



MinnesotaCorn

RESEARCH & PROMOTION COUNCIL

PROGRESS REPORT

PROJECT TITLE: Corn derived materials
PROJECT NUMBER: 1088-18EU
REPORTING PERIOD: March 31 – June 30, 2018
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1.) PROJECT ACTIVITIES COMPLETED DURING THE REPORTING PERIOD. (*Describe project progress specific to goals, objectives, and deliverables identified in the project workplan.*)

In the aspects of this project lead by Professor Bates, the goal is to toughen poly(lactide) (PLA) by using a small mass loading of diblock copolymer. Microphase separated diblock copolymers have been shown to increase the ductility of a solid state homopolymer matrix with limited reduction to the elastic modulus (E) and yield strength (σ_y). The diblock copolymer that was previously investigated is poly(isoprene)-*b*-poly(ethylene oxide) (PI-PEO). PEO is miscible with PLA due to favorable thermodynamic interactions (negative Flory-Huggins parameter) between the two polymers. To enable PLA toughening, rubbery PI, which is thermodynamically incompatible with PLA, was employed as the other block. In previous reports we demonstrated that PI-PEO dispersions significantly toughened PLA, increasing the elongation at break (ϵ_b) by as much as 50x and the toughness, determined as the area under the stress-strain curve measured in tension, by 27x.

During the past quarter additional diblock copolymers were synthesized, replacing the PEO with PLA in order to assess the importance of having a negative heat of mixing between the corona block and matrix polymer. PI-PLA with the same overall molecular weight as PI-PEO was mixed with commercial PLA (Nature Works PDLA) and solvent cast to for a master batch containing 25 wt% diblock copolymer. Subsequent melt blending with additional homopolymer resulted in a mixture containing 5 wt% PI-PLA, which was characterized for morphology (particle dispersion and size) by transmission electron microscopy (TEM). Tensile tests were employed to determine whether this additive leads to mechanically tough material.

In the last three months, the Dauenhauer group has compared the catalytic performance of two classes of solid-acid catalysts, namely, aluminosilicate and borosilicate zeolites, in the dehydration of a biofuel model compound, 2-methyltetrahydrofuran (2-MTHF), to a key C5 monomer, namely 1,3-Pentadiene. Presence of Group-13 elements in the zeolitic framework imparts Brønsted acid sites with different deprotonation energies, establishing that borosilicates are much weaker solid acids than aluminosilicates. Moreover, different pore-topologies show distinct behavior in the

confinement of key transition states, and thus affect the rates and selectivities in chemistries like methanol-to-olefins (MTO), and ethanol dehydration. In addition to studying the effect of these two heteroatoms (A, and B), there is now a more fundamental understanding of 2-MTHF dehydration by studying these framework effects

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

As demonstrated in previous reports from the Bates group, melt blending 5% wt. PI-PEO with commercial PLA (Nature Works PDLA) significantly increases the toughness of this plastic. To test the hypothesis that a negative heat of mixing is required to disperse the PI rubber, we prepared complimentary PI-PEO and PI-PLA diblocks using the same hydroxyl-terminated PI obtained from anionic polymerization as a macronitiator. Because the PLA block is chemically identical to the homopolymer there is no heat of mixing with the matrix homopolymer (i.e., the Flory-Huggins interaction parameter equals zero). Figure 1 shows the chemical structures of the two diblock copolymers and Table 1 lists the number average molecular weights (M_n), dispersities (\mathcal{D}), and volume fraction of the PEO and PLA blocks, which form the corona when dispersed as particles.

Table 1. Molecular characteristics of synthesized diblock copolymers

Polymer	M_n (g/mol)	M_n PI (g/mol)	M_n corona (g/mol)	f_{corona}	\mathcal{D}
PI-PEO-5	134,000	68,000	66,000	0.45	1.12
PI-PLA	140,000	68,000	72,000	0.44	1.24

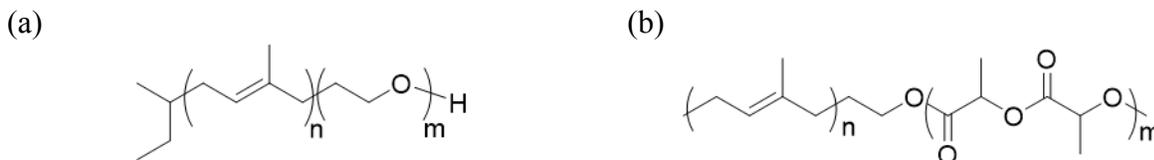


Figure 1. Chemical structure of (a) PI-PEO-5 and (b) PI-PLA.

Representative TEM images obtained from ruthenium tetroxide stained microtomed sections of the two blends are presented in Figure 2. Contrary to our expectation, the PI-PLA particles are smaller (approximately 55 ± 13 nm (the error reflects one standard deviation from the mean) in diameter versus 88 ± 20 nm for PI-PEO) and appear to be more uniform in size than the PI-PEO domains. This leads us to conclude that a negative interaction parameter between the corona and matrix is not required to effect dispersion of the highly immiscible PI blocks at this molecular weight. This result is beneficial towards the goal of producing fully sustainable toughened PLA, based on biosourced isoprene.

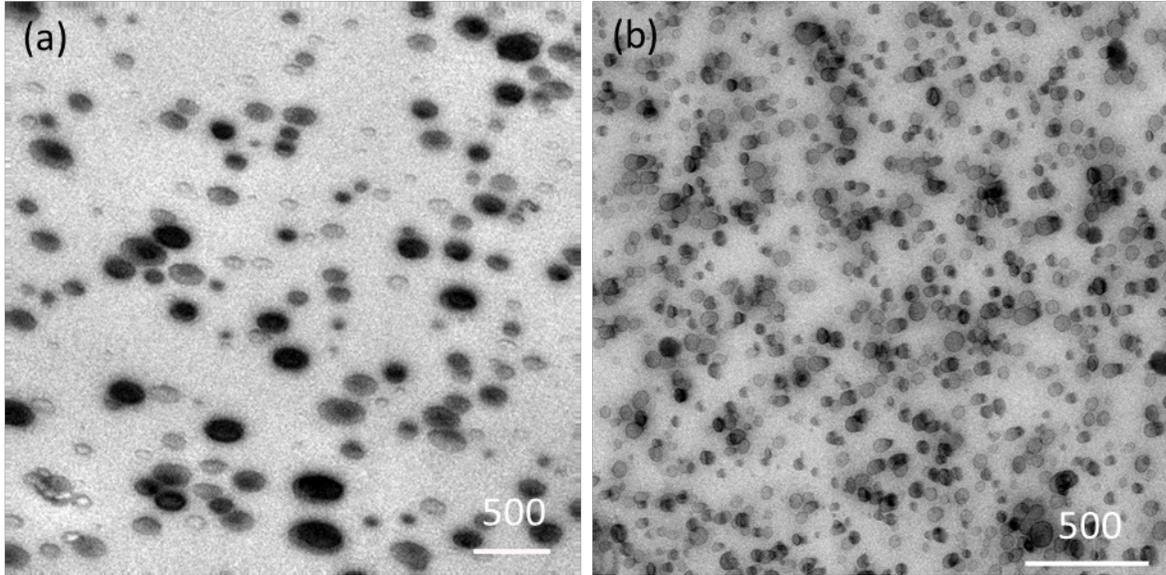


Figure 2. TEM images of diblock copolymer dispersions (a) PI-PEO-5 and (b) PI-PLA in PLA. The scale bars is 500 nm.

The tensile properties of each blend were also examined, and the stress-strain curves are shown in Figure 3 and a summary of the tensile properties are provided in Table 2. The tensile properties of the PI-PLA and PI-PEO- modified PLA are very similar. However, the PI-PLA based blend has a high T_g component as the corona (PLA, $T_g \sim 55^\circ\text{C}$) while PI-PEO-5 has a low T_g corona (PEO, $T_g \sim -65^\circ\text{C}$). Both systems provide excellent toughness with a strain at break of about 250% compared with 5% for the pure PLA. Therefore, we can conclude that the physical properties of the corona do not appear to affect the mechanical properties of the dispersions, confirming that the rubbery polyisoprene nanodomains play the key role in toughening the material.

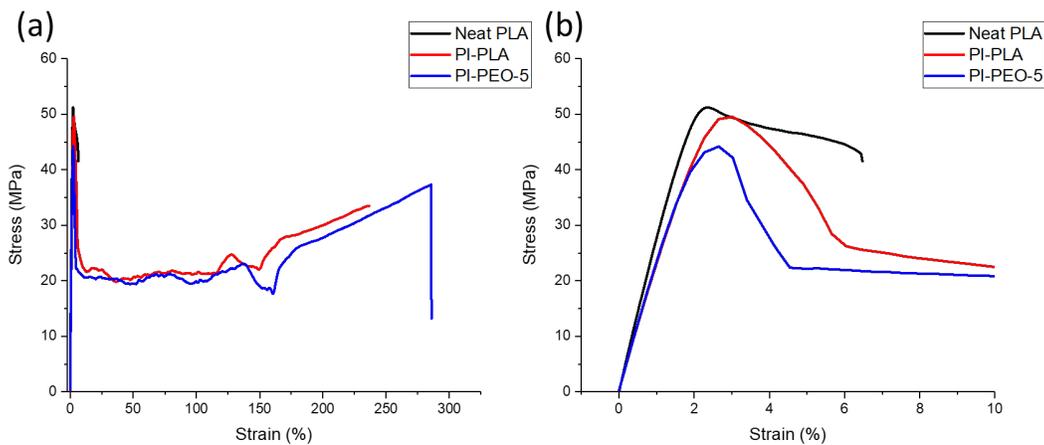


Figure 3. Representative stress-strain curves for PI-PLA (red) and PI-PEO (blue). Curve (a) is the full curve and curve (b) is the same as (a) but with a different x scale to view the yield point.

Table 2. Summary of mechanical properties obtained from pure PLA and blends containing 5 wt% PI-PEO and PI-PLA. Errors reflect one standard deviation based 7 measurements.

Blend	σ_y (MPa)	E (GPa)	ϵ_b (%)	Toughness (MJ/m ³)
Neat PLA	55±7	2.3±0.2	5.2±0.8	2.1±0.4
PI-PEO-5/PLA	44±5	1.8±0.1	250±40	57±20
PI-PLA/PLA	45±4	1.7±0.1	240±50	50±20

From work in the Dauenhauer group, all investigated borosilicates (B-MFI, B-BEA, and B-MWW) show higher overall dehydration selectivity (per carbon basis) than aluminosilicates. It is hypothesized that borosilicates suppress the competing reaction pathways owing to their low Brønsted acid strength, and a comparison of involved activation barriers is currently being investigated to test this hypothesis. Interestingly, the selectivity to 1,3-Pentadiene shows an increase with conversion, indicating its non-primary nature. While the combined selectivity to 1,3- and 1,4-Pentadiene remains invariant with the choice of zeolite framework in borosilicates, the selectivity to 1,3-Pentadiene is higher in a medium-pore borosilicate (B-MFI) than a large pore borosilicate (B-BEA) at both high (>60%) as well as low (<20%) conversion of 2-MTHF. It is believed that this effect is a consequence of longer diffusion lengths in smaller pore systems, leading to secondary reactions which produce the thermodynamically more stable 1,3-Pentadiene. All borosilicates show excellent stability under reaction conditions for over 80 hours. Indeed, their stability on-stream makes them a promising class of materials for this chemistry. Most notably, B-MWW shows ~87% 1,3-Pentadiene selectivity at complete conversion of 2-MTHF sustained over 80 hours on-stream at 385 °C, which is the highest reported yield of 1,3-Pentadiene for this chemistry to the best of our knowledge.

Aluminosilicates are more active than borosilicates but show lower selectivity towards dehydration products. Furthermore, they show rapid deactivation under reaction conditions, with the conversions dropping by ~30% within the first 24 hours on-stream. Unlike with borosilicates, total selectivity to dehydration products is found to be dependent on the framework, with medium pore-aluminosilicates (ZSM-22, and ZSM-5) showing a higher diene selectivities than a large-pore material (Al-BEA). However, it remains to be investigated if these effects are a consequence of transition-state confinement differences or diffusional artifacts.

In the next three months, researchers want to deconvolute the role of different pore systems in MWW by post-synthetic modifications to include meso-porosity in the framework of B-MWW and MCM-22. By selectively poisoning the acid sites in different pore-systems of resulting materials, the hypothesis that smaller pore-systems result in higher 1,3-Pentadiene selectivities will be tested. In addition, the goal is to unambiguously identify the rate-limiting and selectivity-controlling steps in this transformation by carrying out detailed steady-state kinetic measurements on our packed bed flow-reactor setups.

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

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.*)

Professor Paul Dauenhauer delivered a “Beyond the Classroom” lecture to all members of the Center for Sustainable Polymers on the topic of Process Chemistry. The session is recorded and preserved on the center’s You Tube channel, and therefore available to the general public (https://youtu.be/Gzk21Q_fV88?list=PLTzinWmIz88tob-AZ3tcIGxfeiKcB1--X)

The purpose of the Beyond the Classroom sessions are to help center researchers learn about topics relevant to the center that are not covered in their typical classroom curriculum. This particular presentation gave researchers an understanding of industrial processing that is relevant to their day-to-day work in the lab.