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Toughening of Polylactide with Polymerized Soybean Oil

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ABSTRACT: Polymerized soybean oil (polySOY) and isotactic poly(L-lactide) (PLLA) were melt blended to increase the toughness of PLLA in an all renewable blend. The polySOY samples were prepared by crosslinking soybean oil by the addition of a free radical crosslinking agent or by heating the oil in the presence of oxygen. Soybean oil is relatively nonreactive compared to other vegetable oils, and conjugation of the double bonds within the fatty acid chains of the soybean oil triglyceride prior to crosslinking led to significantly increased reactivity. Poly(isoprene-*b*-L-lactide) block copolymers were used to compatibilize the blends due to the high degree of immiscibility between PLLA and polySOY. The blending of polySOY and PLLA resulted in significant improvements in the tensile toughness of the blend compared to neat PLLA. The blend morphology was dependent on the polySOY gel fraction or weight-average molar mass; the polySOY characteristics were key indicators of the tensile toughness.

Introduction

The finite availability of petroleum and environmental considerations have placed recent emphasis on the development of raw materials for polymers from renewable, non-petrochemically derived resources.[1−8] One extensively studied renewable resource polymer is polylactide, which can be derived from various starch sources such as corn.[9−13] Polylactide is not only renewable but also biodegradable; therefore, it has been used in biomedical materials, disposable plastics, and fiber applications.[10,14,15] Nevertheless, the brittleness of polylactide, as evidenced by low impact strength, strain at break, and tensile toughness, has limited more widespread implementation.[10,16] Many approaches have been taken to improve these properties; the effects of polymer stereochemistry, processing history, and the addition of plasticizers have all been studied.[16] In addition, PLLA has been blended with a variety of materials[16] including (but not limited to) polyethylene,[17] polyurethanes,[18] poly(ethylene oxide),[19] poly(ε-caprolactone),[20] polyhydroxyalkanoates,[21] poly(butylene succinate),[22] poly(ethylene−octene),[23] and various types of synthetic rubber[24] with varied results. The challenge remains to find a completely renewable and biodegradable toughening agent that enhances PLLA properties as effectively as the nonrenewable and nonbiodegradable blending partners.

Vegetable oils are triglycerides that typically contain unsaturated fatty acids. The modification of vegetable oils and their subsequent use as raw materials for polymers has been a subject of much interest.[8,25,26] Recent work by our group and others focused on the use of soybean oil (SOY) to toughen PLLA. We explored the morphology of PLLA/SOY blends using unmodified SOY and discovered that the binary blend undergoes phase inversion at low concentrations of SOY, leading to the loss of SOY during blending, which is highly dependent on the choice of block copolymer used to compatibilize the blend.[27] Ali et al. demonstrated that moderate improvements in the elongation at break of PLLA were gained by the addition of epoxidized SOY.[28] In this article we explore how the polymerization of SOY prior to blending improves its level of incorporation into PLLA and how optimization of the polymerized SOY characteristics can yield blends with increased toughness compared to the parent PLLA.

The presence of an average of 4.5 double bonds per SOY molecule allowed for the creation of intermolecular linkages between the molecules through the addition of a free radical crosslinking agent or through autoxidation by heating the oil in the presence of air.[8,25,26,29,30] The effect of conjugation of the double bonds prior to crosslinking on the soybean oil reactivity was also probed. Variation of the reaction parameters allowed for control over the polymerized soy (polySOY) molecular characteristics that in turn were found to have a significant impact on the morphology of the PLLA/polySOY blends prepared by melt blending techniques. Due to the high degree of immiscibility between PLLA and polySOY,[27] block copolymers with varying composition were also added to the blends as compatibilizers. Finally, the tensile toughness of the blends was probed, and a direct correlation between blend morphology and toughness was uncovered.

Experimental Details

Polymer Synthesis and Characterization. Poly(L-lactide) (PLLA) was supplied by Toyota Motor Corp. Wesson soybean oil (SOY) was obtained from a local grocery store. Conjugated soybean oil (CSOY) was synthesized using the following procedure.[31] SOY was mixed with 1.5 mol % carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (Strem Chemical) in benzene. The solution was degassed and heated at 60 °C under argon for 2 days. Benzene was removed from the reaction vessel with a rotary evaporator, and the CSOY was dried under reduced pressure at room temperature overnight. To remove the catalyst,[32] tris(hydroxymethyl)phosphine (Strem Chemical) and dichloromethane were added to the reaction vessel containing the crude product in an inert atmosphere glovebox. The reaction vessel was sealed, removed from the glovebox, and stirred for 2 days. The solution was passed through a silica gel column (using dichloromethane as the mobile phase). The solvent was removed on a rotary evaporator, and the CSOY product was dried under reduced pressure for 2 days at 50 °C. Proton nuclear magnetic resonance (^{1}H NMR) spectra obtained from the purified CSOY were consistent with the literature.[31] For all of the reactions, $>95\%$ of the nonisolated double bonds (on the linoleic and

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Table 1. Characteristics of PI−PLLA Block Copolymers[a]

name	f_{PLLA}	$M_{\mathrm{n,PLLA}}$ (kg/mol)	PDI
PI−PLLA(51)	0.51	35	1.15
PI−PLLA(63)	0.63	57	1.21
PI−PLLA(69)	0.69	76	1.30
PI−PLLA(71)	0.71	82	1.30
PI−PLLA(81)	0.81	140	1.50

[a] f_{PLLA} is the volume fraction of PLLA in the block copolymer at 190 °C. For all of the block copolymers, the PI-block M_{n} = 24 kg/mol and PDI = 1.02. Throughout this study, PI−PLLA(69) and PI−PLLA(71) have been used interchangeably in blends. Therefore, PI−PLLA(70)* will be used to refer to either block copolymer.

linolenic fatty acids) were conjugated, as determined by the disappearance of the bisallylic proton peak at 2.8 ppm.

Polymerized SOY (polySOY) and polymerized CSOY (polyCSOY) were prepared by one of the following methods. In method A, dicumyl peroxide (DCP) was added to degassed SOY or CSOY. The mixture was purged by bubbling with nitrogen gas for 2 h and then heated (under nitrogen) at 150 °C for 12 h (unless otherwise specified). The DCP decomposition products were removed by heating the polySOY or polyCSOY under reduced pressure for 6 days at 190 °C. In method B, 0.5 g of SOY or CSOY was heated at a specified temperature in the presence of air in an open 50 mL round-bottom flask with stirring. No further purification was utilized. The kinetics of the polymerization of SOY or CSOY by method B were found to be dependent on the size of the sample and the size of the reaction vessel (likely due to the surface area available for oxygen incorporation). Unless otherwise specified, the polySOY samples discussed in this article were prepared with method A. Poly(isoprene-*b*-L-lactide) (PI−PLLA) block copolymers were prepared with a combination of anionic and ring-opening polymerization, as described in refs 27 and 33.

Number-average and weight-average molecular weights (M_{n} and M_{w}, respectively) and the polydispersity index (PDI = $M_{\mathrm{w}}/M_{\mathrm{n}}$) of the polySOY materials and the PLLA supplied by Toyota Motor Inc. were characterized with size exclusion chromatography (SEC) using a Hewlett-Packard 1100 series chromatograph equipped with a Hewlett-Pakard 1047A refractive index detector (in chloroform at 35 °C). The values reported for these polymers are based upon polystyrene standards. The commercial PLLA pellets supplied by Toyota had the following characteristics: M_{n} = 54 kg/mol and PDI = 1.73. The molecular weight of the PLLA is greater than the entanglement molecular weight.[34] The gel fractions of the polySOY samples were measured using Soxhlet extraction in dichloromethane. Absolute M_{n} based upon end-group analysis and the fraction of 1,4 regioisomer (> 93%) of the PI-block of the PI−PLLA block copolymer and the block copolymer composition were determined from ^{1}H NMR spectroscopy (Varian INOVA-500). The characteristics of the PI−PLLA block copolymers are given in Table 1. The PDI values of the PI−PLLA block copolymers were determined with SEC using polystyrene standards.

Rheological measurements were conducted on the polySOY samples with a Rheometrics ARES strain-controlled rheometer using 25 mm parallel plates. The polySOY samples were prepared by heating the sample in the rheometer oven to 100 °C and gently applying a force until the sample filled the space in between the plates. The storage and loss moduli (G' and G'', respectively) were measured as a function of frequency at a variety of temperatures. Unless otherwise noted, appropriate strain values were used for each measurement such that the response was in the linear viscoelastic region.

Blend Preparation and Characterization. The blend components (PLLA, polySOY, and PI−PLLA block copolymers) were melt blended in a twin-screw DACA mixer with 4 g batch size. PLLA was dried in a vacuum oven overnight at 80 °C prior to mixing and stored in a desiccator under reduced pressure until use. PLLA and PI−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 polySOY was subsequently added to the mixer. Unless otherwise noted, the mixing temperature was 190 °C, the mixing rate was 300 rpm, and the total mixing time was 20 min. After mixing, the sample was extruded into liquid nitrogen to preserve the morphology.

A portion of the extrudate was saved for observation of the blend morphology. 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 polySOY droplets were often removed from the surface during the microtoming process due to the weak adhesion between the PLLA and polySOY domains, 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. This indicates that at the edge of the hole some of the polySOY was pulled out away from the matrix but is still attached to the sample. ImageJ analysis software was used to analyze the average particle diameter (or, rather, 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 100−1000 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, particles 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 refs 17 and 35.

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

The blend was 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. After a minimum of 24 h of aging at room temperature, the tensile properties of the blends were then measured 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.[9,10,16] The tensile properties, particularly the strain at break, modulus, and tensile toughness, were dependent on the geometry of the test specimen used. It was discovered that if the gage width was 3 mm and the thickness was 0.5 mm, the gage length needed to be at least 12 mm to obtain the standard values for neat PLLA. If a shorter test specimen was used, nonstandard values were obtained (the strain at break was as high as 14% for PLLA using the shorter bars). Therefore, all of the measurements reported in this paper used the same tensile bar geometry: a dogbone with gage dimensions 12 mm × 3 mm × 0.5 mm. One of the pressed dogbone samples was used for NMR analysis to determine the percent of polySOY incorporated into the blend. Differential scanning calorimetry analysis (TA Instruments Q1000 under nitrogen gas at a scan rate of 10 °C/min from 0 to 220 °C) was used to determine the percent

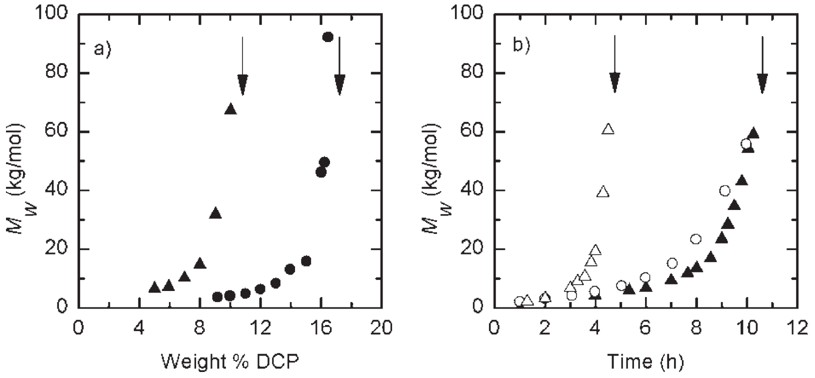

Figure 1. (a) Dependence of the weight-average molecular weight (M_w) of polySOY (●) and polyCSOY (▲) on the percent of dicumyl peroxide (DCP) for reactions conducted at 150 °C for 12 h by method A. (b) Dependence of the weight-average molecular weight (M_w) on reaction time in air for polySOY at 190 °C (○) and polyCSOY at 150 °C (▲) and 190 °C (△) by method B. The gel points are indicated by arrows.

crystallinity and glass transition temperature of the PLLA post-molding. Fracture surfaces from the tensile bars were also coated with 10 nm of platinum and analyzed with SEM as described above.

Results and Discussion

Polymerization of Unmodified Soy (SOY) and Conjugated Soy (CSOY). SOY and CSOY were free radically polymerized following method A in the Experimental Details section. The effects of the DCP concentration on the polymerized SOY (polySOY) and polymerized CSOY (polyCSOY) molecular weights are shown in Figure 1a. The molecular weight is based on size exclusion chromatography with polystyrene standards and thus is not an absolute molecular weight. For both, the molecular weight of the polymer increased with increasing DCP concentration. The gel point, the point at which the sample contains a measurable insoluble fraction as determined by Soxhlet extraction with dichloromethane, is reached at a critical concentration of DCP, indicated by the arrows in Figure 1a. Above the gel point, as the concentration of DCP increases, the gel fraction also increases (the gel fraction is defined by the insoluble portion of the sample). Significantly less DCP is required for the polymerization of CSOY as compared to SOY, consistent with previous work on the increased reactivity of conjugated vegetable oils.[36,37]

SOY and CSOY were also polymerized through autooxidation following method B in the Experimental Details section. The resulting molecular weights of polySOY and polyCSOY are plotted as a function of time in Figure 1b. Using method B, the reaction progress is controlled by the reaction time in the presence of oxygen; conjugation significantly increases the reaction rate.

The molecular weight distributions of selected fully soluble (i.e., no gel fraction) polySOY samples (method A) are shown in Figure S1 (Supporting Information). Due to the uncontrolled nature of the polymerization, the PDIs of the materials range from 2 to as high as 30 for the highest molecular weight samples. In all of the samples, there is a fraction of unpolymerized SOY (or CSOY) remaining. The molecular weight distributions in Figure S1 (Supporting Information) are similar to those reported in the literature for the cross linking of monodisperse polymers.[38]

The polySOY samples used for the blending studies were prepared by the polymerization of SOY using method A. Similar polySOY materials can be easily prepared in the absence of a crosslinking agent (method B). The use of CSOY enhances the oil reactivity in both methods. The polySOY samples used in this study will be referenced in the following manner: polySOY samples that do not contain a gel fraction will be characterized by M_w (based on size exclusion chromatography with polystyrene standards) whereas polySOY samples that do contain a gel fraction will be characterized by the gel fraction (based on Soxhlet extraction with dichloromethane). The characteristics of the polySOY used in the blends in this paper are given in Table S1 of the Supporting Information.

Improving the Incorporation of SOY through Polymerization. Previous work by our group focused on the preparation of blends of PLLA and unpolymerized SOY.[27] Because of the large viscosity difference between PLLA and SOY (roughly 5 orders of magnitude), phase inversion during melt mixing occurs at a relatively low concentration of SOY, resulting in the loss of SOY from the blend during mixing. As a result, it was not possible to incorporate more than 6 wt % SOY into the binary blend, regardless of the initial concentration of SOY added to the mixer.[27] Our initial hypothesis was to polymerize the SOY, resulting in an increase in its viscosity to suppress phase inversion at the SOY concentrations of interest (i.e., > 6 wt %), and prevent the loss of SOY during mixing. Binary blends containing 85 wt % PLLA and 15 wt % polySOY were prepared in a twin-screw melt mixer at 190 °C. All the blends containing polySOY effectively incorporated all of the material loaded into the melt mixer. The lowest molecular weight polySOY sample (M_w = 19 kg/mol, no gel fraction) had a viscosity of 0.01 Pa s at 190 °C. As the viscosity of SOY at 190 °C is 0.002 Pa s, a factor of 5 increase in the viscosity is apparently sufficient to eliminate the loss of SOY during mixing. Furthermore, phase inversion was not observed in any of the PLLA/polySOY blends.

Morphology of Binary and Ternary Blends. Binary blends were composed of 85 wt % PLLA and 15 wt % polySOY, and the gel fraction of the polySOY samples used in the binary blends was varied from 0 to 0.67. The mixing rate had a dramatic effect on the blend morphology for blends containing polySOY with a gel fraction; thus, all of the blends containing polySOY discussed in the balance of the article were mixed at 300 rpm.[39] SEM images obtained from selected binary blends are shown in the left column of Figure 2.[40] From these images there appears to be an optimal polySOY gel fraction that results in the smallest average polySOY particle diameter. The polySOY particle size distributions at intermediate polySOY gel fractions (0.23 and 0.41) appear to be more uniform with a smaller average particle diameter when compared to the blends with polySOY gel fractions of 0.02 or 0.67. At the highest polySOY gel fractions, the particles are apparently nondeformable and are no longer spherical.

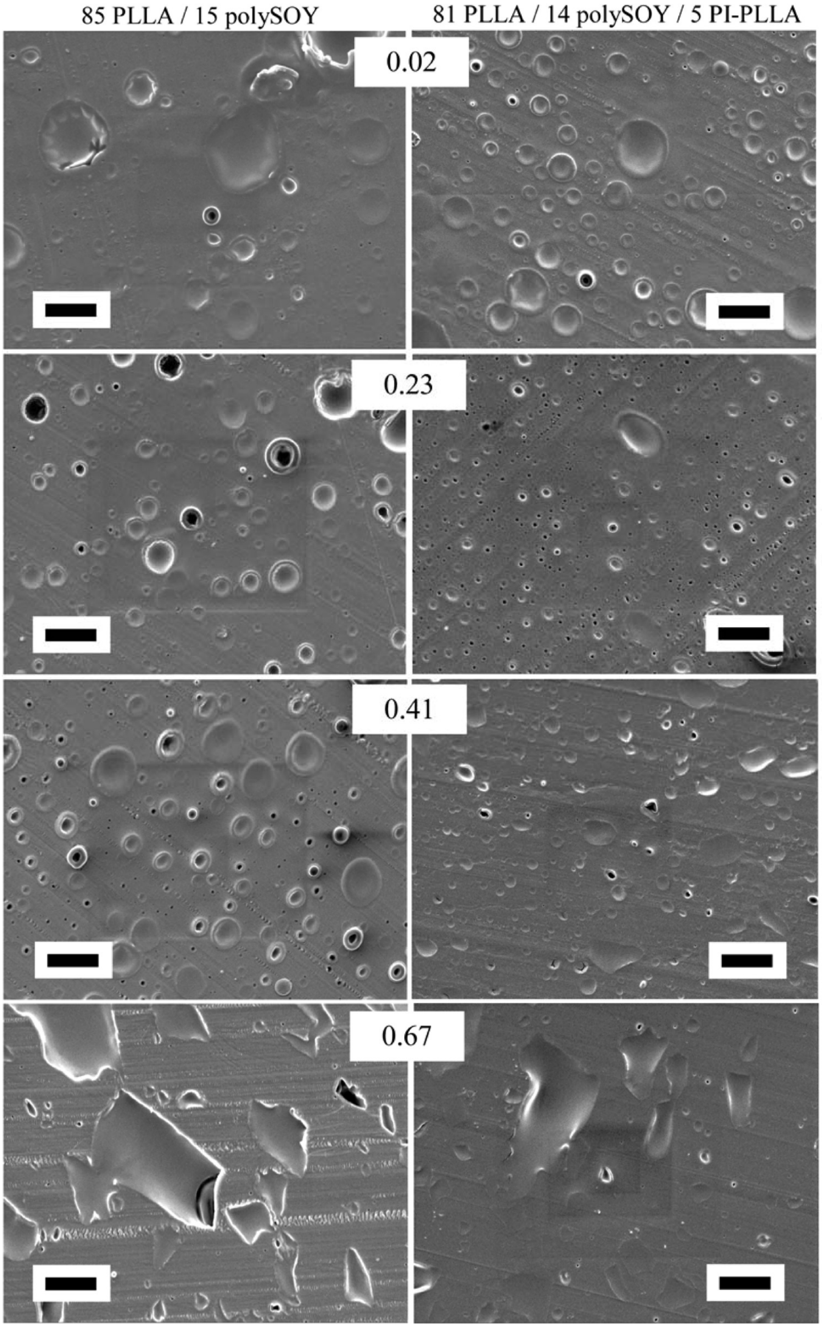

Figure 2. SEM images of (left) 85 wt % PLLA/15 wt % polySOY blends and (right) 81 wt % PLLA/14 wt % polySOY/5 wt % PI−PLLA(70)* blends. The polySOY gel fraction is shown for each pair of images. The scale bars are 5 μm.

PI−PLLA block copolymers (Table 1) were used to compatibilize the PLLA/polySOY blends. The corresponding PI−PLLA(70)* compatibilized blends are shown in the right column of Figure 2.[41] The weight ratio of PLLA to polySOY was held constant at 85:15, and 5 wt % PI−PLLA, based on the total blend weight, was added. Again, the most uniform and smallest sized particles occur at intermediate values of the polySOY gel fractions. In comparing the left and right columns of Figure 2, the presence of the block copolymer reduces the average particle size of the samples.

The volume-average particle diameters (D_v) for each of the samples were determined using image analysis software and are shown in Figure 3. As observed qualitatively in Figure 2, there is a minimum in the particle diameter for both series of blends at intermediate values of the polySOY gel fraction. The addition of PI−PLLA(70)* further reduces the particle diameter in each of the blends. The particle size distributions for two representative samples are given in Figure S3 (Supporting Information). Blends with larger average particle diameters exhibit larger distributions in particle size.

In ref 27, we determined that binary blends of PLLA and SOY exhibited SOY domains with $D_v \approx 10\,\mu$m. Thus, the use of polySOY significantly decreases the dispersed phase particle diameter. Polymerizing the SOY results in competing effects on the particle diameter. We expect the degree of immiscibility between PLLA and polySOY[43,44] to increase as the molecular weight of the polySOY increases, and this should lead to larger particles based on interfacial tension arguments.[45,46] Furthermore, a larger fraction of polySOY can be incorporated into the blend as compared to unpolymerized SOY, and the average particle size is known to increase as the dispersed phase concentration increases.[47]

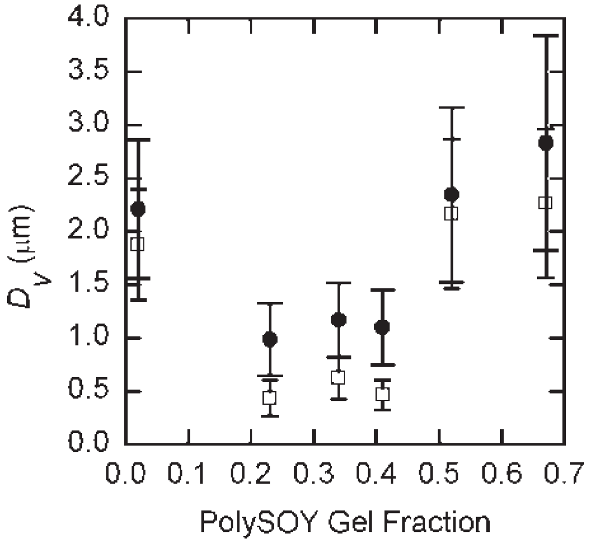

Figure 3. Dependence of the volume-average particle size (D_v) on the polySOY gel fraction for binary 85 wt % PLLA/15 wt % polySOY blends (●) and ternary 81 wt % PLLA/14 wt % polySOY/5 wt % PI−PLLA(70)* blends (□). The error bars represent one standard deviation calculated for the particles observed within one SEM micrograph. We verified the sample-to-sample reproducibility for multiple samples.[42]

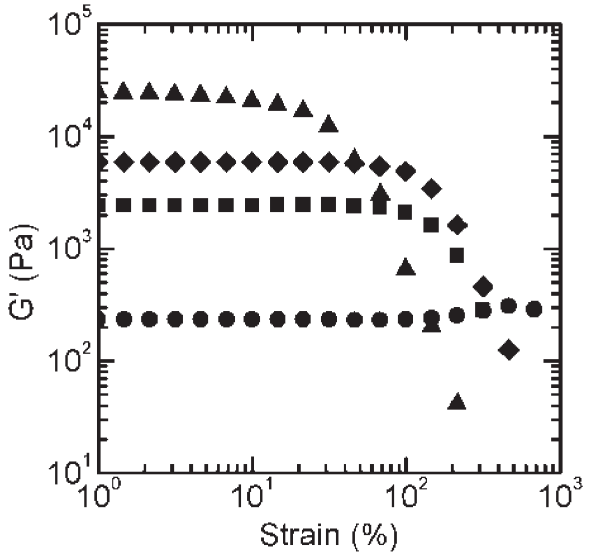

Figure 4. Storage modulus (G') obtained from selected polySOY samples under oscillatory shear using a parallel plate geometry and ω = 50 s^{-1} at T = 190 °C. The polySOY samples had the following gel fractions: 0.23 (●), 0.34 (■), 0.41 (◆), and 0.67 (▲).

On the other hand, optimization of the viscosity ratio (the dispersed phase viscosity divided by the matrix viscosity) can greatly reduce the average dispersed phase particle diameter in a melt-mixed blend.[48,49] The minimum observed in Figure 3 is reminiscent of the minimum in particle size reported in refs 48 and 49 for melt-mixed blends with an optimal viscosity ratio. As the rheological properties of the particle phase are an important factor in determining the blend particle diameter, we conducted dynamic mechanical analysis experiments on the polySOY samples.

Rheological Properties of PolySOY. The storage modulus (G') as a function of strain for polySOY samples with varying gel fractions is shown in Figure 4. At low strain, the rheological data (G' and G'' as a function of frequency) for all polySOY samples containing a gel fraction are consistent with elastic, solidlike behavior.[50,51] However, as the strain is increased, there is a critical strain value at which G' drops off (Figure 4). After such a large strain treatment, the polySOY appeared to have broken up into smaller pieces upon inspection of the samples post-analysis. We propose that the drop off in G' is an indication of particle breakup. PolySOY samples with a gel fraction of ≤ 0.23 did not show a decrease in G' over the range of accessible strains. In comparing the data sets shown in Figure 4, the strain required for particle breakup decreases as the polySOY gel fraction increases. This is consistent with the known finite extensibility of a network that decreases as the molecular weight between crosslinks decreases,[52] with the reasonable assumption that the molecular weight between crosslinks decreases as the gel fraction of the polySOY increases.

The plateau value of G' increases by over 2 orders of magnitude as the polySOY gel fraction is varied from 0.23 to 0.67. It is well-known that the plateau modulus of a polymer network increases as the molecular weight between crosslinks decreases, again indicating that in these samples there is an inverse relationship between the molecular weight between crosslinks and the gel fraction, as expected.[53]

The rheological properties of polySOY offer one explanation for the minimum average particle diameter observed in the melt mixed PLLA/polySOY blends (Figure 3). For polySOY samples with low gel fractions (such as 0.23), the strain at which the particles began to break up during the rheology experiment was high (> 700%) and the modulus was low (ca. 10^2 Pa). The high strain at break allows for greater extension of the polySOY, which limits the breakup of the polySOY into smaller particles during mixing. For polySOY with high gel fractions (such as 0.67), the strain at which the particles began to break up during the rheology experiment was low (< 100%) and the modulus was high (ca. 10^4 Pa). Although the polySOY is quite brittle and would break up under lower strains, the stresses during mixing may not be high enough to significantly deform the particles due to the relatively high modulus. Evidence for this is given by the nonspherical particles observed in the blends containing polySOY with gel fraction 0.67 (Figure 2). Therefore, at intermediate values of the polySOY gel fraction the polySOY particle size can be most easily reduced; for these samples there is the optimal balance between the modulus and strain at which the polySOY breaks up. It is important to note that the rheology experiments conducted here do not necessarily reproduce the stresses acting on the polySOY during the melt mixing process. The mixing process is a combination of both shear and elongational stresses. Therefore, it is still possible that the polySOY particles flow during mixing and that the optimum viscosity ratio of the matrix and particle phases is achieved at the lowest particle diameters, following refs 48 and 49. However, we offer an alternative explanation based on the assumption that the solidlike behavior observed in the rheology experiment is consistent with the behavior of the polySOY during the mixing process.

Tensile Properties of Binary and Ternary Blends. The tensile toughness for binary blends and ternary blends containing PI−PLLA(70)* as a function of polySOY gel fraction is given in Figure 5a.[54] For all of the blends, the stress at break was in the range of 21−30 MPa and the modulus was in the range of 0.9−1.7 GPa (for neat PLLA, the stress at break and modulus are 68 MPa and 2.0 GPa, respectively). Neither the stress at break nor the modulus showed a dependence on the polySOY gel fraction. The yield point was in the range of 26−40 MPa for all of the blends; the yield point decreased slightly as the gel fraction of polySOY increased. As shown

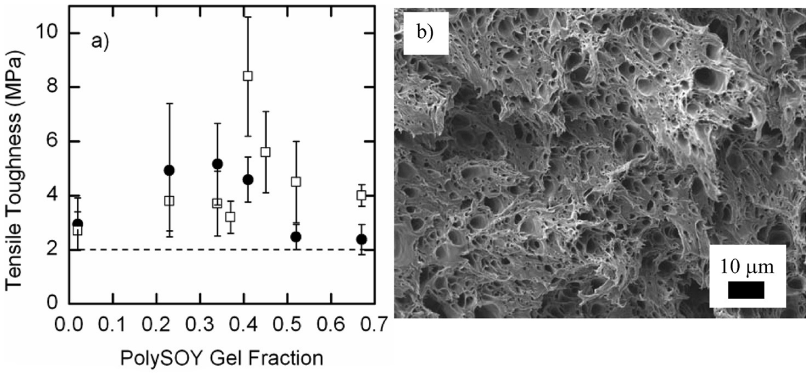

Figure 5. (a) Tensile toughness of 85 wt % PLLA/15 wt % polySOY (●) and 81 wt % PLLA/14 wt % polySOY/5 wt % PI−PLLA(70)* (□) blends as a function of polySOY gel fraction. The error bars represent one standard deviation. (b) SEM micrograph of a fracture surface of a tensile bar after tensile testing for a blend containing 81 wt % PLLA/14 wt % polySOY(gel fraction = 0.41)/5 wt % PI−PLLA(70)*.

in Figure 5a, the binary and ternary blends exhibited a maximum in the tensile toughness at a critical polySOY gel fraction (or, equivalently, strain at break in Figure S6a, Supporting Information). The maximum in tensile toughness occurs at approximately the same polySOY gel fraction that gives the minimum in particle diameter (Figure 3). The maximum tensile toughness was 4 times greater than unmodified PLLA. Similary, the maximum strain at break was 6 times greater than unmodified PLLA. Representative stress−strain curves for some of the blends are given in Figures S6b−g in the Supporting Information. Table S2 in the Supporting Information summarizes the key characteristics of the stress−strain curves for all of the blends. A SEM image of a fracture surface of the blend with the highest tensile toughness [PLLA/polySOY(gel fraction = 0.41)/PI−PLLA(70)*] is given in Figure 5b. The fracture surface shows evidence of matrix deformation due to shear yielding, a known mechanism of toughening in rubber-toughened polymers.[55] Additionally, there appears to be debonding of the particles from the matrix, indicating a lack of interfacial adhesion even in the presence of block copolymer.[56] The percent crystallinity of the samples (based on DSC measurements) is given in Table S3 (Supporting Information). For both series, the percent crystallinity increases as the polySOY gel fraction increases. Furthermore, the DSC measurements indicated there was no plasticization of the PLLA matrix (the glass transition temperature was around 60 °C for all samples).

We also prepared blends with PI−PLLA block copolymers of varying composition. The tensile toughness for these blends is shown in Figure 6 for blends containing polySOY of various M_w or gel fraction. For polySOY with M_w = 19 kg/mol (and no gel fraction), the blend tensile toughness was independent of block copolymer composition and lower than that of neat PLLA (SEM images from these blends are given in Figure S4, Supporting Information). The particle diameters are larger than for the samples containing polySOY with a gel fraction shown in Figures 2 and 3. For polySOY samples with gel fractions of 0.02 and 0.34, the blend tensile toughness was still fairly independent of block copolymer composition, with the 0.34 sample giving higher values of tensile toughness. Finally, at the highest polySOY gel fractions, 0.41 and 0.52, there was a strong dependence of the tensile toughness on the block copolymer composition. The volume-average particle diameters as a function of block copolymer composition are given in Figure S9 (Supporting Information).

As a comparison, tensile data obtained from selected PLLA/SOY blends (in which the SOY was not polymerized) are shown in Table S4. The binary PLLA/SOY blend (with 5 wt % SOY incorporated into the blend) had a strain at break of 20 ± 6% and a tensile toughness of 6 ± 2 MPa. The blends containing PI−PLLA block copolymers (with f_{PLLA} varying from 0.54 to 0.71) were not significantly different from the PLLA/SOY binary blend under the testing conditions reported in this article.[57]

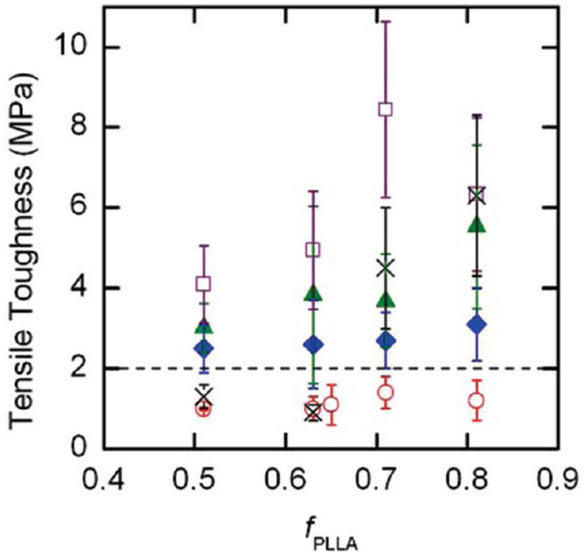

Figure 6. Tensile toughness of PLLA/polySOY/PI−PLLA blends as a function of block copolymer composition with the following polySOY characteristics: M_w = 19 kg/mol (with no gel fraction) (○), gel fraction = 0.02 (◆), 0.34 (▲), 0.41 (□), and 0.52 (×). The dashed lines indicate values for neat PLLA.

The tensile toughness for binary blends and ternary blends containing PI−PLLA(70)* is plotted as a function of particle diameter (D_v) in Figure 7a and the matrix ligament thickness (interparticle distance) (T) in Figure 7b. A direct correlation is readily apparent in both cases. The tensile toughness increases as the particle diameter and matrix ligament thickness decrease. Previous work on the toughness of polymer blends determined that for a brittle polymer matrix there is an optimal particle diameter for maximum toughness.[58] For blends with a ductile matrix, there is a critical matrix ligament thickness below which the toughness increases.[59] Furthermore, theoretical work concerning semicrystalline polymers indicates the toughness may be a function of both the particle diameter and the matrix ligament thickness.[60] The data in Figure 7 indicate that there is a strong dependence of the toughness on both parameters, but at present we

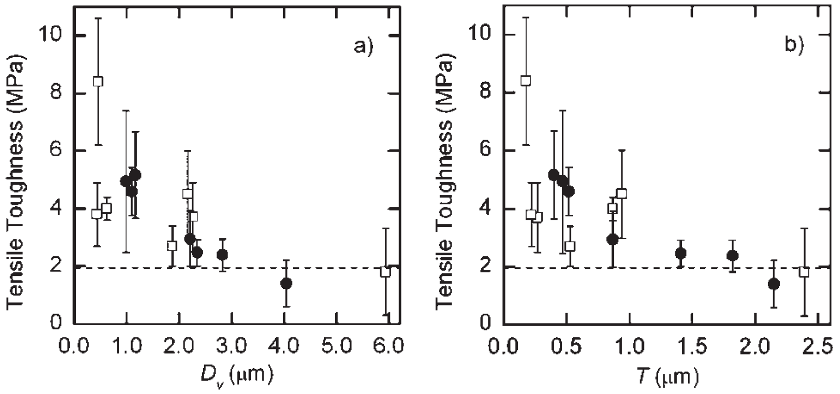

Figure 7. Relationship between the tensile toughness and (a) volume-average particle diameter (D_v) and (b) matrix ligament thickness (T) for 85 wt % PLLA/15 wt % polySOY (●) and 81 wt % PLLA/14 wt % polySOY/5 wt % PI−PLLA(70)* (□) blends. The dashed line indicates the tensile toughness of neat PLLA.

cannot distinguish between the above scenarios. Figure 7b is consistent with data in refs 17 and 61; in all cases the toughness begins to increase below a critical value of the matrix ligament thickness of around 1 μm. It is important to note that the data in Figure 7 represent blends containing polySOY samples of various characteristics. The polySOY characteristics appear to be important only in how they affect the morphology of the blend. Presumably, the polySOY particles are able to initiate crazing or cavitate regardless of their average molecular weight or gel fraction.[58] Furthermore, the addition of block copolymer theoretically could improve the adhesion between the phases,[62,63] however; the data for the compatibilized blends lie on the same curve as the data for uncompatibilized blends in Figure 7. Therefore, the block copolymer also appears to only affect the blend morphology, and no further increases in toughness are observed due to improved interfacial adhesion. This is further evidenced by the fracture surface in Figure 5b.

Conclusions

Polymerization of SOY allowed for the preparation of PLLA/polySOY blends with full incorporation of polySOY. The blends retained relatively high moduli and ultimate tensile strengths. The addition of free radical crosslinking agents to SOY and heating SOY in the presence of air were facile methods of preparing crosslinked polySOY samples. The gel fraction of the polySOY was a key variable in determining the blend morphology, and the tensile properties of the blends were highly dependent on morphology. As in our previous work, there appeared to be a critical interparticle distance of around 1 μm, below which increases in the tensile toughness were observed. With this approach, we have successfully prepared PLLA/polySOY blends with tensile toughnesses as high as 4 times greater than that of unmodified PLLA, with corresponding strain at break values as high as 6 times greater than that of unmodified PLLA.

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Supporting Information Available: SEC traces of selected polySOY samples (Figure S1), molecular characteristics of polySOY samples used in melt blends (Table S1), effect of mixing rate on ternary blend morphology (Figure S2), particle size distributions of selected ternary blends (Figure S3), SEM images of binary and ternary blends containing polySOY with M_w = 19 kg/mol and no gel fraction (Figure S4), rheological characteristics of polySOY (Figure S5), strain at break vs polySOY gel fraction for binary and ternary blends (Figure S6a), stress−strain curves for selected binary and ternary blends (Figures S6b−g), tensile parameters for binary and ternary blends (Table S2), effect of polySOY concentration on strain at break in binary blends (Figure S7), % crystallinity of binary and ternary blends (Table S3), tensile properties of PLLA/SOY and PLLA/SOY/PI−PLLA blends (Table S4), SEM images of PLLA/SOY/PI−PLLA blends (Figure S8), and particle diameter dependence on block copolymer composition in PLLA/polySOY/PI−PLLA blends (Figure S9). This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) To highlight the effect of mixing rate on the morphology, see Figure S2 (Supporting Information) for data obtained from a selected blend prepared at 100 rpm. Blends containing unpolymerized SOY showed no dependence on the mixing rate.

(40) All of the blends included in Figure 2 contain polySOY which has a gel fraction. Representative blends containing polySOY without a gel fraction are shown in Figure S4 (Supporting Information).

(41) Throughout this study, PI−PLLA(69) and PI−PLLA(71) have been used interchangeably in blends. Therefore, PI−PLLA(70)* will be used to refer to either block copolymer.

(42) For example, two independent measurements have been made for the volume-average diameter of the blend with 81 PLLA/14 polySOY (with gel fraction 0.52)/5 PI−PLLA(70)* using SEM micrographs obtained from two separately prepared blends. The two volume-average diameters are 2.2 μm (standard deviation = 0.7 μm) and 1.8 μm (standard deviation = 0.6 μm).

(43) The Flory−Huggins interaction parameter (χ) for PLLA and SOY has been previously determined to be $\chi_{\mathrm{PLLA/SOY}} = 0.35$ at 190 °C in ref 27 (based on a reference volume of 163 $\mathrm{\AA}^3$). This value is large compared to other commonly used immiscible polymer pairs. For example, χ for polystyrene and polyisoprene is 0.07 at 190 °C based on the same reference volume (ref 44).

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