PROJECT TITLE: Corn Derived Materials
PROJECT NUMBER: 1088-18EU
PRINCIPAL INVESTIGATOR AND CO-INVESTIGATOR(S): Marc Hillmyer, Frank Bates, Paul Dauenhauer

ABSTRACT
Provide a project summary describing an overview of the project including principle findings. Include a statement on how the project was of benefit to corn farmers.

Poly(lactide) (PLA) is a compostable plastic that is derived from corn, and has been widely studied as an alternative to petroleum-based plastics. However, PLA is intrinsically brittle limiting its potential for many applications. In this work, the Bates group was able to significantly toughen PLA by the addition of small amounts of a diblock copolymer additive (5 % wt.). The diblock copolymer forms spherical dispersions in PLA that can cavitate to form voids when the material is stressed upon elongation. Crazing is initiated from these voids which delays mechanical failure to much longer extension than with the unmodified material. In addition, elimination of mechanical aging, which occurs in about one day after molding unmodified PLA, was discovered with one of the additives.

The Dauenhauer group’s research evaluated the conversion of sugar-derived furfural to diene monomers that serve as the basis for rubbers including car tires and gloves as well as hard ABS plastics used in consumer products. As shown in Figure 1, there exists four-part chemistry and purification to manufacture butadiene. This large-volume chemical is a natural product of sugars, being unsaturated and significant in market size to have an impact on the usage of corn. In this work, a chemical process is designed and optimized to evaluate the efficacy of renewable butadiene production. Chemical process design includes reactor and separator design and sequencing, along with economic sensitivity analysis and identification of conditions leading to economic viability.

INTRODUCTION
Provide background information related to the project including such item as the problem statement, knowledge gaps, and relevant previous work completed on this issue.

Mechanically toughened PLA
Rising concerns about environmental pollution and plastic waste disposal have led to an increase in research focused on sustainable polymers. To date, 8300 million metric tons of plastic have been produced in the
world, of which only 9% has been recycled and 79% has been collected in landfills.\footnote{1} A strategy to limit the buildup of plastic waste in landfills is to develop products made from degradable polymers. One such polymer that is commercially available is poly(lactide) (PLA). PLA is derived from fermentation products of corn and degrades in an industrial composter at 65°C.\footnote{2} However, PLA undergoes physical aging and becomes brittle in a short time scale. During aging, the polymer chains rearrange to a more stable and dense configuration resulting in loss of chain mobility and therefore brittle failure.\footnote{3} Over the years there have been many attempts to toughen PLA such as using plasticizers\footnote{4-7} or blending\footnote{8-11} PLA with rubbery polymers. Plasticizers require high mass loadings to achieve a ductile blend which lower the glass transition temperature. In comparison, rubbery polymers are often immiscible with PLA leading to large dispersions sizes, which decrease the modulus of the material, and affect the transparency of PLA.\footnote{12} To avoid these limitations, diblock copolymers that form smaller dispersion sizes (i.e. sub-micron sized) are an attractive alternative. Previous researchers have investigated toughening PLA with diblock copolymers,\footnote{13-15} but this study has focused on the effect of diblock copolymer on the toughening mechanism and role of physical aging on the mechanical properties of PLA. Understanding the aging and toughening of PLA with block copolymer additives will be crucial for future applications.

**Sugar derived butadiene**

The utilization of sugars for basic chemicals requires the catalytic chemistry optimized for each reaction as well as the chemical process design to achieve economic manufacturing at large scale. In this work, a previous laboratory-scale reaction of the conversion of tetrahydrofuran to butadiene was evaluated as a complete chemical process to evaluate the design of chemical reactors and separators. The chemical process was optimized by varying key parameters including reactor and separation conditions using experimental data as well as process simulation predictions. Using a sensitivity analysis approach, the key chemical manufacturing parameters were identified and conditions leading to the most economic design were identified.

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**Figure 1.** Three step process from furfural to tetrahydrofuran to butadiene.
OBJECTIVE AND GOAL STATEMENTS

Mechanically toughened PLA
The goal of this work is to establish additives that can be combined with PLA to result in blends that are mechanically tough regardless of aging time. With improved mechanical properties, the number of potential applications and demand for PLA is expected to increase.

For the purpose of converting sugar-derived furfural to butadiene:
- Develop a reactor-recycle system to hydrogenate and decarbonylate furfural to THF
- Design a reactor-recycle system to ring open and dehydrate THF to butadiene
- Identify reactor system or separation scheme for addressing separation of THF, butadiene and propylene
- Optimize the system design to minimize the cost of butadiene

MATERIALS AND METHODS
As appropriate, describe the site(s), experimental design, and other relevant methodology used in completing the project.

Mechanically toughened PLA

Materials. Commercial PLA (Ingeo 4060D) was acquired from NatureWorks. Poly(ethylene oxide)-b-poly(butylene oxide) (PEO-PBO) diblock copolymer (available under the tradename Fortegra™ 100) with a number average molecular weight $M_n = 7,000$ g/mol and containing 35 % wt. PEO was obtained from Olin Chemical. All materials were dried in a vacuum oven for 24 hrs before micro compounding. A series of poly(isoprene)-b-poly(ethylene oxide) (PI-PEO) diblock copolymers were synthesized by a two-step anionic polymerization. Isoprene (Sigma-Aldrich, ≥99%) was purified by distillation from n-butyllithium twice and transferred into a dry burette. The polymerization initiator, sec-butyllithium, was injected into the solvent in the reactor under 3 psi argon pressure. The purified isoprene was then added and allowed to react overnight at 40°C to 100% conversion. The polymer was end functionalized by the addition of a single unit of ethylene oxide (Sigma-Aldrich, ≥99.5%) (EO) and recovered by precipitation in methanol and then vacuum dried. EO, was purified twice over butyl magnesium chloride, then transferred to a cold dry burette. PI-OH was dissolved in purified tetrahydrofuran and initiated by titrating with potassium naphthalenide followed by addition of purified EO and allowed to react overnight at 40°C. The reaction was terminated by the addition of acidic methanol to produce a PI-PEO copolymer. The copolymer was precipitated in cold acetone and then freeze dried from benzene before further use. Six PI-PEO diblock copolymers were synthesized; the one that is discussed here has $M_n = 134,000$ g/mol and contains 49 % wt. PEO.

Sample Preparation. The samples for mechanical property testing were made from a master batch. The master batch was prepared by dissolving 75 % wt. PLA and 25 % wt. diblock copolymer into chloroform followed by solvent casting. Once dry, the master batch and additional PLA were micro compounded at 180°C for 5 mins to produce a 5 % wt. diblock copolymer in PLA blend.

Morphology Characterization by Microscopy
Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the microstructure and deformation mechanism of the blend. Before SEM imaging, samples were cryo-micromanotomed at -120°C to create a fresh face, followed by dissolving PEO-PBO diblock copolymer on the exposed surface with ethanol. The resulting cross section was sputter coated with 2nm of iridium and imaged with JEOL 6500 SEM. TEM samples were prepared by cryo-micromanotoming at -120°C with a diamond knife to produce ultra-thin sections (around 70nm thick). The sections were then vapor
stained for 15 min with 0.5 % wt. ruthenium tetraoxide solution (RuO$_4$) and imaged with a FEI Tecnai Spirit TEM with a 120 kV accelerating voltage.

**Tensile Properties**
After micro compounding, blends were hot pressed at 130°C to form 0.5mm thick films. The films were then cut into dog bone shapes with a SDMK-1000 dumbbell cutter to a width of 5 mm and a gauge length of 22 mm, in accordance of ASTM D1708. All tensile tests were performed at room temperature at a strain rate of 10 mm/min.

**Small Angle X-ray Scattering (SAXS)**
Tensile bars were strained under the same conditions as described above but stopped before failure at specified strains. These samples were then investigated with SAXS to understand the craze formation and growth. SAXS was conducted at the Characterization Facility at the University of Minnesota using a SAXS Lab Ganesha instrument with a CuKα x-ray source ($\lambda = 1.54$ Å) and a position sensitive Eiger 1 M detector.

**Sugar-derived butadiene**
The conceptual design of a process to convert furfural to butadiene via THF was developed to assess the industrial feasibility of this synthetic route. The process comprises three stages, as shown in Figure 1: (1) decarbonylation of furfural to furan and carbon monoxide, along with the associated separations and recycle, (2) furan hydrogenation to THF, and (3) dehydra-decyclization of THF to butadiene followed by butadiene purification. Aspen Plus (V8.6 Aspen Technology) was used with the non-random two-liquid (NRTL) activity coefficient model and the Redlich-Kwong equation of state to simulate the proposed process. The simulation included the Heater, HeatX, RStoic, RadFrac, Flash2, Compr, Sep2, Pump, and Extract modules. Aspen Economic Analyzer was used to estimate capital and operating costs and Microsoft Excel was used for economic analysis.

**Table 1. Feedstock, Product, and Utility Prices.**

<table>
<thead>
<tr>
<th>Process Component</th>
<th>Economic Metric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural purchase price ((\text{\text{$ kg}^{-1}\text{]}^{[61]}))</td>
<td>1.843</td>
</tr>
<tr>
<td>Hydrogen purchase price ((\text{\text{$ kg}^{-1}\text{]}^{[62]}))</td>
<td>1.57</td>
</tr>
<tr>
<td>Butadiene sale price ((\text{\text{$ kg}^{-1}\text{]}^{[63]}))</td>
<td>1.1</td>
</tr>
<tr>
<td>Electricity ((\text{\text{$ kWh}^{-1}\text{]}))</td>
<td>(7.75 \times 10^{-2})</td>
</tr>
<tr>
<td>Cooling Water ((\text{\text{$ kg}^{-1}\text{]}))</td>
<td>(3.17 \times 10^{-5})</td>
</tr>
<tr>
<td>Refrigerant ((\text{\text{$ kg}^{-1}\text{]}))</td>
<td>(1.87 \times 10^{-4})</td>
</tr>
<tr>
<td>Steam, 100 psi ((\text{\text{$ kg}^{-1}\text{]}))</td>
<td>(1.79 \times 10^{-2})</td>
</tr>
<tr>
<td>Wastewater treatment ((\text{\text{$ kg-organic}^{-1}\text{]}^{[64]}))</td>
<td>0.33</td>
</tr>
</tbody>
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**RESULTS AND DISCUSSION**

**Mechanically Toughened PLA**
The morphology of the blends were observed with SEM (Figure 2A), after selectively removing the PEO-PPO diblock copolymer with ethanol. Based on the SEM images, the particles were found to be spherical with an average diameter of 0.66±0.35 \(\mu\text{m}\).
To observe the morphology of the PI-PEO/PLA blends with TEM, the ultrathin sections were exposed to RuO$_4$ which preferentially stains PI causing it to appear darker in the image. The particles produced by blending PI-PEO with PLA are also spherical, with an average diameter of 90±20 nm (Figure 2B).

![Figure 2. (A) SEM image of 5% wt. PEO-PBO in PLA, after washing the microtomed surface with ethanol to dissolve the PEO-PBO diblock copolymer. (B) TEM image of 5% wt. PI-PEO in PLA and stained with RuO$_4$ for 15 mins.](image)

To investigate the mechanical properties of the blend, tensile tests were performed. Each sample was tested at several different aging times and the stress-strain results are displayed in Figure 3. From the tensile curves of neat PLA (Figure 3A), it is evident that physical aging significantly effects the mechanical properties and occurs on a short time scale. Two hours after processing, PLA behaves as a ductile plastic and can elongate to 250% strain before breaking. However, after 24 hours of aging, PLA densifies and becomes brittle, breaking at 7% strain. This short aging time at room temperature limits potential applications. The mechanical properties of the PI-PEO/PLA blend show similar signs of aging as PLA, but this happens at a slower rate. As with PLA, the PI-PEO/PLA blend, at short aging times (24 hours), is a ductile material reaching strain values greater than 225% (Figure 3B). After aging for additional 24 hrs, the material can only be extended half as far, stretching to 100% strain. Finally, by 5 days of aging, PI-PEO/PLA blends are brittle. Although, this shows that the aging of PLA can be slowed by the addition of PI-PEO, the blend is still not practical for many applications. However, by the addition of only 5% wt. PEO-PBO, the mechanical properties can be completely altered. PLA/PEO-PBO blends show no signs of physical aging and are ductile at low aging times (2 days) and remain ductile through 40 days of aging (Figure 3C). This is a significant result and to further understand why the blend does not show signs of physical aging, the toughening mechanism will have to be investigated. Here we note that we discovered that subtle variations in the molecular characteristics of the PEO-PBO diblock copolymer can have a major influence over the efficacy of this additive. In particular, a batch of Fortegra™ 100 with about 15% higher molecular weight but the same composition did not produce long lasting ductility.

There is a clear difference between the mechanical properties and aging of the PI-PEO/PLA and PEO-PBO/PLA blends. There are several potential reasons for these differences, one such reason being the difference in diblock copolymer particle size. The particle size of PEO-PBO/PLA blend is more than 5 times larger than PI-PEO/PLA. Particle size plays a crucial role in rubber particle cavitation. Particle cavitation is a balance between strain energy released from cavitation (proportional to volume of the particle) and energy required to form a new surface (proportional to surface area) during void formation.$^{19}$
Therefore, larger particles are more favorable to cavitate than smaller ones. In the present study, PEO-PBO particles can cavitate at lower stresses which may allow for superior toughening. These results are still being investigated and the follow up study will focus on the success of the PEO-PBO/PLA blend.

PLA is known to deform by crazing, which leads to the formation of a network of fine cracks separated by load bearing fibrils that are spaced apart by approximately 5-30 nm. The creation of a craze is associated with energy absorption during fibril formation, which inhibits crack propagation and results in a tough plastic. However, if the craze fibrils begin to fail, the fine cracks will coalesce and result in larger cracks that will lead to macroscopic failure. To investigate crazing at the fibril length scale, SAXS has been employed.

To understand the toughening mechanism of the PLA/PEO-PBO blend, SAXS was performed on stretched tensile bars (Figure 4). Three different tensile bars were analyzed: i) “tough” neat PLA (aged < 2hrs), ii) brittle neat PLA (aged > 24 hrs), and iii) PLA/PEO-PBO blends (aged for 2 days). The 90° and 0° axes in Figure 4 are referred to as the meridional and equatorial axes, respectively, where the sample is stretched parallel to the meridional axis. The 2-D scattering patterns of PLA and PLA/PEO-PBO have some similar characteristics but the crazing patterns develop differently. In the case of “tough” PLA, at low strains (10%...
strain), there is a clear equatorial lobe, which is indicative of crazing. As the sample is continually strained, the equatorial lobe intensity decreases; as the material is stretched further, no further crazing occurs and the fibrils separating the fine cracks break. Therefore, the cracks grow in size and fibrils are spaced further apart than what can be detected by SAXS.

After aging for 24 hrs, PLA becomes brittle and breaks at low strains. Based on the 2-D SAXS pattern, absence of an equatorial lobe indicates that there is no craze formation; the sharp meridional band can be inferred as uncorrelated void formation. Therefore, at long aging times, PLA is unable to craze and instead unstable voids form that lead to brittle failure.

In contrast to “tough” and “brittle” PLA, the 2-D scattering patterns produced by the PLA/PEO-PBO blend demonstrates a much different sequence of deformation events. At low strains, the PLA/PEO-PBO blend exhibits relatively uniform intensity at all azimuth angles. Upon further straining to 50%, there is a large intensity increase in the equatorial lobe, which continues to intensify as the material is strained to 100%. Thus, in PLA/PEO-PBO crazing does not occur until 50% strain, beyond which the blend continues to deform by crazing, either as a result of propagation of existing crazes or by formation of new crazes. These results demonstrate that the significant differences in mechanical properties between PLA and PLA/PEO-PBO blend are a result of differences in the toughening mechanisms. Due to the presence of PEO-PBO, PLA is able to uniformly and continually deform by crazing, allowing it to be stretched to high strains irrespective of aging time.

![Figure 4. The left hand images are tensile stress-strain curves of samples at a specified aging time where the different X symbols correspond to the strain at which the tests were terminated and the material was subsequently analyzed by SAXS. The right hand images are 2-D SAXS patterns at specified strains, where the samples were stretched in the vertical direction. (A) “Tough” neat PLA (aged < 2 hrs), (B) “brittle” neat PLA (aged> 2 days), and (C) PLA/PEO-PBO blend (aged for 2 days).]
To confirm the conclusions drawn from SAXS and further develop our understanding of the role of the PEO-PBO diblock copolymer during deformation, TEM was performed on the same strained tensile bars. As shown in Figure 5A, “tough” PLA strained to 10% exhibits thick, long crazes that span the width of the TEM image. In Figure 5B, the PEO-PBO/PLA blend shows voids with black lines going through them. The black lines are thin and vary in length. These black lines are believed to be plastically deformed material that is stained by RuO$_4$. However, according to the SAXS data, at 10 % strain the PEO-PBO/PLA blend does not show evidence of crazing. So these features will need to be studied further. The TEM image in Figure 5B clearly shows void formation, and these voids can be modeled as ellipses having an average area of 0.35±0.21 µm$^2$. Notably, this area is the same as the spherical particles in Figure 2 (0.35±0.26 µm$^2$). Therefore, this indicates that the spherical particles cavitate to form the ellipsoidal voids once the material is stressed. These voids act as stress concentrators where plastic deformation can occur. This is confirmed by Fig. 5B which shows plastic deformation being initiated from the voids and propagating outward from them.

![Figure 5. TEM images of (A) “tough” neat PLA stretched to 10 % strain and (B) a PLA/PEO-PBO blend stretched to 10 % strain. The tensile bar in the right corner of the images shows the direction the bars were pulled.](image)

Sugar-derived butadiene

Our findings are described in Figure 6, which outlines all three chemical steps to manufacture butadiene from corn-derived sugars. The initial green components include the decarbonylation reactor (R-1) followed by separating distillation columns D-1 and D-2; carbon monoxide and hydrogen are removed in a flash tank. In the purple reactor R-2, furan is then hydrogenated. In reactor R-3, tetrahydrofuran undergoes ring-opening dehydration to make butadiene; the energy is conserved via an economizing heat exchanger. Separations than occur in distillation columns D-3 and D-4 followed by drying in A-1.
The process economics to manufacture butadiene from furfural were broken down into feedstock and processing costs with further subdivisions of utilities, capital and operating costs as shown in Figure 7. The base case design of the chemical process achieved a minimum sale prices of butadiene of $5.521 kg⁻¹; this is the price that butadiene could be sold at to break even for a discounted chemical process over 20 years with an initial capital investment and yearly sales while also accounting for all costs. As shown, the entire process is controlled by the cost of furfural feedstock, which takes into account the lost carbon due to side reactions, predominantly propylene formation from THF and furfuryl alcohol (overhydrogenation) from furfural.

Figure 6. Chemical Process Design of Optimized Furfural to Butadiene.

Figure 7. Total base case cost of minimum sale price of butadiene broken into process and feedstock costs.
Figure 8. Sensitivity of the minimum selling price (MSP) of butadiene to selected process parameters. Parameters were varied ±10% relative to the base case design of 100 kmol hr$^{-1}$ at furfural and hydrogen purchase prices of $1.843 \text{ kg}^{-1}$ and $1.57 \text{ kg}^{-1}$, respectively.

To further improve the chemical process economics, a sensitivity analysis was conducted as shown in Figure 8. The key process parameters were selected including the purchase price of furfural, the size of the chemical process, the total capital investment, the hydrogen price, the wastewater treatment cost, and the catalyst price of the hydrogenation precious metal catalyst. Each parameter was varied by +/- 10%, and the resulting minimum sale price of butadiene was calculated. It is clear that the furfural purchase price dominates the chemical process design, indicating that the economics of renewable butadiene will be determined by the purchase price of furfural.

**CONCLUSIONS**

**Mechanically Toughened PLA**

Blending PLA with an appropriate grade of PEO-PBO diblock copolymer results in a tough PLA material that shows no signs of physical aging up to 40 days. The PEO-PBO diblock copolymers form spherical domains in PLA that cavitate once the material is stressed. The cavitated particles can act as stress concentrators for craze initiation and propagation, allowing the material to be strained to long extensions.

**Sugar-derived butadiene**

The process to convert furfural to butadiene can be technically achieved using a series of three chemical reactor systems with combined recycle and distillation achieving purity requirements for commercial grade butadiene. The key side products separated from the process are furfuryl alcohol and propylene. Economic analysis using a 20 year discounted cash flow analysis identified conditions leading to a minimum sale price of butadiene that achieves breakeven conditions. From this optimization strategy, it was shown via sensitivity analysis that the overwhelming economic predictor of economic viability was the furfural price. Improvements in reducing lost carbon (i.e., better catalytic chemistry) have the most potential for improving economic viability. For a furfural purchase price of ~$1.00 \text{ kg}^{-1}$, butadiene could be manufactured and sold for ~$2.00 \text{ kg}^{-1}$. Further research in the improvements of catalyst selectivity and reduced chemical process unit operations are necessary to further improve the overall economics of renewable butadiene.

**EDUCATION, OUTREACH, AND PUBLICATIONS**

*Identify conferences, workshops, field days etc. at which project results were presented. Include number of farmers estimated to be present. List articles and/or manuscripts in which project results were published.*
In August 2017, Frank Bates, Chris Ellison, Charles McCutcheon, Jennifer Henderson and Laura Seifert attended Farm Fest to discuss the toughening PLA project. According to Farmfest, approximately 30,000 people attended the festival.

In January 2019, Chris Ellison, Charles McCutcheon and Jennifer Henderson presented a poster on the toughening PLA project at the MN Ag Expo. According to Mn Ag Expo, approximately 1,500 people attended the expo.

In April 2019, Charles McCutcheon presented a poster at the toughening PLA project at the CSP annual meeting.

REFERENCES