Toughening of Polylactide by Melt Blending with Linear Low-Density Polyethylene

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ABSTRACT: Melt blending of polylactide and linear low-density polyethylene (LLDPE) was performed in an effort to toughen polylactide. In addition, two model polylactide–polyethylene (PLLA–PE) block copolymers were investigated as compatibilizers. The LLDPE particle size and the impact resistance of binary and ternary blends were measured to determine the extent of compatibilization. For the amorphous polylactide (PLA), toughening was achieved only when a PLLA–PE block copolymer was used as a compatibilizer. For the semicrystalline polylactide (PLLA), toughening was achieved in the absence of block copolymer. To decrease the variability in the impact resistance of the PLLA/LLDPE binary blend, as little as 0.5 wt % of a PLLA–PE block copolymer was effective. The differences that were seen between the PLA and PLLA binary blends were investigated with adhesion testing. The semicrystalline PLLA did show significantly better adhesion to the LLDPE. We propose that tacticty effects on the entanglement molecular weight or miscibility of polylactide allow for the improved adhesion between the PLLA and LLDPE. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3757–3768, 2003

Key words: polylactide; polyethylene; block copolymers; toughness; melt blending

INTRODUCTION

Polylactide, an aliphatic polyester, is a biodegradable polymer derived from renewable resources that has gained much interest in recent years. It is generally prepared through the ring-opening polymerization of lactide, of which there are two commonly used isomers, L-lactide (SS) and D-lactide (RR). By controlling the amount of each isomer in the monomer feed, the tacticity can be easily manipulated. Poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are both isotactic, and they are both semicrystalline materials as a result of this stereoregularity. When more than 15% of the mesolactide (SR) is present in PLLA or PDLA an atactic, amorphous material is formed (PLA).[1] Atactic materials can also be formed by the copolymerizations of L- and D-lactide. However, the higher end-use temperature and the superior mechanical properties of semicrystalline PLLA make it the more desirable stereoisomer for commercial applications.[2]

Currently, polylactide is primarily used for biomedical applications such as sutures and drug delivery devices because of its biodegradable and biocompatible nature.[3] While the biodegradable aspects of polylactide are important for the biomedical applications, the fact that it is derived from renewable resources makes it even more attractive from an environmental standpoint. PLLA could foreseeably become an alternative to traditional commodity plastics for everyday applications. Unfortunately, the broad substitution of commodity plastics by PLLA is thwarted by its brittle behavior under impact loads.[4] This brittleness limits its applications to those that do not require high impact resistance.

In analogy to other brittle materials, PLLA can be toughened by blending it with another polymer. However, the blending of two polymers to increase the toughness of one of the constituents has had varying degrees of success.[5–9] The mechanical performance of two-phase polymer systems is generally limited due to the low degree of interfacial adhesion and the large minor phase particle size that result from the inherent immiscibility of most polymer pairs.[10] This limitation can be overcome through the addition of a corresponding block copolymer, which will segregate to the polymer interfacial region.[11] The presence of the block copolymer at the interface reduces the interfacial tension and inhibits coalescence, both of which allow the minor phase to remain dispersed as small particles.[12,13] Additionally, the block copolymer can also increase interfacial adhesion through segregation to the interface and entanglement with their respective homopolymers. The existence of these interfacial entanglements is necessary for improved polymer–polymer adhesion.[14] The interfacial adhesion between the polymers is important for the mechanical performance of the polymer blend, in that it allows for the stresses to be transferred from the brittle matrix across the interface to the rubber particles.

Although numerous attempts have been made to toughen polylactide through blending, focus has typically been on biomedical applications, so biocompatible polymers such as polycaprolactone and various polyurethanes have generally been used as the dispersed (minority) phase.[4,15,16] For commercial applications of PLLA blends, a more cost effective blending constituent is desirable. In this regard, polyethylene would be an ideal material. Furthermore, the tunable properties of polyethylene would be beneficial for preparing toughened polymer blends. In particular, the impact resistance of low-density polyethylene (700 J/m)[17] is far greater than that of PLLA (22 J/m)[8] and thus makes it a potentially useful PLLA blend component.

Polylactide and polyethylene blends have been reported, but not always for the purpose of toughening. In two studies, blends of polylactide and polyethylene were prepared to determine the effect of polyethylene on polylactide degradation.[18,19] A subsequent patent suggests the use of polyethylene as an impact modifier but provides no data on whether successful toughening of polylactide was achieved.[20] Based on thermodynamic arguments, polylactide and polyethylene should be very immiscible, and a block copolymer should therefore be necessary for compatibilization purposes.[21] In a previous study, we performed solution blending of PLLA with linear low-density polyethylene (LLDPE) and demonstrated that the addition of the corresponding block copolymer (PLLA–PE) did lead to toughened PLLA composites.[8] While solution blending is convenient on a lab scale, practical production is not feasible using this blending method. As such, we have explored the melt blending of these polymers.[22]

In addition to toughening polylactide, we sought to gain an understanding of the compatibilization mechanism when a block copolymer is introduced into a semicrystalline/semicrystalline polymer blend. Presumably entanglements at the interface are important for increasing the interfacial adhesion and improving the mechanical properties of a polymer blend; on the other hand, with a semicrystalline polymer blend, the ability of the block copolymer segments to crystallize with the corresponding homopolymers may also have an effect on the resultant toughening. To help clarify the contributions of crystallization and entanglements to the compatibilization mechanism, one can lower the molecular weight of the block copolymer constituents below their respective entanglement molecular weights and evaluate the resulting toughness.

In this study, melt blending of polylactide with LLDPE was performed, and the effect of the PLLA–PE block copolymer on the morphology and impact resistance was examined. The polylactides investigated included an isotactic commercial-grade poly(L-lactide) and a predominantly atactic polylactide (PLA). The polyethylene used was a linear low-density polyeth-ylene that contained 13.2 mol % of octene as the comonomer. We also attempted to determine the compatibilization mechanism of the block copolymer by using two block copolymers, one with the PLLA block below its entanglement molecular weight and one with the PLLA block above its entanglement molecular weight. These block copolymers were used in blends with both amorphous PLA and semicrystalline PLLA as the matrix polymer to explore the effect of the block copolymer when it is able to crystallize with the matrix material. Differences that were noted between the semicrystalline PLLA and amorphous PLA binary blends were investigated through the use of adhesion testing.

EXPERIMENTAL

Materials

Commercial-grade PLLA (98.7 mol % L-isomer) and predominately atactic PLA (86.4 mol % L-isomer) were supplied by Cargill-Dow Polymer, LLC (Minnetonka, MN) (trade name: Natureworks). The LLDPE was obtained from Dow Chemical Company (Midland, MI) (Engage EG 8100, ethylene/octene copolymer containing 13.2 mol % octene; melt flow index = 1.0 g/10 min). The PLLA–PE block copolymers were prepared using the general procedure previously described.[8] Briefly, 1,3-butadiene (Aldrich, Milwaukee, WI) was anionically polymerized in cyclohexane using *sec*-butyl-lithium (1.3 M in cyclohexane, Aldrich) as the initiator and subsequently end-capped with ethylene oxide to give hydroxyl-terminated 1,4-polybutadiene containing ∼ 93% of the 1,4 regioisomer. This polybutadiene was then hydrogenated to give hydroxyl-terminated polyethylene, which was used in combination with $AlEt_3$ as a macroinitiator in the ring-opening polymerization of L-lactide. Two block copolymers were prepared, both with a PE block of about 30 kg/mol. One block copolymer had a PLLA block of about 5 kg/mol [PLLA–PE(5–30)] and the other had a PLLA block of about 30 kg/mol [PLLA–PE(30–30)], as determined by ^{1}H-NMR spectroscopy. The detailed molecular characteristics of the homopolymers and copolymers are given in Table I, and the polymer structures are shown in Figure 1.

Equipment/general procedures

The molecular weights of the PLLA and PLA homopolymers were determined on a Hewlett–Packard 1100 series liquid chromatograph (Hewlett–Packard, Palo Alto, CA) equipped with a Hewlett–Packard 1047A refractive index detector and three Jordi poly-(divinylbenzene) columns with 10^4-, 10^3-, and 500-Å pore sizes. The mobile phase was tetrahydrofuran (40°C and 1 mL/min). The columns were calibrated using polystyrene standards from Polymer Laborato-

TABLE I
Characterization of Homopolymers and Copolymers

Sample	Crystallinity[a] (%)	T_g (°C)	T_m (°C)	Viscosity[b] ($\times 10^{-6}$) (cP)	M_n[c] (kg/mol)	PDI[c]
PLLA[d]	11	58	167	1.6	85.6	1.67
PLA[e]	0	54		1.3	92.1	1.59
LLDPE[f]	6	−58	60	2.2	60.5	1.94
PLLA–PE(5–30)	11/27	—[g]	143/102		29.3	1.18
PLLA–PE(30–30)	48/33	—[g]	170/102		53.9	1.21

[a] Calculated from DSC (see Experimental section).
[b] Viscosity at processing shear rate determined at 190°C.
[c] Determined by SEC versus polystyrene standards (see Experimental section).
[d] Nature Works™, 98.7 mol % L-isomer, supplied by Cargill-Dow Polymer, LLC.
[e] Nature Works™, 86.4 mol % L-isomer, supplied by Cargill-Dow Polymer, LLC.
[f] Engage EG8100, ethylene/octene copolymer with 13.2 mol % octene, supplied by Dow Chemical Company.
[g] The T_g of the PLLA block could not be determined because of the broad melting peak of the PE block.

ries. The molecular weights of the LLDPE and the PLLA–PE block copolymers were determined on a Waters 150-C at 135°C in 1,2,4-trichlorobenzene with a flow rate 1 mL/min. The columns were calibrated using polystyrene standards from Polymer Laboratories with molecular weights ranging from 1.8 to 380 kg/mol.

Images of the cryofractured samples and the adhesion sample surfaces were obtained using a Hitachi S-800 scanning electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 5 kV. The samples were coated with about 50 Å of platinum before viewing.

Particle size analysis was performed on the LLDPE particles that were dispersed in the PLA and PLLA matrices. The samples were taken from the tested impact bars with the polylactide matrix was dissolved in chloroform. The analysis was done using a Coulter LS 230 particle analyzer (Coulter Beckman, Fullerton, CA). A sonicator was used to prevent coalescence of the LLDPE particles. For each sample, the average particle diameter d and the particle size distribution

Figure 1 Chemical structures of the polymers used in this study. PLLA, isotactic poly(L-lactide); PLA, atactic polylactide; PLLA–PE, poly(L-lactide)–polyethylene block copolymer (the PE block contains approximately two ethyl branches per 100 carbon atoms); LLDPE, linear low-density polyethylene (statistical copolymer of ethylene and octene).

parameter σ were determined from the following equations[23]:

$$\ln d = \frac{\sum\limits_{i=1}^{N} n_i \ln d_i}{\sum\limits_{i=1}^{N} n_i} \quad (1)$$

$$\ln \sigma = \sqrt{\frac{\sum\limits_{i=1}^{N} n_i (\ln d_i - \ln d)^2}{\sum\limits_{i=1}^{N} n_i}} \quad (2)$$

where n_i is the number of particles having the diameter d_i. The particle size distribution parameter is a measure of the polydispersity of the particle size, with $\sigma = 1$ being monodisperse.

Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). For all analyses, a 5- to 10-mg sample was heated at 5°C/min. To remove the thermal history of the samples prior to testing, the samples were annealed for 5 min at their highest test temperature and then cooled to 5°C at 2°C/min and held for 5 min before heating again for the thermal analysis. For the PLA, PLLA, and PLLA–PE block copolymers, the samples were heated from 5°C to 200°C. The LLDPE sample was heated from 5°C to 100°C. One sample was tested for each data point reported. The percent crystallinity was calculated using the following equation:

$$\% \text{ Crystallinity} = 100 \times \frac{\Delta H_m}{f \Delta H_m^{\text{ideal}}} \quad (3)$$
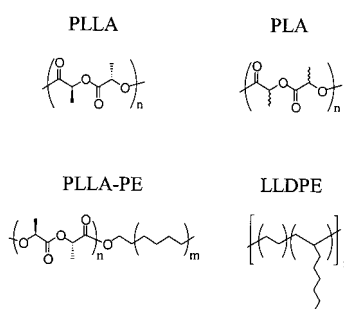
where ΔH_m is the measured heat of fusion, f is the weight fraction of the component in question, and $\Delta H_m^{\text{ideal}}$ is the enthalpy of fusion for a crystal having infinite crystal thickness (94 J/g for PLLA,[24] 277 J/g for PE[25]). To determine the glass-transition temperature, T_g, of the LLDPE, DSC analysis for this sample was also performed on the Perkin–Elmer Pyris-1 instrument.

Viscosity testing was performed on a Rheometrics dynamic stress rheometer (TA Instruments, New Castle, DE) at 190°C under a nitrogen purge using a dynamic frequency sweep from 500 to 0.05 rad/s.

Blend preparation

The melt blending was performed at 190°C in a Haake Rheomix 600 batch mixer (ThermoHaake, Karlsruhe, Germany). Before blending, the polymers were manually premixed in the desired compositions. All blends were prepared with 80 wt % of PLLA or PLA and 20 wt % of LLDPE. When the block copolymer was used, the weight percent of the block copolymer added was based on the total weight of the 80 : 20 blend. To prepare the melt blends, the premixed material was added to the chamber of the mixer, which was heated to 190°C and had the blades rotating at 30 rpm. Once all of the material was in the chamber, the plunger was lowered to enclose the chamber and the rotation was increased to 50 rpm. The maximum shear rate in the mixer at 50 rpm was 65 s^{-1}.[26] After 15 min at 50 rpm, the blades were stopped and the blends were removed from the chamber using a spatula. The hot blend was cut into small pieces using scissors and allowed to cool to room temperature on the bench top.

Because polylactide can degrade by hydrolysis of the ester bond, drying of polylactide pellets is commonly performed before processing.[4] Several melt blends were prepared using PLLA pellets that had been dried at 40°C under vacuum for 24 h and we determined that there was no significant effect on the ultimate properties. Therefore, for the preparation of the melt blends, predrying of the polylactide was not performed.

Impact testing

Impact test bars (dimensions 12.7 × 63.5 × 3.2 mm) were prepared by compression molding the blends and homopolymers at 200°C for 10 min at an ultimate pressure of 0.20 MPa. The samples were then cooled to 100°C over the course of 1 min using circulating water and held for 5 min, after which they were directly cooled to room temperature.

Notched Izod impact testing was performed on a Resil 25 (CEAST, Pianezza, Italy) at room temperature according to ASTM D256. The notch depth was cut to 2.54 mm. The impact resistance was calculated by dividing the total energy required to break the sample by the thickness of the impact bar. A minimum of three samples were tested for each material.

Adhesion testing

The adhesion testing was performed by the dual-cantilever beam crack propagation test.[14] The plaques for the adhesion test samples were prepared by compression molding under a maximum pressure of 0.50 MPa for 9 min. The PLLA plaques were pressed at 200°C, whereas the PLA plaques and the LLDPE plaques were pressed at 130°C. To form the bilayer adhesion samples, the PLLA and LLDPE plaques were put into contact and pressed together with an ultimate pressure of 0.50 MPa at 200°C for 9 min and then cooled to 50°C over 4 min. Additional PLLA/LLDPE bilayer samples were prepared that were held under a maximum pressure of 0.50 MPa at 200°C for 5 min and then cooled to 100°C and held for 5 min before being quenched to 50°C. The PLA and LLDPE bilayer adhesion samples were pressed together at 130°C under a maximum pressure of 0.5 MPa for 9 min and then cooled to 50°C over 4 min. Spacers were used to control the final thickness of the samples. Any overflow that was formed during pressing was trimmed away using a hot wire cutter.

To perform the adhesion testing, a razor blade was inserted at the interface of the bilayer adhesion sample. The samples were left unperturbed for 1 h, after which the crack length ahead of the razor blade tip was measured. In addition, the thickness of each layer was measured after testing. In general, the PLLA layers had a thickness of 1.2 mm, the PLA layers had a thickness of 1.7 mm, and the LLDPE layers had a thickness of 1.5 mm.

The strain energy release rate was then determined using the following equation[14]:

$$G_c = \frac{3\Delta^2 E_1 E_2 h_1^3 h_2^3 (C_1^2 E_2 h_2^3 + C_2^2 E_1 h_1^3)}{8a^4 (C_1^3 E_2 h_2^3 + C_2^3 E_1 h_1^3)^2} \tag{4}$$

where $C_i = 1 + [0.64(h_i/a)]$, Δ is the razor blade thickness, E_i is the elastic modulus, a is the crack length ahead of the razor blade, and h_i is the layer thickness.

RESULTS AND DISCUSSION

In this study, melt blending of polylactide and polyethylene was performed with the intent of toughening polylactide. To compatibilize these two immiscible polymers, corresponding PLLA–PE block copolymers were introduced into the binary blends. The detailed molecular characteristics of these materials are given in Table I. All blends were prepared with 80 wt % of polylactide and 20 wt % of LLDPE.[27] The amount of block copolymer added to the binary blend was cal-

TABLE II
Particle Size Analysis and Impact Resistance of PLA Homopolymer and Blends

PLA : LLDPE : PLLA–PE block[a]	PLLA–PE block used[b]	LLDPE particle size[c,d] (μm)	Particle size distribution parameter (σ)[e]	Izod impact resistance[d] (J/m)
100 : 0 : 0				12 ± 4
80 : 20 : 0		6.4	1.4	34 ± 1
80 : 20 : 5	(5–30)	4.3	1.4	36 ± 5
80 : 20 : 5	(30–30)	0.9 ± 0.1	1.5	460 ± 60

[a] Given in weight ratios of the components.
[b] See Table I.
[c] Determined by light scattering (see Experimental section).
[d] ±1 SD.
[e] Defined in the Experimental section.

culated on the basis of the total weight of the binary blend. To assess the compatibilization mechanism of the block copolymer, two block copolymers with a PE block of molecular weight ~ 30 kg/mol were studied, one with the PLLA block above the polylactide entanglement molecular weight (~ 30 kg/mol) and one with the PLLA block below the entanglement molecular weight (~ 5 kg/mol). (The entanglement molecular weight of polylactide is approximately 9 kg/mol.[28]) To determine the extent of compatibilization, the LLDPE particle size and the impact resistance were measured (see Experimental section for details).

To begin with, the amorphous PLA blends were prepared to investigate a system where only entanglements would take place at the interface for the polylactide, given that the atactic PLA is not able to crystallize. In this case, we would be able to determine the extent of compatibilization obtainable with the block copolymers in the absence of polylactide crystallization.[29]

PLA/LLDPE blends

Three sets of blends were prepared with the amorphous PLA, one without block copolymer, one with the PLLA–PE(5–30) block copolymer (5 wt %), and one with the PLLA–PE(30–30) block copolymer (5 wt %). The LLDPE particle size, determined by light scattering, and the impact resistance were measured (Table II). In addition, SEM images of the cryofractured surfaces are shown in Figure 2.

The binary blend behaves as expected for a highly immiscible polymer blend; large dispersed phase particles and smooth, distinct particle interfaces, indicating poor interfacial adhesion, were obtained. When the PLLA–PE(5–30) block copolymer was added to the binary blend (5 wt %), the LLDPE particle size decreased slightly (4.3 versus 6.4 μm). This is most likely attributable to the presence of the block copolymer at the interface, which inhibits the coalescence of the particles.[26] With the addition of the PLLA–PE(30–30) block copolymer to the binary blend (5 wt %), the LLDPE particle size decreased significantly (0.9 versus 6.4 μm). The difference in the LLDPE particle size between the PLLA–PE(5–30) blend and the PLLA–PE(30–30) blend would appear to be attributed to the difference in molecular weight of the PLLA block. Lepers and Favis[12] suggested that the length (i.e., molecular weight) of the block forming the outer shell around the dispersed phase particles was critical for coalescence suppression. While coalescence suppression is important for maintaining small dispersed phase particle size, the block copolymer also lowers the interfacial tension between the immiscible polymers, thus decreasing the particle size.[30] However, the length of the block forming the outer shell was shown to have less of an influence on the interfacial tension reduction compared to coalescence suppression.[12]
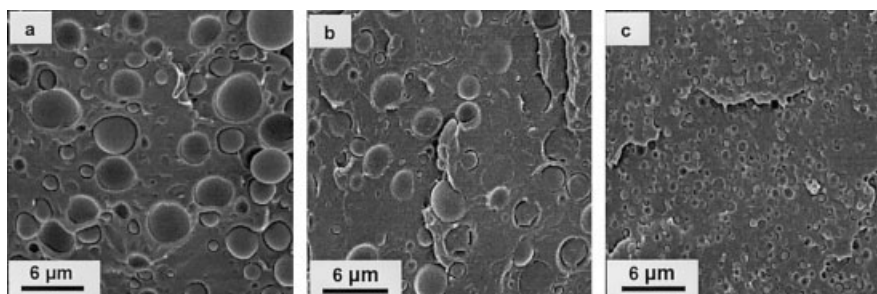

Figure 2 Representative SEM images of cryofractured surfaces of (a) 80 : 20 PLA/LLDPE; (b) 80 : 20 : 5 PLA/LLDPE/PLLA–PE(5–30); (c) 80 : 20 : 5 PLA/LLDPE/PLLA–PE(30–30).

TABLE III
Particle Size Analysis and Impact Resistance of PLLA Homopolymer and Blends

PLLA : LLDPE : PLLA–PE block[a]	PLLA–PE block used[b]	LLDPE particle size[c,d] (μm)	Particle size distribution parameter (σ)[e]	Izod impact resistance[d] (J/m)
100 : 0 : 0				20 ± 2
80 : 20 : 0		2.8 ± 1.3	1.4	350 ± 230
80 : 20 : 5	(5–30)	1.9 ± 0.2	1.4	510 ± 60
80 : 20 : 5	(30–30)	0.9 ± 0.2	1.5	660 ± 50

[a] Given in weight ratios of the components.
[b] See Table I.
[c] Determined by light scattering (see Experimental section).
[d] ±1 SD.
[e] Defined in the Experimental section.

Therefore, the difference in the dispersed phase particle size for the PLLA–PE(5–30) and PLLA–PE(30–30) block copolymer blends is presumably due to the superior ability of the block copolymer with the long PLLA block to suppress the coalescence.

A comparison of the impact test results (Table II) showed that the PLA/LLDPE binary blend impact resistance increased only slightly over that of the homopolymer PLA. Due to the large dispersed phase particle size and low interfacial adhesion, the poor mechanical properties were expected.[10] Upon addition of the PLLA–PE(5–30) block copolymer, the impact resistance did not increase over that of the binary 80 : 20 blend. For this block copolymer, the PLLA block is below the entanglement molecular weight and unable to entangle with the matrix PLA. In addition the PLLA block is unable to crystallize with the matrix PLA since it is atactic; therefore, the PLLA–PE(5–30) block copolymer does not increase the interfacial adhesion and is not an effective compatibilizer even though the LLDPE particle size decreased somewhat. On the contrary, when the PLLA–PE(30–30) block copolymer was added, the average impact resistance increased significantly over that of the binary blend (460 versus 34 J/m), presumably due to the ability of the block copolymer to entangle with the homopolymers, which allowed for well-dispersed LLDPE particles and improved interfacial adhesion.

After the addition of the PLLA–PE(30–30) block copolymer to the immiscible binary blend we obtained tough blends, which is consistent with other related studies.[8,9] However, compared to the previous solution blending study, the toughening achieved by melt blending is exceptional. The impact resistance for the melt blend containing the PLLA–PE(30–30) block copolymer was almost three times higher than that of the blend containing the PLLA–PE(30–30) block copolymer in our related solution blending study.[8]

Comparison of PLA/LLDPE and PLLA/LLDPE blends

To determine the efficacy of the PLLA–PE block copolymers as compatibilizers in the semicrystalline PLLA/LLDPE polymer blends, three sets of blends were prepared with the semicrystalline PLLA, one without block copolymer, one with the PLLA–PE(5–30) block copolymer (5 wt %), and one with the PLLA–PE(30–30) block copolymer (5 wt %). The LLDPE particle size, determined by light scattering, and the impact resistance were measured (Table III). In addition, SEM images of the cryofractured surfaces are shown in Figure 3.

For the semicrystalline PLLA/LLDPE binary blend, the LLDPE particle size is much smaller than expected based on the amorphous PLA/LLDPE binary blend
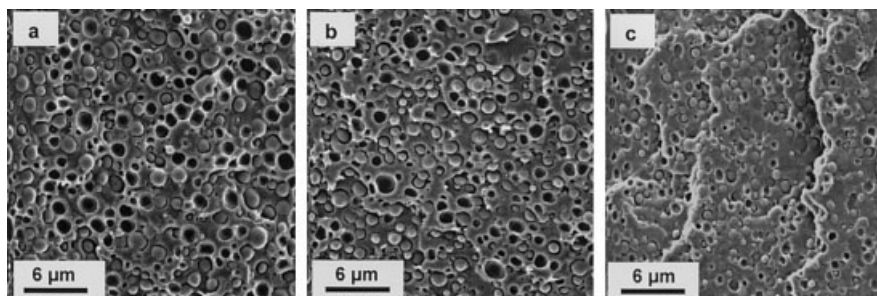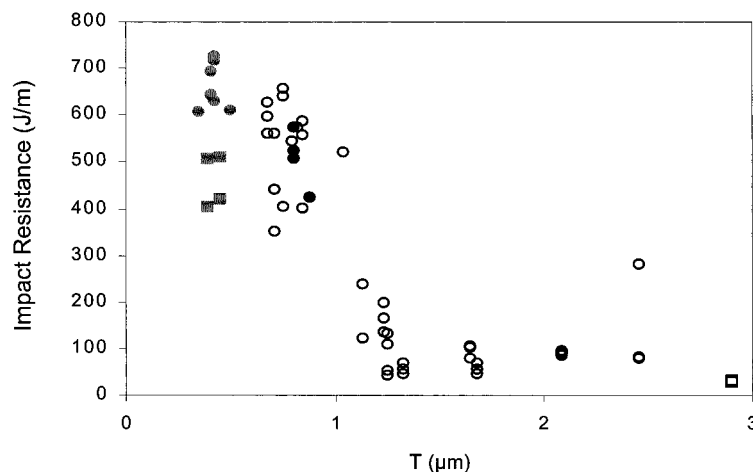

Figure 3   Representative SEM images of cryofractured surfaces of (a) 80 : 20 PLLA/LLDPE; (b) 80 : 20 : 5 PLLA/LLDPE/PLLA–PE(5–30); (c) 80 : 20 : 5 PLLA/LLDPE/PLLA–PE(30–30).

Figure 4 Relationship between matrix ligament thickness and impact resistance for: 80 : 20 PLLA/LLDPE binary blend (open circles); 80 : 20 : 5 PLLA/LLDPE/PLLA–PE(5–30) (black circles); 80 : 20 : 5 PLLA/LLDPE/PLLA–PE(30–30) (gray circles); 80 : 20 PLA/LLDPE binary blend (open squares); and 80 : 20 : 5 PLA/LLDPE/PLLA–PE(30–30) (gray squares).

observations (2.8 versus 6.4 μm). When the PLLA–PE(5–30) block copolymer was added to the PLLA/LLDPE binary blend (5 wt %), the LLDPE particle size decreased only slightly compared to the binary blend (1.9 versus 2.8 μm). However, with the addition of the PLLA–PE(30–30) block copolymer to the binary blend (5 wt %), the LLDPE particle size decreases further (0.9 versus 2.8 μm). As in the PLA/LLDPE blends, the difference in the dispersed phase particle size for the PLLA–PE(5–30) and PLLA–PE(30–30) block copolymer blends is presumably due to the superior ability of the block copolymer with the long PLLA block to suppress the coalescence.

The impact test results (Table III) of the PLLA/LLDPE binary blend showed significantly higher impact resistance than that of the homopolymer PLLA (350 versus 20 J/m). The addition of the PLLA–PE(5–30) block copolymer increases the average impact resistance from 350 to 510 J/m, and the PLLA–PE(30–30) block copolymer increases the impact resistance even further, to 660 J/m. In addition to increasing the impact resistance, a noticeable decrease in the standard deviation of the impact resistance was noted upon addition of the block copolymers, and we address this in a subsequent section.

The improvement in the impact resistance with the PLLA–PE(30–30) block copolymer compared to the PLLA–PE(5–30) block copolymer is most likely attributed to the smaller LLDPE particle size in the PLLA–PE(30–30) blend (see later discussion on matrix ligament thickness). In addition, the interfacial adhesion for the PLLA–PE(30–30) blend is potentially better than that in the PLLA–PE(5–30) blend. For the PLLA–PE(5–30) blend, the block copolymer can only crystallize with the PLLA matrix since it is below the PLLA entanglement molecular weight; however, the PLLA–PE(30–30) block copolymer can entangle as well as crystallize with the matrix PLLA, thus potentially im-

proving the interfacial adhesion compared to the PLLA–PE(5–30) blend.

The most surprising result from the impact testing of the PLLA/LLDPE blends was the extremely tough binary blend. This was unexpected based on the results obtained from the previous solution blending study of the semicrystalline PLLA, as well as the PLA/LLDPE melt blend results. Both showed that the binary blend exhibited poor mechanical properties.[8] A primary difference between these blends is the LLDPE particle size. The binary PLLA/LLDPE blend in the solution blending study and the amorphous PLA/LLDPE blend in this study had LLDPE particle sizes that were significantly larger than what was found for the PLLA/LLDPE melt blend. The effect of the LLDPE particle size on the impact resistance can be investigated by determining the critical matrix ligament thickness. Wu[31,32] suggested that the matrix ligament thickness (T) was the primary controlling factor for rubber toughening in polymer blends. The matrix ligament thickness is defined as the surface-to-surface dispersed phase interparticle distance. Wu stated that if the average matrix ligament thickness was below the critical value, then the blend would be tough; if it was above the critical value, the blend would be brittle. The large variability in the LLDPE particle size for the PLLA/LLDPE binary blend allowed us to evaluate this relationship. To calculate the matrix ligament thickness eq. (5) was used, given that not only the particle size but also the particle size distribution parameter were determined to be important for calculating the matrix ligament thickness.[23]

$$T = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3} \exp(1.5 \ln^2\sigma) - \exp(0.5 \ln^2\sigma)\right] \quad (5)$$

In eq. (5), ϕ is the volume fraction of rubber, d is the average particle diameter, and σ is the particle size

distribution parameter, which were calculated on the basis of eqs. (1) and (2), respectively. The open circles in Figure 4 show the relationship between the matrix ligament thickness and the impact resistance for the binary PLLA/LLDPE melt blends.[33] As the matrix ligament thickness decreases, the impact resistance increases, and the critical matrix ligament thickness is approximately 1.0 μm.

The data for the PLLA/LLDPE/PLLA–PE(5–30) (black circles) and the PLLA/LLDPE/PLLA–PE(30–30) (gray circles) ternary blends are also plotted in Figure 4. From the PLLA–PE(30–30) data, it appears that the impact resistance shows a leveling off when the matrix ligament thickness goes below the critical value; however, the effect of the interfacial adhesion on the toughening in these blends is not known, so the comparison with this data is limited.

The PLA/LLDPE binary blend data are also plotted in Figure 4 (open squares). For the amorphous PLA/LLDPE binary blend the matrix ligament thickness is much larger than the critical value, thus providing a potential explanation for the brittle behavior. Interestingly, the PLA/LLDPE/PLLA–PE(30–30) data [also plotted in Fig. 4 (gray squares)] show that for the same matrix ligament thickness ($\sim$ 0.4 μm), the PLA/LLDPE/PLLA–PE(30–30) blend gives an impact resistance that is statistically lower than that of the PLLA/LLDPE/PLLA–PE(30–30) blend. This may be an indication that the block copolymer is crystallizing with the matrix in the PLLA-containing blend and increasing the interfacial adhesion for the semicrystalline blend, thus increasing the impact resistance.

Another possible explanation for the increased toughness for the semicrystalline PLLA/LLDPE/PLLA–PE(30–30) blend is the presence of overlapping crystallites. Argon et al.[34,35] have proposed a toughening mechanism for semicrystalline blends in which the rubber/matrix interface nucleates crystallization of the matrix to produce crystallographically oriented material in the near interface region. The percolation of these oriented layers throughout the matrix results in tough behavior. In addition, they propose that the existence of these oriented layers promotes the plastic response of the material. Therefore, based on this model, below the critical matrix ligament thickness a semicrystalline blend should be tougher than an amorphous blend due to the presence of the oriented layer around the rubber particles. Further studies would need to be conducted to determine whether local orientation of crystallites was occurring in the PLLA at the PLLA/LLDPE interface and causing the increased toughness.

By comparing the PLA/LLDPE and the PLLA/LLDPE binary blends, we see that the LLDPE particle size in the PLA blend was almost three times larger than that in the PLLA blend. A possibility that was investigated for the increased LLDPE particle size was whether, after removal from the mixing chamber, the

LLDPE in the amorphous PLA blend had more time to coalesce (i.e., coarsen) and thus form larger particles. Because the blends were removed from the melt mixer (at 190°C) and cooled to room temperature on the bench top, the amorphous PLA should be well above its T_g of 54°C directly after removal from the mixer and the LLDPE particles would be able to coalesce. On the other hand, the semicrystalline blend should start to solidify below about 120°C.[36] Thus the LLDPE would have less time for coalescence after being removed from the mixer in the semicrystalline PLLA/LLDPE blend. To determine whether the coalescence after mixing was the cause of the increased LLDPE particle size for the PLA blends, samples of both the PLA and PLLA binary blends were removed from the mixer after blending and immediately quenched in liquid nitrogen. The LLDPE particle size of the quenched PLA blend was found to be 1.5 times larger than that of the quenched PLLA blend. The fact that the LLDPE particle size of the quenched PLA blend is still somewhat larger than that of the semicrystalline blend indicates that the additional time for coalescence is not the only reason that the amorphous binary blend has a larger LLDPE particle size.

Material differences between PLLA and PLA were also investigated as a potential reason for the increased particle size, even though the PLA and PLLA are chemically identical and comparable in molecular weight and thus should blend in a similar manner with LLDPE. Taylor modeled the drop size for a Newtonian fluid in a simple shear field using the viscosity ratio η_r (ratio of dispersed phase to matrix phase viscosities) and the capillary number [$Ca = \dot{\gamma}\eta_m D/(2\Gamma)$].[37,38] By balancing the interfacial forces and the shear forces, Taylor obtained a relationship for the maximum drop size (D) that would be stable, given by eq. (6):

$$D = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma}\eta_m\left(\frac{19}{4}\eta_r + 4\right)} \tag{6}$$

where $\dot{\gamma}$ is the shear rate, η_m is the matrix viscosity, and Γ is the interfacial tension. From this equation, the LLDPE particle size could be affected by differences in the viscosities of the PLLA and PLA or differences in the interfacial tensions between PLLA and PLA with LLDPE.

The viscosities at the processing temperature (190°C) and shear rate (65 s^{-1}) were found to be 1.6 $\times$ 10^6 cP, 1.3 $\times$ 10^6 cP, and 2.2 $\times$ 10^6 cP for PLLA, PLA, and LLDPE, respectively.[39] The value of η_r is 1.4 for PLLA/LLDPE and 1.7 for PLA/LLDPE. Using eq. (6) we can estimate the LLDPE particle size for both the PLLA/LLDPE and the PLA/LLDPE blends by assuming that they have the same interfacial tensions.[40] For the PLLA/LLDPE blend the LLDPE particle size (D)
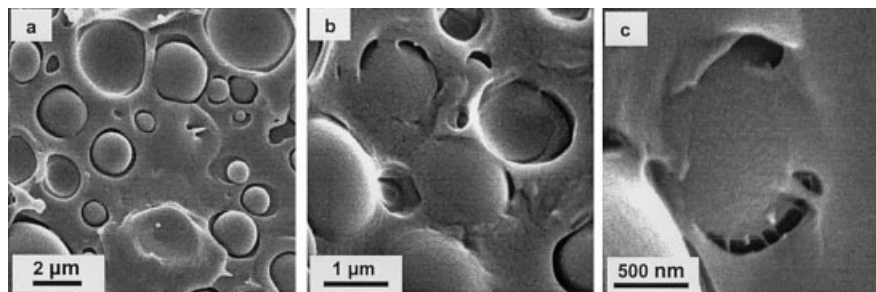
Figure 5 SEM image. Interface comparison between the amorphous and semicrystalline binary blends: (a) PLA/LLDPE 80 : 20 binary blend; (b) PLLA/LLDPE 80 : 20 binary blend; (c) higher magnification image of PLLA/LLDPE 80 : 20 binary blend.

was calculated to be 0.12 μm, and for the PLA/LLDPE blend the LLDPE particle size (D) was calculated to be 0.15 μm. On the basis of the viscosity ratio difference, the particle sizes are not significantly different. Interestingly, the particle sizes calculated using this equation are significantly smaller than what was obtained in this study (2.8 μm for the PLLA/LLDPE blend and 6.4 μm for the PLA/LLDPE blend). This has been attributed to the fact that eq. (6) does not account for the non-Newtonian nature of polymers or the coalescence of the particles during blending.[26] As seen from eq. (6), the small increase in viscosity ratio would not give the almost threefold increase in LLDPE particle size that was seen for the PLA/LLDPE blend compared to the PLLA/LLDPE blend. In a study by Favis and Chalifoux[41] with polycarbonate/polypropylene blends, by changing the molecular weights of the blend constituents and hence the viscosity ratio, an increase of 3 to 4 times for the particle size was obtained; however, the viscosity ratio had increased from 4.5 to 17.3. In the polylactide/LLDPE system, a larger LLDPE particle size was obtained in the blend with the larger viscosity ratio, which is consistent with the study by Favis and Chalifoux.[41] Nevertheless, a much larger difference in the viscosity ratios would be necessary for the large increase in the LLDPE particle size.

While the viscosity ratio difference does not appear to be a contributing factor to the LLDPE particle size difference, the interfacial tension between PLLA and LLDPE could be different from the interfacial tension between PLA and LLDPE. The interfacial tension between two polymers is proportional to the square root of the Flory–Huggins interaction parameter χ, which is a measure of the miscibility of two polymers.[42] If the interfacial tension between PLLA and LLDPE were different from that of PLA and LLDPE, the miscibility of these polymers would be different. Evidence that the interfacial interactions between the semicrystalline PLLA and the LLDPE are different from those with the amorphous PLA is given in Figure 5. The SEM images show that the particle interfaces for the PLA blend are distinct, whereas with the PLLA blend the particle interfaces are not as clear. In addition, the

higher magnification image of the PLLA blend shows what appear to be polymer fibrils that span across the particle interface into the matrix material. This could be an indication that the entanglements at the interface are becoming trapped when the PLLA and LLDPE crystallize.[43] We would expect, based on the immiscibility of these polymers, that polylactide and LLDPE would have a small interfacial thickness and significant entanglements at the interface would be unlikely. However, the existence of the polymer fibrils would seem to indicate that the PLLA and LLDPE are mixing at the interface more than expected, perhaps due to the stereoregularity of the PLLA.

The PLA and PLLA do differ in tacticity and this may be the ultimate cause of their blending behavior differences. Several researchers have shown that the tacticity can affect the relative miscibility of two polymers, with certain configurations being more miscible with a given polymer.[44-47] In the case of this study, PLLA may be more miscible with LLDPE than PLA, which would allow the LLDPE to be dispersed into smaller particles in the PLLA matrix due to the lower interfacial tension between PLLA and LLDPE. In addition, the existence of the polymer fibrils could be explained if PLLA and LLDPE were more miscible than expected, given that they would have a larger interfacial thickness and thus more entanglements in the interfacial region. The increased thickness of the interfacial region would increase the likelihood that interfacial entanglements would become trapped upon crystallization of the PLLA and LLDPE.

Besides miscibility effects, the tacticity of the polymer chain has also been shown to affect the rheological properties for both poly(methyl methacrylate) and polypropylene.[48,49] In both of these cases, the syndiotactic polymer exhibited a lower entanglement molecular weight than that of either the isotactic or the atactic variants. Therefore, in the case of polylactide, for the same interfacial thickness, the tacticity could be allowing for more entanglements at the interface with the semicrystalline material. To investigate this further, adhesion testing was performed since the increased interfacial thickness and the trapping of en-
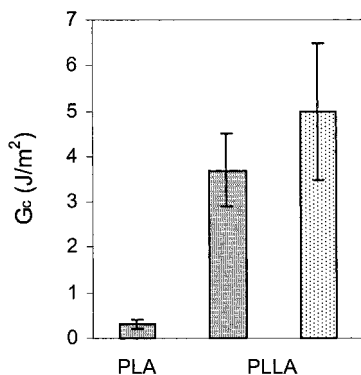
Figure 6 Comparison of strain energy release rates for PLA and PLLA with LLDPE obtained from the dual-cantilever beam crack propagation test: (solid gray) quenched to 50°C; (dotted) held at 100°C for 5 min. (Error bars indicate ±1 SD).

tanglements should cause the interfacial adhesion to increase.

The adhesion testing was done using the dual-cantilever beam crack propagation test, in which a razor blade was inserted between the polymer layers and the crack was allowed to propagate along the interface.[14] The strain energy release rate was then calculated using eq. (4). The values for the PLLA/LLDPE interface and the PLA/LLDPE interface are given in Figure 6. Using this test, the semicrystalline PLLA did have a considerably higher value for the strain energy release rate than that of the amorphous PLA, indicating better adhesion between the PLLA and LLDPE. The increased adhesion for the PLLA was seen even when the samples were quenched from the melt. When the PLLA samples were given time to crystallize at 100°C, the strain energy release rate increased only slightly over that of the quenched PLLA samples.

The surfaces of the adhesion samples were also examined using SEM (Fig. 7). The LLDPE that was in contact with the semicrystalline PLLA appears to have large crystallites on the surface. For the LLDPE that was in contact with the amorphous PLA, no large crystallites were observed. The presence of the large crystallites may be attributable to the molten LLDPE being pulled across the interface as the PLLA contracts upon crystallization and thus an "imprint" is left on

the LLDPE side. The surfaces of the LLDPE samples that were allowed time to crystallize at 100°C while in contact with the PLLA also showed the presence of crystallites similar to the quenched LLDPE surface. However, no polymer fibrils were seen that would indicate that interfacial entanglements were being trapped across the PLLA/LLDPE interface. Due to the low strain rates experienced in the dual-cantilever beam crack propagation test, the fact that extended polymer fibrils were absent is not surprising.[50] Using this test the existence of the trapped interfacial entanglements cannot be verified, but the increased adhesion for the PLLA/LLDPE interface does indicate that there are enhanced interfacial interactions between these polymers compared to the amorphous PLA. The improved adhesion for the PLLA/LLDPE interface would allow for stresses to be transferred more readily to the LLDPE during the impact testing. This may be a contributing factor, in addition to the better dispersion of LLDPE in PLLA, to increased impact resistance for the PLLA/LLDPE binary blend compared to that of the PLA/LLDPE binary blend.

Block copolymer influence on the impact test results of PLLA/LLDPE blends

The impact test results for the binary PLLA/LLDPE blend showed that exceptional toughening of PLLA was achieved even without the use of a compatibilizer; however, significant variability was seen. The addition of the block copolymer not only increased the average impact resistance, but also significantly decreased the variability. Several blends were prepared with varying amounts of the PLLA–PE(30–30) block copolymer to determine how much block copolymer was necessary to achieve the benefits of its use. In ternary blends, block copolymers will form micelles once the critical micelle concentration is surpassed rather than segregate to the interface once the critical micelle concentration is surpassed.[51] Therefore, determining the lowest level of block copolymer that is necessary to maintain the desired properties will result in wasting less block copolymer as micelles in the homopolymers. The results, shown in Figure 8, indi-
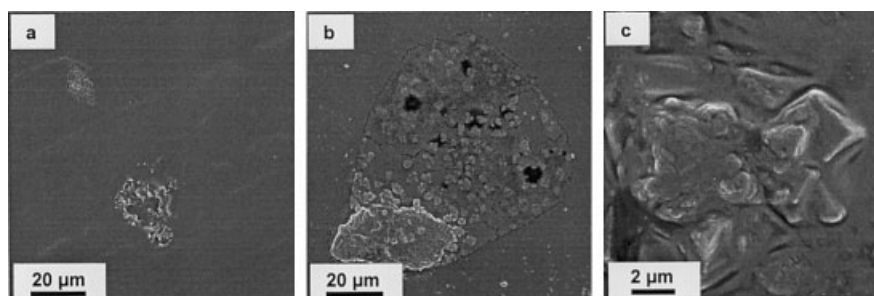
Figure 7 SEM images of LLDPE side of adhesion sample surfaces after testing: (a) adhesion sample prepared with PLA; (b) adhesion sample prepared with PLLA; (c) higher magnification of adhesion sample prepared with PLLA.
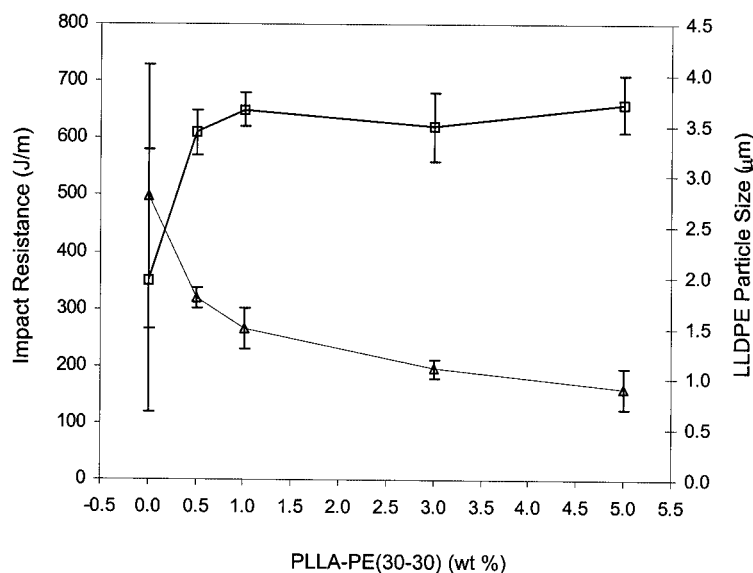
Figure 8 Effect of the amount of PLLA–PE(30–30) block copolymer on the impact resistance (squares) and the LLDPE particle size (triangles) of 80 : 20 PLLA/LLDPE blends.

cate that using only 0.5 wt % of the PLLA–PE(30–30) block copolymer based on the total weight of the binary blend is enough to help minimize the standard deviation in the impact test results while retaining the high impact resistance. The highest value for the impact resistance was obtained with 5 wt % of the block copolymer (660 J/m). However, all of the block copolymer blends are within one standard deviation of each other, showing that to achieve optimum toughness and less variability for this system, as little as 0.5 wt % of the block copolymer could be used.

Figure 8 also shows how the LLDPE particle size was affected by the amount of block copolymer. After addition of 3 wt % of the PLLA–PE(30–30) block copolymer, the LLDPE particle size begins to level off at around 1.0 μm. While 3 wt % of the block copolymer is necessary to achieve the minimum LLDPE particle size, only 0.5 wt % of the block copolymer is necessary to achieve optimum toughness. This is attributed to the matrix ligament thickness. At 0.5 wt % of block copolymer the matrix ligament thickness is below the critical value, and further reduction of the matrix ligament thickness below the critical value does not enhance the toughness obtained.

CONCLUSIONS

Using melt blending, we were able to achieve exceptional toughening of polylactide by incorporating LLDPE. In the case of the amorphous PLA/LLDPE blend, to toughen the polylactide the PLLA–PE(30–30) block copolymer was necessary for compatibilization purposes. With the semicrystalline PLLA/LLDPE blend, significant toughening was seen in the absence of a compatibilizer, although the toughening was enhanced and the variability was reduced by the pres-

ence of as little as 0.5 wt % of the PLLA–PE(30–30) block copolymer.

The toughening achieved in this study is comparable to, and in some cases better than, the toughening seen for some of the "supertough" polylactides of Pennings et al.[15] Interestingly, the study by Pennings also found a difference in the toughening that could be achieved between semicrystalline and amorphous polylactide blends, but the differences were not investigated. We propose that the differences between the PLA/LLDPE and the PLLA/LLDPE binary blends are due to tacticity effects on either the entanglement molecular weight of polylactide or the degree of miscibility of polylactide with LLDPE. The adhesion testing that was performed gave an indication that such an effect may exist, given that improved adhesion was seen for the PLLA/LLDPE interface compared to the PLA/LLDPE interface. Investigation into these tacticity effects is under way.

The results from the PLA/LLDPE/PLLA–PE(30–30) blend and the PLLA/LLDPE/PLLA–PE(30–30) blend appear to indicate that the crystallization of the block copolymer allows for improved toughening at the same matrix ligament thickness. However, the existence of an oriented crystallite layer around the rubber particles in the PLLA/LLDPE blend may also be contributing to the observed toughness.

References

1. Drumright, R. E.; Gruber, P. R.; Henton, D. E. Adv Mater 2000, 12, 1841.
2. Perego, G.; Cella, G. D.; Bastioli, C. J Appl Polym Sci 1996, 59, 37.
3. Vert, M.; Li, S. M.; Spenlehauer, G.; Guerin, P. J Mater Sci Mater Med 1992, 3, 432.
4. Hiljanen-Vainio, M.; Varpomaa, P.; Seppala, J.; Tormala, P. Macromol Chem Phys 1996, 197, 1503.
5. Fayt, R.; Jerome, R.; Teyssie, P. J Polym Sci Part B: Polym Phys 1989, 27, 775.
6. Muratoglu, O. K.; Argon, A. S.; Cohen, R. E. Polymer 1995, 36, 4771.
7. Yu, Z. Z.; Ou, Y. C.; Hu, G. H. J Appl Polym Sci 1998, 69, 1711.
8. Wang, Y.; Hillmyer, M. A. J Polym Sci Part A: Polym Chem 2001, 39, 2755.
9. Kim, H. C.; Nam, K. H.; Jo, W. H. Polymer 1993, 34, 4043.
10. Paul, D. R.; Bucknall, C. B. Polymer Blends; Wiley: New York, 2000; Vol. 1, p. 11.
11. Shull, K. R.; Kramer, E. J. Macromolecules 1990, 23, 4769.
12. Lepers, J. C.; Favis, B. D. AIChE J 1999, 45, 887.
13. Lyu, S.-P.; Bates, F. S.; Macosko, C. W. Polym Prepr (Am Chem Soc Div Polym Chem) 1999, 40, 1016.
14. Creton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. Macromolecules 1992, 25, 3075.
15. Joziasse, C. A. P.; Topp, M. D. C.; Veenstra, H.; Grijpma, D. W.; Pennings, A. J. Polym Bull 1994, 33, 599.
16. Yuan, Y.; Ruckenstein, E. Polym Bull 1998, 40, 485.
17. VanKrevelen, D. W. Properties of Polymers, 3rd ed.; Elsevier Science B.V.: Amsterdam, 1997.
18. Raghavan, D.; Emekalam, A. Polym Degrad Stab 2001, 72, 509.
19. Sinclair, R. G. U.S. Pat. 5,216,050, 1993.
20. Sinclair, R. G.; Preston, J. U.S. Pat. 5,252,642, 1993.
21. An estimate of the degree of immiscibility can be obtained by the difference in the solubility parameters for the two materials. The solubility parameter of polylactide has been reported as 22.8 $(J\ cm^{-3})^{1/2}$, see: Joziasse, C. A. P.; Topp, M. D. C.; Veenstra, H.; Grijpma, D. W.; Pennings, A. J. Polym Bull 1994, 33, 599. Upon independent calculation using VanKrevelen group contributions the solubility parameter of polylactide was found to be 19.7 $(J\ cm^{-3})^{1/2}$. Therefore, the average value of 21.3 $(J\ cm^{-3})^{1/2}$ can be used as an estimate for the polylactide solubility parameter. The solubility parameter for polyethylene is 17.1 $(J\ cm^{-3})^{1/2}$, see: VanKrevelen, D. W. Properties of Polymers, 3rd ed.; Elsevier Science: Amsterdam, 1997. As a reference the solubility parameter of polypropylene is 18.8 $(J\ cm^{-3})^{1/2}$, see: VanKrevelen, D. W. Properties of Polymers, 3rd ed.; Elsevier Science: Amsterdam, 1997. Based on these values, the degree of immiscibility between polylactide and polyethylene is expected to be much greater than that of polyethylene and polypropylene, since the interaction parameter χ is proportional to the square of the solubility parameter difference, see: Helfand, E.; Tagami, Y. J. Chem Phys 1972, 56, 3592.
22. Melt blending of LLDPE with a biodegradable aliphatic polyester (described as a copolymer of aliphatic glycols and dicarboxylic acids), similar to polylactide, has been performed; however, tough blends were not obtained until the blend contained 80% LLDPE, see: Kim, J.; Kim, J. H.; Shin, T. K.; Choi, H. J.; Jhon, M. S. Eur Polym J 2001, 37, 2131.
23. 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.
24. Witzke, D. R.; Narayan, R.; Kolstad, J. J. Macromolecules 1997, 30, 7075.
25. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989.
26. Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647.
27. For the binary blends, this blend composition was found to be optimum with respect to toughness in another study where the blend composition was varied from 90 : 10 PLLA : LLDPE up to 50 : 50 PLLA : LLDPE.
28. Palade, L. I.; Lehermeier, H. J.; Dorgan, J. R. Macromolecules 2001, 34, 1384.
29. This is neglecting the possibility of crystallization occuring between the PLLA blocks of the block copolymer.
30. Retsos, H.; Margiolaki, I.; Messaritaki, A.; Anastasiadis, S. H. Macromolecules 2001, 34, 5295.
31. Wu, S. Polymer 1985, 26, 1855.
32. Wu, S. J Appl Polym Sci 1988, 35, 549.
33. Additional blends were prepared, sometimes using different blending conditions, to obtain a range of particle sizes. Also, one blend was obtained that had an average impact resistance of 1480 J/m. However, this blend could not be reproduced so it was not included in the analysis.
34. Muratoglu, O. K.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1995, 36, 921.
35. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2331.
36. Schmidt, S. C.; Hillmyer, M. A. J Polym Sci Part B: Polym Phys 2000, 39, 300.
37. Taylor, G. I. Proc R Soc London 1932, A138, 41.
38. Taylor, G. I. Proc R Soc London 1934, A146, 501.
39. The maximum shear rate in the Haake mixer at 50 rpm is 65 s^{-1}, see: Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647. The viscosities at this shear rate were obtained from the viscosity versus frequency plot by using the Cox–Merz rule, see: Tadmor, Z.; Gogos, C. G. Principles of Polymer Processing, Wiley-Interscience: New York, 1979.
40. The interfacial tension was calculated based on the Flory–Huggins interaction parameter χ and the statistical segment length b, see: Datta, S.; Lohse, D. J. Polymeric Compatibilizers: Uses and Benefits in Polymer Blends; Hanser Publishers: Munich, 1996; pp. 25–27. The value used for χ was 0.2, which was estimated based on the solubility parameter difference, see: ref. 21, and b was taken as 7.8 Å, the root mean square average for PE and PLLA (calculated based on the characteristic ratios of PE and PLLA). Using these values the interfacial tension was found to be 1.38×10^{-6} J/cm².
41. Favis, B. D.; Chalifoux, J. P. Polym Eng Sci 1987, 27, 1591.
42. Datta, S.; Lohse, D. J. Polymeric Compatibilizers: Uses and Benefits in Polymer Blends; Hanser Publishers: Munich, 1996.
43. Chaffin, K. A.; Knutsen, J. S.; Brant, P.; Bates, F. S. Science 2001.
44. Beaucage, G.; Stein, R. S. Macromolecules 1993, 26, 1609.
45. Silvestre, C.; Cimmino, S.; Martuscelli, E.; Karasz, F. E.; MacKnight, W. J. Polymer 1987, 28, 1190.
46. Schurer, J. W.; Boer, A. D.; Challa, G. Polymer 1975, 16, 201.
47. Jones, T. D.; Chaffin, K. A.; Bates, F. S.; Annis, B. K.; Hagaman, E. W.; Kim, M.; Wignall, G. D.; Fan, W.; Waymouth, R. Macromolecules, to appear.
48. Fuchs, K.; Friedrich, C.; Weese, J. Macromolecules 1996, 29, 5893.
49. Eckstein, A.; Suhm, J.; Friedrich, C.; Maier, R. D.; Sassmannshausen, J.; Bochmann, M.; Mulhaupt, R. Macromolecules 1998, 31, 1335.
50. Preliminary testing using a higher strain rate tensile butt joint test was performed, see: Yuan, B. L.; Wool, R. P. Polym Eng Sci 1990, 30, 1454. Extended polymer fibrils were observed on the PLLA surface.
51. Dai, K. H.; Kramer, E. J.; Shull, K. R. Macromolecules 1992, 25, 220.