PROJECT ACTIVITIES COMPLETED DURING THE REPORTING PERIOD. (Describe project progress specific to goals, objectives, and deliverables identified in the project workplan.)

Uniaxially and biaxially oriented poly(lactide) (PLA) films toughened by commercial diblock copolymer additives

In previous quarterly reports, it was shown that the mechanical toughness of poly(lactide) (PLA) films was greatly enhanced by adding small amounts of Fortegra, a commercially available poly(ethylene oxide)-block-poly(butylene oxide) (PEO-PBO) diblock copolymer. It was further demonstrated that the PEO-PBO diblock molecular architecture is essential to enable toughening of PLA, i.e., adding homopolymers in similar proportion was not effective. This report investigates the micromechanical deformation process of neat PLA and a 4.7 wt % PEO-PBO in PLA blend via in-situ small angle X-ray scattering (SAXS) during tensile testing. The results of this study indicate that adding PEO-PBO to PLA introduces controlled crazing and this is the mechanism of toughening in the blend.

Mechanically tough PLA based multiblock copolymers

In previous reports, we displayed tensile data and tensile bar gauge area images that provided a macroscopic view of the poly(ethylene oxide)-b-poly(butylene oxide)/poly(lactide) (PEO-PBO/PLA) blend deformation behavior and the toughening effects provided by PEO-PBO. In the current report, we aim to gain more fundamental insight into the deformation mechanisms behind the toughening enhancements at the microscopic level. To achieve this goal, in-situ small angle x-ray scattering (SAXS) experiments were performed during tensile tests to probe craze fibril development during elongation.\textsuperscript{1,2,3,4,5} We note that the tensile specimens for in-situ SAXS measurements were elongated at the same rate as those used for regular tensile tests. All specimens for in-situ SAXS measurements were aged for 2 days at room temperature, and they exhibited stress-strain behavior nearly identical to those obtained in the previous reports.
**Efficient synthesis of lactone chain-end polyesters**
During the last three months, we continued our work on the synthesis of a novel, fully biobased, and potentially biodegradable graft copolymer. Efforts were put towards the optimization for the graft through copolymerization and synthesizing graft with different variables. Some selected graft polymers were characterized to determine their thermal and mechanical properties.

**Direct process design of efficient renewable isoprene (Dauenhauer)**
We recently completed our work on the catalytic conversion of biomass-derived cyclic ether 2-methyltetrahydrofuran (2-MTHF) to C5 linear dienes on borosilicates, which resulted in the discovery of catalysts which can convert \(~86\%\) of this renewable carbon to 1,3-pentadiene.\(^6\) In parallel, we also completed a process-design and technoeconomic analysis of a furfural-to-butadiene technology to assess its industrial potential. This evaluation made it clear that the yield loss of a carbon going from a five-carbon species (furfural) to a four-carbon species (butadiene) hurts the overall economic prospects of this process, leading to minimum butadiene prices nearly \(~3x\) of those achievable by petrochemical routes.\(^7\) Furthermore, this design still utilized P-zeosils to convert tetrahydrofuran to butadiene (the dehydra-decyclization step in Figure 1). While these catalysts are shown to be extremely diene selective at low conversions, overall butadiene yields have still remained low (< 65\%) at high conversions, which was another contributing factor driving butadiene prices.

Buoyed by our discovery of new and more promising materials which are expected to drive down energy-intensive downstream separation costs, as well as the recognition that upgrading furfural to a C5 (rather than a C4)-diene is more likely to be cost-effective, we started a new process design project evaluating the furfural-to-piperylene technology. As noted earlier and shown in Figure 1, this process contains one less unit operation (no decarbonylation reactor) compared to the butadiene process, which is expected to drive down capital equipment cost substantially.

**New catalytic routes to valerolactone monomers from biobased starting materials**
Our current aim is to regioselectively create linear polyesters through tuning the catalyst system. 10-undecenol has been shown previously to lead to aldehydes when polymerized with a catalyst system that promotes linear ester products.\(^8\) In this reporting period the focus has been on creating a monomer with an ether linkage that will prevent isomerization to an aldehyde in the hopes of creating monomers that will isomerize back to terminal alkenes thus leading to linear polymers. Additionally, the impact of pressure on conversion and regioselectivity has been examined.
New hydrogel materials from corn-based raw materials

The publication of our studies of the synthesis and properties of the novel polymer poly(4-ketovalerolactone) was Received: April 2, 2020; Revised: May 7, 2020; and Published: June 10, 2020. The full citation is Xu, S.; Wang, Y.; Hoye, T. R. Poly(4-ketovalerolactone) from levulinic acid: Synthesis and hydrolytic degradation. Macromolecules 2020, 53, 4952–4959. The abstract and table of contents graphic succinctly summarize the work:

“ABSTRACT: We report here the synthesis of poly(4-ketovalerolactone) (PKVL) via ring-opening transesterification polymerization (ROTEP) of the monomer 4-ketovalerolactone (KVL, two steps from levulinic acid). The polymerization of KVL proceeds to high equilibrium monomer conversion (up to 96% in the melt) to give the semicrystalline polyketoester PKVL with low dispersity. PKVL displays glass transition temperatures of 7 °C and two melting temperatures at 132 and 148 °C. This polyester can be chemically recycled through hydrolytic degradation. Under aqueous neutral or acidic conditions, the dominating pathway for polyester hydrolysis is through backbiting from the chain end. Under basic conditions, mid-chain cleavage, accelerated by the ketone carbonyl group in the backbone, promotes the hydrolysis of nearby backbone ester bonds. The final hydrolysis product is 5-hydroxylevulinic acid, the ring opened hydrolysis product of KVL. PKVL was also observed to degrade under the action of a Brønsted acid to a bis-spirocyclic dilactone natural product altaicadispirolactone, which is a dimer of KVL. This constitutes a rare example of a one-step synthesis of a secondary metabolite of non-trivial structure in which a polymer was the starting material and the sole source of matter. Analogous ROTEP of the isomeric 4-membered lactone 4-acetyl-β-propiolactone (APL) was also explored, although this chemistry was not as well-behaved as the KVL to PKVL polymerization.”

2.) IDENTIFY ANY SIGNIFICANT FINDINGS AND RESULTS OF THE PROJECT TO DATE.

Uniaxially and biaxially oriented poly(lactide) (PLA) films toughened by commercial diblock copolymer additives

Deformation mechanism of neat PLA: Simultaneous SAXS-tensile testing data for neat PLA (amorphous, NatureWorks 4060D) yields several different key pieces of information which are indexed in Figure 2A. 2-D SAXS patterns (Figure 2B-F) are used to provide a qualitative comparison between neat PLA and the PEO-PBO/PLA blends, while referencing the azimuthal angle vs. intensity (I) plot (Figure 2G) for quantitative analysis of the results. (Note that the detailed experimental setup and testing procedures can be found in the complementary report by Christopher Ellison and Frank Bates.) During deformation, the 2-D SAXS pattern of neat PLA remained featureless until right before the yield point at ~2.3% strain (Figure 2C), where a sharp increase in scattering intensity along the tensile direction, or 90° (meridional axis), was observed (as shown in Figure 2G), indicative of void formation within the sample. These voids are likely initiated from impurities in the PLA matrix such as dust particles and residual catalyst. Due to the inhomogeneous distribution of these defects, the strain is localized near these defects and therefore additional deformation is necessary before the material can macroscopically yield. As
the material is progressively elongated, and more voids are formed, the meridional streak intensity further increased until it plateaued at 3.1% strain (Figure 2D-F). At 3.1% strain, there was a slight increase in the intensity perpendicular to the tensile direction (Figure 2D), or 0° (equatorial axis), which can also be seen in Figure 2G. This increase in scattering intensity is due to the contrast between the newly formed craze fibrils and void spaces. Because of the limited volume fraction associated with the formed voids and crazes in the neat PLA, the stress and strain are highly localized near those features. The already deformed material can be further deformed at a lower tensile stress than the surrounding material, further enhancing strain localization and leading to early failure. The equatorial scattering intensity continued to increase to a maximum of $1.1 \times 10^6$ before failure.

Deformation mechanism of PEO-PBO/PLA blends: The 4.7 wt % PEO-PBO in PLA blend was prepared using a let-down approach, following the same procedure described in the last quarterly report. The stress-strain data (Figure 3A and B), 2-D SAXS patterns at various strains (Figure 3C-I), and azimuthal angle vs. $I$ plot (Figure 3J) are displayed in Figure 3. The PEO-PBO particles are too large to be detected by SAXS. Therefore, the observed scattering should reflect electron density differences between any formed voids and polymer.

Prior to the yield point (~2.8% strain), all 2-D SAXS patterns of the 4.7 wt % PEO-PBO in PLA blend observed in the elastic regime were identical to those at 0% strain (Figure 3C and D). At the yield point, there was a sharp increase in scattering along the meridional axis, indicative of void formation (Figure 3E and K). The void formation for all the PEO-PBO/PLA blends occurs either right at or slightly after the yield point, never prior to yielding as is the case for neat PLA. This is due to the cavitation of PEO-PBO particles and subsequent void expansion which relieves stress in the matrix resulting in the observed stress decrease after the yield point.
the yield point, at 3.2% strain, there was a sharp increase in the scattering intensity in the equatorial axis (Figure 3F and K), indicative of craze fibril formation. According to Figure 3K, the crazing intensity at the 0° axis is much greater for the 4.7 wt % PEO-PBO in PLA blend than neat PLA due to the presence of PEO-PBO particles. These well-dispersed particles can act as craze initiating sites that allow crazes to grow in a controlled manner throughout the entire sample, dissipating energy by craze fibril formation. These conclusions are further supported by TEM images of elongated tensile bars as displayed in Figure 4. A 4.7 wt % PEO-PBO in PLA sample was elongated to 10% strain and removed for TEM preparation. TEM images reveal that there are voids, about the same size as or slightly larger than the particles (~800 nm in diameter), distributed throughout the sample due to cavitated particles with crazes extending from the voids perpendicular to the tensile direction. The scattering intensity in the equatorial region continually increased until about 100% strain (Figure 3I), at which a maximum value of approximately 10 times that of neat PLA was reached. At 100% strain, the toughening mechanism changed from crazing to shear yielding (i.e., material flow) since the equatorial scattering plateaued, indicating the cessation of craze fibril formation. At 201% strain, the scattering intensities in both the meridional and equatorial directions decreased (Figure 3J and K), which is likely due to the necking phenomenon leading to a decreased sample thickness and scattering volume.

Figure 3. (A) Representative tensile stress-strain data acquired from in-situ tensile SAXS for 4.7 wt % PEO-PBO in PLA. (B) Zoom-in view of (A) at low strain (0-25% strain) to reveal the low-strain tensile properties. The color of the × labels on A and B corresponds to the border of the 2-D SAXS patterns from (D) to (J). (K) 1-D SAXS plot of azimuthal angle vs intensity constructed from radial integration of 2-D SAXS patterns. The sample was aged for 2 days.
Based on the in-situ tensile SAXS results, both neat PLA and PEO-PBO/PLA blends can form crazes when elongated. The neat PLA sample starts to form voids before the yield point and then slowly begins to develop crazes in a small localized area as the material is extended to failure. In comparison, PEO-PBO/PLA blends have well dispersed PEO-PBO particles (stress concentrators) that can act as craze initiating sites and allow the material to develop more crazes uniformly throughout the entire material. This enables the applied stress to be evenly distributed among the numerous crazes throughout the entire sample.

**Mechanically tough PLA based multiblock copolymers**

Synchrotron SAXS data were acquired from the DND-CAT 5ID-D beamline at the Advanced Photon Source at Argonne National Laboratory (Argonne, IL). The data were collected using a sample to detector distance of 8.5 m and a photon wavelength of $\lambda = 1.3776 \, \text{Å}$. 2-D scattering patterns were recorded using a Rayonix CCD detector. The experimental setup can be seen in Figure 5A-B. The tensile bars for all SAXS measurements were elongated in the vertical direction identified as 90°. The 2-D SAXS patterns were then integrated over azimuthal angles from -10° to 10° (i.e., perpendicular to the strain direction of 90°) (an example 2-D SAXS pattern and integration limits are shown in Figure 5C) generating a plot of scattering vector $q = 4\pi\lambda^{-1}\sin(\theta/2)$ vs. intensity. The intensity displayed in the 1-D plots is presented as “Intensity (normalized)”, where the measured intensity was divided by the sample thickness so that comparisons among samples in this study can be made on a relative basis.

![Image](image1.png)

**Figure 4.** TEM images of the gauge region of a 4.7 wt % PEO-PBO in PLA sample at 10% strain taken at different magnifications. Samples were stained with RuO$_4$.

![Image](image2.png)

**Figure 5.** (A) Linkam tensile stage that was used for the in-situ SAXS experiments. (B) A higher magnification image of the grips and x-ray slit. (C) Representative 2-D SAXS pattern (from 4.7 % wt PEO-PBO/PLA at 100% strain) with 10° and -10° azimuthal angles labeled and a tensile bar to show the pulling direction.

In previous reports, along with the current report, we have shown enhanced toughness of the PEO-PBO/PLA blends, and representative stress-strain data of varying PEO-PBO concentrations can be seen in Figure 6A. These curves have distinct features which are labeled in Figure 6B and
were discussed in detail in the previous report. In summary, at the yield point, the particles cavitate and act as stress concentrators for craze initiation. The material continually deforms by crazing, evidenced by the equatorial streak seen in Figure 5C, until the flow stress is reached, leading to the necking transition. This is where the toughening mechanism changes from crazing to shear yielding. Although all PEO-PBO/PLA blends exhibited similar stress-strain characteristics and ductility, they differed in the stress and strain of the unique features. To investigate the effect of loading on PEO-PBO, SAXS was performed to better characterize the craze development and the amount of gauge volume engaged in craze deformation. To analyze the crazes formed in the neat PLA and the PEO-PBO/PLA blends, the invariant of the equatorial axis (0° azimuthal angle) \((Q_{0°})\) was calculated by integration of the \(q\) vs. \(I\) 1-D SAXS plots (Figure 7A-B) according to,\(^{17}\)

\[
Q_{0°} = \int_0^\infty I(q) \times q^2 \times dq
\]  

and related to the volume of crazes \(V\), fibril volume fraction in a craze \(v_f\), and electron density difference (for crazes, \(\Delta \rho\) is between polymer and void) by,

\[
Q_{0°} = Vv_f(1 - v_f)\Delta \rho^2
\]

Assuming \(v_f\) has limited variability at low concentrations (<10 wt %) of PEO-PBO\(^{18,19}\) and \(\Delta \rho\) is a constant for all blends, the changes in \(Q_{0°}\) are a direct result of \(V\). \(Q_{0°}\) is plotted versus strain for five PEO-PBO concentrations in Figure 7C. The maximum \(Q_{0°}\) values at each block copolymer loading are plotted against the total surface area of particles (i.e., product of the surface area of one particle times the total number of particles in the gauge region) in Figure 7D, resulting in a linear fit. The total craze volume, \(V_c\), is linearly dependent on the particle surface area due to the fact that crazes are initiated at the void/polymer interface. With increasing \(V_c\), a greater strain is required to reach the necessary flow stress for necking to occur, thus increasing the necking transition strain (\(\varepsilon_N\)) labeled on Figure 6B; \(\varepsilon_N\) of each blend can be extracted from Figure 6A.(Note, the necking transition strain was identified in the previous report as the double yield strain). This is due to increased energy dissipation from craze formation and an increase in load bearing fibrils resulting in greater fibril stability. It is also worth noting that, with increasing PEO-PBO concentration, both \(Q_{0°}\) and the strain at which \(Q_{0°}\) reaches a maximum (\(\varepsilon_M\))

![Figure 6](image-url)

**Figure 6.** (A) Representative stress-strain data of PEO-PBO/PLA blends at various PEO-PBO concentrations. All stress-strain data is after aging at room temperature for 2 days. (B) Representative stress-strain data (from 1.8 wt % PEO-PBO/PLA blend) with features labeled for reference.
increased (Figure C) while $\varepsilon_M$ coincided with $\varepsilon_N$ for all the PEO-PBO/PLA blends. $Q_{0°}$ leveling off or decreasing at $\varepsilon_M$ provides additional evidence that at $\varepsilon_N$, the deformation mechanism changes from crazing to shear yielding as the material necks.
In conclusion, the loading of PEO-PBO in PLA impacts the particle-matrix interfacial area from which crazes can be initiated. Increasing the loading of PEO-PBO also results in greater total craze volume and tougher blends.

**Figure 7.** 1-D SAXS patterns obtained by the integration of the azimuthal angles from -10° to 10° for (A) neat PLA and (B) 4.7 wt % PEO-PBO in PLA. (C) Plot of invariant ($Q_W$) vs. strain for various wt % PEO-PBO in PLA, using the normalized intensity described earlier. (D) Max invariant $Q_W$ from (C) vs. total particle surface area (which is equal to surface area of an average-sized particle times the average number of particles in the gauge area) for PEO-PBO/PLA blends (solid line is a linear fit of the data), and the dotted line represents the $Q_W$ of neat PLA. All samples were aged for 2 days before testing.

**Efficient synthesis of lactone chain-end polyesters**

Using previously developed one-pot synthesis, 15 g of 3 batches of macromonomer of different molecular weight (2.9, 7.1 and 14 kg/mol) were produced. The conditions for the copolymerization of the macromonomer with a lactone (Figure 8) were optimized. Conditions of temperature and concentration were selected as the best to give good control of the graft-through polymerization. Using those conditions, with an organocatalyst, several graft polymers were synthesized with different graft density and side chain length. Thermal and physical properties of those graft will be measured and compared in order to determine the chemical architecture that gives the best mechanical behavior.
Direct process design of efficient renewable isoprene
The process is currently being simulated in the Equation Oriented (EO) approach in Aspen, where standard modules like Heater, HeatX, RStoic, RadFrac, Flash2, Compr, Sep2, Pump, and Extract modules are being utilized to simulate and optimize the various design parameters. While catalyst choice for second step is our own discovery of B-MWW, the catalyst choice for the first step for the hydrogenolysis of furfural to 2-MTHF has been taken to be from a report by Li and co-workers in which a Cu-Pd bimetallic catalyst affords ~97% 2-MTHF yields at quantitative furfural conversion at atmospheric pressure and mild temperatures. Since the overall thermodynamic favorability of 1,3-pentadiene (1,3-PD) is significantly higher than its isomer and a deleterious side product 1,4-pentadiene (1,4-PD), it is possible to operate the second reactor at a 1,3-PD/1,4-PD ratio of ~50. However, given the high purity standards of piperylene needed from the process (>99.5%), an additional isomerization reactor may be employed to reach equilibrium pentadiene ratios before separation. Once the process parameters have been optimized, an economic analysis will be undertaken using Aspen Economic Analyzer to calculate the capital as well as operational costs. Setting the net present value of the entire project to zero will enable calculation of the minimum selling price of piperylene, which will ultimately dictate if this approach is economically viable for industrial implementation.

New catalytic routes to valerolactone monomers from biobased starting materials (Tonks)

The synthesis and purification of 2-(undec-10-en-1-yloxy)ethan-1-ol has been carried out and initial polymerizations have been performed. When polymerized under the conditions previously shown to yield polymers with 10-undecenol (Figure 9) an ester yield of 75%, calculated via an internal standard, was achieved. This ester product was only 80% linearly regioselective. Dtbpx has been shown previously to yield linear selective small molecule esters. Therefore, this monomer was polymerized using dtbpx and conditions previously reported by Beller. Isomerized alkene was the major product of this reaction with only 7% conversion to ester. Future experiments will examine if lower temperatures and longer reaction times will preference polyesters over isomerized alkenes.
The other aim pursued since our previous report was an investigation of the impact of pressure on the regioselectivity of the resulting ester. Screens of various pressures used alongside typical reaction conditions (Table 1) have shown that while yield improves as the pressure increases the regioselectivity is not impacted by CO pressure. An additional screen when tris(2-methoxyphenyl) phosphine as the ligand showed no impact of pressure on regioselectivity and only a modest increase of conversion from 61% to 72% when the pressure is increased from 290 psig to 500 psig.

**Table 1:** Examining the impact of pressure on the regioselectivity of 10-undecenol polymerization.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pressure (psig)</th>
<th>Ester Yield(%)</th>
<th>Linear : Branched</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>86</td>
<td>74 : 26</td>
</tr>
<tr>
<td>2</td>
<td>203</td>
<td>92</td>
<td>76 : 24</td>
</tr>
<tr>
<td>3</td>
<td>290</td>
<td>93</td>
<td>72 : 28</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 5 mmol 10-undecenol (in toluene), 100 ºC, 22 h, and ran in a Parr reactor. 
*b Based on standardization of $^1$H NMR signals against DMT internal standard. 
*c Based on $^1$H NMR integrations.

New hydrogel materials from corn-based raw materials

Coumalic acid (1, R = H) is readily available from malic acid, which, like levulinic acid in the PKVL study above, is a commodity chemical derivable from glucose (and many other sugars) through fermentation. It is known that coumalate esters (1, R = alkyl) can be photochemically converted to strained bicyclic lactones 2 (Figure 10a). We have initiated a study of molecules like 2 with the goal of exploiting their inherently high potential energy to drive polymerization to novel materials with potential useful properties.

We are also studying the equilibrium ring-opening reaction of simple lactones to their corresponding hydroxy acids (in acidic water) or methyl hydroxyesters (in acidic methanol) (Figure 10b). The fundamental tenet driving this study is that the equilibrium concentration for each lactone:hydroxyacid/ester (3:4) will correlate with the extent (at equilibrium) to which the lactone will polymerize to polyesters via ring-opening transesterification polymerizations.
3.) CHALLENGES ENCOUNTERED. (Describe any challenges that you encountered related to project progress specific to goals, objectives, and deliverables identified in the project workplan.)

As previously reported, all research labs involved in this project moved their labs into hibernation in mid-March in response to the Covid-19 pandemic. Progress continued virtually during this time, and in late May research labs began a phased re-opening. Research is happening now by relying on physical distancing and staggered shifts.

Efficient synthesis of lactone chain-end polyesters
We encountered a challenge trying to calculate the kinetics of the graft-through polymerization. By $^1$H NMR, the signals of both lactones overlap, despite investigating many different solvents. It is thus impossible to determine if the copolymerization has a statistical or more of a gradient behavior. Next, we will try to measure kinetics using SEC, it is less precise but good enough to give us an idea of the copolymerization nature.

4.) FINANCIAL INFORMATION (Describe any budget challenges and provide specific reasons for deviations from the projected project spending.)

5.) EDUCATION AND OUTREACH ACTIVITIES. (Describe any conferences, workshops, field days, etc attended, number of contacts at each event, and/or publications developed to disseminate project results.)

The Green and Sustainable Workshop for Chemistry teachers was promoted and modified to a virtual setting during this reporting period.

Figure 10. a) The photocyclization of coumalate esters 1 (R = alkyl) gives strained lactones 2, which are potential monomers for polymerization reactions. b) The equilibration of lactones 3 with their ring-opened analogs 4 in water (R = H) or methanol (R = Me) may correlate with the degree to which the lactones will proceed to polyesters at equilibrium.
Please note: A publication titled “Crazing Mechanism and Physical Aging of Poly(lactide) Toughened with PBO-PEO Diblock Copolymer” will be submitted to the journal *Macromolecules* by the end of July.

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**Citations**


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