electrospun Poly(lactic acid) Nanofibers, Bacterial Cellulose, and Nanocrystalline Cellulose

**Principal Investigator(s):** Chunhui Xiang* and Nuria C. Acevedo

**Site:** Iowa State University

**Project Objectives.** The objective of this work is to develop sustainable hydrophilic/hydrophobic nanocomposites from poly(lactic acid) (PLA), bacterial cellulose (BC), and nanocrystalline cellulose (NCC). PLA nanofibers will be produced by electrospinning, generating nanofibers with exceptional properties due to their minute diameter and high surface to mass ratio. BC nanofiber membranes will be developed from fermented tea. NCC will be incorporated into the BC culture media and PLA nanofibers to improve the mechanical properties of the BC and PLA nanofiber membranes. The surface chemistry of the nanocomposites will be controlled by adjusting the ratio of hydrophilic to hydrophobic fibers. PLA is a flexible chain, hydrophobic, thermoplastic polymer. Cellulose, however, is a semi-rigid, hydrophilic, non-thermoplastic polymer. The nanocomposites can be used as sponges to selectively absorb chemicals based on their hydrophilic/hydrophobic properties; the small pore size formed between the fibers and the large surface area of the fibers favors the sorption phenomena. The biodegradable nanocomposites can also be used for controlled release delivery of specific ingredients such as pharmaceuticals or agricultural chemicals.

**Industrial Relevance, Need, and Appropriateness for the Center.** Blending and compatibilization technologies using available biobased polymers such as PLA have great potential in industry. The central research questions for this study are how the BC nanofibers interact with PLA nanofibers and NCC, and how this influences the final nanocomposite structure and its mechanical properties. This knowledge will make it possible to tailor hierarchical biobased products with specific functionalities and properties for several industrial applications. For example, agrochemical companies may be interested in the varying hydrophobic/hydrophilic balance of the nanocomposites for their agrochemical applications. The mechanical properties of the nanocomposites. This study will identify the physical characteristics of nanocomposites from two biorenewable and biodegradable polymers and assess the potential of the nanocomposites for agricultural and medical applications.

Various research groups in the CB² have worked on different nanocomposites from casting films, but few have worked on biobased fiber systems. This research would create the potential for collaboration opportunities among CB² members. The project could provide a novel carrier for the controlled release delivery of pharmaceuticals or agricultural chemicals. The nanocomposites could also be used as biodegradable food packaging (e.g., edible food packaging).

**Experimental Plan.**

1. **Preparation of PLA/BC/NCC nanocomposites**

   In this study, nanocomposites will be produced using two different approaches: (1) PLA and PLA/NCC nanofiber membranes will be produced by electrospinning and then the electrospun PLA and PLA/NCC nanofiber membranes will be incorporated on the surface of the bacteria and yeast culture media (fermented tea) to act as a base/foundation for BC nanofiber growth and (2) the BC and BC/NCC nanofiber membranes will be fabricated and used as a collector of the electrospun PLA and PLA/NCC nanofibers. A hot press will be used to improve the blending and compatibilization of the BC/PLA/NCC nanocomposites.
2. Characterization of PLA/BC/NCC nanocomposites

The PLA/BC and PLA/BC/NCC nanocomposites will be characterized by the following methods:

- Structural properties: Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) will be used to examine the morphology of the nanocomposites. X-ray patterns of the nanocomposites will be analyzed using a powder X-ray diffractometer.
- Performance: Water contact angle and water/oil absorbency will be measured using a Tensiometer (KSV Sigma 701).

3. PLA/BC/NCC applications: Selective absorbency of chemicals and controlled release of model chemicals (Rhodamine B).

The PLA/BC/NCC nanocomposites will act as a sponge to selectively absorb chemicals. Rhodamine B will be used as the model chemical to demonstrate the controlled release delivery mechanism offered by the nanocomposites.

Proposed Deliverables

1. Develop nanocomposites with various hydrophilic/hydrophobic behaviors.
2. Characterize the morphology, mechanical properties, and functionality of the nanocomposites developed.
3. Investigate the selective absorbency and controlled release delivery of chemicals by the nanocomposites.

Research Facilities. The key equipment needed for this project to evaluate the hydrophilic/hydrophobic properties of the nanocomposites is a Tensiometer (KSV Sigma 701), which measures the force on a sample being pulled through a fluid/fluid interface to measure surface or interfacial tension and dynamic contact angle.

Timeline and Budget

<table>
<thead>
<tr>
<th>Tasks</th>
<th>2015</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>Fabrication of PLA &amp; PLA/NCC, and BC &amp; BC/NCC nanofiber mats</td>
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<tr>
<td>Formation of PLA/BC/NCC nanocomposites</td>
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<tr>
<td>Characterization of nanocomposites</td>
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<tr>
<td>Measure the selective absorbency and study controlled release of chemicals from nanocomposites</td>
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<tr>
<td>Writing up manuscripts and external funding proposals</td>
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<td>FY 15 Base</td>
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<td>Total Salaries</td>
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<td><strong>BENEFITS</strong></td>
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<td>Total Benefits</td>
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<td>Materials and Supplies</td>
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<td>Characterization</td>
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<tr>
<td>Equipment (Tensiometer KSV Sigma 701)</td>
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<td>Other (travel, other direct costs)</td>
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<td>Total Other Direct</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 2.3 – Sustainable Hydrophilic/Hydrophobic Nanocomposites from Electrospun Poly(lactic acid) Nanofibers, Bacteria Cellulose, and Nanocrystalline Cellulose  
**Principal Investigator(s):** Chunhui Xiang* and Nuria C. Acevedo  
**Site:** Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

**Level of Interest**

- [ ] Very Interested  
- [ ] Interested  
- [ ] Interested with Change  
- [ ] Not Interested  
- [ ] Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: ______________________________________
THRUSTR AREA: BIOBASED PRODUCTS

4.1 — Mechanochemically Activated and/or Functionalized Cellulose Powders and Their Reinforced Plastic Compounds for More Demanding Applications

Principal Investigator(s): Michael P. Wolcott*, Jinwu Wang, and Jinwen Zhang
Site: Washington State University

Project Objectives. The overall objective is to develop a form of cellulose with an enhanced metering capability that can be well dispersed into matrices to make high-performance cellulose modified composite materials for demanding applications. Specifically for the present proposal: (1) to develop a process to simultaneously and cost-effectively pulverize, activate (breaking up hydrogen bonds), and functionalize (derivatize hydroxyl groups) fibrillar wood pulp to produce a series of property-tuned meterable cellulose powders; (2) to formulate and extrude the compositions of polymers, cellulose powders, and other additives and process aids into pellets of cellulose reinforced compounds; and (3) to injection mold the pellets into test specimens of cellulose reinforced composites and characterize them morphologically, thermo-mechanically, and by yellowness index.

Industrial Relevance, Need, and Appropriateness for the Center. Wood cellulosic material, in the forms of wood flour, wood pulps, regenerated cellulose fibers (rayon & lyocell), microcrystalline cellulose (MCC), nanocellulose (cellulose nanofibrils–CNFs & cellulose nanowhiskers - CNWs), has been intensively investigated for use as a reinforcement for polymer composites in the past decades. The PIs have helped commercialize wood flour reinforced plastic composites (WPC) for roofing and decking materials. The success of WPC commercialization is built on its comparatively low wood flour cost and functions as the filling rather than reinforcing properties of cellulose. Using high-purity cellulose other than wood flour will open up a variety of new possibilities. However, cellulose fiber and nanocellulose reinforced composites have been constrained by difficulties in achieving a good dispersion in matrix and strong interface between the cellulose and the matrix. The strength and strain at break often decrease with increasing the cellulose content indicating induced brittleness. The removal of the lignin, hemicelluloses and extractives in pulping, bleaching, and other separation processes causes the cellulose fibrils to aggregate and form tight structures in drying due to restructured hydrogen bonds between hydroxyls of cellulose chain. Extrusion itself cannot break them up by dispersive and distributive forces due to the low decomposition temperature of cellulose. Grinding dried aggregated nanocellulose is necessary for good dispersion. The question concerning nanocellulose is that why should anyone want to go through an energy-intensive isolation of cellulose fibrils and crystals in a dilute consistence and again grind them after drying? In considering these factors, we suggest that wood pulps composed mainly of cellulose be subjected to mechanical or mechanochemical activation with selected chemicals to prepare surface-activated cellulose powders through ball-milling for reinforcements. The advantage of the mechanochemical activation and modification is the reduced solvent consumption, or complete elimination of the solvent, thus eliminating the need for energy-intensive drying. The utility of mechanochemical modification has been tested in previous literature. Maleated polyolefin was grafted on the surface of cellulose particles by ball milling yielding improved composites. Surface-acetylated cellulose powder was prepared by milling acetic anhydride and wood pulp resulting in improved composites. The combination of dry mechanical activation and/or mechanochemical modification will result in fruitful information,
which will enable the industry members to design scalable processes to commercialize cellulose reinforced composites. Further, prepared cellulose powders may find applications as thickeners, binders, film formers, and water-retention agents for construction products.

**Experimental Plan.** Loose dry softwood Kraft pulp, used as a model cellulose, will be processed to several different cellulose powders by a ring and puck vibratory mill and planetary ball mills under designed conditions. Firstly, chemically unmodified cellulose powders will be prepared by grinding pulp to the different particle size and crystallinity. Secondly, chemically modified powders are prepared by co-milling with chemicals, so-called mechnochemistry. Several potential chemistries of cellulose functionalization will be scoped and screened. Carboxymethylation and oxidation are two routes of adding ionic groups on the surface of cellulose. Esterification and silylation of cellulose hydroxyls will render cellulose more hydrophobic and reduce agglomeration in hydrophobic polymer matrices. Maleic anhydride polypropylene (MAPP)-grafted cellulose powders will be prepared by co-milling cellulose pulp and MAPP pellets and used as the master batch to improve cellulose dispersion and interfacial adhesion in PP-based composites. Model polymers will be selected to test cellulose powder reinforcing ability. Application is expected to extend to other matrices such as mineral and bituminous products. Polyvinyl alcohol is a hydrophilic polymer compatible with mechanically activated amorphous cellulose by forming hydrogen bond between hydroxyls across the cellulose-matrix interface. Polylactic acid and polypropylene are hydrophobic polymers, which may be compatible with surface hydrophobized cellulose powders. Additives functioning as compatibilizer or plasticizer, such as polyethylene glycol or an anionic surfactant, will be identified to improve overall workability. The formulations are extruded, pelletized and injection molded into test specimens. The resulting cellulose reinforced materials will be characterized to see how different variables affect the composite's properties and formulations and processing conditions will be optimized. For comparison, cellulose reinforced composites with commercial available MCC, CNFs, and CNWs will be fabricated to compare the reinforcing ability of the cellulose powders and nanocellulose.

**Proposed Deliverables.** Cellulose powders and cellulosic reinforced compound pellets, which can be distributed to the industrial members for evaluation, and documents: a MS thesis or report, a conference poster and/or presentation, and two referred publications, which describe (1) powdered cellulose preparation, energy consumption, and powder characteristics (size, size distribution, surface area, and crystallinity, viscosity and ash content); (2) mechnochemical preparations of powdered cellulose derivatives and characterization; (3) formulation, compounding, and characterization of cellulose reinforced compounds (pellets); and (4) injection molding conditions and characteristics of cellulose reinforced composites (specimens).

**Research Facilities.** Access to the Composite Materials and Engineering Center and on a fee-for-service base to the Analytical Chemistry Service Center of the WSU Biological System Engineering Department. Key equipment needed for the proposed project is already in place: Rocklab vibratory ring and puck mill, three Across International Ball Mills (4x100 ml, 4x500 ml, 4x5000 ml grinding jars and balls made from various materials), Malvern Mastersizer 3000 particle size analyzer, Malvern Pharma Vision Systems Sample Preparation Device SPD1300 for powder dispensing, TriStar II Surface Area and Porosity Analyzers, and Rigaku, Miniflex 600, x-ray powder diffractometer. Plastics research: Leistritz ZSE-18mm parallel twin screw extruder with a pelletizer, Brabender CWB TSE 20/40 EC Twin Screw Extruder, Sumitomo SE 50D 50-ton injection molding machine, and spectrophotometer.

**Timeline and Budget.** $79,028 includes two-year funding for a graduate student (Stipend: $38,603 and Benefits $30,586), Cellulose and chemicals ($2,000), CMEC and ACSE service fees ($1,500), and travel to conferences ($1,500).
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<tr>
<th>Task</th>
<th>Year 1</th>
<th>Year 2</th>
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<tbody>
<tr>
<td>Powdered cellulose, preparation, and characterization</td>
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<tr>
<td>Powdered cellulose derivatives, synthesis, and characterization</td>
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<tr>
<td>Cellulosic reinforced compounds (pellets), formulation, and formation through melt extrusion compounding</td>
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<tr>
<td>Cellulose reinforced composites (specimens), injection molding, and characterization</td>
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<tr>
<td>Data reduction and deliverable preparation</td>
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</table>
Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 4.1 – Mechanochemically Activated and/or Functionalized Cellulose Powders and Their Reinforced Plastic Compounds for More Demanding Applications

**Principal Investigator(s):** Michael P. Wolcott*, Jinwu Wang, and Jinwen Zhang

**Site:** Washington State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

**Level of Interest**

- [ ] Very Interested
- [ ] Interested
- [ ] Interested with Change
- [ ] Not Interested
- [ ] Abstain (Outside my group’s ability to evaluate)

**Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.**

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: _____________________________________
4.2 — Pyrolytic Lignin-polyester-based Hot-melt Adhesives and Sealants

Principal Investigator(s): Armando G. McDonald* and Karl Englund
Site: University of Idaho and Washington State University

Project Objectives. To develop and demonstrate industrial biobased hot-melt adhesives for use in composite materials. The project is focused on making biobased adhesives with no volatile organic compounds (VOC) emissions from pyrolytic lignin (PL). The novelty of the proposed project is the utilization of lignocellulosic constituents and other biobased building blocks to make hot-melt adhesives. The proposed research integrates advances in biomass conversion/fractionation technologies and polymer chemistry to make the adhesives. The proposed project objectives are: (1) isolation of PLs from wood pyrolysis bio-oil; (2) synthesis of polyester prepolymer and reaction with PL to produce PL-polyester hot-melt adhesives; and (3) performance evaluation of PL-hot-melt adhesives on wood veneer substrates.

Industrial Relevance, Need, and Appropriateness for the Center. This project will establish the viability of utilizing biomass-derived PL and chemical building block streams to produce VOC-free hot-melt adhesives from domestically produced feedstocks (e.g. wood). In addition, this new hot-melt adhesive system will be evaluated in composite and packaging applications. The research will also result in the development of a renewable resource, biobased chemical economy for the United States, and will ultimately provide new rural businesses and markets for these bioproducts.

Experimental Plan. We aim to produce biobased linear polyester prepolymer (~1000 g/mol) by melt condensation and then subsequent co-condensation reaction with PL to form PL-copolymers. Properties will be tuned by a combination of modification in PL fractionation and functionalization, polyester composition and molar mass (diacid+diol or hydroxyacid, lactic acid), and by PL content.

1. PL will be isolated from bio-oil produced from our ½ ton/d pilot reactor and functionalized.
2. Polyester prepolymer will be prepared using two approaches: (1) lactide will be partially polymerized by melt condensation in a vacuum chamber at 130°C to form the prepolymer and (2) a mixture of adipic acid (C6) (or sebacic acid (C10)) and 1,4-butanediol (BDO) will be melt condensed at 150°C at 120 mm Hg to create the polyester prepolymer. The reactions for 1 and 2 should proceed to form a viscous liquid and not a gel in order to obtain good solubility/dispersability with PL for subsequent copolymerization. A series of prepolymer will be made using a design of experiments approach to evaluate the influence process variables on properties (viscosity, molar mass).
3. PL will be dispersed in the polyester prepolymer. The highly viscous mixtures will be transferred to a prepared aluminum pan and placed into vacuum oven at 80°C to remove residual moisture. Then the reaction temperature increased to 120°C at 650 mm Hg, and the reaction proceeded for 40 h to obtain the PL-copolyester hot-melt adhesives.
4. The PL, precursor, and PL-copolyester will be chemically, mechanically, and thermally characterized by a combination of FTIR spectroscopy, GPC, ESI-MS, TGA, TMA, DSC, DMA, mechanical tests, and rheology. The criteria for acceptable resins will be based not only on their adhesive performance but also their process-ability. Lap shear tests will be used to assess bonding. Laminated composites will be manufactured using straight grain maple veneers. The manufactured composites will be evaluated for flexure and internal bond strength along with durability tests when exposed to moisture and thermal changes.
Proposed Deliverables.

- Prepare adhesive precursors (PL and polyester prepolymers) and determine properties.
- Prepare PL-polyester hot-melt adhesives and determine properties.
- Manufacture fully biobased laminate composites and assess performance.

Research Facilities. McDonald/Englund have a combined laboratory facilities with the necessary equipment/instruments to undertake this research. A ½ ton/d pyrolysis unit is available for the production of bio-oil and subsequent PL. A series of reactors 50 ml to 1000 ml are available for polymer preparation. Both labs have a full suite of polymer characterization tools available (GCMS, FTIR, ESI-MS, GPC, DSC, TMA, DMA, TGA, rheometers, MFI, Instron test machines, optical microscopes, contact angle, xenon-arc weatherometers) and materials processing facilities (extruders, injection molders, hot-presses, mills, etc). On campus facilities include, SEM, TEM, x-ray diffraction, XPS, and NMR.

Timeline and Budget. The $60,000 per year (for two years) budget includes in year one approximately $15,000 for materials and supplies and lab fees, $35,000 for graduate tuition and stipend, $5,000 for undergraduate irregular help, and $5,000 for indirect costs. One graduate student (MS) and one undergraduate student are needed for the proposed project. The MS student will work on the synthesis and characterization of PL-polyester hot-melt polymers. The undergraduate will prepare the pyrolysis bio-oil, fractionation of the PL material, and characterization of the PL for the project. The following Gantt chart summarizes the project timeline.

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<th>5-8M</th>
<th>9-12M</th>
<th>13-16M</th>
<th>17-20M</th>
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<td>PL isolation and characterization</td>
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<td>PL-copolyester synthesis</td>
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<td>3 PL-copolyester adhesive evaluation</td>
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<td>MS thesis and publications</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 4.2 – Pyrolytic Lignin-polyester-based Hot-melt Adhesives and Sealants
Principal Investigator(s): Armando G. McDonald* and Karl Englund
Site: University of Idaho and Washington State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested

☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: ______________________________________
**4.3 — Technical Evaluation of Cellulose-based Plastic Composite Materials**

**Principal Investigator(s):** Samy Madbouly* and Melissa Montalbo-Lomboy

**Site:** Iowa State University

**Project Objectives.** Biobased polymers and composites have received extensive attention as sustainable alternatives to petroleum-based composites for a wide range of applications, such as textiles, resins, and rigid or flexible foams. Applications that use biobased polymers/composites include food containers, waste bags, packaging, and agricultural plastics. Efforts to replace petroleum-based polymer composites are motivated by environmental, social, and economic issues. The main objectives of this proposal are to prepare and characterize novel biobased composites from natural cellulosic fiber (e.g., corn stover, corn fibers, and switchgrass) and biobased polymer matrix (e.g., PLA, PHA, bio-PA) with improved morphology, physical, mechanical, and thermal properties. Mixing cellulosic fiber with a biobased polymer matrix can significantly enhance the mechanical properties and reduce the material cost. The development of biobased polymer/cellulosic fiber composites with the desired property enhancements are often determined by the degree of interaction and the interface between the cellulosic fiber and the polymer matrix. The surface of cellulosic fiber has hydroxyl groups that allows chemical modification to enhance the interaction and improve the interface between cellulosic fiber and the polymer matrix. Therefore, in the case of poor compatibility between cellulose fiber and polymer matrix, the surface of cellulosic fiber will be modified and functionalized prior to mixing with a polymer matrix through acetylation or silane coupling agents. Based on these chemical modifications, the surface of cellulose fiber will be functionalized with more reactive group such as amine end groups.

**Industrial Relevance, Need, and Appropriateness for the Center.** Glass and carbon fibers are common types of fibers widely used in polymer matrix composite production. Glass fiber is inexpensive and has adequate strength, stiffness, and high failure strain, but the density is very high and the composites tend to have fatigue failure. In contrast, carbon fibers are relatively expensive but have excellent mechanical properties and low densities. Cellulosic fibers can be obtained with relatively low cost and have comparable density to that of carbon fiber and good mechanical properties. The reduction in cellulosic composites compared to glass fiber composites offer the adoption of biobased polymer composites in aerospace, automotive, and turbine blades productions. In addition, this makes the final products more eco-friendly. This project can play a critical role in developing new, high-value cellulosic fiber and biobased polymer composites products that greatly enhance U.S. competitiveness in the fast-growing global market for multifunctional advanced biomaterials and their use in different applications.

**Experimental Plan.** Different natural cellulosic and lignocellulosic fibers will be considered in this project. The surfaces of cellulosic fiber will be modified and functionalized using acetylation and silane coupling agents. The surface chemistry on the cellulosic fiber surface will be characterized by Fourier-transformed infrared spectroscopy (FTIR) and mechanical testing. The best modification method based on hydrophilic functional groups and the mechanical and physical properties of polymer composites will be identified. Different commercially available biobased polymers, such as PLA (NatureWorks LLC), PHA (Metabolix Inc), and PA (Arizona Chemical Inc) will be used in this project. Compounding will be completed using a twin-screw extruder (Leistritz Micro18, L/D ratio 30, American Leistritz Corp., Somerville, NJ) to produce plastic extrudate that will then be pelletized with a pellet mill (Scheer Bay Inc. WI). The temperature profile during extrusion will be identified for the different composites. Compression and injection molding will be used to prepare composite films and dog-bone specimens for characterization. Differential scanning calorimeter (DSC) measurements will be used to evaluate the Tg temperature and crystallization behavior of various
cellulosic fiber polymer composites. The DSC measurements will be conducted using a TA Instruments Q2000. The dynamic mechanical analysis (DMA) measurements will be performed on a Q800 DMA from TA Instruments in tensile mode. The thermal stability of different fiber composites will also be studied using a Q50 thermogravimetric analyzer (TA Instruments, New Castle, DE) under nitrogen and oxygen atmospheres. The ultimate mechanical properties will be studied using an Instron universal testing machine to measure the tensile and compressive strength of the fiber composites following standard ASTM methods. The morphology of the fiber composites will be investigated using scanning electron microscopy (SEM). The SEM will be observed using a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250, ISU) operating at an acceleration of 3-10 kV under high vacuum. The viscoelastic behavior of the biobased cellulosic fiber polymer composites will be investigated using a controlled stress/strain rheometer (TA Instruments ARES-G2) with 25 mm diameter parallel plates. All measurements will be performed under very accurate thermal conditions (±0.1 K) using an air/N₂ gas convection oven designed with twin element heater guns, a barrel-shaped chamber, and three internal platinum resistance thermometers (PRT) for optimum temperature stability.

**Proposed Deliverables.** (1) Develop fiber pretreatment procedures, formulations and processing conditions for producing high-value biorenewable cellulosic fiber/polymer composites with enhanced benefits compared to petrochemical composites. (2) Surface modification of cellulosic fiber and composite processing conditions will be developed as needed to maximize biobased polymer composite performance. (3) Evaluate overall suitability of cellulosic fiber/polymer composites as low cost sustainable materials for replacement of petrochemical plastics. (4) A database of cellulosis fiber/polymer composite properties will be available for industrial partners, including processing, rheological behavior, morphology, thermal, and mechanical properties.

**Research Facilities.** The facilities and other resources available to the PIs include everything needed to undertake and complete the proposed research project successfully (please see the experimental plan section). This project can play a crucial role for developing new, high-value-added biobased polymers that will greatly enhance U.S-industrial competitiveness in the fast-growing global market of advanced bioplastics. The project involves collaboration between the Materials Science and Engineering Department and Agricultural and Biosystems Engineering Department at Iowa State University. The PI and Co-PI have expertise and extensive experience in biobased polymers and composites, rheological property, characterization and analysis, synthesis and processing, and materials structure and property relationships.

**Timeline and Budget.** This is a two-year project. The budget is $60,000 per year to hire one graduate student and cover the cost of materials and supplies, testing, and one month salary for each PI.

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<th>Task</th>
<th>Year 1</th>
<th>Year 2</th>
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<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
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<tr>
<td>Surface modification and functionalization of cellulosic fibers</td>
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<tr>
<td>Processing of biobased polymers (PLA, PHA, or PA) with the surface modified cellulosic fiber</td>
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<tr>
<td>Characterization of the biobased cellulosic fiber/polymer composites using different techniques</td>
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<tr>
<td>Identify new industrial applications for the biobased cellulosic fiber/polymer composites</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 4.3 – Technical Evaluation of Cellulose-based Plastic Composite Materials  
**Principal Investigator(s):** Samy Madbouly* and Melissa Montalbo-Lomboy  
**Site:** Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

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**Level of Interest**

- [ ] Very Interested  
- [ ] Interested  
- [ ] Interested with Change  
- [ ] Not Interested  
- [ ] Abstain (Outside my group’s ability to evaluate)

**Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.**

Provide any comments about this project here.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: _____________________________________
4.4 — Development of a Life Cycle Assessment Tool for Screening of Trade-offs among Processing Costs, Environmental Impacts, and End-of-life Options

Principal Investigator(s): Kurt A. Rosentrater*, David Grewell, Darren Jarboe, and James Schrader

Site: Iowa State University

Project Objectives. The last decade has seen an explosive growth in the use of biology to transform various agricultural resources into fuels, chemicals, and industrial materials. Most research and development efforts have focused on raw material processing, conversion processes, and end-use functionality/performance. Very little work has been done to determine costs, environmental impacts, or end-of-life options for biobased materials. Further, the industry needs a tool, which can rapidly assess these at the beginning stages of commercialization, to help guide development efforts. This project will develop a tool to estimate the eco-profiles of a variety of biobased and biodegradable plastic materials for use at early stage development in order to better understand the impacts of manufacturing and using bioplastics and biocomposites. This tool will be used to estimate production costs, use costs, greenhouse gas emissions/offsets, biodegradability at end-of-life, and best end-of-life options.

Industrial Relevance, Need, and Appropriateness for the Center. This industry is growing in response to high petroleum prices as well as environmental concerns regarding widespread use of conventional polymers. The tool developed will give industry partners a way to compare costs, energy demands, environmental impacts, and end-of-life options for biomaterials. It will also help industry further differentiate biobased products from other products, allowing them to gain further market penetration. The tool will aid technology commercialization efforts by helping identify specific modifications for a bioplastic to improve its environmental performance, both in terms of manufacturing as well as throughout the entire life cycle. Member companies will have access to biobased material performance data and the model, allowing them to make educated decisions on material selection, part design, and processing. This will help them reduce costs and to improve the environmental performance of their products.

Experimental Plan. In order to understand the environmental impacts and sustainability of bioplastics and biocomposites being developed by members of the CB², we will use a multi-tier life cycle assessment LCA approach. First, we will model specific manufacturing systems for a variety of bioplastics. We will:

1. develop thermo-mechanical models that will allow the mechanical, thermal, and processing performance of bioplastics to be normalized to petrochemical plastics. The models will be based on existing thermo-mechanical properties provided by center partners, other material suppliers, and databases such as Material Data Center (a database containing 500 bioplastics produced by M-Base);

2. develop processing models that will allow flow and processing characteristics of bioplastics to be normalized to petrochemical plastics. These will include constraints such as maximum flow path distances and minimum wall thicknesses. Again, the models will be based on existing data as well as data produced by our partners; and

3. develop geometric constraint models that will allow dimensional tolerances and recommended geometries to be normalized to petrochemical plastics. This will include recommendations on minimum radii and addition of stiffness features as well as recommended draft angles.
Second, we will model the broader life cycle for each bioplastic, not just the manufacturing stage. This broader analysis will consist of a cradle-to-grave approach and will examine every step of the life cycle, including extraction of raw materials from the earth (i.e., cradle), processing these materials into a product, use of that product by consumers or other end users, and then disposal/recycling of any wastes, including the product itself, at the end of its useful life (i.e., the grave). This will include compostability and biodegradation. We will also include analysis of energy use, water use, greenhouse gas emissions (CO₂, NOₓ, CH₄), and costs throughout the life cycle.

Third, we will determine what physical or processing changes are needed for a given bioplastic to achieve the same performance as a traditional petroleum-based plastic as well as cost and environmental impacts. To accomplish these, we will develop a rules-based artificial intelligence system using the above detailed models to determine the normalized material/processing requirements to produce parts from bioplastics that have the same performance and processibility as petrochemical-based plastics. We will calculate environmental and cost trade-offs necessary to achieve this performance.

**Proposed Deliverables.** An encrypted web-based simulation tool that member companies can access by password will be created. This system will house material data, performance data, end-of-life (including compostability and biodegradation) data, and cost data. The custom life cycle assessment (LCA) system can be used to provide estimates of costs and environmental impacts, and will propose steps required for a given bioplastic to achieve similar cost/performance to traditional petroleum-based plastics.

**Research Facilities.** Researchers at ISU have already worked with M-Base to develop an initial database, which allows users to examine costs and CO₂ emissions for products produced from bioplastics and petrochemical plastics. We will incorporate this database into our online LCA system. To accomplish this, we will have to develop custom computer/database programs. We will purchase two computers and various computer programs, but no other durable goods will be purchased during this project.

**Timeline and Budget.** An encrypted web-based simulation tool that member companies can access by password will be developed. This system will house material data, performance data, end-of-life (including compostability and biodegradation) data, and cost data. The custom LCA system will be used to provide estimates of costs and environmental impacts and will propose steps required for a given bioplastic to achieve similar cost/performance to traditional petroleum-based plastics.

**Proposed Budget** $53,116

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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 4.4 – Development of a Life Cycle Assessment Tool for Screening of Trade-offs among Processing Costs, Environmental Impacts, and End-of-life Options

Principal Investigator(s): Kurt A. Rosentrater*, David Grewell, Darren Jarboe, and James Schrader

Site: Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested
☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.

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Note: This information will not be divulged during the review.

Your Name:  

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Your Organization:  

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4.5 — Understanding Consumer and Industry Perceptions of and Willingness to Pay for Bioplastic Products

Principal Investigator(s): John Beghin* and Erin MacDonald

Site: Iowa State University

Project Objectives. The objectives of this project are to (1) understand consumer and business-to-business (B2B) perceptions of bioplastics within broader contexts such as sustainability, eco-friendliness, and green attributes; (2) estimate consumers’ willingness to pay (WTP) for bioplastic products under various scenarios and other valuations such as “warm glow” effect on brand; and (3) explore the motivations of companies to include (or not include) bioplastics in their products and how they are marketed to their customers. The outcome of this work will be reports based on survey results: one focused on end consumers and another focused on B2B sales, where product manufacturers are the customers. CB2 members will have access to aggregations of raw survey data for their own use. If successful, this project will aid bioplastic raw material producers and consumer goods manufacturers in determining price points, marketing messages, and appropriate material choices and blends. If extended, this project will be able to track the shift in perceptions and valuation of bioplastics over time.

Industrial Relevance, Need, and Appropriateness for the Center. Perception and willingness-to-pay (WTP) studies for bioplastics are few. With any new product or material, it is useful to gauge consumer and industry understanding and valuation. The members of the CB2 represent a variety of stakeholders in the bioplastic manufacturing supply chain, but each has a “customer” whose needs must be met. Additionally, all stakeholders face challenges in effectively pricing their products. It is difficult to understand, at this early stage, whether bioplastics offer a value-added that consumers (and businesses) have a WTP a premium for. Therefore, it will be useful to understand perceptions of bioplastics and how these perceptions are related to potential monetary gains. Positioning bioplastics as “sustainable,” “green,” and/or “eco-friendly” is complex. It is likely that not all bioplastics are alike in the eyes of the customer, yet little is known about differences in perception. In some product categories there may be a “green enough” heuristic, whereas in others there may be a specific WTP for bioplastics.

The types of questions this study will explore include: **Sustainability:** What does sustainability (and related terms) mean to the customer? Is sustainability a brand attribute for a product portfolio or a specific product attribute irrespective of the brand? Are bioplastics closely related to this meaning? Is it important/economically advantageous that a bioplastic be compostable as well as composed of plant material? Is it acceptable as sustainable if bioplastics are incinerated as part of “energy recovery?” What percentage of a plastic product must be bioplastic in order for the whole product to be considered sustainable? Is it important that the bioplastic processing procedure exclude the use of toxic chemicals, even if none are left in the final product? **Labeling and Appearance:** Is it important that the products look “natural” or that they are differentiated from other plastic products? Is labeling recognized and trusted? **Value (utility):** Do businesses and consumers have a WTP a premium for bioplastic content and under what conditions? Is this a sliding-scale premium, where they will pay more for higher bioplastic content? Do different departments within a business value bioplastics differently, and if so, how are differences resolved?

Experimental Plan. The project consists of the design, refinement, administration, analysis, and report of three online surveys. Consumer survey 1 is directed at consumers and administered using Amazon Mechanical Turk. Consumer survey 2 is similar to survey 1, but administered instead via a survey hosting company, such as Harris Interactive, Gongos, or Luth Research. This smaller, yet more expensive survey will
allow for controlled populations and reliability testing. The B2B survey is directed at manufacturers that use or could use bioplastics in their products. The consumer survey will have multiple conditions. Both of the consumer surveys and the B2B survey will include a variety of question types, including choice, sliding scale, and write-in response.

**Design:** There will be an information collection period in which the members can provide input to direct the scope of the surveys. Depending on the level of interest, this input can be collected via in-person meetings, phone calls, and/or e-mails. Target products for the consumer survey will be selected. Examples include: packaging, small disposable consumer goods, and vehicles. Then, draft surveys will be created in Qualtrics and sent to CB² members to collect feedback on specific questions. Sample responses will be compiled and analysis procedures verified. Statisticians and colleagues will be consulted to ensure the validity of the experimental method. ISU Institutional Review Board (IRB) approval will be obtained.

**Refinement:** During the refinement stage, pilot versions of the survey will be sent to a small subset of consumers and businesses. The first iteration will happen in-person, to query respondents on impressions afterward. The second iteration will occur online using survey hosts and manufacturer interviews. Surveys will be refined based on these initial results.

**Administration:** Consumer survey 1 will be administered via Amazon Mechanical Turk. Consumer survey 2 will be administered via a survey hosting company (e.g., Luth Research). The co-PI has used both services before. Bucket targets will be identified to ensure a good variety of consumer types by demographics, locations (U.S. distribution), and type of green consumer. For the B2B survey, the launch procedure will be more complex. The survey is more open-ended and will require an interview-like procedure. A list of target companies and contacts will be compiled. The CB² members will assist by providing potential contacts, who will be contacted by phone and/or e-mail, to request participation in the survey. Responses may be collected by phone and e-mail depending on the respondent’s preference. B2B survey data collection can occur at professional conference venues.

**Analysis:** For quantitative data: typical statistical approaches such as compilation of percentages, analysis of variance (ANOVA), and logistical regression will be used, for example, to predict the socio-economic determinants of WTP. For qualitative data: compilations for themes, analysis of language, and direct quoting will be used to draw useful generalizations.

**Proposed Deliverables.** The analyses will be compiled into three sub-reports of findings on consumer and B2B perceptions and motivations and associated WTP: two regarding consumers and one regarding B2B transactions, and one final report. CB² members will also receive aggregated raw survey data. The survey(s) will remain “live,” and can be used to track changes in perceptions and valuations over time (pending funding for continued data collection and analysis). See also the section below on duration and milestones.

**Research Facilities.** Existing computer resources and software are the only resources needed at ISU.

**Timeline and Budget.** The Gantt chart below naturally follows the same sequence of milestones as the three surveys. Consumer survey 1 is directed at consumers and administered using Amazon Mechanical Turk. The first report is the deliverable for the summer of year 1 one of the project. Consumer survey 2 is similar to Consumer survey 1, but administered instead via a survey hosting company, such as Harris Interactive, Gongos, or Luth Research. This smaller, yet more expensive survey will allow for controlled populations and reliability testing. By fall of year 2 (Fall 2015) we expect the report on the Consumer survey 2 survey to be ready. The B2B survey is directed at manufacturers that use or could use bioplastics in their products. By the end of spring 2016, we expect to report on the B2B survey findings. The consumer survey will have
multiple conditions. Both of the consumer surveys and the B2B survey will include a variety of question types, including choice, sliding scale, and write-in response. The final report is expected to be ready in summer 2016.

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The total budget is $71,211. It includes two-year funding for a graduate student ($59,211), survey-hosting services ($9,000), Mechanical Turk fees ($1,500), and travel to conferences to collect B2B participant information ($1,500). The fall 2014 starting date is negotiable. The timeline of stages and deliverables is explained for the three surveys in the Gantt chart above with completion expected in summer 2016.
Level of Interest Feedback Evaluation (L.I.F.E.) Form

**Project Name:** 4.5 – Understanding Consumer and Industry Perceptions of and Willingness to Pay for Bioplastic Products

**Principal Investigator(s):** John Beghin* and Erin MacDonald

**Site:** Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization's level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

**Level of Interest**

- [ ] Very Interested
- [ ] Interested
- [ ] Interested with Change
- [ ] Not Interested
- [ ] Abstain (Outside my group’s ability to evaluate)

**Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.**

Provide any comments about this project here.

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Note: This information will not be divulged during the review.

Your Name: ____________________________________________________________

Your Organization: ______________________________________________________
4.6 — Development of Biobased VOC-free Powder Coating Resin Systems

PI and Co-PIs: Jinwen Zhang* and Shyam Sablani
Site: Washington State University

In this work we propose to develop biobased powder coatings including epoxy, polyester-epoxy hybrid, and polyurethane powder coating resins using rosin and dipentene as feedstocks. We will collaborate with the Powder Coating Research Group, a member of CB2, in this research exploration. In recent years, Zhang’s group has conducted a significant amount of fundamental investigation on use of rosin, dipentene, and other natural chemicals as building blocks in synthesis of epoxies and other thermosetting polymers. The work proposed here is within the continuum of research that is being pursued by the PIs, but it does not overlap with what have been accomplished. Instead, it will greatly benefit from what we have learned and make an extension to a specific application – powder coatings.

Project Objectives. The long-term goal of the proposed research is to develop a viable technology that replaces or partially replaces petroleum-based powder coating resins with biobased counterparts. Specifically, the overall objective of this application is to demonstrate that some natural cyclic compounds are feasible feedstocks in replacing petroleum-based aromatic compounds for synthesis of powder coating resins. This objective will be achieved by: (1) identifying the molecular structures of biobased powder coating resins, (2) investigating the curing behaviors, and (3) determining the primary coating properties of the biobased resin systems. The findings from this study will provide an important guideline in the next step of research that may eventually lead to the development of commercial biobased powder coatings, and set up a framework for developing other biobased polymers.

Industrial Relevance, Need, and Appropriateness for the Center. Since volatile organic compound (VOC) release from traditional coatings is subject to strict government regulations, powder and waterborne coatings have been developed as alternatives to eliminate or reduce VOCs. On the other hand, increasing public environmental concern and awareness of sustainable development has motivated researchers to pursue renewable feedstocks for polymer materials. Current epoxy resins are entirely based on petrochemicals, while polyurethanes based on soybean oil-derived polyols have only found a niche application for foams. Therefore, there is an urgent need for enabling technology to develop cost effective, high performance, biobased epoxy and polyurethane powder coatings. The proposed research is aligned with the interest of the Center for Bioplastics and Biocomposites that aims to bring sustainable solutions for polymer materials including coating resins in collaboration with industrial partners.

Experimental Plan. Besides resisting corrosion and weathering, superior abrasion, impact strength, and hardness are also required for protective coating. For most polymers, the high mechanical performance relies on the inclusion of rigid molecular building blocks such as aromatic or cycloaliphatic moieties. Among various natural chemicals rosin and dipentene are two important ones with large productions and relatively low price and have found many industrial applications.

Rosin is a resinous exudate from pines, conifers, etc. Rosin acids, which consist of 90% of rosin, are a family of isomeric acids (abietic acid is the dominant component) with a rigid fused ring structure. Diptetene (limonene) is also a readily available cycloaliphatic chemical in a variety of softwood trees, plants, and fruits. Both rosin and dipentene can be conveniently converted to dicarboxylic acid and anhydride (Figure 1). Current polyesters
used for polyester, polyester-epoxy hybrid, and polyurethane powder coatings are mainly based on the copolyesters of rigid terephthalic acid (TPA), isoterephthalic acid (iTPA), and trimellitic anhydride (TMA) with neopentyl glycol and trimethylol propane. Our approach is to replace TPA, iTPA and TMA with the biobased alternatives, the Diels-Alder adducts of rosin acid and dipentene with acrylic acid (acrylopimaric acid, or APA) and with maleic anhydride (MPA & DPMA) (Figure 1). Small amounts of the flexible adipic acid and sebacic acid will be added in the synthesis of copolyesters to regulate the balance of molecular rigidity/flexibility and physical properties. For polyester and polyester-epoxy hybrid powder coatings, carboxy-polyesters are needed, while for polyurethane powder coatings hydroxy-polyesters are required. Further, for the powder coating, the resins with high glass transition temperature (Tg > 50°C), low melting or softening point (80-110°C), and melt viscosity are preferred. These requirements demand a fine tune of the stoichiometry of the reactants.

Rosin can also be converted to epoxies which may either serve as base resins for powder coatings or as curing agents for carboxy-polyesters. For example, diglycidyl ether of APA and triglycidyl ether of MPA can be easily synthesized and used as potential curing agents. Further, by manipulating the stoichiometry of epichlorohydrin and APA and/or MPA, rosin-derived epoxies with desirable Tg and softening point for powder coating base resins are likely synthesized. In addition, curing agents can be selected from the commercial products, e.g., triglycidyl isocyanurate, for the curing of rosin-derived carboxy-polyesters. For curing of hydroxy-polyesters, biobased blocked isocyanates will be synthesized. In this effort, dipentene will be first converted to dicarboxylic acid and then to diisocynate. The resulting diisocynate will be blocked with ε-caprolactam.

Curing behavior of the biobased powder coating will be studied by DSC and chemorheology, and the mechanical, dynamic mechanical, and adhesion properties will be evaluated by following ASTM standards. Particularly, the applications of developed powder coatings will be evaluated with metal cans filled with food simulants under sterilization conditions. The coatings will be tested for their corrosion resistance, adhesion to metal surface, physical deformation during fabrication of the container, thermal and chemical resistances. Transport of low molecular weight additives and unreacted monomers from coatings into food simulants will be tested under industrial food processing and storage conditions.

Figure 1. Rosin and dipentene-derived diacid and acid-anhydride versus their petroleum-based aromatic counterparts.
We do not anticipate any risks and hazards from the proposed research. The polymer synthesis, handling of coatings, sterilization experiments will be carried out in compliance with recommended safety precautions and requirements, as specified by university and regulatory agencies. The PIs have extensive experience with the polymer synthesis, use of food processing systems and analytical instrumentation, and their laboratories are well equipped for conducting this project. We anticipate that biobased coatings on metal cans will be able to sustain chemical environment of foods and high temperatures of sterilization process. If necessary we will chemically modify the coatings.

**Proposed Deliverables.**
- Identify the structures and synthesis methods of biobased resins for powder coatings
- Determine curing behavior of the biobased powder coatings
- Evaluate fundamental mechanical, physical, and adhesion properties of the biobased coatings
- Quantify the level of migrating substances from coatings under high temperature sterilization

**Research Facilities.** For this work a powder coating spray device will be purchased for coatings of metal cans. Otherwise, our labs at CMEC and BSE are well equipped for materials synthesis and characterizations.

**Timeline and Budget.** The fund requested include $35,744 for a PhD student, $13,850 for faculty time, $4,000 for materials and supply, $1,000 for travel, totaling $58,800 (including 10% overhead).

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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 4.6 – Development of Biobased VOC-free Powder Coating Resin Systems
Principal Investigator(s): Jinwen Zhang* and Shyam Sablani
Site: Washington State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

- Very Interested
- Interested
- Interested with Change
- Not Interested
- Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Note: This information will not be divulged during the review.

Your Name: _____________________________________________

Your Organization: ____________________________________
Project Objectives. The long-term goal of this study is to develop starch-based packaging materials for a wider range of applications. Native and modified starches with different structures and properties will be selected to understand important factors affecting the application of starch for both food and non-food film usages. The specific objectives are to understand the role of (1) starch sources and their composition (amylose/amylopectin ratio), (2) the degree of branching, (3) the choice of plasticizer, and (4) the choice of blending materials (e.g., nanoclay, fiber) on the properties of the resulting starch-based packaging films. The properties (i.e., strength, barrier properties, hydrophobicity, glass-transition, thermal degradation) and functionality of starch films will be evaluated.

Industrial Relevance, Need, and Appropriateness for the Center. There is increasing interest in using biopolymers from renewable resources for producing materials and products to reduce dependence on petroleum sources, control environmental pollution, and reduce carbon footprint. Starch, the second most abundant biomass in nature, can be used to produce bioplastics, nanoparticles, biomedical products, and carrier material for drug-delivery. Starch-based films are biorenewable, biodegradable, and possess good oxygen barrier properties.

Native starch exists in a semi-crystalline granule and is comprised of two major polysaccharides: amylose and amylopectin. Native starch does not possess the thermoplastic properties needed for polymer-related applications; however, they could be modified to possess these properties with the addition of plasticizers, heat, and shear, usually via extrusion.

Processing factors and starch structure/composition influence starch film properties, thus, their applications. The water-solubility of a film is a very important characteristic in determining its food and non-food applications. Starch films could be made either hydrophilic or hydrophobic based on blends and additives. There is growing market demand for hot-water dissolvable (hydrophilic) packaging materials for pre-mixed food ingredients and pre-packed detergents. Such packages reduce packaging material waste. Hydrophobic starch films could be created to possess properties such as greater mechanical strength, elasticity, flexibility, and surface and barrier properties. The relative proportion of amylose in starch and addition of composite materials affect the barrier and mechanical properties of films. There is a need to understand the structure-property relationship on the thermoplastic properties of starch, targeting a broader range of applications.

Experimental Plan. Selection and modification of starch (source and composition): The ratio of amylose and amylopectin in starch will be varied between 10% to 80% in model starch blends to prepare cast films and property characterization. Natural sources of starch with varying degrees of amylose content (e.g., cassava, 15%; normal yellow dent corn, 24%; waxy rice and corn <2%) will be used for the preparation of hot-water-dissolvable and water insoluble starch films. Preliminary data obtained in our laboratory showed that film prepared from acid-hydrolyzed waxy corn starch could completely dissolve in boiling water in less than 1.5 min. Partially de-branched or partially acid-hydrolyzed starch will be used to reduce the molecular size of the waxy corn and waxy rice starch to increase the water solubility of the developed starch films while maintaining the tensile properties. High-amylose yellow dent corn, normal yellow dent corn, and normal rice starch will be used alone and in mixtures to prepare films with strong mechanical properties for packaging materials. De-branching reactions will be applied to produce more linear starch molecules to increase the
strength of the starch films. Hydroxypropylated, hydroxyethylated, or acetylated starch will be used to prepare starch-based films with improved processability, film clarity, mechanical properties, and stability.

**Plasticizers:** Water, sorbitol, and glycerol will be evaluated for their plasticizing effects on starch films at various ratios (25-40% w/w, dry starch basis).

**Blowing extrusion of films:** Cast films will be produced for optimizing amyllose content, degree of modification, plasticizer types, and content. For producing proof-of-concept verification at optimal conditions, extruded-blown films will be produced and evaluated. Native or chemically/enzymatically modified starch will be dried, mixed with plasticizer, and compounded using a twin-screw extruder. The extrudate will be pelletized and the pellets will be used to produce starch films using a single-screw extruder with a blowing die and tower. To further improve the mechanical properties and water resistance of the starch films, nanoclay (montmorillonite) and fibers will be added at optimal ratios (to be determined experimentally) and the films will be tested for enhanced mechanical and barrier properties.

- Testing of starch or blended starch films: Film samples will be equilibrated in a desiccator with 50% relative humidity for three days prior to testing.
- Mechanical properties: of the starch films: Mechanical properties will be analyzed using an Instron Universal Testing Machine (model 4502, Instron Corporation, Canton, MA) following ASTM protocols. The tensile strength, percentage elongation at break, and Young’s modulus will be determined at a crosshead speed of 5 mm/min. TGA evaluations will be carried out for degradation of films at higher temperatures.
- Water solubility test of starch films: The film will be weighed to the nearest 0.0001 g and placed into a test beaker with 80 mL of deionized water at different temperatures (25, 40, 55, 70, 85, and 100°C) and stirred for 10 min. The remainder of the film after soaking will be recovered and dried at 60°C to a constant weight. The percentage of total soluble matter (% solubility) will be calculated as: % solubility = 100% × (initial dry weight – final dry weight)/initial dry weight.
- Barrier properties: The oxygen transmission rate of the films will be measured using a MOCON OXTRAN instrument following the ASTM D3985 standard method. There is an oxygen stream on one side of the film and a nitrogen stream on the other side of the film. The outlet of the nitrogen side is equipped with an oxygen detector. The test will be conducted at 23°C and 0% relative humidity, and the rate will be expressed at cc/m2/24 hr. The vapor transmission rate will be related to the amount of water allowed to absorb onto dry beads until saturation per unit time.
- Starch structure: A crystal diffraction refractometer (XDR) will be used to quantify the change in crystallinity in starch molecules. Nuclear magnetic resonance (NMR) will be used to quantify changes in the molecular structure of starch and blend materials in forming complexes.

**Proposed Deliverables.** We will gain a very good understanding of feedstock and processing factors that affect resultant starch film properties and functionality, along with demonstration of two types of thermoplastic starch films as described above.
Year 1
1. A variety of starch films will be developed using de-branching and partial acid-hydrolysis. Different starches (e.g., high-amylose and normal yellow dent corn, normal rice), and plasticizers and blend materials will be evaluated. Spectroscopic evaluation of films will be done. Most of the evaluations will be on cast films.

Year 2
1. Films will be made using blown extrusion.
2. The mechanical properties, water solubility, and barrier properties will be tested for the blown films.

Research Facilities. The Center for Crops Utilization Research at Iowa State University has pilot plant equipment for mixing, compounding, and blowing extrusion of starch films. They include high-speed mixers, a melt flow indexer, single-screw and twin-screw extruders, and Instron Universal Testing Machine. We will use these facilities to prepare films at pilot plant-scale. We will need to identify a MOCON OX-TRAN instrument for oxygen-transmission rate test.

Timeline and Budget. The project will be a two-year project. A postdoctoral research associate will be hired to conduct the project. The estimated budget is:

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<th>Year</th>
<th>Budget</th>
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<td>Year 1</td>
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Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 4.7 – Improving Thermoplastic Properties of Starch for Food and Non-food Packaging Applications

Principal Investigator(s): Buddhi Lamsal*, Yongfeng Ai, and Jay-lin Jane

Site: Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested
☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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Provide any questions about this project you would like the PI to address.
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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.
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Note: This information will not be divulged during the review.

Your Name: ____________________________________________

Your Organization: ______________________________________
THRUST AREA: MODELING

5.1 — Interfacial Healing of Biopolymers

Principal Investigator(s): David Grewell
Site: Iowa State University

Project Objectives. This work will use first principle governing equations to model and calculate the activation energy of interfacial healing of molten biopolymer interfaces. These models and the resulting activation energies can be used to predict interfacial healing of weld lines generated during secondary welding processes as well as internal weld lines generated during injection molding. Temperature fields will be predicted using validated models for ultrasonic welding. These one-dimensional, time dependent temperature fields will be used to predict interfacial healing through analytic methods. In more detail, these temperatures will be coupled to molecular diffusion models developed by the PI to allow the interfacial healing activation energy of various biopolymers to be calculated.

Industrial Relevance, Need, and Appropriateness for the Center. This work will characterize the ultrasonic welding of rigid polylactic acid (PLA) and PHA (polyhydroxyalkanoate) components, both materials manufactured from renewable feedstock. The team has characterized the welding of various PLA films for such applications as packaging; however, there is no information on the ultrasonic welding of rigid PLA or PHA components. Ultrasonic welding is one of the most common methods to join plastics because it is fast, with cycle times of less than 1 s, efficient, and easily automated. However, there are many equipment parameters that affect weld quality, such as vibrational amplitude, weld time, and weld force. In addition, there are part design constraints that influence weld quality, such as joint design and weld distance (distance between ultrasonic tooling and weld interface). While most plastics can be welded under near field conditions, where the distance between the ultrasonic tooling and the weld interface is less than 6 mm, many cannot be welded under far field conditions, where the distance between the weld interface and the ultrasonic tooling is greater than 6 mm.

In order to determine whether there is a design limitation for producing parts that must be welded with ultrasonics, this study will evaluate the effect of weld distance on PLA and PHA weldability. In addition, there are two major categories of joint designs for ultrasonic welding, energy directors and shear joints. Each has its own advantages and limitations. Also, some materials are not well suited for one or both of the joint designs. Thus, to determine if this is also a design constraint for PLA and PHA components that must be welded, the effect of joint design will also be studied. Once weldability of these materials is characterized, the welding process will be modeled using standard models based on heat generation, molecular diffusion, squeeze flow and interfacial healing. These models will be validated with experimental data for the determination of temperature dependent activation energy. This will allow end users to model and predict interfacial healing with a range of possible processes, including other welding techniques, such as hot plate welding and vibration welding as well as weld lines produced during injection molding.

Experimental Plan. Two common grades each of PLA and PHA (total of four) will be molded into American Welding Society (AWS) samples with the energy director and shear joint design as well as into basic material test samples. The final selection of grades will be based on feedback from CB² members. The samples will be welded at 20 kHz under various conditions:
• Weld distance: near and far field (2 values)
• Weld joint design: energy director and shear joint (2 values)
• Weld time (5 values)
• Weld force (5 values)
• Weld amplitude (4 values)

Screening experiments will be conducted to determine the proper design space. Based on the design space, a full factorial experimental design will be constructed, including replicates of five for a total of 2000 welds for each material. Welds will be characterized in terms of:
• Tensile strength
• Part marking or damage
• Dissipated energy as reported by welding system
• Relative amount of flash

Statistical procedures will be used to develop models for the dependent and independent variables. The results of the welding trials will be provided to the CB2 members.

In addition, the work will use models developed by the PI based on first order principles to estimate the activation energy and material constants for the various materials that will be studied. These models will be validated with temperature measurements and interfacial weld strength. This will allow industry to model diffusion related processes such as mold weld lines.

**Proposed Deliverables.** A progress report on the outcomes of the first selected material, including its weldability and sensitivity to welding parameters will be done. The proposed work will give designers and manufacturers the critical knowledge regarding the weldability of PLA and PHA materials so that products can be properly designed and assembled. In year two, the activation energy of the materials will be determined, including temperature sensitive activation energy if applicable.

**Research Facilities.** The PI has several ultrasonic welding systems as well as a long history of developing fundamental models of welding processes. In addition, the PI has mechanical characterization equipment as well as access to microscopy systems, including scanning electron beam microscopy for failure analysis.

**Timeline and Budget.** The proposed work requires approximately $40,000 of funding each year for two years. The detailed work plan and budget is detailed below:
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**Total Budget:** $79,450
Level of Interest Feedback Evaluation (L.I.F.E.) Form

Project Name: 5.1 – Interfacial Healing of Biopolymers
Principal Investigator(s): David Grewell
Site: Iowa State University

To facilitate a dialogue between center faculty and member organizations, each industry representative is asked to indicate his/her organization’s level of interest in each project.

Unless the individual organizing L.I.F.E. feedback has instructed you otherwise, your identifying information will be handled as follows: it will not be shared during public IAB feedback sessions; it will be shared with center director and faculty in order to facilitate follow-up on specific suggestions.

Level of Interest

☐ Very Interested
☐ Interested
☐ Interested with Change
☐ Not Interested
☐ Abstain (Outside my group’s ability to evaluate)

Please provide any comments, questions, or suggestions you have about this project, the progress made, and technical or implementation issues.

Provide any comments about this project here.

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PROJECT PRESENTATIONS 79
Provide any questions about this project you would like the PI to address.

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Provide any suggestions you have for improving this project or making it more relevant to your needs or interests.

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Note: This information will not be divulged during the review.

Your Name: ________________________________

Your Organization: __________________________
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THRUST AREA: SYNTHESIS AND COMPOUNDING

1.4 — Blending and Compatibilization of Biobased Materials with Condensation Polymers Including Poly(L-lactic acid) and Polybutylene Succinate

**Principal Investigator(s):** Eric W. Cochran* and Nacu B Hernandez  
**Site:** Iowa State University

Many important biomonomers may only be economically polymerized through step growth polymerization. For example, L-lactic acid is a chiral biomolecule that forms a high-melting semicrystalline homopolymer, poly(L-lactic acid), or PLLA. However, while block copolymers based on PLLA have excellent mechanical properties, for example as thermoplastic elastomers (TPEs), the only known route for polymerization of these materials involves a ring opening polymerization of L- or D-lactide, a precursor far more costly than lactic acid. However, the use of polycondensation-type polymerizations does not allow for the well-defined addition of other polymer building blocks such as thermoplastic rubbers that could be used to form PLLA-based TPEs. We propose the application of a novel strategy we have developed for the compatibilization of condensation polymers such as PLLA or Polybutylene Succinate (PBS) with other acrylic and vinyl based polymers (e.g. thermoplastic polymerized soybean oil, EVA, polystyrene, poly(n-butyl acrylate), etc.).

Our technique converts these step growth polymers into macromolecular initiators for subsequent controlled radical polymerizations, e.g. Re-versible Addition-Fragmentation chain Transfer polymerization. By doing so, these polymers may now be upgraded to block copolymers with monomers such as: acrylates, acrylamides, acrylonitrile, styrenics, dienes, and vinyl monomers. The materials created will be evaluated both as a stand-alone thermoplastic elastomers as well as compatibilization agents for blends of PLLA/PBS with other homopolymers.

1.5 — Production of Lignin-based Thermoplastic Elastomers

**Principal Investigator(s):** Xianglan Bai*, Eric Cochran, and Marjorie Rover  
**Site:** Iowa State University

In this project, it is proposed to produce a phenolic monomer stream from lignin-based fast pyrolysis. These monomers will then become a feedstock to produce hard segments in thermoplastic elastomer (TPE) formulations. To achieve thermoplastics rather than thermosets, a patent pending implementation of a polymerization technology known as Re-versible Addition-Fragmentation chain Transfer (RAFT) will be used. RAFT has already been demonstrated for developing a vegetable oil-based TPE. The presence of high abundance of vinyl groups in the phenolic monomer stream is expected to be advantageous in RAFT polymerization since the polymerization could occur through unsaturated side chain C=O bonds. The economic feasibility of lignin-based TPE will also be evaluated. If successful, the outcome of the proposed research will provide a low-cost biobased TPE using phenolic monomers as hard segments. The significant of the proposal includes (1.) Producing phenolic monomer stream from low-cost lignin; (2.) Synthesizing biobased TPE from lignin-derived phenolic monomers; and (3.) Evaluating economics of lignin-based TPE.
1.6 — Biobased Polyurethane Powder Coatings

**Principal Investigator(s):** Jason Chen* and Samy Madbouly  
**Site:** Iowa State University

Most organic powder coatings are produced primarily or entirely from petroleum. It is proposed to develop a biobased polyurethane powder coating, with emphasis on the development of a new castor oil-derived isocyanate curing agent. Both castor oil and hydrogenated castor oil (i.e., castor wax) will be converted into blocked polyisocyanate curing agents by mixing these readily-available building blocks with common diisocyanates such as IPDI and blocking agents such as \( \varepsilon \)-caprolactam. The blocked polyisocyanates will be cured with biobased polyols such as hydroxyl-terminated polybutylene succinate (PBS) and/or other model biobased diols selected by the member companies. The properties of blocked polyisocyanates prepared from partially-hydrogenated castor oil will be simulated by using different ratios of castor oil- and castor wax-derived polyisocyanates. Curing kinetics will be characterized in detail using dynamic rheology and DSC measurements over a wide temperature range (50-220°C). Understanding the curing kinetics will allow designers to tune the blocking group in the isocyanate curing agent and the use (or absence) of polymerization catalysts. These blocked polyisocyanates have the potential to reduce the cost of powder coatings based on isocyanate curing agents by reducing the weight percentage of diisocyanate (e.g., IPDI) in the overall formulation.

1.7 — Converting Products of Fast Pyrolysis into Terephthalic Acid

**Principal Investigator(s):** George Kraus* and Robert Brown  
**Site:** Iowa State University

Functionalized aromatic compounds are ubiquitous in industry as commodity and value-added fine chemicals. The potential applications are enormous and range from building blocks in the chemical industry to precursors for pharmaceutical drug development to polymers. Among the range of aromatic chemicals, terephthalic acid has emerged as a potential high-volume product from renewable sources. Our source for aromatics is lignin. Lignin, a renewable phenylpropane-based polymer, is a large and untapped source of renewable aromatic compounds. Fast pyrolysis is able to convert lignin into phenolic-rich oil, which mostly consists of lignin-derived oligomers of high reactivity. If these reactive primary products could be in-situ converted to more stable intermediates or directly converted to desirable products, it would be a significant discovery. George Kraus will work with Robert Brown to develop a setup where the products of fast pyrolysis of lignin will be passed into a cold solution. The Kraus group will try several reaction conditions to determine the optimal conditions for cyanohydrin formation. The cyanohydrin will react with an oxaphilic catalyst, such as an iron or manganese catalyst, to isomerize the cyanohydrin to a benzylic alcohol. The benzylic alcohol will be oxidatively converted into terephthalic acid.
1.8 — Biobased Multi-functional Air Filtering Materials and Their Stability Evaluation

**Principal Investigator(s):** W. H. Katie Zhong* and Tian Liu  
**Site:** Washington State University

Air pollution is the introduction of chemicals, particulate matter, or biological materials that cause harm or discomfort to humans or other living organisms, or that damage the natural atmosphere environment. Air filters are widely used in practice, e.g. residential, hospitals automotive and airplane, etc. Thus far, only synthesized materials or petroleum-based materials, such as polypropylene and fiberglass, are available for air filters, but they cause serious environment problems worldwide. This global situation leads to a critical demand for biobased air filtering materials, especially lack of air filters in many developing countries though their air pollution is getting worse. In this proposed project two different processing methods, based on treatment and functionalizing cellulose-based paper towel substrate and electrospinning of biobased nanocomposite hybrids, will be utilized to develop cost-effective, biobased, and multi-functional air filtering materials for high efficiency air filters. Besides the features of natural materials, such as environment-friendliness and disposability, and abundant plants, such as soy and gelatin, possess broad range of functional groups that have been shown to be effective with many polar molecules, and thus can be utilized to adsorb some toxic chemicals in the air. Therefore, the resulting material cannot only possess particulate air filtration properties, but also have the potential for chemical absorption capability. The proposed project will not only expand the application of abundant natural plants, but also will contribute the environment through developing disposable air filters with similar or even higher efficiency than current air filters that are needed worldwide.

1.9 — Biobased Green Self-healing Multifunctional Anti-corrosive Coatings

**Principal Investigator(s):** Vijay Kumar Thakur* and Thomas F. Garrison  
**Site:** Washington State University

Protective coatings are commonly used for corrosion control of metallic structures located in harsh environments such as offshore platforms, bridges, and underground pipelines. These protective surface layers are continually exposed to damage and depletion during transportation, installation, and service. The existing protective coating systems do not adequately address these issues because the damages typically occur at the micron level and are hard to detect. Furthermore, coatings based on petroleum-derived materials are less desirable from a sustainability and environmental point of view. The objective of this proposed research work is to prevent or reduce the rate of corrosion by using an environmentally friendly, anti-corrosive, biobased self-healing polymer layer. Biorenewable polymers will be used in combination with green corrosion inhibitors and micro-/nano-capsules (carrying a self-healing agent) to induce self-healing properties. The project aims to develop innovative, biobased materials that exhibit self-healing and anti-corrosion properties.
Starch is a biodegradable polysaccharide composed of linear amylose and branched amylopectin. Because it is produced by most green plants, it is one of the most abundant renewable resources found in nature. Starch is a granular solid in its natural form, although when plasticized with hydrophilic liquids (such as water, glycerol, or other polyols) becomes a thermally processable biobased and biodegradable plastic known as thermoplastic starch (TPS). The mechanical properties of TPS are strongly dependent on the plasticizers employed and the environmental conditions, especially humidity due to the volatile or hygroscopic nature of the plasticizers. For this reason, TPS falls short of an engineering thermoplastic and requires innovation to bring consistency to the material. Examples of such innovations are mechanically processed blends of TPS with petroleum-based polymers ranging from polyvinyl alcohol (excellent compatibility with TPS, poor properties) to polypropylene (excellent properties, poor compatibility with TPS). The main objectives of this project will be to

1. Study the fundamental principles that govern the physical and mechanical properties of TPS and how these properties are affected by different parameters such as monomer variability (i.e. crops’ source), their molecular architecture, molecular weight, composition, etc.

2. Moreover, we will introduce a new plasticizer based on thermoplastic PAG (poly(acrylated glycerol)), a new thermoplastic rubber developed by our group with tunable branching (through degree of acrylic functionality) and hydrophilicity/hydrophobicity (through acetylation –OH groups). We anticipate that PAG/TPS blends will have desirable mechanical properties due to a combination of excellent thermodynamic compatibility and complementary constituent material properties.
THRUST AREA: BIOCOMPOSITES

2.4 — Blending and Compatibilization Technologies Using Available Partially and Fully Biobased Polymers

**Principal Investigator(s):** Samy Madbouly  
**Site:** Iowa State University

Most biobased and partially biobased polymer mixtures are immiscible and separate into a two-phase morphology. Immiscible blends with coarse, irregular, and unstable domain sizes typically have relatively weak interfaces result in blends with poor mechanical properties and have limited uses. To address these problems it is possible to use block, graft, or star copolymers as compatibilizing agents. These compatibilizing copolymers can migrate to the polymer/polymer interface, reducing surface tension and increasing the stability of the blends. A homopolymer can also act as a compatibilizer if it has a good miscibility with the two polymer components of the blend. The major objective of this proposal is to use different types of compatibilizers, such as block-, graft-, star-copolymers, or homopolymer to improve the compatibility, and morphology of various immiscible biobased and partially biobased polymer blends, such as nylon-11, polylactide (PLA), polyhydroxyalkanoate (PHA), polyethylene, (PE), styrenic thermoplastic elastomers (e.g., styrene-butadiene-styrene (SBS)), urethane thermoplastic elastomers (TPU), and ethylene vinyl acetate (EVA). Reactive blending and in-situ polymerization and compatibilization of polymer blends during mechanical mixing will also be studied in this work. Various analytical techniques will be used to characterize the polymer blends with and without compatibilizers including rheology; DMA; DSC; TGA; x-ray; TEM; SEM; and Instron mechanical tester.

2.5 — Green Composites from Waste Biomass and Biopolymers for Multifunctional Composite Materials Applications

**Principal Investigator(s):** Vijay Kumar Thakur* and Thomas F. Garrison  
**Site:** Washington State University

The prevalent usage of synthetic polymers in consumer and industrial applications has raised concerns over environmental impacts and potential health risks. Synthetic polymers made from petroleum-based feedstock pose risks to manufacturers caused by short-term disruptions in the global supply chain and by long-term shortages caused by dwindling petroleum reserves. These concerns have motivated recent developments in economical and environmentally friendly composites made from biorenewable resources. The purpose of this proposed research is to make multifunctional nano- and micro-composites with excellent mechanical and thermal properties for applications in the packaging and automotive industries. Biorenewable materials, including cellulosic fibers, saw dust, rice hulls, and wheat straw, are available as waste biomass in large quantities in the United States. This research seeks to improve current technology by effectively utilizing waste biomass as nano- and micro-fillers in composites with biobased polymer matrices.
2.6 — Liquid Molding of Wood Strand Panels with Large Curvature Using VARTM for Automotive Applications

**Principal Investigator(s):** V. Yadama* and L.V. Smith

**Site:** Washington State University

Auto body and interiors make up 40% of the total vehicle weight, providing a promising opportunity to improve fuel efficiency. Liquid molded wood strand composites provide a sustainable alternative (economical and renewable) to using biobased natural fibers. The PIs have shown that low-cost wood strands can be formed with controlled orientation and consolidated using resin transfer molding (RTM) to yield high performance panels. The objective of this work is to investigate the forming of wood strand preforms with complex geometries using low consolidation pressure and vacuum bags (VARTM process) with single-sided tooling as a precursor to forming using RTM. The study will identify resin flow and viscosity requirements for applications in automotive interiors.

The influence of wood strand preform thickness, corner bend angles, and bend curvatures will be investigated to study the effects of single-curvature bending. Wood strand preforms will be consolidated, shaped, and cured using vacuum bags and a thermosetting polymeric resin. Dome-forming experiments will be used to study the formability or ease of forming when the wood-strand preform is subjected to double-curvature bending. Panels’ shape stability, thickness variations (thinning or wrinkling), void contents, and mechanical properties will provide performance metrics. Effects on resin flow and the influence of viscosity will be studied. Results will identify geometry and flow limits on forming complex geometries during vacuum forming of wood strand preforms using VARTM, thus enabling further development of technology for producing automotive parts with renewable material such as wood strands using RTM in the future.
THRUST AREA: BIOBASED PRODUCTS

4.8 — Zein-based Nano-functionalized Biodegradable Films for Active Packaging of Food

**Principal Investigator(s):** Buddhi Lamsal* and Chenxu Yu  
**Site:** Iowa State University

Biopolymers from corn protein (zein) could be utilized to prepare biodegradable packaging films or coatings with antimicrobial functionality by embedding nanoparticles, which could also reinforce the films for enhanced mechanical strength. The overall goal is to create and test corn zein-based packaging materials that exhibit bactericidal functionality resulting in extended shelf life of fresh foods. The α-zein will be extracted from corn gluten meal or whole zein using organic solvents, 70% 2-propanol, 55% 2-propanol, or 70% ethanol. Surface coatings or films will be produced using extracted corn α-zein with specially designed functional nanomaterials TiO$_2$/SiO$_2$ core/shell particles. The design and synthesis of doped TiO$_2$/SiO$_2$ core/shell nanoparticles will be tailored to maximize inactivation of microorganisms by radicals under sunlight or UV exposure. Conditions for incorporating nanoparticles into zein film matrices or surface coats will be optimized and physico-chemical and mechanical properties of cast films evaluated. The functionalized zein films will be tested for packaging effectiveness in keeping quality (oxidation of lipids and proteins) and microbial safety in fresh meat or fruit applications. Successful completion of the research will add value to zein applications as biorenewable and biodegradable packaging materials with antimicrobial functionality.

4.9 — Life Cycle Assessment of Lignocellulosic-based Bioplastics

**Principal Investigator(s):** Kurt A. Rosentrater* and Matt Darr  
**Site:** Iowa State University

In order to understand the environmental impacts and overall sustainability of lignocellulosic-based bioplastics and biocomposites being developed by members of the CB, we will use a multi-stage life cycle assessment (LCA) approach. First, we will model specific feedstock collection, delivery, and manufacturing systems in order to understand the impacts of upstream processes. Second, we will model the broader life cycle for lignocellulosic-based bioplastics. This broader analysis will consist of a cradle-to-grave approach and will examine every step of the life cycle, including extraction of raw materials from the earth (i.e., cradle), harvesting, transportation, logistics, processing those materials into a product, use of these products by consumers or other end users, and then disposal/recycling of any wastes, including the product itself, at the end of its useful life (i.e., the grave). SimaPro (or equivalent) software will be used to conduct the LCA modeling, and will include analysis of embedded energy use, water use, greenhouse gas emissions (CO$_2$, NOx, CH$_4$), and other environmental impact metrics.

Deliverables will include life cycle models for lignocellulosic-based bioplastics and biocomposites, quantification of environmental impacts of feedstock collection, delivery, including manufacturing processes for lignocellulosic-based bioplastics and biocomposites, as well as quantification of environmental impacts for entire life cycle for lignocellulosic-based bioplastics and biocomposites.
3-hexenedioic acid (HDA) can be produced at high selectivity and yield by the fermentation of glucose to cis-cis muconic acid followed by direct electrocatalytic hydrogenation, without an intermediate separation step. While HDA is not currently regarded as a commodity chemical, its chemical similarity to adipic acid suggests that when polymerized with diamines, the resulting polymer (preliminarily termed nylon-6,HDA) may have properties analogous to the Nylon family. Moreover, the alkene unit in the polymer backbone provides opportunities for the subsequent construction of designer materials, e.g. graft/comb copolymers, differentiating the materials from Nylons in an advantageous manner. In this project we will improve the synthesis of HDA, polymerize the biobased monomer with 1,6-hexamethylenediamine, and examine the material and chemical properties. The Tessonnier group will focus on improving the activity of the Pb electrocatalyst and its stability in the presence of the biogenic impurities found in the fermentation broth. The Cochran group will synthesize Nylon-6,HDA and conduct direct comparisons with the analogous Nylon-6,6 family of polymers. It is further proposed to investigate nylon-6,HDA as a thermal- or photo-curable thermoset and as a grafted copolymer compatibilizer between nylon-6,6 and other polymers such as those of the polystyrene or polyacrylate families. This research will introduce HDA as an economical bio-advantaged substitute for adipic acid, a major commodity chemical projected to enjoy a $7.5 billion market by 2019. The project will establish the commercial potential for biobased polyamides derived from this bio-monomer. Investigation of new bio-monomers is synergistic with CB3.
NURIA ACEVEDO
Department of Food Science & Human Nutrition
(515) 294-5962 | nacevedo@iastate.edu
Research Interests: Physicochemical and structural properties of foods, lipids, food nanotechnology, and material science in foods

JOHN BEGHIN
Department of Economics
(515) 294-5811 | beghin@iastate.edu
Research Interests: Agricultural economics, international trade, international economics, trade and the environment, policy analysis, obesity, food policy

JASON CHEN
Department of Chemistry
(515) 294-7409 | jschen@iastate.edu
Research Interests: Using practical and scalable chemistry to design and synthesize novel monomeric and polymeric substances with a variety of potential properties and applications

ERIC COCHRAN
Deputy Director, Center for Bioplastics and Biocomposites
Department of Chemical & Biological Engineering
(515) 294-0625 | ecochran@iastate.edu
Research Interests: Synthesis and characterization of heterogeneous block copolymers and polymer nanocomposites for applications ranging from asphalt modification to adhesives to directed self-assembly for photolithographic masks
MATTHEW DARR
Department of Agricultural & Biosystems Engineering
(515) 294-8545 | darr@iastate.edu
Research Interests: The use of embedded systems and advanced instrumentation to enhance the efficiency, productivity, and control capacity of agricultural systems including those for food, fiber, and energy production

WILLIAM GRAVES
Department of Horticulture
(515) 294-6954 | graves@iastate.edu
Research Interests: Biology of rare woody plants

DAVID GREWELL
Director, Center for Bioplastics and Biocomposites
Department of Agricultural & Biosystems Engineering
(515) 294-2036 | dgrewell@iastate.edu
Research Interests: Developing soy and corn-based protein plastics as well as developing and characterizing processing techniques

DARREN JARBOE
Center for Crops Utilization Research and BioCentury Research Farm
(515) 294-2342 | jarboe@iastate.edu
Research Interests: Technology commercialization and entrepreneurship, rural development, farm machinery sanitation, and biomass marketing and utilization

GEORGE KRAUS
Department of Chemistry
(515) 294-7794 | gakraus@iastate.edu
Research Interests: Organic synthesis, bio-agricultural chemistry, and toxicology

BUDDHI LAMSAL
Department of Food Science & Human Nutrition
(515) 294-8181 | lamsal@iastate.edu
Research Interests: Food processing and engineering, crops utilization and industrial value-addition via enzyme application, and fermentations, biobased products, engineering properties of food and structure-functional properties- proteins, polysaccharides, food rheology
SAMY MADBOULY  
Department of Materials Sciences & Engineering  
(515) 294-1214 | madbouly@iastate.edu  
Research Interests: Dynamic and static rheology of biopolymers, blends, composites, dispersions, and gels; shape-memory polymers and their biomedical applications; formulation of aqueous polyurethane dispersions and its applications in coating and adhesive industries; processing, phase behavior, and morphology of polymer blends and composites under static condition and shear flow; and characterization of polymeric materials

CHRIS MARTIN  
Department of Art & Design  
(515) 294-1639 | chmartin@iastate.edu  
Research Interests: Application of biopolymers and biocomposites to evaluate and maximize their potential for practical uses in building and design

REZA MONTAZAMI  
Department of Mechanical Engineering  
(515) 294-8733 | reza@iastate.edu  
Research Interests: Smart materials and structures, functional thin-films (energy harvesting, sensors and actuators), polymer-metal nanocomposites (green energy), nature-inspired soft microrobotic (biomedical devices and military applications), and MEMS and NEMS

MIKESCH MUECKE  
Department of Art & Design  
(515) 294-8786 | mikesch@iastate.edu  
Research Interests: Biocomposites; green design; compact-footprint design-build construction, passive house technology; design for the elderly; electronic architectures; rapid prototyping; architectural history, theory, and culture; mobility and architecture

BALAJI NARASIMHAN  
Department of Chemical & Biological Engineering  
(515) 294-8019 | nbalaji@iastate.edu  
Research Interests: Molecular design of nanoscale polymer systems and biomaterials to precisely control molecular architecture and functionality in these systems

RUDY PRUSZKO  
Center for Industrial Research and Service  
(563) 583-6496 x18 | rpruszko@iastate.edu  
Research Interests: Economics, social issues, and commercialization
D. RAJ RAMAN
Department of Agricultural & Biosystems Engineering
(515) 294-0465 | rajraman@iastate.edu
Research Interests: Developing early-stage techno-economic models of bioprocessing systems

DAVID RINGHOLZ
Department of Art & Design
(515) 294-0454 | ringholz@iastate.edu
Research Interests: Demonstrate how industrial design can act as a vehicle for showcasing what is possible with biopolymers and moving this technology into the mainstream

IRIS RIVERO
Department of Industrial and Manufacturing Systems Engineering
(515) 294-7944 | rivero@iastate.edu
Research Interests: Biomedical manufacturing, nanomaterials, carbon nanotubes, manufacturing processes, materials characterization, aerospace applications, nondestructive testing (NDT)-X-ray diffraction, and fatigue/failure analysis

KURT ROSENTRATER
Department of Agricultural & Biosystems Engineering
(515) 294-4019 | karosent@iastate.edu
Research Interests: Sustainability of biorenewable systems and processes, development of value-added products and coproducts, design of bioprocess engineering systems, and mathematical modeling and simulation

JAMES SCHRADER
Department of Horticulture
(515) 230-3408 | jschrade@iastate.edu
Research Interests: Identifying, evaluating, and improving emerging bioplastic container materials to replace petroleum-based plastic containers in specialty crop production

JOEY TALBERT
Department of Food Science & Human Nutrition
(515) 294-7015 | jotalber@iastate.edu
Research Interests: Biocatalysts, nanobiotechnology, non-aqueous enzymology, green processing, and immobilized enzymes
KEITH VORST
Department of Food Science & Human Nutrition
(515) 294-6957 | kvorst@iastate.edu
Research Interests: Design, safety, and function of polymeric food packaging with an emphasis on cost optimization and conversion processes of polymer and bioplastic food packaging, biological and chemical safety of food contact surfaces, and shelf-life extension and nutritive value retention

TONG WANG
Department of Food Science & Human Nutrition
(515) 294-5448 | tongwang@iastate.edu
Research Interests: Characterization and processing of soybeans, corn, eggs, and microalgae for producing functional lipids and proteins as food, feed, and fuels

CHRIS WILLIAMS
Department of Civil, Construction & Environmental Engineering
(515) 294-4419 | rwilliam@iastate.edu
Research Interests: Asphalt materials characterization; asphalt design, performance and construction; asphalt rheology; and pavement design

CHUNHUI XIANG
Department of Apparel, Events & Hospitality Management
(515) 294-7474 | chxiang@iastate.edu
Research Interests: Modifying the properties of existing textile products with nanomaterials, i.e. nanofibers, nanopartiles
WASHINGTON STATE UNIVERSITY FACULTY AND STAFF

BIRGITTE AHRING
School of Chemical Engineering and Bioengineering
(509) 372-7683 | bka@wsu.edu
Research Interests: Renewable energy and applied biotechnology, anaerobic bacteria, and renewable products from lignocellulosic biomass

DON BENDER
Department of Civil and Environmental Engineering
(509) 335-2829 | bender@wsu.edu
Research Interests: Design and construction of timber structures, engineering properties of wood-based materials, and hygrothermal properties of building envelopes

KARL ENGLUND
Department of Civil and Environmental Engineering
(509) 335-6259 | englund@wsu.edu
Research Interests: Wood and natural fiber composites, polymer processing with natural fiber reinforcement, and natural fiber composite properties

THOMAS GARRISON
School of Mechanical and Materials Engineering
(509) 335-8491 | thomas.garrison@wsu.edu
Research Interests: Synthesis of biobased polyols and polyurethanes, processing and characterization of biobased polymers and composites, and sustainable use of biorenewable resources

MICHAEL KESSLER
Site Director, Center for Bioplastics and Biocomposites
School of Mechanical and Materials Engineering
(509) 335-8654 | MichaelR.Kessler@wsu.edu
Research Interests: Processing and characterization of polymer composites, vegetable oil-based polymers, self-healing polymer composites, and evaluation of polymers and composites using experimental solid mechanics and thermal analysis
VIJAY KUMAR
School of Mechanical and Materials Engineering
(509) 335-8491 | drivijay.kumar@wsu.edu
Research Interests: Synthesis and processing of biobased polymers, nanomaterials and polymer micro/nano composites; green synthesis of nanomaterials; and surface functionalization of polymers/nanomaterials

ARMANDO MCDONALD
Composite Materials and Engineering Center
(208) 885-9454 | armandm@uidaho.edu
Research Interests: Biobased composite materials, fiber modifications, and product prototype development and synthesis of carbohydrate, protein, and polyphenolic based polymers for use as thermoplastics and adhesives

PIZHONG QIAO
Department of Civil and Environmental Engineering
(509) 335-5183 | qiao@wsu.edu
Research Interests: Advanced polymer composite materials in civil infrastructure, mechanics of composite materials and structures, smart composites and structures, and fracture of bonded interfaces

SHYAM SABLANI
Biological Systems Engineering
(509) 335-7745 | ssablani@wsu.edu
Research Interests: Polymeric packaging for advanced food technologies and engineering nanoparticle interactions with plant surfaces

LLOYD SMITH
School of Mechanical and Materials Engineering
(509) 335-3221 | lvsmith@wsu.edu
Multi-axial characterization of composite materials, damage and failure modeling, environmental degradation of polymer composites, and sports science

JINWU WANG
Composite Materials and Engineering Center
(509) 335-6362 | jinwuwang@wsu.edu
Research Interests: Biobased resin and composites development
HAIFANG WEN
Department of Civil and Environmental Engineering
(509) 335-2513 | haifang_wen@wsu.edu
Research Interests: Constitutive modeling of pavement materials, recycled materials and byproducts utilization, and pavement evaluation and rehabilitation

MIKE WOLCOTT
Department of Civil and Environmental Engineering
(509) 335-6392 | wolcott@wsu.edu
Research Interests: Composite material development, extrusion processing, viscoelasticity and rheology, adhesion, and anisotropic elasticity

TRAVIS WOODLAND
Office of Commercialization
(509) 335-5593 | t_woodland@wsu.edu
Research Interests: Business development, intellectual property, and corporate relations

VIKRAM YADAMA
Composite Materials and Engineering Center
(509) 335-6261 | vyadama@wsu.edu
Research Interests: Mechanics of wood and wood composites; modeling of engineered wood composites, structure and behavior; behavior of wood joints; and industrial extension and outreach in forest products

JINWEN ZHANG
Composite Materials and Engineering Center
(509) 335-8723 | jwzhang@wsu.edu
Research Interests: Synthesis, processing, and application development of biobased polymer materials; polymer toughening and reinforcing; structure and properties of polymer blends and composites; and polymer foaming and fiber spinning technologies

KATIE ZHONG
School of Mechanical and Materials Engineering
(509) 335-7658 | katie_zhong@wsu.edu
Research Interests: Nanocomposites and multifunctional materials, aerospace materials and composites, composite manufacturing technology, biomaterials and processing, and renewable energy materials