The Hillmyer group has investigated the thermal and mechanical properties of poly((−)-lactide) (PLA) toughened with commercially available castor oil derivatives, specifically, either ethoxylated hydrogenated castor oil (HCO-EO) or ethoxylated castor oil (CO-EO). Two-component blends were prepared using a simple extrusion technique and processed via compression molding to yield colorless, optically transparent films at all compositions (2.5 wt%, 5.5 wt%, and 10 wt% CO-EO or HCO-EO additive). Tensile properties of the films depended on both the additive used and the blend concentration (Figure 1a and 1b). Interestingly, HCO-EO appears to be a more effective toughening agent than castor oil and CO-EO at moderate loadings. Although the toughening mechanism is currently unknown, we plan to investigate this subject in future work.

Table 1. Thermal Properties of PLA Blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^aT_g$ (°C)</th>
<th>$^aT_c$ (°C)</th>
<th>$^a\Delta H_c$ (J g$^{-1}$)</th>
<th>$^aT_m$ (°C)</th>
<th>$^a\Delta H_m$ (J g$^{-1}$)</th>
<th>$^bT_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>58.0</td>
<td>111.5</td>
<td>40.5</td>
<td>172.2</td>
<td>41.3</td>
<td>321</td>
</tr>
<tr>
<td>CO-EO-2.5%</td>
<td>55.9</td>
<td>103.6</td>
<td>30.8</td>
<td>171.5</td>
<td>40.7</td>
<td>318</td>
</tr>
<tr>
<td>CO-EO-5.5%</td>
<td>52.6</td>
<td>96.7</td>
<td>25.9</td>
<td>170.1</td>
<td>37.5</td>
<td>309</td>
</tr>
<tr>
<td>CO-EO-10%</td>
<td>49.1</td>
<td>90.9</td>
<td>23.1</td>
<td>170.0</td>
<td>38.8</td>
<td>302</td>
</tr>
<tr>
<td>HCO-EO-2.5%</td>
<td>54.4</td>
<td>103.9</td>
<td>30.8</td>
<td>170.6</td>
<td>44.7</td>
<td>311</td>
</tr>
<tr>
<td>HCO-EO-5.5%</td>
<td>52.4</td>
<td>98.3</td>
<td>26.6</td>
<td>169.6</td>
<td>48.0</td>
<td>306</td>
</tr>
<tr>
<td>HCO-EO-10%</td>
<td>48.7</td>
<td>92.7</td>
<td>28.7</td>
<td>170.1</td>
<td>40.9</td>
<td>302</td>
</tr>
</tbody>
</table>

$^a$Thermal properties were determined using DSC at a ramp rate of 10 °C min$^{-1}$ and are reported on the first heating ramp. $^b$Degradation temperature was determined using TGA, heating under nitrogen at a ramp rate of 10 °C min$^{-1}$ and are reported as the temperature at which 5% mass loss was observed.
The Tonks group has been working on optimizing hydroesterificative olefin polymerization (HOP) reaction conditions to remove unwanted byproducts and make higher molecular weight polymers. First, we have explored the idea of “prefunctionalizing” our biomass starting materials with formate groups, and polymerizing these new formate monomers. The rationale behind this approach is that many bio-derived alcohols were sluggish to undergo HOP, and thus tethering the CO to the alcohol prior to polymerization may yield higher conversions. In fact, preliminary results have now shown that Pd(OAc)$_2$/PPh$_3$ is highly efficient in catalyzing hydroesterification between aryl olefins and excess amounts of phenyl formate in toluene at 90 °C (Figure 2, top), which was previously impossible with our generation 1 catalytic system. Inspired by the success of the phenyl formate optimized reaction conditions, we revisited our initial catalytic system for HOP, and modified the conditions to better match those found to be successful for phenyl formate. Excitingly, with 5% catalyst loading (Pd(OAc)$_2$: PPh$_3$: TsOH = 1:4:1), HMS in toluene (1:3 v/v) reached a conversion of 94% under 120 psig of CO at 50 °C after 24 h, yielding polymer with molecular weights in excess of 3000 and dispersities of 2. We are currently exploring the characterization and optimization of this material such that we can produce even higher molecular weight polymer (Figure 2, bottom).

**Figure 1.** Representative uniaxial extension data for a) blends of ethoxylated castor oil and PLA and b) ethoxylated hydrogenated castor oil and PLA. Samples were tested at a constant crosshead velocity of 5 mm min$^{-1}$.

**Figure 2.**
The Hoye group is continuing to explore ways to capitalize on the highly efficient formation of the adduct 1, formed in 94% yield upon simple mixing of furfuryl alcohol (FA) and IA at ambient temperature. In particular, improvements in its conversion to 3-isochoromanone (2) and 2-methylstyrene (3) continue to be explored. We have also built an apparatus that allows us to carry out the (known) isomerization of FA to 4-hydroxycyclopent-2-enone (4) under the action of weak Brønsted acid catalysis. We view 4 as a precursor to several potential AB monomers and will soon be exploring those possibilities. Finally, we have also begun a study of the use of chloromethylfurfural (CMF, 5) as a precursor to new monomers. CMF is readily available upon treatment of 6-carbon sugar sources like glucose and cellulose with aqueous HCl (muriatic acid). We have smoothly converted CMF to 2,5-furandialdehyde (6) simply by warming 5 in DMSO. This dialdehyde is a difunctional monomer we hope to exploit. Alternatively, we have learned how to convert CMF to ester aldehydes 7 simply by exposure to carboxylic acids in the presence of a tertiary amine base. We will soon explore this reaction using acrylic and methacrylic acids.

Figure 3. Conversion of compounds from corn to new molecules with potential as arene and polymer precursors.

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


Provisional Patent Application:
Title: COMPOUNDS FROM RENEWABLE RESOURCES
First Inventor: Thomas R. Hoye
Application No.: 62/320,087
Filing Date: April 08, 2016

3.) CHALLENGES ENCOUNTERED. (Describe any challenges that you encountered related to project progress specific to goals, objectives, and deliverables identified in the project workplan.)

Nothing to report.

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 Center for Sustainable Polymers (CSP) began preparations for high school teacher workshops focused on green chemistry. Two high school chemistry teachers were recruited in June 2016 to serve as peer leaders for the future workshops. These two teachers are currently enrolled in an online green chemistry course offered through “Beyond Benign”, a national green chemistry education organization. These teachers will collaborate with Professor Jane Wissinger (UMN Chemistry) and Gillian Roehrig (UMN STEM Education Center) to develop two workshops. One workshop will be offered in the summer of 2017 in the Twin Cities metro area and one workshop will be offered in the summer of 2018 in outstate Minnesota.

During 2014-2016, lesson plans were also developed for 4-H youth in grades K-2 (“Cloverbuds”). Seven modules were developed and content areas included the role of scientists and engineers, material properties, plastics in everyday life, recycling, and sustainability. In this reporting period, the modules were field tested in the states of Minnesota, New York, and California. Twelve 4-H clubs participated in these tests and each group completed one or two modules. After the completion of field tests to try out the activities in each module, seven 4-H clubs were scheduled to complete pilot tests (competition of all modules in sequential order) during June, July, and August 2016. In total, over 200 youth from the three states have completed either the field or pilot test activities. Feedback from adult 4-H leaders will be collected and used to structure the revisions of the modules before a national rollout of the Cloverbud content.

\[\text{Robertson, M. L.; Paxton, J. M.; Hillmyer, M. A.} \quad \text{ACS Applied Materials and Interfaces 2011, 3, 3402-3410}\]