ACS APPLIED MATERIALS & INTERFACES

RESEARCH ARTICLE

www.acsami.org

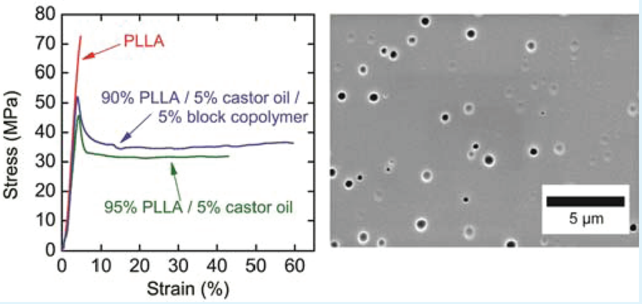
Tough Blends of Polylactide and Castor Oil

Megan L. Robertson,[†] Jessica M. Paxton, and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, United States

S *Supporting Information*

ABSTRACT: Poly(L-lactide) (PLLA) is a renewable resource polymer derived from plant sugars with several commercial applications. Broader implementation of the material is limited due to its inherent brittleness. We show that the addition of 5 wt % castor oil to PLLA significantly enhances the overall tensile toughness with minimal reductions in the modulus and no plasticization of the PLLA matrix. In addition, we used poly(ricinoleic acid)-PLLA diblock copolymers, synthesized entirely from renewable resources, as compatibilizers for the PLLA/castor oil blends. Ricinoleic acid, the majority fatty acid comprising castor oil, was polymerized through a lipase-catalyzed condensation reaction. The resulting polymers contained a hydroxyl end-group that was subsequently used to initiate the ring-opening polymerization of L-lactide. The binary PLLA/castor oil blend exhibited a tensile toughness seven times greater than neat PLLA. The addition of block copolymer allowed for control over the morphology of the blends, and even further improvement in the tensile toughness was realized—an order of magnitude larger than that of neat PLLA.



KEYWORDS: renewable resource polymers, polylactide, castor oil, ricinoleic acid, block copolymer compatibilization, polymer blends, sustainable materials

INTRODUCTION

The derivation of materials from renewable resources has been the subject of much interest in the literature because of the finite availability of petroleum and the environmental implications of petroleum processing.[1−9] For example, polymers derived from plant sugars[10] and terpenes,[11] vegetable oils,[5] naturally occurring polysaccharides,[12] and microbial syntheses[13] have been the subject of intensive study. Poly(L-lactide) (PLLA) is a commercially available polyester derived from plant sugars that has recently gained much attention as an alternative to petroleum-derived plastics.[10,14−17] PLLA is not only derived from an annually renewable resource, but is also hydrolytically degradable and compostable. The mechanical properties of PLLA are similar to that of polystyrene,[15,18] and like polystyrene, one of the deficiencies of the material is its brittleness, as evidenced by relatively low values of the tensile strain at break, tensile toughness, and impact strength. The focus of this study is the development of all-renewable, tough PLLA blends.

This paper follows a series of papers from our group on the utilization of triglyceride oils as toughening agents for PLLA. The oils do not plasticize the PLLA matrix; rather, the PLLA and oil form a phase separated mixture. The mechanism of toughening in these blends follows an expansive literature on rubber toughening of brittle polymers.[19] Our motivation for using triglyceride oils is to create a tough PLLA (analogous to the rubber toughening techniques used to produce high-impact polystyrene) derived entirely from renewable resources. Though other studies have shown that the tensile and impact toughness of PLLA can be improved by the preparation of phase separated blends containing PLLA and a minority phase rubbery polymer, the blending partners used were derived from petroleum.[20−25] In recent work, we have explored the rubber toughening of PLLA by the incorporation of triglyceride oils, primarily soybean oil. We discovered that PLLA/soybean oil mixtures underwent phase inversion at low concentrations of soybean oil, limiting the maximum amount of oil incorporated in the blend.[26] In the phase inverted blends, the minority phase (soybean oil in this case) formed the matrix surrounding particles of the majority phase (PLLA in this case). Block copolymer compatibilization of the PLLA/soybean oil blends allowed for suppression of phase inversion and increased concentrations of incorporated oil,[26] and the reactive compatibilization of a modified PLLA and conjugated soybean oil resulted in blends with significantly higher strain at break values than neat PLLA.[27] Similarly, the polymerization of soybean oil prior to mixing with PLLA prevented the phase inversion of the blends and resulted in enhanced values of the strain at break relative to neat PLLA.[28]

In this work, we focus on castor oil, a triglyceride containing the hydroxyl bearing ricinoleic acid as 90% of its fatty acids.[3] Castor oil as a raw material for polymers has found applications in polyamides (such as Nylon-11),[29] polyurethanes,[30] and interpenetrating networks,[31] among others. To evaluate the efficacy of castor oil as a renewable resource blending partner for PLLA we

Received: May 18, 2011
Accepted: July 22, 2011
Published: August 08, 2011

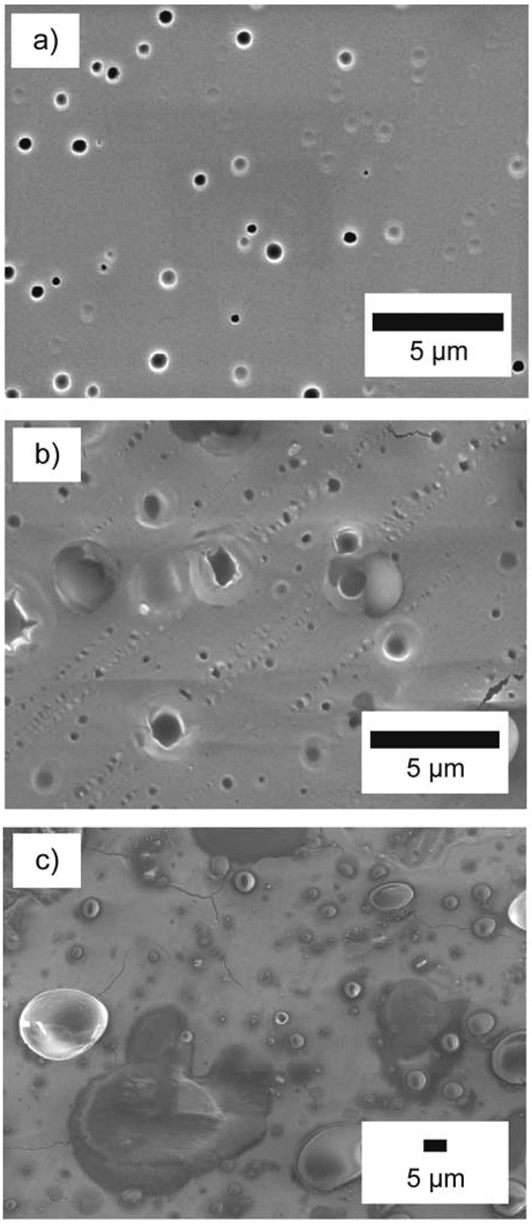


Figure 1. SEM micrographs of PLLA/castor oil blends containing (a) 5, (b) 10, and (c) 15 wt % castor oil. Note the lower magnification of micrograph c compared to micrographs a and b.

explored the morphology and tensile properties of melt blends of PLLA containing 5−15 wt % castor oil.

The utilization of block copolymers as compatibilizers to improve the properties of immiscible blends has been well established in the literature.[32] To further enhance the binary blends of castor oil and PLLA, we explored the use of block copolymer compatibilizers to control the blend morphology and improve the interfacial adhesion. Building upon the work of Domb and co-workers,[33,34] we synthesized diblock copolymers containing a poly(ricinoleic acid) (PRA) block and a PLLA block using the synthetic scheme developed by Ebata and co-workers for the preparation of high molecular weight PRA,[35,36] followed by the ring-opening of L-lactide. Blends were subsequently prepared and analyzed containing PLLA, castor oil, and the PRA-PLLA block copolymers.

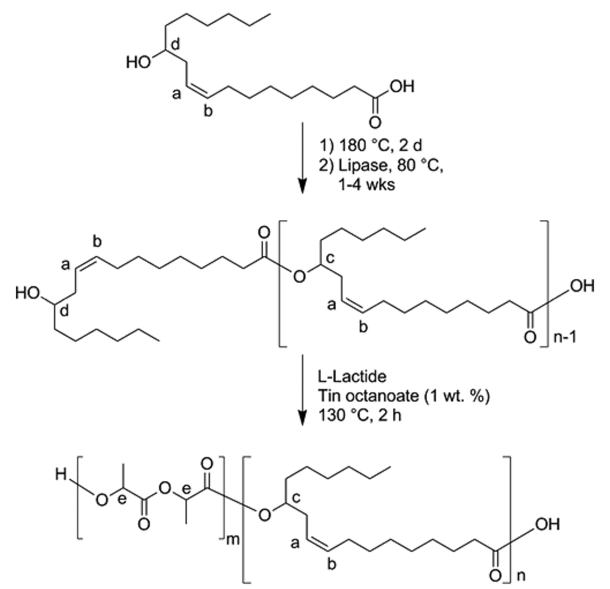
RESULTS AND DISCUSSION

Morphology of Binary Poly(L-lactide)/Castor Oil Blends. Binary blends of poly(L-lactide) (PLLA) and castor oil were prepared by melt mixing using a DACA twin-screw mixer. Blends containing 5−15 wt % castor oil were prepared, and in all cases the castor oil was fully incorporated into the blend based on proton nuclear magnetic resonance (^{1}H NMR) analysis. This is a substantial improvement over the case of the PLLA/soybean oil blends in which no more than around 6 wt % of soybean oil could be incorporated due to phase inversion phenomena.[26] SEM images obtained from the castor oil blends are given in Figure 1 and the blend characteristics are summarized in Table S1 in the Supporting Information. The blend containing 95 wt % PLLA and 5 wt % castor oil exhibits a volume average particle diameter $D_v = 0.70 \pm 0.20\ \mu$m (Figure 1a). The droplets were significantly smaller and more uniform than an analogous blend prepared with soybean oil, in which $D_v = 9.6 \pm 7.0\ \mu$m.[26] When the concentration of castor oil in the blend was increased to 10 wt %, D_ν increased slightly ($1.6 \pm 0.52\ \mu$m) and the droplets became less uniform (Figure 1b and Table S1 in the Supporting Information); at 15 wt % castor oil there was a drastic increase in $D_\nu = 24 \pm 4.3$ (Figure 1c and Table S1 in the Supporting Information). The stability of the blend containing 5 wt % castor oil was probed by quiescent annealing at 190 °C for 2 h in an oil bath. The blend morphology did not change significantly during the annealing process as seen in the scanning electron micrograph (SEM) images obtained from the blend pre- and post-annealing (see Figure S1 in the Supporting Information).

The size and uniformity of the 95 wt % PLLA/5 wt % castor oil blend (Figure 1a) was unexpected for a noncompatibilized blend with a seemingly high interfacial tension based on our previous work with 95 wt % PLLA/5 wt % soybean oil blends.[26] The interfacial tension of a binary blend depends on the Flory−Huggins interaction parameter, χ.[37,38] We previously determined $\chi_{\mathrm{PLLA/SOY}}$[26] and similar cloud point measurements were conducted on PLLA/castor oil blends. At 195 °C, $\chi_{\mathrm{PLLA/SOY}}$ is 0.34, while we have determined $\chi_{\mathrm{PLLA/CASTOR}}$ to be 0.18. Though the interaction parameter for PLLA/castor oil is smaller than that of PLLA/soybean oil, the PLLA/castor oil blends with $M_{\mathrm{n,PLLA}} = 54$ kg/mol used in the melt blending experiments are still expected to be immiscible (i.e., $\chi N \gg 2$). An explanation for the size and uniformity of the droplets in the 95 wt % PLLA/5 wt % castor oil blend is that the pendant hydroxyl groups on the castor oil triglyceride possibly undergo an esterification reaction with PLLA during the melt mixing process. This would result in the formation of PLLA-castor oil hybrid molecules of varying architectures (there are on average 2.8 hydroxyl groups per molecule on the castor oil triglyceride), which could act as compatibilizers for the PLLA/castor oil blend in a reactive compatibilization scenario.[39] A previous study on blends of PLLA and branched polymers containing a castor oil core and PLLA arms showed that a content of 5% of the branched polymers increased the strain at break of the PLLA.[40]

To explore the possibility of transesterification, a model 50 wt % PLLA/50 wt % castor oil blend was studied in which the PLLA had the following characteristics: $M_n = 4$ kg/mol (^{1}H NMR) and PDI = 1.10 (size exclusion chromatography, SEC, with polystyrene standards). The lower M_n value of PLLA was chosen to increase the likelihood of observing changes in the molecular weight distribution resulting from coupling of the PLLA and castor oil molecules. The blend was mixed in the melt in a glass

Scheme 1. Synthesis of PRA and PRA-PLLA[a]



[a] The labels a−e correspond to ^{1}H-NMR signals shown in Figure S4 in the Supporting Information.

Table 1. PRA and PRA-PLLA Characteristics

polymer name	$M_{n,PRA}$ (kg/mol)[a]	f_{PLLA}[b]	$M_{n,PLLA}$ (kg/mol)[a]	PDI[c]
PRA(3)[d]	2.6			3.67
PRA(6)	6.3			3.16
PRA(8)	8.4			5.69
PRA-PLLA(3−17)	2.6	0.17	0.72	1.47
PRA-PLLA(3−41)	2.6	0.41	2.5	1.36
PRA-PLLA(3−51)	2.6	0.51	3.7	1.37
PRA-PLLA(3−62)	2.6	0.62	5.8	1.30
PRA-PLLA(3−70)	2.6	0.70	8.2	1.34
PRA-PLLA(3−82)	2.6	0.82	17	1.62
PRA-PLLA(6−10)	6.3	0.10	0.91	3.47
PRA-PLLA(6−17)	6.3	0.17	1.7	4.01
PRA-PLLA(6−43)	6.3	0.43	6.4	1.94
PRA-PLLA(6−52)	6.3	0.52	9.3	4.86
PRA-PLLA(6−56)	6.3	0.56	11	1.94
PRA-PLLA(6−73)	6.3	0.73	24	2.68
PRA-PLLA(6−80)	6.3	0.80	34	3.28
PRA-PLLA(8−17)	8.4	0.17	2.2	3.08
PRA-PLLA(8−39)	8.4	0.39	7.2	4.01
PRA-PLLA(8−52)	8.4	0.52	12	2.20
PRA-PLLA(8−66)	8.4	0.66	22	4.01
PRA-PLLA(8−78)	8.4	0.78	40	3.57

[a] ^{1}H NMR spectroscopy [b] Volume fraction of PLLA through ^{1}H NMR analysis [c] SEC using polystyrene standards [d] The synthesis of PRA(3) was completed without the addition of lipase.

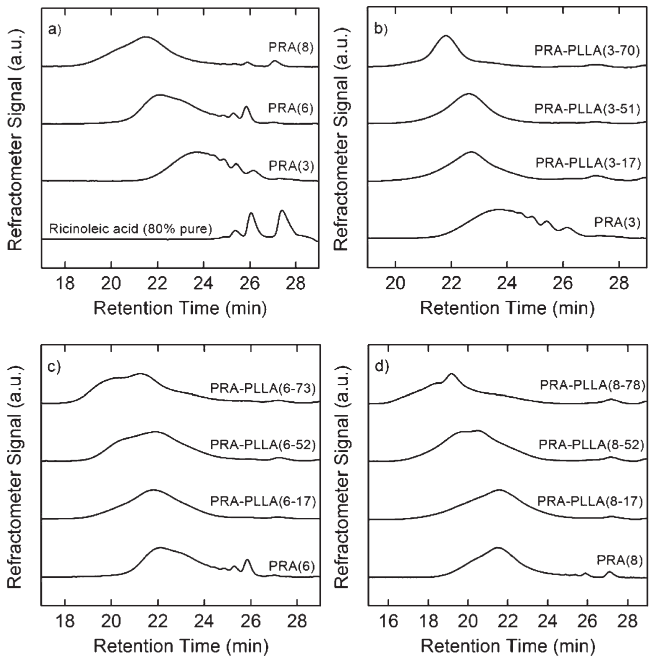


Figure 2. SEC traces of selected (a) PRA polymers and PRA-PLLA diblock copolymers containing (b) PRA(3), (c) PRA(6), and (d) PRA(8). The ricinoleic acid peak shown in a) was obtained on a sample which was 80% pure and thus other fatty acids are also present in the mixture (ricinoleic acid elutes at 27.5 min). The fatty acid impurities were removed during precipitation of the diblock copolymer. All diblock copolymer SEC traces are postprecipitation. The SEC traces have been shifted in order to delineate the data. SEC traces for all polymers used in this study are given in Figure S5 in the Supporting Information.

ampule at 190 °C for 2 h, and then analyzed by SEC. The SEC data (see Figure S2 in the Supporting Information) did not show any broadening of the PLLA or castor oil peaks. We saw no clear evidence for the coupling of PLLA and castor oil. However, a compatibilizer concentration of 1% (or less) would likely be sufficient to reduce the interfacial tension of the blend,[41] and such a small concentration would be difficult to detect with standard NMR or SEC techniques.

Tensile and Impact Properties of Binary Poly(L-lactide)/Castor Oil Blends. Tensile testing was conducted on dogbone shaped samples of the PLLA/castor oil blends. While PLLA exhibited brittle fracture at around 5% strain, the incorporation of 5−10 wt % castor oil into PLLA increased the strain at break to around 40%. The strain at break for the blend containing 15 wt % castor oil was about 13%. It is important to note that the castor oil did not plasticize the PLLA matrix in the binary and ternary blends, as evidenced by the value of the glass transition temperature of PLLA (58 °C) determined from differential scanning calorimetry experiments which is consistent with the neat polymer. The tensile toughness of the blend containing 5 wt % castor oil was seven times greater than that of neat PLLA (14 MJ m^{-3} vs 2 MJ m^{-3}). Further addition of castor oil to the binary blend reduced the tensile toughness due to a decrease in the stress at break (see Table S2 in the Supporting Information). The impact strengths of neat PLLA and the binary blend containing 95 wt % PLLA/5 wt % castor oil were tested, and the impact strength of neat PLLA was found to be 26 ± 2 J/m while that of the PLLA/castor blend was 42 ± 7 J/m, representing 150% increase. Large-scale blends were also prepared using a variety of compounders; the results are summarized in Table S3 and Figure S3 in the Supporting Information. The use of a twin screw extruder resulted in comparable blends to those prepared in the DACA mixer, with slightly enhanced tensile properties.

Synthesis and Characterization of Poly(ricinoleic acid-*b*-L-lactide) Diblock Copolymers. In an effort to further enhance

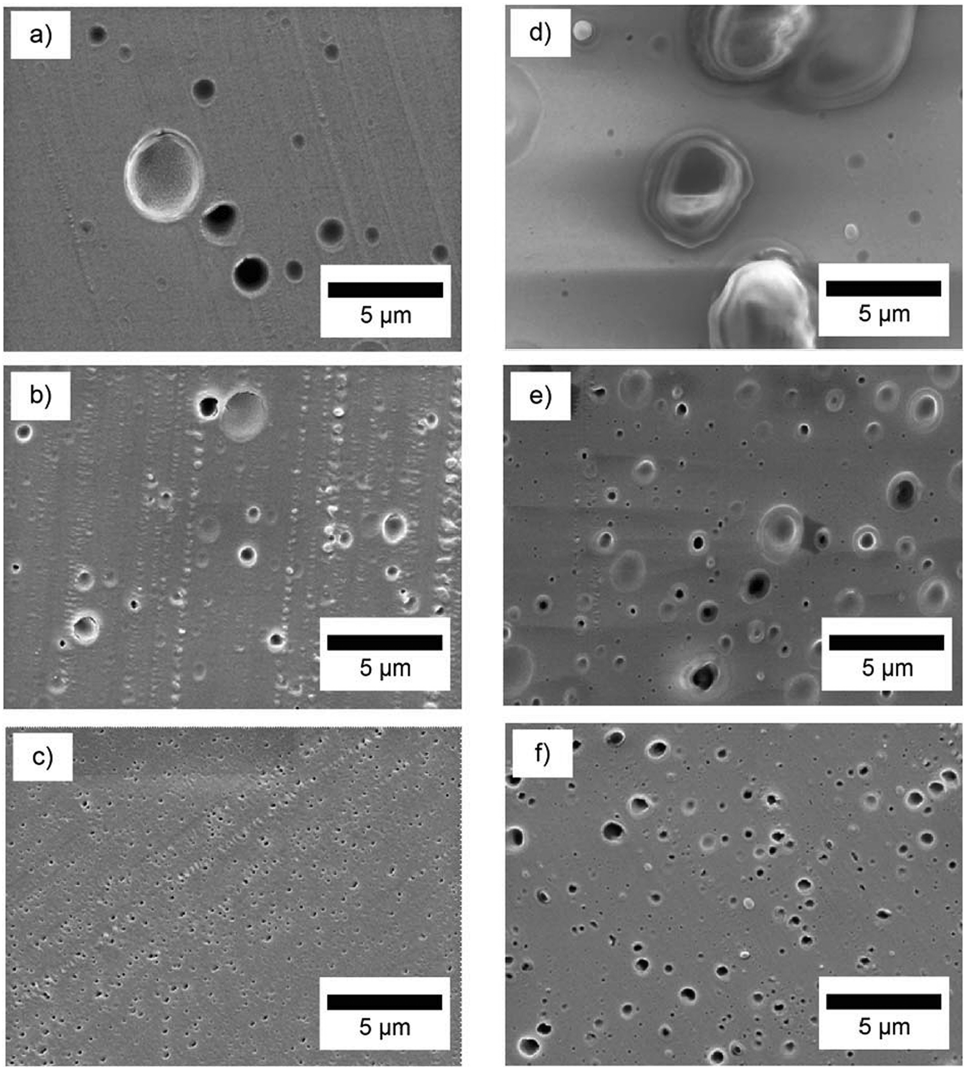


Figure 3. SEM micrographs of a 95 wt % PLLA/5 wt % castor oil blend with the addition of 5 wt % PRA-PLLA containing PRA(3) and the following f_{PLLA}: (a) 0.17, (b) 0.51, and (c) 0.70. SEM micrographs are also shown of a 90 wt % PLLA/10 wt % castor oil blend with the addition of 5 wt % PRA-PLLA containing PRA(3) and the following f_{PLLA}: (d) 0.17, (e) 0.51, and (f) 0.70. f_{PLLA} = the volume fraction of PLLA in the block copolymer.

the properties of the PLLA/castor oil blends, we sought potential compatibilizers that would be suitable for these blends. To this end, three poly(ricinoleic acid) (PRA) samples were synthesized through a lipase-catalyzed condensation polymerization (Scheme 1).[35,36] Their molecular characteristics are listed in Table 1. ^{1}H NMR end-group analysis was used to determine the absolute M_n for each of the PRA polymers assuming one free OH end group per chain, using the areas of peaks c and d in Figure S4 in the Supporting Information. SEC data obtained from the PRA samples are given in Figure 2a. A clear shift to lower elution volumes is observed upon increasing the molecular weight for the three polymers (the data for the ricinoleic acid starting material is also included as a reference). The polymers exhibit broad molecular weight distributions with PDI values in the range of 3.7−5.7, which is higher than expected for condensation polymerizations, possibly because of inhomogeneities in the reaction mixture.

Poly(ricinoleic acid-*b*-L-lactide) (PRA-PLLA) diblock copolymers were synthesized using each of the three PRA polymers as macroinitiators for the ring-opening of L-lactide (Scheme 1). The characteristics of the PRA-PLLA block copolymers are given in Table 1. The volume fraction of PLLA in the PRA-PLLA diblock copolymers was determined by ^{1}H NMR analysis (see Figure S4 in the Supporting Information). Selected SEC data obtained from each series of diblock copolymers are shown in Figure 2b−d (additional samples are shown in Figure S5 in the Supporting Information). In general, the peak position shifts to lower elution volume with increasing PLLA content although the breadth of the peaks leaves open the possibility for PRA homopolymer contamination. Though the block copolymerizations with PRA(3) proceeded smoothly because of the miscibility of PRA(3) and the lactide monomer, PRA(6) and PRA(8) were immiscible with the lactide monomer. All of the PRA-PLLA block copolymers reported in this manuscript were prepared with lactide polymerizations in the bulk; however, a separate set of reactions in solution were conducted. These samples exhibited multimodal molecular weight distributions with PDI values far exceeding that of the samples prepared in the bulk. Therefore, even though the PRA polymers at higher molecular weights were not miscible with lactide, bulk polymerization techniques were utilized.

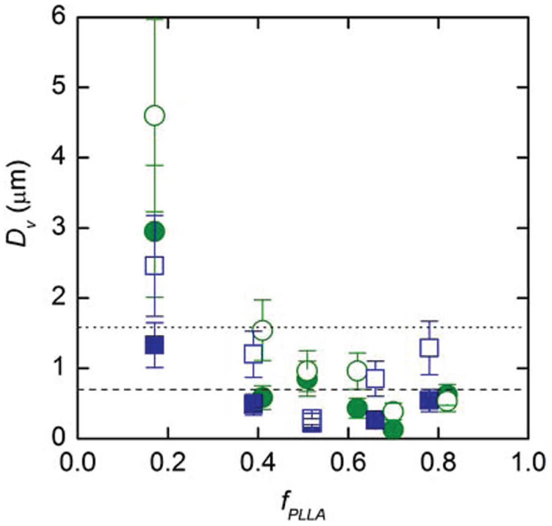


Figure 4. D_v vs f_{PLLA} are shown for 90 wt % PLLA/5 wt % castor oil/5 wt % PRA-PLLA blends. The PRA-PLLA block copolymers contain (green ●) PRA(3) and (blue ■) PRA(8). D_v vs f_{PLLA} are also shown for 85 wt % PLLA/10 wt % castor oil/5 wt % PRA-PLLA blends. The PRA-PLLA block copolymers contain (green ○) PRA(3) and (blue □) PRA(8). f_{PLLA} = the volume fraction of PLLA in the block copolymer. The D_v values are also shown for the 95 wt % PLLA/5 wt % castor oil (- - -) and 90 wt % PLLA/10 wt % castor oil (···) binary blends.

To determine the homopolymer content in the PRA-PLLA diblock copolymers, the PRA end-groups were analyzed by ^{1}H NMR spectroscopy. For the series of diblock copolymers containing PRA(3), 5−10 mol % PRA homopolymer was present relative to the PRA in the diblock copolymer. This calculation could not be completed with certainty for the diblock copolymers containing PRA(6) and PRA(8) due to the vanishingly small size of the PRA end-group (peak d in Figure S4 in the Supporting Information) resulting from the larger values of M_n. To probe further the possibility of PRA homopolymer contamination in the other series of diblock copolymers, preparatory SEC experiments were conducted, which also indicated the presence of homopolymer PRA (see Figure S6 in the Supporting Information).

Differential scanning calorimetry (DSC) experiments indicated that the PRA-PLLA diblock copolymers were microphase separated. In most cases a melting peak was observed for PLLA and distinct glass transition temperatures were observed for PLLA and PRA (see Table S4 in the Supporting Information). The glass-transition temperatures of the PRA blocks in the diblock copolymers (ranging from −65 to −77 °C) were consistent with the PRA homopolymers (ranging from −70 to −72 °C). Most of the glass transition temperatures of the PLLA blocks (ranging from 49 to 60 °C) were consistent with previous studies on a PLLA homopolymer.[28] Many of the PLLA-block melting temperatures (ranging from 109 to 176 °C) were depressed relative to the homopolymer PLLA melting temperature (reported to be 178 °C in ref 10), which could be a result of the small PLLA molecular weight[42] or the microphase separation of the domains.[43] Small-angle X-ray scattering (SAXS) experiments confirmed the presence of microphase separation (see Figure S7 in the Supporting Information), although the specific nature of the morphology could not be elucidated from the SAXS data.

Morphology of Compatibilized Blends. The efficacy of PRA-PLLA diblock copolymers for the compatibilization of PLLA/castor oil mixtures was probed by the preparation of ternary blends by melt mixing. SEM micrographs obtained from the blends are given in Figure 3 and the blend characteristics are summarized in Table S5 in the Supporting Information. The addition of PRA-PLLA block copolymers resulted in variation of the blend morphology, as shown in Figure 3 for blends containing 5 and 10 wt % castor oil. D_v ranged from 0.1 to 10.0 μm for the compatibilized blends (Figure 4 and Table S5 in the Supporting Information). There appears to be an optimal block copolymer composition at which the blend droplet diameter is minimized (Figure 4). A similar trend was observed previously in poly(isoprene)-*b*-poly(L-lactide) compatibilized PLLA/soybean oil blends.[26] This optimal block copolymer composition depends on the overall molecular weight of the block copolymer; however, no significant effect of the fraction of castor oil was observed. The minimization of D_v is most likely due to the minimization of the interfacial tension of the system, which depends on the block copolymer composition in compatibilized blends.[44,45] The stability of the compatibilized blends was also probed by annealing selected samples at 190 °C. No significant changes were observed in the blend morphology postannealing (see Figure S1 in the Supporting Information).

Tensile Properties of Compatibilized Blends. Stress vs strain data are given in Figure 5a for representative binary and ternary blends containing 5 wt % castor oil, and neat PLLA for comparison. While PLLA exhibited brittle fracture at around 5% strain, the incorporation of 5% castor oil into PLLA increased the elongation to around 40%. Compatibilization with block copolymers further increased the elongation to around 60%. As with the binary blends, plasticization of the PLLA matrix was not observed (see Table S5 in the Supporting Information). The tensile properties of all of the compatibilized blends studied are summarized in Table S6 in the Supporting Information. Figure 5b focuses on the relationship between the morphology and tensile toughness for all of the binary and ternary blends studied. The tensile toughness is plotted as a function of the interparticle distance determined from the SEM micrographs. The binary blends containing 5 and 10 wt % castor oil exhibited significantly higher values of the tensile toughness than neat PLLA (the dashed line in Figure 5b). Addition of block copolymer resulted in an order of magnitude increase in the tensile toughness relative to neat PLLA. The block copolymer characteristics, which ultimately influence the interparticle distance, appear to have little influence on the tensile toughness; most of the 5 wt % castor oil blends exhibited high tensile toughness values, regardless of the block copolymer characteristics.

Previous work has shown that there is a critical interparticle distance for the toughening of PLLA, which was around 1 μm.[46−48] Furthermore, more recent theoretical work has proposed that there is a critical range of particle diameters for improvements in the toughness of a blend, rather than a critical interparticle distance.[49] For semicrystalline polymers, it has been proposed that the critical interparticle distance is dependent on the particle diameter.[50] In the present study, toughened blends were obtained with interparticle distances and average particle diameters ranging from around 0.1−3 um. Blends containing similar levels of castor oil were not studied with interparticle distances or average particle diameters outside of this range. Therefore, while the present results are consistent with the current theoretical descriptions, we cannot clearly distinguish between them.

In most cases the ternary blends containing 10 wt % castor oil did not show improved values of the tensile toughness when

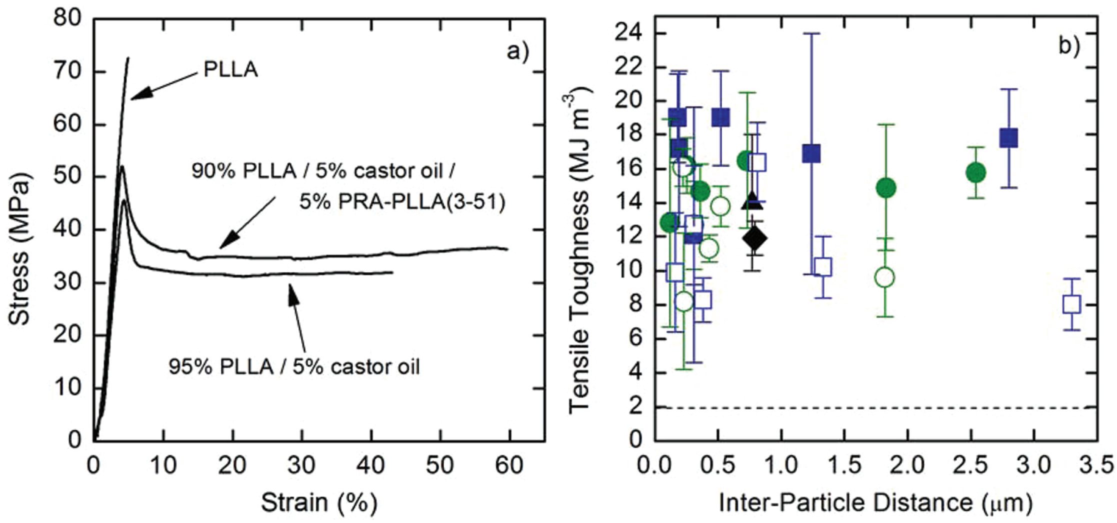


Figure 5. (a) Stress vs strain data for neat PLLA, a 95 wt % PLLA/5 wt % castor oil binary blend, and a 90 wt % PLLA/5 wt % castor oil/5 wt % PRA-PLLA(3–51) ternary blend. b) Tensile toughness vs the interparticle distance for 90 wt % PLLA/5 wt % castor oil/5 wt % PRA-PLLA blends. The PRA-PLLA block copolymers contain (green ●) PRA(3) and (blue ■) PRA(8). Tensile toughness vs the interparticle distance are shown for 85 wt % PLLA/10 wt % castor oil/5 wt % PRA-PLLA blends. The PRA-PLLA block copolymers contain (green ○) PRA(3) and (blue □) PRA(8). The binary 95 wt % PLLA/5 wt % castor oil (▲) and 90 wt % PLLA/10 wt % castor oil (♦) blends are also indicated. The dotted line is the tensile toughness of neat PLLA.

compared to the binary 90 wt % PLLA/10 wt % castor oil blend. The tensile elongations of the ternary blends containing 10 wt % castor oil were in some cases as high as in the ternary blends containing 5 wt % castor oil; however, values for the stress at break were significantly reduced.

The fracture surfaces of tensile test bars were imaged with SEM and are shown in Figures S8 and S9 in the Supporting Information. The images are consistent with deformation of the PLLA matrix due to shear yielding,[51] which in some cases has been shown to be induced by cavitation of the rubbery particles.[52] Similar fracture surface images have been observed in previous studies of rubber toughened PLLA.[28,46] In some cases, there appears to be debonding of the particles from the matrix, possibly due to a lack of interfacial adhesion even in the presence of block copolymer (see Figures S8 and S9 in the Supporting Information).[53]

CONCLUSIONS

Castor oil could be fully incorporated into the PLLA matrix (observed up to 15 wt % of the total blend), in contrast to previous studies on PLLA/soybean oil blends. The castor oil droplets in the 95 wt % PLLA/5 wt % castor oil blend were unexpectedly small and uniform, especially compared to that of the 95 wt % PLLA/5 wt % soybean oil blends. Preliminary experiments to explain the small size and uniformity of the droplets resulted in the conclusion that the Flory–Huggins interaction parameter is not significantly different for PLLA/castor oil compared to PLLA/soybean oil. The most likely explanation is the coupling between PLLA and castor oil molecules during the mixing process, however this phenomenon was not directly observed in model experiments.

Renewable resource PRA-PLLA diblock copolymers were synthesized through a combination of condensation and ring-opening polymerization techniques. The diblock copolymers exhibited microphase separation in the bulk, as evidenced by SAXS and DSC experiments. The morphology of the PLLA/castor oil blends was significantly impacted by the addition of the PRA-PLLA diblock copolymers, with D_v ranging from 0.1–10 μm. Furthermore, the blend morphology was found to be stable to annealing at 190 °C, for both binary and ternary blends. All of the blends studied showed improvements in the tensile toughness relative to neat PLLA. The binary 95 wt % PLLA/5 wt % castor oil blend exhibited a tensile toughness seven times greater than neat PLLA, and with block copolymer compatibilization, an order of magnitude increase in the tensile toughness was observed relative to neat PLLA. The fracture surfaces from the tensile bars are consistent with shear yielding of the PLLA matrix. Also, the impact strength of the 95 wt % PLLA/5 wt % castor oil blend was 1.5 times greater than neat PLLA. A variety of compounders were employed to probe the possibility of scaling up the castor oil-toughened PLLA. The use of a twin screw extruder, an industrially relevant preparation technique, resulted in comparable blends, with slightly higher values of the tensile toughness than the blends prepared in the smaller-scale DACA mixer.

EXPERIMENTAL DETAILS

Polymer Synthesis and Characterization. Ricinoleic acid (80% pure, Sigma Aldrich) was polymerized (without prior purification) through a condensation reaction by heating it under reduced pressure at 180 °C for 2 days. Ricinoleic acid (99% pure) and methyl ricinoleate (99% pure) (both from Sigma Aldrich) were also used in small scale polymerizations. The higher monomer purity had no noticeable effect on the resulting polymer molecular weight distribution. Therefore, the 80% pure ricinoleic acid was used for simplicity in all of the polymerizations reported in this manuscript. The fatty acid impurities were removed from the block copolymers during precipitation. To further increase the molecular weight of the resulting polymer, 10–20 wt % lipase from *candida antarctica* supplied on an acrylic resin (with an activity of 11,200 propyllaurate units per gram, as determined by the supplier, Sigma Aldrich; used as-purchased) was added to the ricinoleic acid (at room temperature) and it was further heated under reduced pressure at 80 °C for 1−4 weeks following Ebata et al.[35,36] Poly(ricinoleic acid) (PRA) was dissolved in dichloromethane, filtered through a frit funnel to remove the lipase, and then dried under reduced pressure at 60 °C for 3 days. PRA and L-lactide (purchased from Purac, recrystallized in ethyl acetate) were evacuated overnight in a pressure vessel. Tin octanoate (1 wt % based on lactide; used as-purchased from Sigma-Aldrich) was added to the reaction mixture (in air) and the vessel was sealed and heated to 130 °C for 2 h. The lactide conversion under these conditions was 90−95%. The poly(ricinoleic acid-*b*-L-lactide) (PRA-PLLA) diblock copolymers were precipitated twice in methanol and dried under reduced pressure at 80 °C for 3 days.

The number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n where M_w is the weight-average molecular weight) of the PRA, PRA-PLLA, and PLLA homopolymer (supplied by Toyota Motor Inc.) were characterized with analytical size exclusion chromatography (SEC) using a Hewlett-Packard 1100 series chromatograph equipped with three PLgel 5 μm MIXED-C columns and a Hewlett-Packard 1047A refractive index detector (in chloroform at 35 °C). The values reported from SEC are based upon polystyrene standards. The commercial PLLA pellets supplied by Toyota had the following characteristics determined from SEC: M_n = 54 kg/mol and PDI = 1.73. The molecular weight of the PLLA is greater than the entanglement molecular weight.[54]

Preparatory size exclusion chromatography experiments (prep SEC) were performed on selected PRA-PLLA diblock copolymers using the same chromatograph and two PLgel 10 μm MIXED-D columns. Chloroform at 35 °C was used as the mobile phase at a flow rate of 6 mL/min as to keep the internal pressure of the columns approximately equal to the pressure used during analytical SEC experiments.

Absolute M_n based upon end group analysis of the PRA polymers and the compositions of the PRA-PLLA diblock copolymers were determined from ^{1}H NMR spectroscopy (Varian INOVA-500). The mole fraction of each block in the block copolymer, as determined from NMR experiments, was converted to the volume fraction of each block using the molecular weight of a repeat unit and density of each block. The densities for PLLA and PRA used in this calculation were 1.264 g/mL and 0.93 g/mL, respectively at 23 °C. The characteristics of the PRA polymers and PRA-PLLA diblock copolymers are given in Table 1.

Small-angle X-ray scattering (SAXS) experiments were performed at the Advanced Photon Source (APS) at Argonne National Laboratories at the Sector 5-ID-D beamline maintained by the Dow-Northwestern-Dupont Collaborative Access Team (DND-CAT). The X-ray wavelength was 0.84 Å, the sample to detector distance was 5.65 m, and the detector radius was 81 mm. The scattering intensity was monitored by a Mar 165 mm diameter CCD detector with a resolution of 2048 × 2048. The two-dimensional scattering patterns were azimuthally integrated, resulting in one-dimensional scattering intensity (I) versus scattering vector (q) profiles.

Differential scanning calorimetry analysis (TA Instruments Q1000 under nitrogen gas at a scan rate of 10 °C/min from 0−220 °C) was used to determine the glass transition temperatures of the PLLA and PRA and the melting point of PLLA in the PRA-PLLA diblock copolymers.

Blend Preparation and Characterization. Poly(L-lactide) homopolymer (PLLA) was supplied by Toyota Motor Corporation and castor oil was purchased from Sigma Aldrich (used as-purchased). Unless otherwise noted, the blend components (PLLA, castor oil, and PRA-PLLA diblock copolymers) were melt blended in a recirculating, corotating, conical twin-screw DACA Micro Compounder with 4 g batch size. For selected blends, a Haake internal batch mixer (Haake Rheomix OS, 20 g batch size) and a PRISM model corotating twin screw extruder (16 mm, L/D ratio = 25, 1 kg collected extrudate) were also employed. A more complete description of the three mixers is given in ref 55. PLLA was dried in a vacuum oven overnight at 80 °C prior to mixing, and stored in a desiccator under reduced pressure until use. In the DACA and Haake mixers, PLLA and PRA-PLLA (in the case of ternary blends) were first added to the mixer, and the torque was allowed to equilibrate for a few minutes. The castor oil was subsequently added dropwise to the mixer. For the DACA mixer, the mixing temperature was 190 °C, the mixing rate was 300 rpm, and the total mixing time was 20 min. For the Haake mixer, the mixing temperature was 190 °C, the mixing rate was 50 or 100 rpm, and the total mixing time was 20 min. For the twin screw extruder, the flow rates of the PLLA pellets and castor oil (supplied using a syringe pump) were set to achieve the desired concentration of castor oil. The PLLA flow rate was 26.0 g/min and the castor oil flow rate was 1.3 g/min. Five heating zones were utilized in the twin screw extruder (listed from sample inlet to sample outlet): 190, 190, 190, 180, and 170 °C. After mixing, the sample was collected into liquid nitrogen to preserve the morphology (from the extruder port in the DACA and twin screw extruder, and transferred manually in the Haake, which does not have an extruder port).

A portion of the sample was saved for observation of the blend morphology (taken from the extrudate in the DACA mixer and twin screw extruder). The sample (from a middle portion of the extrudate) was cryo-microtomed (Ultracut Microtome, Reichert) using a glass knife at −150 °C. The polished surface of the specimen was coated with 10 nm of platinum. The specimen was imaged with scanning electron microscopy (SEM) using a JEOL 6500 instrument operating at an accelerating voltage of 5 kV and containing a Everhart Thornley secondary electron detector. The castor oil particles were sometimes removed from the surface during the microtoming process and thus holes in the sample were observed. The centers of the holes often appear darker than the matrix, with a bright ring around the holes. ImageJ analysis software was used to analyze the average droplet (or hole) diameter from the SEM images. The area of each particle was calculated and then converted to an equivalent diameter of a sphere ($D_i = 2(A_i/\pi)^{1/2}$). Using 100−700 particles, a volume-average diameter (D_v) was calculated as shown in eq 1. Though the Sauter mean diameter, which is the ratio of the volume to surface area average diameters, has been used (eq 1), it will be referred to as the volume-average diameter in this manuscript for simplicity. No further correction of D_i was made for the underestimation of D_i due to the two-dimensional projection of the sphere. Additionally, droplets of a size too small to be observed at the magnification chosen have been neglected. The volume average diameter is used as it places more weight on the larger particles than the number average diameter. The interparticle distance, or matrix ligament thickness (T), was also calculated following ref 56. Selected samples were annealed in an oil bath at 190 °C for 2 h and subsequently analyzed with SEM to probe the stability of the morphology (after microtoming the surface and coating with 10 nm of platinum).

$$D_v = \frac{\sum_i^n D_i^3}{\sum_i^n D_i^2} \tag{1}$$

The blends were pressed at 200 °C (after annealing for 10 min at 200 °C) at an approximate pressure of 1 MPa into a dogbone-shaped mold with gage width =3 mm, gage length =12 mm, and thickness = 0.5 mm. The samples were removed from the press and allowed to cool at room temperature for 10 min. The tensile properties of the blends were then measured (after 1 day to 1 week of room temperature aging) on a Rheometrics Minimat tensile tester at a rate of 10 mm/min. Though this dogbone shape does not conform to ASTM standards, the tensile properties of neat PLLA measured using this method (strain at break = 5%, stress at break = 68 MPa, tensile modulus = 2 GPa, and tensile toughness = 2 MPa) were in agreement with the literature.[14,15,18] Further discussion of this dogbone sample is found in ref 28. One of the pressed dogbone samples was used for ^{1}H NMR analysis (Varian INOVA-500) to determine the percent of castor oil incorporated into the blend, and in all cases the castor oil was fully incorporated. SEM analysis was also conducted on the fracture surfaces of the tensile bars (after coating with 10 nm of platinum).

The pressed samples were analyzed with differential scanning calorimetry analysis (TA Instruments Q1000 under nitrogen gas at a scan rate of 10 °C/min from 0−220 °C) to determine the glass transition temperature and percent crystallinity of PLLA in the blends.

A model blend was prepared to probe the potential coupling between the PLLA and castor oil by melt mixing in a glass vial with a stir bar at 190 °C for 2 h. The absolute M_n of the PLLA used in the model blend was characterized with end group analysis of ^{1}H NMR spectroscopy data (Varian INOVA-500), and the M_n was determined to be 4.1 kg/mol. The PDI of the PLLA was 1.10 determined from SEC with polystyrene standards.

Additional PLLA/castor oil blends were solution cast for the purpose of determining the Flory−Huggins interaction parameter (χ). Two blends were prepared with $M_{n,\mathrm{PLLA}}$ = 2.0 kg/mol (^{1}H NMR) and PDI = 1.08 (SEC with polystyrene standards) containing 80 and 85 wt % PLLA. The cloud points of the blends were determined by heating them in an oil bath and noting the temperature at which they transitioned from cloudy to clear. The cloud points were 205 and 195 °C (± 5 °C) for the blends containing 80 and 85 wt % PLLA, respectively. The equations for the binodal curve obtained from Flory−Huggins theory[57−59] were fit to the two data points, with $\chi_{\mathrm{PLLA/CASTOR}}$ as a fitting parameter (a more detailed explanation of the cloud point experiments and fitting procedure is found in the Supporting Information for ref 26). The result of this analysis was the determination that $\chi_{\mathrm{PLLA/CASTOR}} = 0.18$ at 195 °C (±5 °C), and that $\chi_{\mathrm{PLLA/CASTOR}} = 0.16$ at 205 °C (± 5 °C). A reference volume of 0.163 nm^3 was used, consistent with ref.[26]

Impact testing bars were prepared by pressing the sample into a mold ($12.7 \times 63.5 \times 3.2$ mm^3) at 200 °C (after annealing for 10 min at 200 °C) at an approximate pressure of 1 MPa. The samples were removed from the press and allowed to cool at room temperature for 10 min. Notched izod impact testing was performed on a Resil 25 impact tester (CEAST) at room temperature per ASTM D256. The notch depth was cut to 2.54 mm. The impact strength was calculated by dividing the total energy required to break the sample by the thickness of the impact bar (3.2 mm). A minimum of five samples were tested for each material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Binary blend characteristics and tensile properties (Tables S1−S2), SEM images of binary and ternary blends pre- and postannealing (Figure S1), SEC data from a model blend to probe the coupling between PLLA and castor oil (Figure S2), characteristics and tensile properties of the 95 wt % PLLA/5 wt % castor oil blend obtained from various compounders (Table S3), SEM images of the 95 wt % PLLA/5 wt % castor oil blend obtained from various compounders (Figure S3), ^{1}H NMR data obtained from PRA and PRA-PLLA polymers (Figure S4), SEC data obtained from PRA-PLLA diblock copolymers (Figure S5), preparatory SEC data obtained from PRA-PLLA(6−56) (Figure S6), SAXS data obtained from PRA-PLLA diblock copolymers (Figure S7), DSC data obtained from PRA and PRA-PLLA (Table S4), ternary blend characteristics and tensile properties (Tables S5−S6), and fracture surfaces of tensile bars from binary and ternary blends (Figures S8 and S9). This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail:hillmyer@umn.edu.

Present Addresses

†Department of Chemical and Biomolecular Engineering, University of Houston, 4800 Calhoun Road, Houston, TX 77204-4004.

■ ACKNOWLEDGMENT

The authors thank Louis M. Pitet and Mark T. Martello for acquiring the SAXS data, William M. Gramlich for helpful discussions and assistance with the preparatory SEC experiment, and Jie Song, Dr. Hyunwoo Kim, and Dr. Carlos R. Lopez-Barron for assistance with the various compounders used in this study. In addition, the authors would like to thank Grayce C. Theryo for helpful discussions, particularly regarding the tensile and impact measurements, and Raghuram Thiagarajan for assistance with the determination of the binodal curves in the calculation of the Flory−Huggins interaction parameter. The authors are grateful to Toyota Motor Corporation and the United States Department of Agriculture for funding. Parts of this work were carried out in the University of Minnesota I.T. Characterization Facility, which receives partial support from NSF through the NNIN program. SAXS data were acquired at the DuPont−Northwestern−Dow Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by E. I. Dupont de Nemours and Co., The Dow Chemical Co., and the State of Illinois. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.

■ REFERENCES

(1) Demirbas, A. *Energy Sources, Part A* **2007**, *29*, 419–424.

(2) Flieger, M.; Kantorova, M.; Prell, A.; Rezanka, T.; Votruba, J. *Folia Microbiol.* **2003**, *48*, 27–44.

(3) Guner, F. S.; Yagci, Y.; Erciyes, A. T. *Prog. Polym. Sci.* **2006**, *31*, 633–670.

(4) Madison, L. L.; Huisman, G. W. *Microbiol. Mol. Biol. Rev.* **1999**, *63*, 21–53.

(5) Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1788–1802.

(6) Petrovic, Z. S. *Polym. Rev.* **2008**, *48*, 109–155.

(7) Philip, S.; Keshavarz, T.; Roy, I. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 233–247.

(8) van Beilen, J. B.; Poirier, Y. *Plant J.* **2008**, *54*, 684–701.

(9) Young, J. L.; Woerderman, D. L.; Selling, G. W. *J. Biobased Mater. Bioenergy* **2007**, *1*, 171–176.

(10) Garlotta, D. *J. Polym. Environ* **2001**, *9*, 63–84.

(11) Mosnacek, J.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 5509–5511.

(12) Teramoto, Y.; Nishio, Y. *Polymer* **2003**, *44*, 2701–2709.

(13) Madison, L. L.; Huisman, G. W. *Microbiol. Mol. Biol. Rev.* **1999**, *63*, 21–53.

(14) Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, *4*, 835–864.

(15) Bhardwaj, R.; Mohanty, A. K. *J. Biobased Mater. Bioenergy* **2007**, *1*, 191–209.

(16) Datta, R.; Henry, M. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1119–1129.

(17) Sodergard, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123–1163.

(18) Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 85–108.

(19) Perkins, W. G. *Polym. Eng. Sci.* **1999**, *39*, 2445–2460.

(20) Anderson, K. S.; Hillmyer, M. A. *Polymer* **2004**, *45*, 8809–8823.

(21) Li, Y. J.; Shimizu, H. *Macromol. Biosci.* **2007**, *7*, 921–928.

(22) Kim, K. S.; Chin, I. J.; Yoon, J. S.; Choi, H. J.; Lee, D. C.; Lee, K. H. *J. Appl. Polym. Sci.* **2001**, *82*, 3618–3626.

(23) HiljanenVainio, M.; Varpomaa, P.; Seppala, J.; Tormala, P. *Macromol. Chem. Phys.* **1996**, *197*, 1503–1523.
(24) Ho, C. H.; Wang, C. H.; Lin, C. I.; Lee, Y. D. *Polymer* **2008**, *49* (18), 3902–3910.
(25) Ishida, S.; Nagasaki, R.; Chino, K.; Dong, T.; Inoue, Y. *J. Appl. Polym. Sci.* **2009**, *113* (1), 558–566.
(26) Chang, K. H.; Robertson, M. L.; Hillmyer, M. A. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2390–2399.
(27) Gramlich, W. M.; Robertson, M. L.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 2313–2321.
(28) Robertson, M. L.; Chang, K. H.; Gramlich, W. M.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 1807–1814.
(29) Nayak, P. L. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **2000**, *C40*, 1–21.
(30) Petrovic, Z. S.; Cvetkovic, I.; Hong, D.; Wan, X.; Zhang, W.; Abraham, T.; Malsam, J. *J. Appl. Polym. Sci.* **2008**, *108*, 1184–1190.
(31) Sperling, L. H.; Mishra, V. *Polym. Adv. Technol.* **1996**, *7*, 197–208.
(32) Ajji, A.; Utracki, L. A. *Polym. Eng. Sci.* **1996**, *36*, 1574–1585.
(33) Slivniak, R.; Domb, A. J. *Macromolecules* **2005**, *38*, 5545–5553.
(34) Slivniak, R.; Domb, A. J. *Biomacromolecules* **2005**, *6*, 1679–1688.
(35) Ebata, H.; Toshima, K.; Matsumura, S. *Macromol. Biosci.* **2007**, *7*, 798–803.
(36) Ebata, H.; Mayumi, Y.; Toshima, K.; Matsumura, S. *J. Oleo Sci.* **2008**, *57*, 315–320.
(37) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592–3601.
(38) Helfand, E.; Bhattacharjee, S. M.; Fredrickson, G. H. *J. Chem. Phys.* **1989**, *91*, 7200–7208.
(39) Macosko, C. W.; Jeon, H. K.; Hoye, T. R. *Prog. Polym. Sci.* **2005**, *30*, 939–947.
(40) Tsujimoto, T.; Haza, Y.; Yin, Y.; Uyama, H. *Polym. J.* **2011**, *43*, 425–430.
(41) Retsos, H.; Margiolaki, I.; Messaritaki, A.; Anastasiadis, S. H. *Macromolecules* **2001**, *34*, 5295–5305.
(42) Pan, P.; Kai, W.; Zhu, B.; Dong, T.; Inoue, Y. *Macromolecules* **2007**, *40*, 6898–6905.
(43) Douzinas, K. C.; Cohen, R. E. *Macromolecules* **1992**, *25*, 5030–5035.
(44) Chang, K.; Morse, D. C. *Macromolecules* **2006**, *39*, 7397–7406.
(45) Chang, K.; Macosko, C. W.; Morse, D. C. *Macromolecules* **2007**, *40*, 3819–3830.
(46) Anderson, K. S.; Hillmyer, M. A. *Polymer* **2004**, *45*, 8809–8823.
(47) Anderson, K. S.; Lim, S. H.; Hillmyer, M. A. *J. Appl. Polym. Sci.* **2003**, *89*, 3757–3768.
(48) Wu, S. H. *J. Appl. Polym. Sci.* **1988**, *35*, 549–561.
(49) Bucknall, C. B.; Paul, D. R. *Polymer* **2009**, *50*, 5539–5548.
(50) Corte, L.; Leibler, L. *Macromolecules* **2007**, *40*, 5606–5611.
(51) Margolina, A.; Wu, S. H. *Polymer* **1988**, *29*, 2170–2173.
(52) Jansen, B. J. P.; Rastogi, S.; Meijer, H. E. H.; Lemstra, P. J. *Macromolecules* **2001**, *34*, 4007–4018.
(53) Armat, R.; Moet, A. *Polymer* **1993**, *34*, 977–985.
(54) Grijpma, D. W.; Penning, J. P.; Pennings, A. J. *Colloid Polym. Sci.* **1994**, *272*, 1068–1081.
(55) Maric, M.; Macosko, C. W. *Polym. Eng. Sci.* **2001**, *41*, 118–130.
(56) Liu, Z. H.; Zhang, X. D.; Zhu, X. G.; Li, R. K. Y.; Qi, Z. N.; Wang, F. S.; Choy, C. L. *Polymer* **1998**, *39*, 5019–5025.
(57) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51–61.
(58) Huggins, M. L. *J. Chem. Phys.* **1942**, *46*, 151–158.
(59) Eitouni, H. B.; Balsara, N. P., Thermodynamics of Polymer Blends. In *Physical Properties of Polymers Handbook*, 2nd ed.; Mark, J. E., Ed.; Springer: New York, 2007.