Seed Concepts for 2019 CB² Projects

Author: Richard L. Hoch
Affiliate: Diageo
Title: Bio-resistance of bio-filled composites (SC-001(R))

Seed concept: Bio-Composites of polymers and agave fibers, flax, hemp, cellulose, and kenaf have been produced as engineering resins in a variety of industries, including those represented by the CB2 IAB. Ford, John Deere, and Diageo have supported research projects in this space in past funding rounds of the CB2. Hyundai and evolvegolf could also benefit from research in this space. With the introduction of these natural products into polymers, microbiological attack of the resulting composites becomes a concern. Mold and fungi may form on or in the composites under the right conditions and effect their functional life. Researchers at the University of British Columbia’s Okanagan School of Engineering recently completed a study with flax and hemp fiber composites with MIT and the National Research Council of Canada but more work needs to be done. This concept would further explore the organisms and conditions that can result in micro-biological growth on and or in various bio-composites including but not limited to polypropylene and agave fiber and how that growth can affect functional properties. Additional composites of interest could include wood fiber, DDG, bamboo, and rice hulls. It would also look at chemistries and processing conditions that can inhibit and or eliminate growth. The project could allow for collaboration with microbiology and or biochemistry investigators at Iowa State and or Washington State.

Key Thrust Area: Biocomposites

Author: Richard L. Hoch
Affiliate: Diageo
Title: Bioplastic and bio-composite choices for a circular economy (SC-002(R))

Seed concept: The vision of CB² and its 3 goals:

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
3. To support large-scale implementation of renewable materials

Support the three principles of a Circular Economy being:

1. Design out waste and pollution
2. Keep products and materials in use
3. Regenerate natural systems

Many companies, including those IAB partners of CB2, have adopted sustainability goals that are positioned to drive company operations to a more circular economy model. What is not always clear is how circular options being considered are with regards to the principles of the circular economy outline.
Since its inception CB2 has only supported 1 project in the modeling space and it is a thrust area for the center.

The IAB and CB² need a simple tool (model) that could be used to evaluate and rank projects, commercial and developmental, from a circular economy view. The goal of this concept is not to produce another LCA model. Rather, the goal is to produce something new that is designed to weigh and rank different options with regards to the circular economy principles specifically as they relate to the thrust areas of CB². Also, the outcome (tool) would be delivered to all IAB members for general use. It would be great if the output of the model had visual representations that link directly to and weigh circular economy principles and the diagram as presented at: https://www.ellenmacarthurfoundation.org/circular-economy/interactive-diagram

This is the general idea (concept). The PI community can further expand, refine, and improve upon the idea in their proposal(s).

Key thrust area: Modeling

**Author:** Brian Tlach
**Affiliate:** Siegwerk
**Seed Concept:** Degradable pigments and inks for improved packaging biodegradation (SC-003(R))

Printing inks are typically based on organic pigments for coloring due to robust chemical and physical properties. These properties also cause the pigments to persist much longer than most resins used in packaging inks. If the biobased pigments are easier to degrade, the inks could be easier to remove for recycling and also allow the inks to more fully degrade over time. Biobased pigments could reduce the persistence of the pigments and improve ink degradability in the environment. This would be especially advantageous as many industries and CB² members seek the development of biodegradable films, packaging, and consumables. The biobased pigments would improve the renewable content of inks, reduce the reliance on petroleum based raw materials, and improve compatibility of printing inks with composting and recycling. The biobased pigments will need to be free from polychlorinated biphenyls (PCBs) or primary aromatic amines (PAAs) which can be present in pigments and pose long-term environmental and health concerns.

The typically product lifetime printing with Siegwerk inks is 6 – 12 months. This would be the target lifetime of the pigments. The key color shades are Blue 15:4, Yellow 13, and Red 57:1 while black (carbon black) and white (titanium dioxide) are not of concern. Main properties would be color shade, color strength, fade resistance, and bleed resistance. High purity grade pigments should be the focus as this will broaden the applications into printing methods including flexographic, rotogravure, offset, and digital printing as well as pigments/colorants for biodegradable foams and thermoplastics.

Key Thrust Areas:
Synthesis
Biobased Products
Biodegradation

Author: Kevin Lewandowski (SC-004(R))
Affiliate: 3M
Seed Concept: I don’t have specific chemicals in mind, however, our company is still looking for biobased inputs as practical alternatives for bisphenol A type epoxy resins (biobased structural adhesives) as well as biobased resins for pressure sensitive adhesives (such as acrylics and rubber block copolymers). Any projects in these areas that have practical value would be of high interest.
Seed Concept: The biological synthesis of monounsaturated diacids, diols and hydroxy acids has proliferated over the past few years in both the academic and patent literature. Proffering a balance of chemical stability and functionally active handles for incorporating novel properties, these molecules have the potential to transform the properties of existing polyesters and polyamides—or even to stand alone as new polymers if the added value justifies the costs. This seed concept seeks proposals that will explore commercial applications for polymers derived from these monounsaturates. Competitive responses will focus on a specific bio-derived monounsaturate or family thereof, chosen both for the foreseen end-uses and potential for commercial availability at a price-point that is justified by the applications. The variety of functional handles provides an incredible diversity of potential polymer properties. For example, the unsaturation point can be epoxidized and acrylated, further raising the -OH number. The resultant monomer could be highly polar or even water soluble. It could be copolymerized with other acrylics as an effective polarity modifier, facilitating compatibility with other compounding agents in the manufacture of adhesives or coatings. The residual hydroxyl functionality could be further exploited with urethanation reactions to prepare crosslinkable acrylics. Another example germane to monounsaturated diacids would include copolymerization with other diacids in the production of polyamides or polyesters. The resultant polymers would have allylic functionality along the chain backbone that could be exploited to further tune the properties of the material. Structure-property relations, including the relationship of the bio-molecule carbon number to the comonomers, are also of interest.
Seed Concept: With the commercialization of PEF and PTF rapidly approaching by various parties, there are a number of opportunities and challenges to develop new blend compositions to take advantage of unique properties afforded by these materials. Most effort to date on application development of these materials has focused on beverage packaging and the substantial improvement in barrier properties compared to PET. Additional beneficial properties deriving from blending and compounded these materials with other engineering thermoplastics remains substantially unexplored. The furanic backbone would be expected to enable a number of new miscible and compatible blends compared to current polyester offerings bringing about possibilities to combine the outstanding barrier properties, high heat distortion temperatures and greater modulus of PEF with attributes of common engineering thermoplastics. Expected outcomes would be information on physical properties, processing, molding, and recycling as foundational knowledge for application development by member companies.

Starch, a biodegradable polysaccharide produced by most green plants, is one of the most abundant renewable resources found in nature. Starches are used extensively as adhesives since they have great adhesion with porous surfaces. However, some of their disadvantages are poor moisture resistance, poor adhesion to non-porous substrates, aging causes their physical properties to change, and starch adhesives can dissolve and lose tack when the moisture content rises.

Polyacrylated glycerol (PAG) shows excellent tack with porous and nonporous substrates and remains tacky at water dispersions of 50 wt% solids. Our past research has shown that compounding starches with PAG can substantially improve the aging properties of thermoplastic starch while remaining water soluble.

We propose the development of waterborne starch and PAG based pressure sensitive adhesives suitable for applications subject to variable humidity in which the degree of water resistance is controlled by the addition of crosslinkers. The concept idea belongs in the CB² Synthesis and Compounding and in the Biobased Products key thrust areas. ADM is a supporting IAB member for this concept. It will also impact member companies like Siegwerk, Berry Global, Diageo, 3M and other companies that work in the area of packaging, adhesives, and labeling.
Author: Nate Tortorella  
Affiliate: John Deere  
Title: Rotationally molded bio-materials (resins, fibers, fillers) (SC-008(R))

Seed concept:

The concept will benefit member companies that are interested in rotational molding as a method to manufacture hollow parts. John Deere in particular is interested in this technology because of the large tanks that are rotationally molded for applications ranging from fuel to seed. We are interested in controlling water or fuel permeability and tank bulging while diversifying the supply chain.

Key thrust areas:

- Synthesis and compounding  
- Biobased products  
- Processing  
- Biocomposites

Title: Bio-based plastic wrap for bales (SC-009(R))

Seed concept:

The concept will benefit member companies that are interested in durable packaging films. John Deere in particular is interested in this technology because of the large amount of plastic wrap our customers purchase for hay, cotton, and other crop that sit out in the environment for extended periods of time. We are interested in controlling water permeability, tensile strength, elongation, UV resistance, and biodegradability.

Key thrust areas:

- Synthesis and compounding  
- Biobased products
Author: PTTGC

1) Title: Home composting PLA and its applications (SC-010(R))

Seed concept:
PLA is one of the most popular bioplastics in the world. However, there are some properties limitation. PLA itself needs an industrial composting condition for their composting process; for example, temperature of 58°C. It will be beneficial if we can develop PLA and its application to be a home compost (25°C). The waste separation system, industrial composting facility, and energy consumption will be cut off.

2) Title: Application development for biodegradable nanocellulose composite (SC-011(R))

Seed concept:
Industry has gained considerable attention in environmental benefits of nanocellulose material since it is biodegradable and renewable. Nanocrystalline cellulose has high modulus, high tensile strength, low thermal expansion. It can be used as a reinforcement material in composite.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cc)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi Strength Steel</td>
<td>7.9</td>
<td>600</td>
<td>210</td>
<td>~1</td>
</tr>
<tr>
<td>Aluminum 6061-T6</td>
<td>2.7</td>
<td>275</td>
<td>70</td>
<td>~2</td>
</tr>
<tr>
<td>E-glass fiber</td>
<td>2.5</td>
<td>3,500</td>
<td>80</td>
<td>~2</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>1.8</td>
<td>4,000</td>
<td>230</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Cellulosic</td>
<td>1.5</td>
<td>7,500</td>
<td>135</td>
<td>4-10</td>
</tr>
<tr>
<td>Nanocrystals*</td>
<td></td>
<td></td>
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</tbody>
</table>


Considering end-use market, biodegradable material has been considered as a growing market. Polylactic and polybutylene succinate are most important biodegradable materials, but there might be some drawbacks on mechanical properties. Nanocellulose composite will improve mechanical properties of biodegradable plastic which will help to explore for new application. Our interest is looking for new applications and new materials of nanocellulose biodegradable composite in following areas:

- Automotive nanocellulose composite
- Packaging
- 3D printing nanocellulose/biodegradable plastic
- Medical

In automotive application, nanocrystalline cellulose can tremendously improve the mechanical performance and light weighting of vehicles. Works still needs to be done on
how to compatibilize nanocrystalline cellulose with the resin matrix and to reduce cost of nanocrystalline cellulose.

In packaging area, PLA and PBS are good structural material. However, they still have insufficient O2 barrier and water vapor barrier properties. Typically, an oxygen barrier film, typically made of EVOH, is needed to provide barrier to prolong shelf life of products. EVOH is, however, non-biodegradable. It is interesting to see if nanocrystalline cellulose composite with bioplastic can improve both structural performance and barrier properties of bioplastic resins, while maintaining biodegradability.

<table>
<thead>
<tr>
<th>Material</th>
<th>Gas Transmission Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O (WVTR) [g/m²·day]</td>
</tr>
<tr>
<td></td>
<td>20 µm</td>
</tr>
<tr>
<td>BioPBS™ FZ91</td>
<td>520</td>
</tr>
<tr>
<td>PLA</td>
<td>680</td>
</tr>
<tr>
<td>PBAT</td>
<td>900</td>
</tr>
<tr>
<td>LDPE</td>
<td>26</td>
</tr>
</tbody>
</table>

Source: BioPBS Technical Presentation

3D Printing is also another growth area. While there are hundreds of material grades available for injection molding, there are still not many grades of 3D printing materials to choose from. PLA filament is good enough for prototyping, but still insufficient impact resistance. ABS has a better impact resistance, but the emission of styrene monomer during printing requires it to be processed in a closed environment with worker protection.

Furthermore, in medical application, a combination of 3D printing technology and nanocellulose/resin composite can provide a strong biomedical material for bioprinting. There seem to be a lot of activities around using nanocellulose as tissue engineering scaffold for cell culture and medical application.
3) **Title** Conceptual manufacturing process for low cost nanocellulose from bagasse (SC-012(R))

**Seed concept:** Sugarcane bagasse is a major component in waste from sugarcane juice production. Conversion of bagasse to nanocrystalline cellulose and nanofiber cellulose have potential to apply as reinforcement material in biocomposite. They can be applied in various applications including coating, medical, packaging, cosmetic, electronic material and automotive. Literatures report several methods to convert sugarcane bagasse to nanocellulose such as mechanical grinding, acid digestion, or enzymatic method. Fundamental research to support conceptual design on processing condition provide beneficial knowledge for industry. An effective production process with reasonable production cost is still required. The process could be designed for nanocrystalline cellulose or nanofiber cellulose or a combination. Furthermore, oxidation derivatives of nanocellulose in any form can be a part of production process.

**Author:** Bin Yang (PI), Jinwen Zhang (Co-PI)-NEED INDUSTRY PARTNER Affiliate: Washington State University

**Title:** Lignin-Derived Monomeric Aromatics-Based Thermosetting Engineering Materials (SC-013(R))

Seed concept: Current use of lignin or lignin derivatives as feedstocks for polymer applications have attracted increasing interest as sustainable, cost-effective, and biodegradable alternatives for petroleum-based thermosets. However, most lignin-based thermosetting resins exhibited limited poor processability due to solid and insoluble nature of lignin and limited mechanical properties due to the highly branched structure. To improve the processability and mechanical properties, our team will develop and demonstrate the use of reactive monomeric aromatic lignin compounds derived
from biorefinery waste or undervalued lignin streams for high performance thermosetting polymer materials. The proposed research is based on extensive and unique patented technologies: 1) Recently, Dr. Yang’s group at WSU demonstrated efficient using zeolite to hydrolyze the NREL pilot plant corn stover lignin to high yield (> 85% wt/wt) aromatic monomeric compounds with highly etherified side chain structures, and 2) Vanillin-based high performance epoxy materials (Dr. Zhang’s Lab).

In this study, Dr. Yang’s team will develop various chemical approaches/strategies to optimize/tune the reaction conditions and process parameters to produce highly reactive lignin monomeric compounds that are vital for the success of the overall project. Dr. Zhang’s team will work on the conversion of the lignin monomeric compounds to thermosetting engineering polymers. Thermosetting engineering materials are important metrics resins for polymer composites that are widely used in aerospace, automotive, sports good and electronics, coating, and adhesive polymers.

Authors: Tina Tosukhowong (Myriant), Saskia van Bergen (WA Dept of Ecology)

Seed Concept: The Development of Cost-effective Marine Degradable Plastics (SC-014(R))

Ocean pollution by plastics has become a significant global problem impacting marine creatures and coastal ecosystem. Many plastic fragments have been found in deep sea fish in the Northwest Atlantic, which could be directly passed on to human.

Depending on region, the plastic waste compositions in marine environments vary but bottles and bags are frequently a major source.
This seed concept is seeking the development of plastic materials that are biodegradable in the marine environment. It is important that the solution is a cost-effective alternative to common material such as polyolefins. Examples of target applications are plastic bags, films, bottles, single-use containers, adhesives and microbeads.

Marine biodegradability standard can be found at [http://www.okcompost.be/data/pdf-document/Program_OK_12e_a_OK_biodegradable_MARINE_add.pdf](http://www.okcompost.be/data/pdf-document/Program_OK_12e_a_OK_biodegradable_MARINE_add.pdf). Currently, there are many additives and bioplastics that have been developed. However, high prices have deterred consumer adoption. For example, currently the polyolefin price is less than $1/lb, while a marine degradable polymer such as polyhydroxy alkanoate (PHA) is ~$3/lb. Thermoplastic starch and PLA can be quite low cost, however they cannot be used as a single resin to achieve both performance and biodegradability. How can we close the gap in price, performance, and biodegradability?

**Author:** Hongfei Lin (WSU)

**Industry Partner:** Erik Hagberg (ADM)

**Title:** Production of primary amines from waste protein (SC-015(N))

Protein as a very rich natural N-containing feedstock is suitable for conversion into primary amines. Different potential sources for amino acids that could be used for the production of bulk chemicals in a biorefinery include maize and wheat DDGS, sugarcane and sugar beet vinasse and leaves, cassava leaves, press cakes of plant oils, animal slaughter waste, microalgae, macroalgae, grass and alfalfa, etc. The growing amount of waste proteins make the utilization of amino acids as a source for bulk chemicals a possible option in the near future. Though the proportion of protein varies according to the sources and production process, after extraction all the isolated proteins can be hydrolyzed into different amino acids. The hydrolysates can be treated by successive
electrodialysis (ED) in order to extract amino acids into several fractions and further fractionated to achieve the separation of amino acids. Our group has developed a highly efficient heterogeneous process which can convert L-lysine to diamines. The catalytic process for the conversion of L-lysine, the study on the protection strategy of amino group, the C–C and C-N bond cleavage, and reaction pathways are combined to elucidate the mechanistic insight to the deoxygenation of L-lysine to diamines. As a result, the highest yield of diamines (46.6% of cadaverine and 38.6 % of piperidine and its derivatives as other N-containing. We thus gained the knowledge and experience to convert waste proteins to primary amines, which may react with phenol and formaldehyde to form benzoxazines, the individual or mixed monomers that are widely used for production of currently commercially available polymers for the aerospace industry and more specifically for interior applications. In particular, we propose to convert the mixed amino acids to the blended primary amines via selective deoxygenation process. As a result, the waste proteins were converted into a polymeric candidate with excellent fire retardant properties and the improvement processability over existing polymers.

Figure 1 Production of primary amines and their use pattern
Author: Marc Brinkmeyer
Affiliate: Idaho Forest Group
Title: Wood-based cellulose and lignin-derived precursors for biodegradable bioplastics and biocomposites SC-016 (N)

Seed concept: Production of forest-based products such as lumber results in large quantities of low-value post-harvest forest residuals and sawmill waste streams that include sawdust, planar shavings, and wood chips. Lumber production at IFG mills amounts to approximately 60,000-truck loads of wood residuals. Traditional use of these materials has been for energy generation, but lower cost and plentiful natural gas has significantly impacted the economics. Wood chips for newsprint and pulp manufacturing are experiencing lower prices due to closure of antiquated mills, and particleboard is over produced and has resulted in lower prices for sawdust and shavings.

This seed concept calls for research that aims to find more value-added applications for this raw material source resulting from lumber production. Approximately 65% of this feedstock is comprised of six- and five-carbon carbohydrates and 25% lignin, an amorphous and highly branched aromatic polymer. Several products can be derived from these constituents including cellulosic and lignin fibers, glucose and other sugars, and a variety of alcohols. These derived products have the potential to be converted into fibers for textiles and composites, food ingredients, bioplastic additives, specialty chemicals, dispersants, surfactants, bio-based hydrogels, and so forth. Major challenges to monetize lignocellulosic-based chemical products are finding effective and economical methods of fractionating wood and isolating desired chemical building blocks and integrating into existing forest products supply chain for economic viability. These bioproducts are critical for biorefineries to be economically viable. A diversified portfolio of products that includes drop-in biochemicals for petroleum-based products will also revitalize the forest products industry and contribute to a sustainable bioeconomy. Isolation of building blocks from wood-based carbohydrates and lignin to produce drop-in biobased thermoplastics that are also biodegradable would lead to a competitive bioeconomy and displacement of synthetic plastic waste streams. Synthesis of these building blocks to further process into bioplastics/blends of bioplastics and synthetic plastics and biocomposites with attributes such as flame resistance, hydrophobicity, or adhesion would be beneficial.

Key Thrust Areas: Bioplastics, Biocomposites, Synthesis & Compounding, and Feedstock Logistics
Seed concept: Lignocellulosic biomass, consisting of a combination of cellulose, hemicellulose, and lignin in the plant cell wall, is the most abundant renewable resource on earth. Despite a recent focus on their use and conversion to value-added products such as fuels and chemicals, the ligniocellulosic resource remains largely unutilized due to an extremely complex and widely varying nanoscale lignin-carbohydrate complex, and also the lack of cost-effective and environmentally-friendly conversion technologies. However, it is noteworthy to mention that wood has a unique fluid transport system built by nature. It contains active functional groups and aromatic compounds providing wood with hydrophilic and hydrophobic properties. Thus, it would suggest an opportunity to make a breakthrough in fundamental science that will accelerate the development of more efficient and cost-effective green stormwater filter composites.

From the environmental point of view, the heavy metal ions and hydrophobic organic compounds from wastewater must be removed or be reduced to the minimum level before discharged to the environment. To date, in pulp and paper industry, the effect of the adsorption of various metal ions from single, binary, ternary, and quaternary metal ion systems from process aqueous streams onto pulp fibers and bark on behavior and properties of final products has been studied. Also, treatment of wastewater is commonly carried out by physical (filtration using activated carbon), chemical or biological processes. The cost of filtration by activated carbon or chemical methods are relatively expensive. Biological treatment uses microorganisms bacteria, fungi, and yeasts but the process is very slow and may result in some environmental issues. Thus, further investigations are needed to develop a green stormwater composite system with an enhanced longevity and performance of biofiltration media for removal of metal ions (e.g., Cu and Zn) and also toxic organic chemicals (e.g., PAHs, PCBs, oil, grease) form stormwater.

Biofiltration, on the other hand, has clear advantages over the aforementioned methods as it uses inexpensive and environmentally-friendly lignocellulosic materials for removing contaminants from wastewater. In the past, the effectiveness of lignocellulosic-based filters has been mostly attributed to the thermally treated-structure of wood such as torrefied wood and biochar. But in a project conducted by Dr. Wolcott's research team on multi-solute continuous flow column experiments, raw wood crumbles, torrefied wood crumbles, biochar, and pea gravel were used to assess their ability to adsorb soluble copper and zinc that are constituent of concern in municipal stormwater runoff. Interestingly, it was shown that raw wood crumbles outperformed all other media evaluated by adsorbing 97% copper and 89% of zinc. The previous results indicated that wood-based media induces selective adsorption of metal ions. We will particularly focus on organic chemicals and polycyclic aromatic hydrocarbons removal.
and also improving the performance and longevity of the filtration media for stormwater treatment through the use of mechano-chemo approaches. In our experimental work Dr. Wolcott’s research team has demonstrated that how lab and pilot-scale mechanical milling such as ball milling and spring suspended vibratory mill proved capable of micronizing and modifying forest residues and of inducing amorphous wood powders for more demanding applications.

Here, what motivates us is the presence of active functional groups and hydrophobic aromatic structures in raw wood, in which they are acting as the binding sites for pollutants. For example, wood can exhibit ion-exchange properties due to the presence of certain type of functional groups (acidic groups). These acidic groups are mainly carboxylic groups and phenolic hydroxyl groups, acting as the binding sites for metal ions to wood. A model of ion-exchange reactions occurring between the metal ions in the solution (stormwater) and the hydrogen ions in carboxyl groups in the solid phase (wood cell walls) is illustrated in Fig. 1.

![Fig. 1. Schematic illustration of wastewater transport in wood (a) and ion-exchange of metal ions (M²⁺ pollutant) with hydrogen ions to carboxyl groups; chelating heavy metals (b).](image)

The combination of acidic functional groups and aromatic units as it exists in wood has function in synergy with sorption capacity for both metal ions and hydrophobic organic compounds. Our preliminary study offers effective ways to mechanically treat surface of wood for removal of wide range of stormwater pollutants. Raw wood structure as a model system has several major advantages. First, wood is known as a renewable resource built by nature. Second, lifetime of wood can significantly be increased using different natural and or chemical treatments. Third, fluid transport system in wood can
be modified in order to enhance the transport of water in its structure and consequently providing sustainable condition for further absorption. Fourth, various physicochemical treatments can be employed for modifying wood functional groups and providing wood with desirable characteristics.