

PROGRESS REPORT

PROJECT TITLE: Corn derived materials
 PROJECT NUMBER: 1088-17EU
 REPORTING PERIOD: October 1- December 31, 2017
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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.*)

The Bates group's strategy to blend PLA with small amounts of diblock copolymer was recently found to increase ductility of PLA, combatting its brittle nature of PLA without compromising its modulus or strength. This project aims to elucidate the mechanisms responsible for this behavior.

Poly(isoprene)-block-poly(ethylene oxide) (PI-PEO) diblock copolymers have been synthesized by a two-step anionic polymerization process. Isoprene is initiated with sec-butyl lithium and end capped with ethylene oxide and acidic methanol to make PI-OH. The PI-OH was then reinitiated with potassium naphthalenide followed by the addition of ethylene oxide to form PI-PEO.

PEO is known to be miscible with PLA, while PI is thermodynamically incompatible with PLA. To form nanoscale micelles, the favorable interactions of PLA and PEO must outweigh the unfavorable interactions of PLA and PI. It has been experimentally¹ and theoretically² proven that when the molecular weight of the corona (PEO) is greater than that of the matrix (PLA), it is entropically favorable for the matrix polymer to wet the corona and the dispersions will form micelles. Using this information, the volume fraction and the molecular weight of PEO have been increased in an attempt to form micelle dispersions in PLA. A series of the synthesized diblocks are included in Table 1.

Table 1- Molecular weight characteristics of synthesized diblock copolymers

	Mn^a (g/mol)	Mn PI^a (g/mol)	Mn PEO^a (g/mol)	f_{PEO}^c	Wt_{PEO}^a	D^b
PI-PEO-1	11100	8950	2150	0.17	0.19	1.01
PI-PEO-2	10890	7600	3290	0.27	0.30	1.01
PI-PEO-3 ^d	5700	3600	2140	0.34	0.38	1.04
PI-PEO-4 ^d	8700	3900	4800	0.52	0.55	1.05
PI-PEO-5	134000	68000 ^c	66000	0.45	0.50	1.12

^a Calculated from NMR, ^b Calculated from GPC (THF mobile phase), ^c Calculated from light scattering with dn/dc=0.134 ^d Kyungtae Kim synthesized the PI-OH block of the diblock ^e ρ_{PEO}=1.07g/mL ρ_{PI}=0.91g/mL

Each diblock was solvent cast from chloroform with Ingeo 4060D, an atactic PLA (PLDLA) with an $M_n=118\text{kg/mol}$ to form a master batch. The master batch product was then micro-compounded with additional PLA (Xplore 5mL twin screw micro compounder operated at 100 rpm) at 180°C for 5 minutes resulting in 5% wt. diblock in PLA. The blend was then formed into a film using a Carver heat press to a thickness of 0.5 mm and then immediately cooled with water using a Wabash hydraulic press. This film was imaged using transmission electron microscopy (TEM), characterized by differential scanning calorimetry (DSC) (Mettler Toledo) and cut into dogbone shaped specimens with dimensions in compliance with ASTM1708 for tensile testing (Shimadzu AGS-X).

The aim of Dauenhauer group's project has been to evaluate the performance of boron containing siliceous zeolite frameworks as effective catalysts for dehydra-decylization of tetrahydrofuran and methyl tetrahydrofurans to produce C4 and C5 dienes. Previous studies have shown that phosphoric acid supported on siliceous zeolitic frameworks are highly selective catalysts to forming dienes for this chemistry. Additionally, Fan and co-workers have shown that these siliceous P containing zeolites have weak acid sites. H-form of B-zeolites have the highest deprotonation energy values among group-13 heteroatom substituted zeolite frameworks, making them very weak Bronsted acid catalysts. The objective of a careful investigation of B-zeolites has been to develop an understanding of the role of acid strength of catalysts for this chemistry.

In this reporting period, boron containing zeolites with three different framework structures (MFI, MWW, and BEA) and varying Si/B ratios ($13 < \text{Si/B} < 74$; calculated using ICP-OES) were synthesized in-house under hydrothermal conditions and were characterized by various materials characterization tools. PXRD and SEM were used to assess crystallinity and study morphology. Ar-physisorption was performed to calculate the pore volume and micropore surface area. ^{11}B and ^{29}Si MAS NMR experiments were conducted for two samples to study the chemical environments of B/Si. These experiments confirmed the presence of B inside zeolite framework. IR spectroscopy was used to corroborate this observation by studying the OH-stretching frequencies in these materials. All the prepared materials showed detectable Bronsted acid sites which roughly scaled with the amount of B in the framework. The synthesized and characterized materials were then evaluated for dehydra-decylization chemistry using a pulsed injection inline reactor system.

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

For the Bates group - the DSC results obtained from the blends are shown in Figure 1. These results demonstrate that all PI-PEO/ PLDLA blends resulted in PEO crystallization except PI-PEO-5. If the corona is able to crystallize, the PEO chains will pack tightly and therefore cannot be wet by the PLA matrix, leading to coarse dispersions. This can be seen in the TEM images of PI-PEO-3 and PI-PEO-4 illustrated in Figure 2. PI-PEO-3 and PI-PEO-4 contain larger dispersion sizes, which we interpret as evidence that the PEO block lengths are not large enough to facilitate effective corona wetting by PLA. PI-PEO-5 on the other hand, dispersed in a much more uniform way with particle diameters around 100nm. This remarkable result is consistent with the hypothesis that PEO and PLA have a negative heat of mixing in the amorphous state. Although similar in size to the PI-PEO-2 dispersions, PI-PEO-5 has a much higher molecular weight ($\sim 10\times$), and micelle size scales with $N^{2/3}$. These exciting results indicate that the corona is wet more effectively by the matrix PLA at the higher molecular weight.

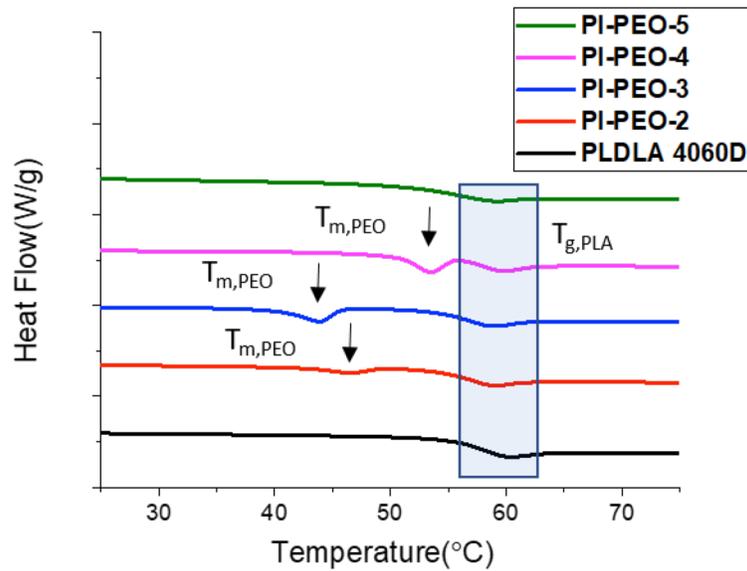


Figure 1- DSC traces (endo down) of neat PLA and PLA/diblock blends containing 5wt.% diblock obtained during the second heat at a rate of 10°C/min

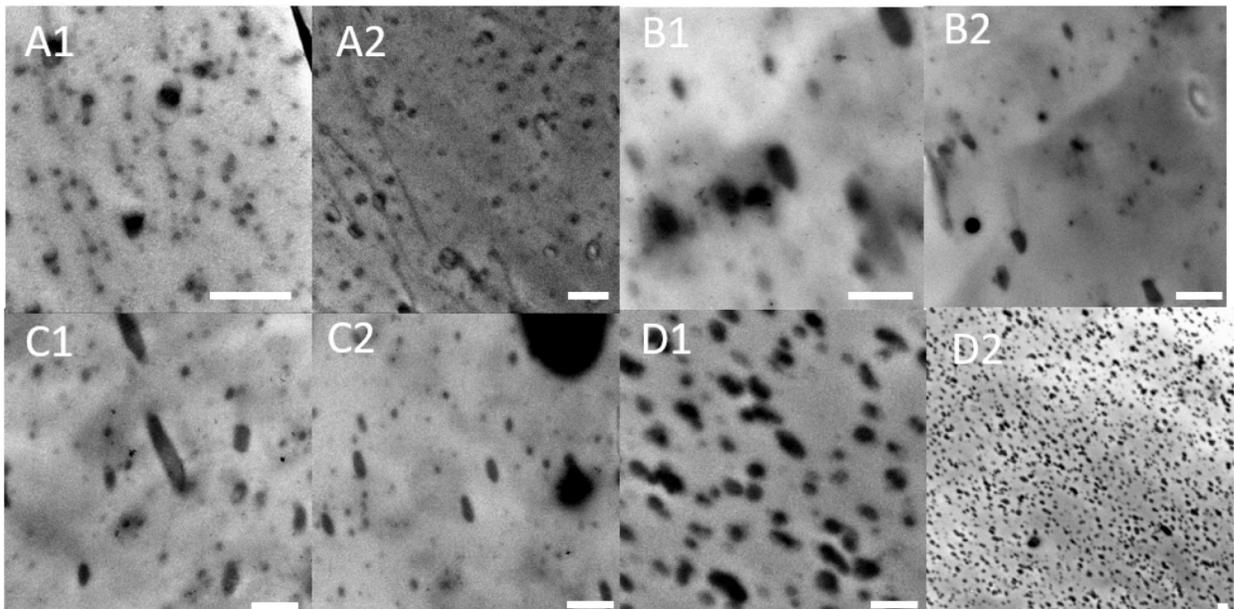


Figure 2-TEM images of 5wt% blend of diblock in PLA. (A) PI-PEO-2 (B)PI-PEO-3 (C) PI-PEO-4 (D) PI-PEO-5. All scale bars are 500nm. The sections were prepared by cryo microtoming at -120°C. The polyisoprene is preferentially stained with 0.5 wt.% Ruthenium tetroxide (RuO₄) aqueous solution for 15 min.

The 5 wt% PI-PEO-5 blend with PLA was tensile tested, with a representative result shown in Figure 3 and a summary of the results are in Table 2. There is a clear increase in toughness, and elongation at break. There is a slight reduction in tensile modulus and yield strength, which is expected once rubber modifiers are added to the system. During the tensile test the neck of the dogbone whitened, indicating cavitation and void formation, which is associated with energy dissipation. TEM images of the deformed area will be collected in the future to evaluate this toughening mechanism.

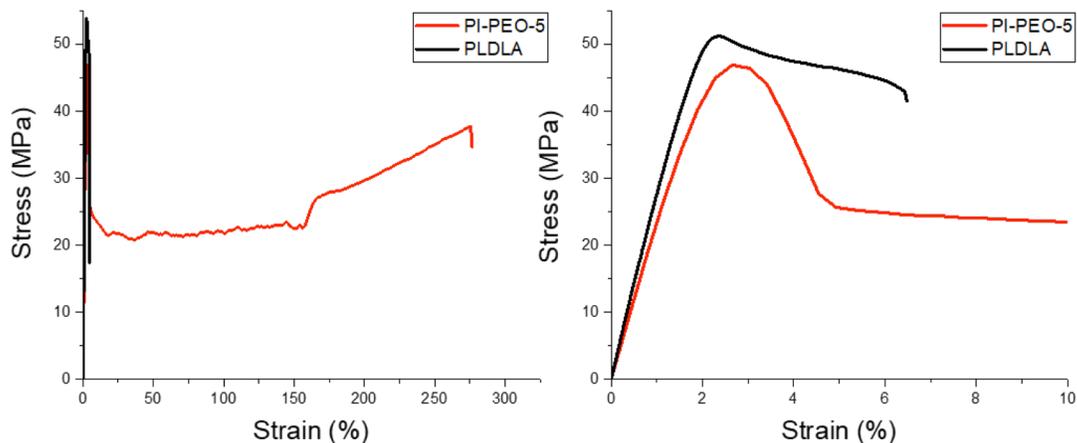


Figure 3- Stress versus strain curve for neat PLDLA and blended PLDLA with 5% wt. PI-PEO-5.

Table 2- Summary of mechanical properties of diblock copolymer/PLA blends

Blend	σ_y (MPa)	E (GPa)	ϵ_b (%)	Toughness (MJ/m ³)
Neat PLDLA	55±7	2.3±0.2	5.2±0.8	2.1±0.4
PI-PEO-5	44±4	1.8±0.1	250±40	58±21

Overall, a uniform dispersion that toughens PLA has been achieved. However, the associated micelles are rather large and lead to some degree of translucency. To reduce dispersion size, the core molecular weight can be decreased, the corona molecular weight can be increased or another rubbery block can be considered.

In the Dauenhauer group's project, while B-zeolites were found to give low selectivity towards isoprene (<30% carbon basis) from 3-methyltetrahydrofuran, they were highly selective to the formation of linear pentadienes from 2-methyl tetrahydrofuran (85-90% carbon basis). Furthermore, they were also found to be selective to formation of butadiene from tetrahydrofuran (70-80% carbon basis). The low selectivity to isoprene from 3-MTHF was attributed to a methyl shift to form a more stable 2° carbocation during the catalytic cycle, and this rearrangement is to be expected on any traditional Bronsted acid catalyst.

1. Loewenhaupt, B.; Steurer, A.; Hellmann, G. P.; Gallot, Y., Microphases and macrophases in polymer blends with a diblock copolymer. *Macromolecules* **1994**, 27 (4), 908-916.
2. Leibler, L.; Orland, H.; Wheeler, J. C., Theory of critical micelle concentration for solutions of block copolymers. *The Journal of Chemical Physics* **1983**, 79 (7), 3550-3557.

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

Initial experiments with low molecular weight PI-PEO diblocks did not reproduce the type of dispersion obtained with PEO-PBO in the Bates project. This hurdle was overcome by preparing higher molecular weight polymer.

Characterization via site counting of the acid sites for the B-based zeolites has been inconclusive for the Dauenhauer group. To address this challenge, all future kinetic measurements will be reports as a site-time yield rather than a turnover frequency.

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.)*

None this quarter