Proposal Topics “Seed Concepts” for 2018 Projects

Thrust Areas
#1) Synthesis and compounding
#2) Biobased products
#3) Modeling
#4) Processing
#5) Biocomposites
Numbering notation (#thrust area, # project, 17 (year))

Benjamin Maloy-Evolvegolf
Title: 1.1.17 Development of biobased ABS (engineered thermoplastic)
Development of a novel 100% bioderived replacement for ABS. Oak Ridge National laboratory made progress towards bio based ABS. It is also my understanding that Dr. Eric Cochran is progressing in this direction at ISU.

Danny Mishek-SelfoEco
Title: 5.2.17 Nutrients run-off of biobased fertilizers
Leaching out of nutrients/additives from bio-polymers into the soil compared to run-off and top fertilizing. This should include alloys of PLA and PBS and evaluating the degradation rates, thermal mechanical properties as well as studying the effects of various fillers.

Ben Caes-Siegwerk
Title: 1.3.17 Biobased UV absorbing biobased coating for food protection
UV radiation is known to cause degradation of food products resulting in decreased taste, nutritional value, and spoilage. To protect food from this degradation, typical packaging is opaque (*e.g.* brown or black) or metallized. Per consumer demand, there is increasing interest among converters to provide a transparent viewing window to allow viewing of foodstuffs before consumer purchase. However, a transparent UV-protective coating must be applied over this viewing window to prevent degradation from occurring. This coating can should be water or solvent based and has to potential to generate millions of dollars in new business opportunities.

Yucheng Peng - Berry Global, Inc.
Title: 2.1.17 Bioplastic packaging for healthcare
Bioplastics and biocomposites materials applications in healthcare, medical and pharmaceutical packaging. This is a general idea introduced to have the teams to propose any ideas using bioplastic in healthcare field. Right now, the strategy of using bioplastic in many companies are for marketing purpose. Two of the biggest hurdles are (1) high cost and (2) low performance. The idea here is to push the application of bioplastics in value-added applications, such as packaging in healthcare if the bioplastics could provide high performance in some areas where the other commodities could not offer or compete. Any new ideas will be welcomed based on the professional teams’ expertise in bioplastics. Pharmaceutical and medical packaging innovations using bioplastics will be the focus.

Yucheng Peng - Berry Global, Inc.
Title: 2.2.17 Transparent bioplastic for glass replacement
Transparent bioplastics and biocomposites with special functionalities to replace glass. The target is to replace the glass in healthcare packaging applications which breakage is one of the major concerns. The other requirements will be barrier, transparence, biocompatibility, etc. The polymer exploration will be one of the goal for this project. Find suitable polymer for suitable healthcare applications and, simultaneously, no other materials will offer the same properties (optional). We are relying on the bioplastics expertise in CB2 program to have innovative ideas. This is also one of the strategies to commercialize bioplastics - using bioplastics in value-added applications,

instead of using bioplastics as of marketing purpose. Two of the biggest hurdles using bioplastics are (1) high cost and (2) low performance.

Yucheng Peng - Berry Global, Inc.

Title: 1.4.17 Degradable plastic for thermal forming processing

Biodegradable and compostable products development from bioplastics and biocomposites using extrusion, injection molding, thermoforming, etc. This project is to develop the processing procedures of bioplastics in industrial scale using extrusion, injection molding, thermoforming, etc. The major limitations using bioplastics in larger scale are the low processing temperature, long cycle time, and low quality of the final parts (brittle, yellowing, smell, etc.). The consumer packaging industry is reluctant to try bioplastics due to the lack of justifying the bioplastics applications in these areas. For the CB2 program project, it will be a good practice to explore the potential of bioplastics in consumer packaging applications, including food, beverage, personal care, etc. This study will help bioplastics find the value proposition in the plastic packaging industry.

Jeff Frantz-Branson Ultrasoncs, Leo Klinstein Dukane-Ultrasonics

Title: 3.1.17 Consumer safe PLA blister packs

Because 6,000 people are injured each year opening "blister packs" and this number may increase with wider acceptance of PLA packaging because of its brittleness and sharp edges, a new design of packaging is important to promote the use of bioplastics for packaging. It is important to design a joint for blister packs that are tailored for PLA mechanical properties that make them easier to open with less hazards (https://www.treehugger.com/green-food/thousands-injured-by-adiabolicala-packaging.html). This will touch a wide range of member companies. This will include PLA/PBS alloys and the measurements of toughness and tear resistance and SEM characterization of the fracture surfaces.

Alper Kiziltas- Ford Motor Company

Title: 1.6.17 Improving Characteristics of Transparent Polymers

In the past years, many transparent polymers including poly (methyl methacrylate), polystyrene, and polycarbonate have gained great interest because of their excellent optical clarity and low density. Despite their huge potential, there are some certain drawbacks including mechanical-dynamical properties (low strength, impact resistance and storage modulus etc.), which limit their efficient use in engineering applications. A general need also exists for increasing the mechanical strength and stiffness of transparent polymers while still retaining their good optical transparency.

Alper Kiziltas- Ford Motor Company

Title: 4.4.17 Nanomaterials

There is a gap between nanotechnology research and markets. This challenge addresses three of the key nano-based industrial value chains: 1) lightweight multifunctional materials and sustainable composites, 2) structured surfaces and 3) functional fluids. The potential of multifunctional nanomaterials and composites has been demonstrated in R&D actions for several industries, such as packaging, automotive and construction. However, a number of barriers hamper to develop cost effective and sustainable industrial scale technologies for the production of nano-based products for specific applications, aiming at the selection, testing and optimization of materials and process parameters. Activities addressing this challenge in CB2 will therefore implement the next steps towards the deployment and market introduction of lightweight, multifunctional, economical and environmentally friendly nano-based products for different applications, by scaling up laboratory experience to industrial scale.

Alper Kiziltas- Ford Motor Company

Proposal Topics "Seed Concepts" for 2018 Projects

Title: 2.3.17 Development of Innovative Technologies/Approaches to Manufacture Added-Value Products with Fewer Resources

To increase the competitiveness of our company and reduce the environmental effects, we should develop innovative technologies and approaches to manufacture added-value products with fewer resources and to ensure a sustainable product life cycle based on reuse and remanufacturing methods and technologies. Most of the materials in composites industry including, long and short fiber composites, nanomaterials and bio-based materials as well as more conventional materials are not considered for re-use because of absence of data on reprocessed performance. The partnership, which falls under the umbrella of CB2 initiative aimed at inspiring this generation to create a better world for the next through conscious actions, will support the aim of recycling, reusing and remanufacturing.

Richard L. Hoch – Diageo

Title: 5.5.17 Spent Distiller Grain Biocomposites for Light-Weighting and New Products

Whiskey, Scotch, and Bourbon distillers around the world produce spent grains as part of the process of making their products. These spent grains amount to hundreds of millions if not billions of pounds every year with a small distillery easily generating over 10 million pounds every year. The spent grains are dealt with either by drying and disposal or by use as-is for live-stock feed. While DDGs from the biofuel industry has been studied as possible fillers from bioplastics composites, there is limited studies on DDGs from the consumer alcohol industry which have the higher levels of residual sugars and other components. Howebwer, because these products are highly regulated, there is a relatively high level of consistency, which may make these grains more attractive compared to DDGs from the biofuel industry. The purpose of this project is to explore the properties of these spent grains for use in biocomposites as either fillers for light-weighting, property improvement, or aesthetic changes. Distiller grains from US bourbon and Canadian whiskey distillers will be evaluated. Grains will be analyzed for moisture content and chemical composition as well as ignition temperature. Composites could be made with PP, HDPE, PLA, and PHA and the resulting composites evaluated for weight reduction, strength, odor, and aesthetic appearance.

Richard L. Hoch – Diageo

Title: 4.2.17 Poly-Lactic Acid: Perfomance Improvements Through Modification, Blending, and Copolymerization

Poly-lactic acid is an established bioplastic that has been used in a variety of applications with much success. However, due to some of its limitations it has not been able to replace conventional polymers like HDPE, PET, or PP in more demanding applications. One of those limitations is due to the water permeation rate of the material. The high MWTR of PLA has kept it from being used in many small format beverage applications as well as large scale containers like drums, carboys, or bins. The other limitation PLA has for more wide-spread use in storage is due to its low Tg. This limitation keeps it from being used for ambient long-term storage of liquids. A PLA container stored in a typical warehouse where temperatures easily reach 40 °C (and higher) will craze in a relatively short period of time and become brittle and break. This research would start with a review of literature and then expand on previous work by and looking at the use of modifiers, blends, and co-polymerization aimed at decreasing the MWTR and increasing the thermal stability of PLA. A possible novel solution would be alloying of PLA and PBS that has higher vapor barrier and thermal properties. While PBS has lower transparency, many of applications do not require transparency.

Richard L. Hoch – Diageo

Title: 1.7.17 Towards Fully Sustainable Polyethylene Naphthalate Production

Polyethylene Naphthalate (PEN) was first synthesized in 1945. It was not offered commercially until the 1990s. PEN has superior properties to polyethylene terephthalate (PET). It has a higher Tg and is therefore more thermally stable making it a better material for packaging products that require hot filling or post-filling thermal treatments. It is also a considerably better moisture, oxygen, and carbon dioxide barrier than PET. These properties make it more suitable than PET for packaging products that require oxygen or carbon dioxide barrier like beer. Lastly, it has better UV resistance than PET. Despite all these superior properties to PET, including the fact that it can processed into products with the same equipment as PET, it has not enjoyed the commercial success of PET. There are many reasons for this commercial reality. The goal of this project would be to develop a synthesis pathway to PEN production utilizing fully sustainable raw materials. One of the main focuses of the proposed work should include a significant TEA model to identify costs reduction opportunities.

Shan Jiang-ISU

Title: 5.6.17 Dispersing and Strengthening Biocomposite Using Colloidal Surfactant

One critical challenge in industrial process and material fabrication is the dispersing and emulsification of different phases. For example, dispersing and stabilizing emulsion is the key to many products such as ink, coating, cosmetic, food, and construction chemicals. Another example is fiber reinforced composite, the dispersion of fiber and adhesion of fiber interface with matrix have been identified as a major factor influencing the final performance.

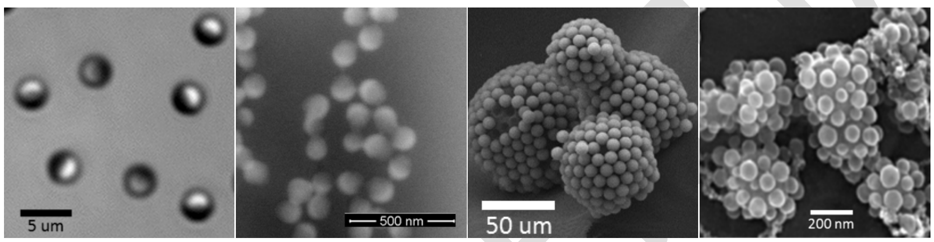


Figure. Left to right: colloidal surfactant of 3 um and 100 nm, black side is hydrophobic, white side is hydrophilic; colloidal surfactant stabilized emulsion and particles;

The common surface modification approach usually involves expensive chemicals and extra purification step. We propose to disperse and strengthen different phases using colloidal surfactant, which has been recently developed in our lab as shown in the figure. The colloidal surfactant is colloidal particles that are either surface active, or have different phases on a single particle. It has been demonstrated that these particles can strongly adsorb at the interface. Since each particle contains many surface active groups, it has much higher adsorption energy than small surfactant and will help stabilize interface for an extended period time. Due to the size of the particles, they will not leach out and may enhance the mechanical strength of the composite. We can further tailor the chemistry of these particles for different applications. Here are a few examples:

1. Agave fiber composite (collaborating with Diageo)

The lignin compatibility and interfacial adhesion with the synthetic polymer matrix can drastically affect the mechanical performance of the composite materials. We propose to modify one side of the colloidal surfactant with adhesion molecules, such as catechol functional groups, which can adsorb and react with lignin surface. The other side of the particle is kept the same material as the matrix, such as poly styrene and PMMA, which can provide the compatibility.

2. Ink and coating applications (collaborating with Siegwerk)

One example is to induce assembly between surfactant colloids with the inorganic component in the formulation. One side of the particle can be modified with anchoring molecules, such as carboxylate and phosphate groups. The other side can be made of acrylic polymers, which provide the compatibility with the matrix.

3. PLA composite with carbon filler

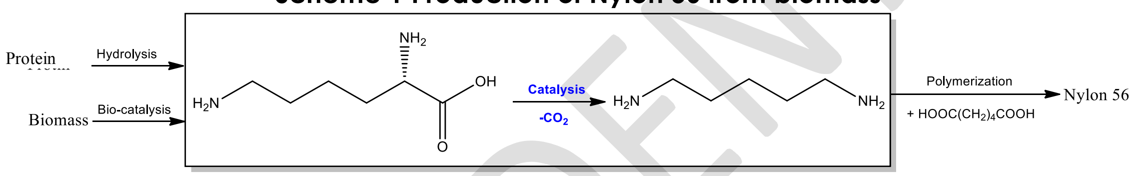
One side of the particle is modified with adhesion molecules, such as catechol, and silane molecules, which can adsorb and react with carbon filler surface. The other side of the particle is composed of acrylic acid, which can provide the compatibility with PLA matrix and improve the mechanical properties.

Hongfei Lin-WSU

Title: 1.8.17 Production of Diamine by Catalytic Decarboxylation of Amino Acids

Objective: The objective of this project is to synthesize biobased polyamides, which have a wide range of applications including synthetic fibers, engineering plastics, resins, etc., from waste protein. In particular, we propose to convert protein derived amino acids to diamines, e.g. L-lysine to 1,5- pentanediamine, via selective catalytic decarboxylation in a liquid-liquid biphasic process. Pentanediamine can replace hexanediamine to react with adipic acid for synthesizing Nylon, .i.e, polyamide. Scheme 1 shows that Nylon 56 is synthesized through the polymerization of 1,5-pentanediamine with adipic acid, both of which can be obtained from renewable biomass resources. We anticipate that a large selection of polyamide products can be synthesized through the combination of various bio-based diacids and diamines. Biobased polyamides are not only the drop-in replacement of the petro-based counterpart but also the unique specialty chemicals with improved properties. In particular, Nylon 56 is a competitive novel fiber for textile material and shows promise for development into highly comfortable clothing. It is pleasing to the touch, absorbs and desorbs moisture nearly as high as cotton, yet has the comparable strength and heat resistance as Nylon 66.

Scheme 1 Production of Nylon 56 from biomass



Scheme 1 Production of Nylon 56 from biomass

Background: Polyamides are widely used in textile industry. Besides, the demand for polyamide resins in the manufacture of engineering plastics sector is continuing to grow: the automotive sector is the largest consumer, while the electrical/electronic branch is the second largest. In addition, polyamides as hard, tough and rigid materials, with excellent properties of high impact abrasion and wear resistance, are also great for applications in packaging and construction. The synthesis of polyamides is usually through condensation of diacid and diamine monomers. Dicarboxylic acids are readily produced from sugars or lipids. For instance, succinic acid, adipic acid, sebacic acid, etc. are already commercialized bio-based chemicals. In contrast, biobased diamines are still not sufficient to meet the fast-growing market demand of biobased polyamides. Our project is to develop a cost-effective process to synthesize a class of these biobased polyamides.

Amino acids are N-containing renewable feedstocks usually obtained from hydrolysis of proteins. Amino acids contain a carboxylic group and an α-amino group, some of which have hydroxyl groups and another carboxylic or amino group (e.g. Lysine, Aspartic acid, Glutamic acid, Serine, Glutamine). Through selective decarboxylation or deamination of amino acids, excessive functional groups may be removed and thus the monomers with only terminal groups could be obtained. Traditionally, diamines are synthesized from di-nitriles originated from petroleum-derived olefins. The commercial biobased 1,5-pentanediamine production process via was developed by Ajimoto [1], which is through the enzymatic decarboxylation of lysine in engineered microorganisms. However, the yield of the 1,5-pentanediamine by fermentation is rather low. Recently, Roman et al. reported a chemical method using hypobromite as the catalyst and a

67.2% yield of 1,5-pentanediamine was obtained in the two-step electrolysis process [2]. However, the scalability of electrolysis is challenging.

Our Approach: Our group has developed a highly efficient decarboxylation process, liquid-liquid biphasic catalytic process (BCP), which can convert a variety of carboxylic acids to hydrocarbons at nearly the highest theoretical carbon atom efficiencies. We demonstrated that a ~94% carbon yield of heptadecane (C17) was achieved from the decarboxylation of C18 fatty acids including stearic acid and oleic acid in a water-hexane system with a supported metal catalyst. In the BCP system, the interfacial water significantly improve the selectivity and the kinetic rate of a decarboxylation reaction. In the project, we will design and screen catalyst that can selectively perform decarboxylation of L-lysine, while leaving the amine groups intact at the same time. The process conditions will be optimized to maximize the yield of diamine and the decarboxylation reaction rate. we will use Aspen to design a continuous BCP for production of 1,5-pentanediamine from waste protein with L-lysine as the intermediate product. Finally, we will synthesize Nylon 56 by reacting 1,5-pentanediamine with adipic acids. The mechanical properties will be measured and the techno-economic analysis will be performed.
Budget: The total budget for one year is $60,000, with includes $40,000 for a full-time postdoc, $20,000 for materials, supplies and characterization fee.

[1] Yoshiaki Murata, Takahiro Kuribayashi, Fumito Onishi and Takehiro Hiura. Method for producing 1, 5-pentamethylene diamine, *WO2015076238 A1*, 2015.
[2] Roman Matthessen, Laurens Claes, Jan Fransaer, Koen Binnemans and Dirk E. De Vos. Decarboxylation of a Wide Range of Amino Acids with Electrogenerated Hypobromite. *Eur. J. Org. Chem.* 2014, 6649–6652.

Jinwen Zhang-WSU

Title: 4.3.17 Preparation of biobased smart material: shape memory, shape changing, reprocessibility, and self-repair

Vitrimer is a class of self-healable and reprocessble cross-linked polymer. It can be prepared by incorporating dynamic covalent bonds into the cross-linked structure, and the cross-linked points in the prepared polymer are mainly constructed by dynamic covalent bonds. At high temperature (> 180 °C), the dynamic covalent bonds are cleaved, and the polymers behave like classic thermoplastics that can be easily reprocessed. At low temperature (< 150 °C), the dynamic covalent bonds are rebuilt, and the vitrimer behaves like thermoset which is neither soluble nor fusible.

Preparation of vitrimer just emerged in the recent 5 years. Current reports are focused on developing vitrimer using petro-based resources which are toxic and nonrenewable. We intend to prepare vitrimer using biobased resources such as eugenol, rosin, plant oil and lignin. To the best of our knowledge, preparation of biobased vitrimer has not been reported yet. Up to now, we successfully developed eugenol-based vitrimer. The prepared material has excellent self-healable and reprocessble properties, and it also has shape memory and shape changing effects. Vitrimer is a thermo-resopnsive material. In the future, we will incorporate more external stimuli responsive functions such as light, pH value, and electricity to the vitrimer. The ultimate goal of our research is to prepare multi-responsive bio-based smart polymer materials.