

Rubber Toughening of Poly(lactic acid): Effect of Stereocomplex Formation at the Rubber-Matrix Interface

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ABSTRACT: In this study, a series of graft copolymers poly(*n*-butyl acrylate)-*g*-poly-L-lactide (PBA-*g*-PLLA) and poly(*n*-butyl acrylate)-*g*-poly-D-lactide (PBA-*g*-PDLA) with various molecular weights and PBA/PLA ratios were prepared from the copolymerization of *n*-butyl acrylate and PLA macromers. The PLA macromers were prepared by ring opening polymerization of L- or D-lactide in the presence of 2-hydroxyethyl acrylate initiator. The synthesized copolymers can be used to toughen brittle PLLA by incorporating them as an elastomeric phase. Interestingly, the much tougher PLLA was obtained when the commercial PLLA was blended with 10 wt % elastomeric graft copolymer containing pendant PDLA chain. It is believed that the formation of stereocomplex between PLLA matrix and PDLA side chain in the elastomer phase differentiates it from the blend of PLLA and PBA-*g*-PLLA, whose side chain has the same configuration as the matrix PLLA. DSC, XRD, and TEM results support this hypothesis. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 2541–2547, 2013

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INTRODUCTION

Poly(lactide) (PLA) has received extensive attention in the medical and pharmaceutical fields due to its biodegradability and biocompatibility properties.^{1,2} In recent years, its bio-renewability as well as its high modulus and strength have made PLA a promising alternative to petroleum-based plastics. It has been used to produce fibers, film, vehicle interiors, appliance components, food wares, food/beverage packaging, etc.³ Fibers produced from polylactide exhibit low odor retention and excellent moisture wicking properties.^{4,5} However, the inherent brittleness of PLA and its low heat deflection temperature (HDT) have greatly restricted its large scale commercial applications.⁶

Many strategies have been developed to alter the mechanical properties of PLA. Analogous to other brittle polymers, mechanical properties of PLA can be modified by plasticization, copolymerization, and melt blending with flexible polymers, etc. A considerable number of PLA toughening studies have been carried out with the objective of balancing and increasing tensile

strength, impact strength, and modulus. Two good reviews on PLA toughening have been published recently.^{7,8} Among various modifications, melting blending is one of the most straightforward and economic approaches to increase its toughness. So far, various biodegradable and nonbiodegradable polymers, such as polycaprolactone,^{9–11} polyhydroxyalkanoate,^{12,13} soybean oil derivatives,^{14,15} poly(butylenes succinate),¹⁶ polyamide elastomers,¹⁷ rubbers,^{18,19} thermoplastic polyolefin elastomer,²⁰ poly(ethylene-glycidyl-methacrylate),²¹ acrylonitrile-butadiene-styrene copolymer,²² polycarbonate,²³ glycidyl methacrylate-grafted poly(ethylene-octene),²⁴ thermoplastic polyurethane elastomer,²⁵ polyamide11,²⁶ ethylene/*n*-butyl acrylate/glycidyl methacrylate (EBA-GMA) terpolymer,²⁷ polyethylene,^{28,29} and so on, have been used as toughening modifiers for PLA.

On the other hand, the thermal and mechanical properties of PLA are influenced significantly by its tacticity.⁷ Due to the chirality of lactide, PLA can exist in three stereochemical forms: poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly-

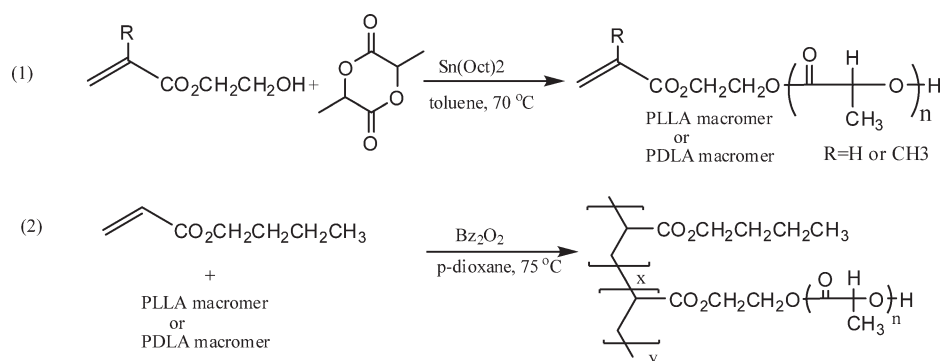


Figure 1. Synthetic scheme of PLA macromers and graft copolymer PBA-g-PLA.

(DL-lactide) (PDLLA).¹ Stereocomplex formed by 1 to 1 blending of enantiomeric PLLA and PDLA was firstly reported by Ikada et al in 1987.³⁰ Since then, stereocomplexation of PLLA and PDLA has been extensively investigated.^{31–36} It not only shows much higher melting point (by 50°C), but also exhibits increased modulus, tensile and elongation at break within a certain molecular weight range, when compared with the corresponding homopolymer.³⁷ The improvement of the properties was attributed to micro-phase structure difference generated as a result of formation of many stereocomplex crystallites which acted as intermolecular cross-links. Attempt to toughen PLA by combining block copolymerization and stereocomplexation has also been reported recently.^{38–40} The increases in Young's modulus and elongation at break of blends were observed in some samples compared to the corresponding enantiopure analogues. These block copolymers were mostly used as thermoplastic elastomers. In a recent paper PDLA-PEG-PDLA triblock copolymer was used as toughening agent for PLLA.⁴¹ The injection molded tensile specimens tested in this study were annealed at 80°C for 4 h. Totally, 5% loss of modulus and 3.6 times increase of elongation at break compared with neat PLLA were seen when 15 wt % of PDLA-PEG-PDLA was added. The improvement of properties was ascribed to a new morphology different from neat PLLA developed in the presence of PDLA-PEG-PDLA. But no comparison between PLLA-PEG-PLLA and PDLA-PEG-PDLA was made in this article.

In many applications, especially in packaging, the transparency of the materials is very important. Blending polymers with different refractive indexes could sacrifice the transparency of the resulted materials. Poly(*n*-butyl acrylate) (PBA) is a sticky, colorless, ductile, and transparent rubbery material. Its refractive index is 1.46–1.47, very close to that of the PLA matrix (1.45). The blend of PLA with PBA has been investigated and it was found that the blend with up to 10 wt % of PBA still displayed good transparency.⁴² Although the elongation at break was increased by about 40 times when 11 wt % PBA was blended with PLA, its modulus decreased by about 60%.

In this article, a series of graft copolymers PBA-g-PLLA and PBA-g-PDLA with various molecular weights and butyl acrylate/PLA ratios were prepared from the copolymerization of *n*-butyl acrylate and PLA macromers. The obtained copolymers, consisting of a plastic phase (PLA) and a rubber phase (PBA), were attempted to toughen PLLA matrix as thermoplastic elastomers.

By employing PBA-g-PLA, the grafted PLA branches act as compatibilizers, while the soft PBA backbone may serve as the toughening agent. In the mean time, because PBA-g-PDLA is capable of forming stereocomplex with the PLLA matrix, we expect that PBA-g-PLLA and PBA-g-PDLA may show different effect as toughening modifiers.

EXPERIMENTAL

Materials

PLA polymer pellets 3051D containing about 96.5% L-lactide (M_w 160,000 with a polydispersity of 1.7) was purchased from NatureWorks LLC. The pellets were dried at 50°C in a vacuum oven overnight before use. L-lactide (99.5%) and D-lactide (99.5%) were purchased from Purac Biochem (Gorinchem, Netherlands) and used as received. 2-hydroxyethyl methacrylate (HEMA) (97%, dried with 4A molecular sieve), 2-hydroxyethyl acrylate (HEA) (97%, dried with 4A molecular sieve), benzoyl peroxide (97%) from Lancaster and tin (II) 2-ethylhexanoate (95%, stannous octoate) from Sigma-Aldrich were used without purification. *n*-Butyl acrylate (*n*-BA) ($\geq 99\%$) from Sigma-Aldrich was passed through a basic alumina column to remove stabilizer. Toluene was purified by passage through an activated alumina column for the removal of protic impurities and through a supported copper catalyst to remove trace oxygen with a solvent purification system connected to glove box. 1, 4-Dioxane was refluxed with KOH and then distilled. Dichloromethane, methanol, and tetrahydrofuran were of analytical grade.

Synthesis of PLA Macromers

Macromers of 2-hydroxyethyl acrylate or methacrylate-terminated PLLA or PDLA having various chain lengths were prepared via ring opening polymerization using HEA or HEMA as initiator in the presence of stannous octoate following a literature method.⁴³ In a typical reaction (macromer PLLA2), 21.6 g (150 mmol) of L-lactide, 0.221 g of stannous octoate (1 wt % of the total weight of lactide and the initiator) were dissolved in 150 mL dry toluene (1 mmol/mL) in a Schlenk flask. To the solution 513.3 mg (4.42 mmol) of HEA was added under Argon. The resulting mixture was stirred at 70°C for 3 days. Toluene was then evaporated using a rotary evaporator. The crude polymer was purified by reprecipitation using CH₂Cl₂ as solvent and methanol as nonsolvent. After drying under vacuum at 60°C for 24 h, 21.3 g of PLLA2 macromer was obtained: GPC

Table I. Polymerization Conditions and Molecular Characteristics of PLA Macromers

Entry	$[LA_0]/[I_0]^a$	M_n (cal.) $\times 10^3$ (g/mol)	M_n (NMR) $\times 10^3$ (g/mol)	M_n (GPC) $\times 10^3$ (g/mol)	PDI	Conv. (%) ^b
PLLA1	33.8	5	5.0	8.5	1.26	99.0
PLLA2	33.8	5	4.8	8.1	1.23	98.2
PLLA3	68.6	10	9.8	14.0	1.07	98.6
PLLA4	139	20	16.7	28.5	1.10	98.5
PDLA1	33.8	5	5.1	8.5	1.23	98.7
PDLA2	33.8	5	4.4	8.3	1.20	98.8
PDLA3	68.6	10	9.8	13.4	1.07	97.2
PDLA4	139	20	16.7	28.4	1.10	98.0

The polymerization was carried out at 70°C in toluene.

^aMolar ratio of monomer to initiator.

^bfrom ¹H-NMR spectroscopy.

For PLLA1 and PDLA1, 2-hydroxyethyl methacrylate as initiator; for PLLA2-PLLA4 and PDLA2-PDLA4, 2-hydroxyethyl acrylate as initiator.

$M_n = 8100$ and $M_w = 10000$; ¹H-NMR: 1.57 (d, 3nH); 5.16 (q, (n-1)H); 5.86 (dd, 1H); 6.12 (dd, 1H); 6.42 (dd, 1H).

Synthesis of PBA-g-PLA Copolymers

PBA-g-PLA copolymers were prepared by free radical polymerization method. In a typical reaction, 9 g of *n*-BA, 3 g of PLLA macromer PLLA2, and 120 mg (1 wt %) of benzoyl peroxide (BPO) were dissolved in 25 mL dioxane in a 100-mL Schlenk flask. The resulting solution was bubbled with argon for about 30 min to remove air or degassed by three cycles of freeze-pump-thaw and then heated to 70°C with stirring overnight. The hot solution was poured into methanol to precipitate the graft copolymer. The precipitate was dried under reduced pressure to yield 10.7 g of graft copolymer PBA-g-PLLA (PBA-g-PLLA2, PLLA2 stands for the corresponding macromer), with GPC $M_n = 53,000$ and $M_w = 185,500$. ¹H-NMR: 0.94 (t, 3nH); 1.36 (m, 2nH); 1.57 (m) + 1.90 (m) + 2.27 (m) (8H); 4.03 (t, 2nH); 5.16 (q, (n-1)H).

Polymer Characterization

NMR spectra were recorded in CDCl₃ and the chemical shifts were expressed in ppm with respect to the residue chloroform signal at 7.26 ppm. The reaction conversion was calculated based on the ratio of the integration of peaks due to methine proton in polymer and monomer. The number and weight average molecular weights (M_n and M_w) and polydispersity indices (M_w/M_n) were measured with a gel permeation chromatography (GPC) system equipped with Waters 515 HPLC pump, 717plus autosampler, 2414 refractive-index detector and Styragel HR4E column. THF was used as eluent (the flow rate: 1 mL/min, 25°C) and mono-dispersed PS as standards.

Melt Blend

Melt blending of PLLA (Natureworks 3051D) and 10 wt % of PBA-g-PLLA or PBA-g-PDLA was carried out at 180°C, 50 rpm for 10 min by using a Barbender mixer.

Compression Molding

Mechanical testing samples were prepared by compression molding the dried melt blends at 200°C and 6000 lb for 5 min

using a Carver press and a square mold of dimensions 100L \times 100W \times 1.2H mm³.

Specimen Preparation

Dumb bell-shaped tensile specimens were punched with a CEAST hollow die punch (die type: ASTM D638 type V) from the hot compression-molded plates.

Wide-Angle X-ray Scattering

2D WAXS patterns of the samples were recorded in the reflection mode with a Bruker D8 DISCOVER with a general area detector diffraction system (GADDS) using Cu K α radiation ($\lambda = 0.154$ nm) generated at 40 kV and 40 mA. Each sample was scanned for 10 min.

Differential Scanning Calorimeter

Thermal analysis of the examined samples (melt blend and then compression molded plates) was conducted using a TA Instruments DSC (TA 2920 or Q100). A sample of (5–10 mg) in an aluminum pan was heated from 20 to 250°C at a heating rate of 10°C/min under nitrogen flow (the first heating scan) and kept at this temperature for 5 min, then cooled to 20°C, and heated again (the second heating scan).

Table II. Results of Copolymerization of Acrylate Terminated PLA Macromers with nBA

Entry	$[W_{nBA}]/[W_{macromer}]$	M_n (GPC) $\times 10^3$ (g/mol)	PDI	W_{PBA}/W_{PLA}^a
PBA-g-PLLA1	3:1	45.0	3.7	2.6
PBA-g-PLLA2	3:1	53.0	3.5	3.0
PBA-g-PLLA3	3:1	61.2	2.7	2.4
PBA-g-PLLA4	3:1	100.3	2.9	2.3
PBA-g-PDLA1	3:1	142.0	2.9	2.8
PBA-g-PDLA2	3:1	59.4	3.8	3.0
PBA-g-PDLA3	3:1	72.7	3.3	2.7
PBA-g-PDLA4	3:1	92.4	3.3	2.4

^aBased on NMR.

Table III. Tensile Data of PLLA and Blends

Entry	Sample	Wt % PBA in blend	Wt % PDLA in blend	Young's Modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
1	PLLA (control)	0	0	3.2 ± 0.2	49.4 ± 4.6	4.2 ± 1.3
2	PLLA + 10 wt % PBA-g-PLLA3	7.1	0	3.2 ± 0.5	37.2 ± 2.5	6.2 ± 2.9
3	PLLA + 10 wt % PBA-g-PDLA3	7.2	2.8	2.5 ± 0.2	25.2 ± 0.9	23.3 ± 12.1
4	PLLA + 10 wt % PBA-g-PLLA4	7.0	0	3.2 ± 0.2	30.5 ± 0.8	7.0 ± 3.1
5	PLLA + 10 wt % PBA-g-PDLA4	7.1	2.9	2.7 ± 0.1	25.9 ± 1.1	29.7 ± 13.2

Tensile Test

Tensile properties were determined using an Instron 5566, at a tensile speed of 1.0 mm/min at room temperature.

TEM Study

The Transmission Electron Microscope (TEM) samples were obtained by cryo-sectioning (Leica) of frozen samples with diamond knife which were subsequently mounted on a carbon coated copper grid. These thin sections were then observed under TEM (JEOL 2100) with an accelerating voltage of 200 keV.

RESULTS AND DISCUSSION

Synthesis and Characterization of Graft Copolymers

The synthetic scheme of acrylate terminated PLA macromers and their copolymerization with nBA to produce PBA-g-PLA copolymers is shown in Figure 1.

The molecular weight of PLA can be easily tailored by adjusting the molar ratio of monomer to initiator. Table I summarizes the average molecular weights of the macromers as determined by NMR and GPC. The conversion of lactide monomer was determined based on ¹H-NMR spectroscopy from the integration ratio of the methine quartets of the lactide monomer (δ 5.02 ppm) and of the polymer (δ 5.16 ppm). The conversions of lactide for all reactions are quite high, close to 100%. M_n calculated from the integration ratio of the methine quartets (δ 5.16 ppm) to CH₂ = (dd, δ 5.86 and 6.42 ppm, respectively) of the acrylate end group is very close to that calculated from lactide/initiator ratio, but lower than that measured by GPC. The higher GPC molecular weight may be attributed to the difference in hydrodynamic radius between poly(styrene) standards and PLA.⁴⁴ The polydispersity (PDI) of all PLA macromers is very narrow.

PBA-g-PLA graft copolymers of various compositions containing either PLLA or PDLA branches were prepared via free radical polymerization. The results are summarized in Table II. The graft copolymers listed in Table II are labeled according to the corresponding macromers. For example, PBA-g-PLLA1 means that the copolymer is made from nBA and the macromer PLLA1. Although the PDI for all macromers is quite narrow (less than 1.3), all graft copolymers have relatively wide PDI, due to the poor control in molecular weight using random radical polymerization. The composition of the graft copolymers can be estimated by ¹H-NMR from the integration ratio of methyl triplets (δ 0.94 ppm) of PBA and the methine quartets

(δ 5.16 ppm) of PLA. Except PBA-g-PLLA2 and PBA-g-PDLA2, the results in Table II show that the weight ratio of PnBA to PLA is always lower than the calculated value, which indicates the incomplete conversion of *n*-butyl acrylate.

PLLA Toughening with As Prepared PBA-g-PLA

Results Obtained. We chose two pairs of the synthesized graft copolymers to test their efficiency as PLLA toughness modifiers. Commercial PLLA (NatureWorks 3051D) was melt blended with 10 wt % of PBA-g-PLA copolymers. The tensile test results are summarized in Table III. It is noted that the amount of PBA rubber in all blends is about 7 wt %. Commercial PLLA is so brittle that its elongation at break is only ~4.2%. When PLLA is blended with the graft copolymers containing PLLA side chains (entry 2 and 4), modulus remains almost unchanged compared to the neat PLLA, while tensile strength decreases obviously and elongation at break increases slightly. However, when PLLA is blended with the graft copolymers containing PDLA side chains (entry 3 and 5), the dramatic increase of elongation at break is achieved, which increases about 6 to 7 times, compared with PLLA control, although both modulus and tensile strength decrease by about 20 and 50%, respectively. However, when 11 wt % PBA was blended with PLA, its modulus decreased by about 60% and tensile strength dropped by about 40%, respectively.⁴² On the basis of the composition of graft copolymers and its weight percentage in the blend, the actual content of PDLA in the blend is less than 3 wt %. It is

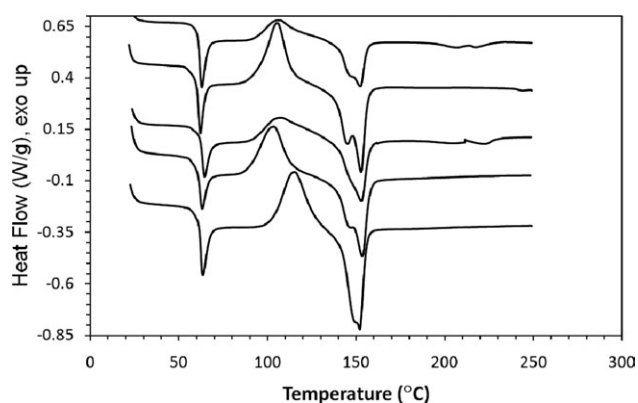


Figure 2. DSC thermograms (1st heating scan with a rate of 10°C/min in N₂ gas flow) for (1) neat PLLA (3051D) and (2 to 5) PLLA melt blends with 10 wt % PBA-g-PL(D)LA graft copolymers. The curves have been offset for clarity. Sample labels follow Table III.

Table IV. Thermal Characteristics of PLLA and Blends

Entry	Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_f (J/g)	$(\Delta H_c + \Delta H_f)$ (J/g)
1	PLLA (control)	62.3	115	152	-26.9	30.2	3.3
2	PLLA + 10 wt % PBA-g-PLLA3	61.9	104	153	-24.6	27.9	3.3
3	PLLA + 10 wt % PBA-g-PDLA3	63.3	107	153 (T_{m2} 203)	-18.5	19.2 (ΔH_{f2} 1.9)	2.8
4	PLLA + 10 wt % PBA-g-PLLA4	61.2	106	153	-26.5	29.3	2.9
5	PLLA + 10 wt % PBA-g-PDLA4	61.7	106	152 (T_{m2} 207)	-13.7	14.1 (ΔH_{f2} 3.7)	4.1

T_g , glass transition temperature; T_{cc} , cold crystallization temperature; T_m , melting temperature; ΔH_{cc} , heat of crystallization; ΔH_f , heat of fusion. Data are not normalized to the fraction of PLA.

also noticed that the graft copolymer containing longer PDLA chain leads to higher elongation at break (compare entry 3 and 5). Much tougher PLLA is achieved by addition of 10 wt % of the as-prepared graft copolymers containing PDLA branches demonstrates that they are efficient toughness modifiers. We propose that the different interfacial interaction between PLLA/PBA-g-PLLA and PLLA/PBA-g-PDLA leads to their different effect as PLLA tougheners. In PLLA/PBA-g-PDLA blend, the stereocomplex between matrix PLLA and side chain PDLA in the graft copolymer (rubber phase) is formed, which provides extra interfacial adhesion and thus results in a different morphology from that of the blend of PLLA/PBA-g-PDLA. This assumption was confirmed by the following DSC, XRD and TEM results.

Thermal Properties Analysis. Thermal properties of the compression molded samples for toughening tests were determined by DSC. Because the initial crystallinity of PLA in the molded samples influences the final mechanical properties of the blends, only DSC data from the first heating scan are presented (Figure 2). Table IV shows that the difference of T_g and melting temperature (T_m) between neat PLLA and PLLA in the blends is very small. However, the cold crystallization peak temperature of PLA in the blends is about 10°C lower than that of neat PLA. The decrease of cold crystallization temperature indicates the enhancement of crystallizability, which is commonly observed for plasticized PLA systems and is due to the increased segmental mobility of the PLA chains by plasticization.^{45,46} The marginal decrease of T_g could be due to the limited plasticization of polymers. What is worth noticing is that for samples containing PDLA components, ΔH_c values are significantly lower than that of the corresponding blends containing the graft copolymers with PLLA branches or PLLA control, which indicates a lower crystallinity. Schmidt and Hillmyer found that the addition of PDLA to PLLA led to the reduction in the overall extent of PLLA crystallization, although it enhanced PLLA crystallization rate due to the nucleating function of the formed stereocomplex.⁴⁷ They attributed the decreased extent of crystallization to the hindered mobility of the PLLA chains due to tethering by the stereocomplex. Indeed, for Samples 3 and 5, there is an extra broad and small melting peak at ca. 205°C, suggesting the formation of stereocomplex between matrix PLLA and pendant PDLA chains in the graft copolymers and it is at low amount. When the blend contains PBA-g-PDLA copolymer, the stereocomplex crystallites formed between PLLA ma-

trix and graft copolymers containing PDLA branches during compounding or hot compression process trap the soft PBA segments within the amorphous regions of the crystalline lamellae. The decrease in chain mobility because of the formed stereocomplex crystals will then trap the rest of polymers into the amorphous phase, which prevents the formation of more PLLA crystallites (thus lower ΔH_c values and lower crystallinity).⁴¹ Most percentage of the stereocomplex should be formed during compounding or hot compression process, which can be confirmed by WAXS (Figure 3). WAXS patterns of the blend Samples 3 and 5 are consistent with those of the stereocomplex.⁴⁸ In addition, the sums of ΔH_c and ΔH_f for all samples are very small, indicating the amorphous property of all samples due to the slow crystallization of PLLA under our experimental conditions, which rules out the effect of crystallinity on tensile property.

Morphological Features. Besides the level of crystallinity, the mechanical property of a polymer also depends largely on their solid-state morphology. When PBA-g-PLA copolymer is added to PLLA, a two phase structure with PBA particles dispersed in continuous PLLA phase should be developed. To confirm this and verify the difference of microstructures, TEM images of blend of PLLA/PBA-g-PLLA and PLLA/PBA-g-PDLA (before and after tensile tests) were obtained. The specimens were cut in direction perpendicular to the direction of tensile force.

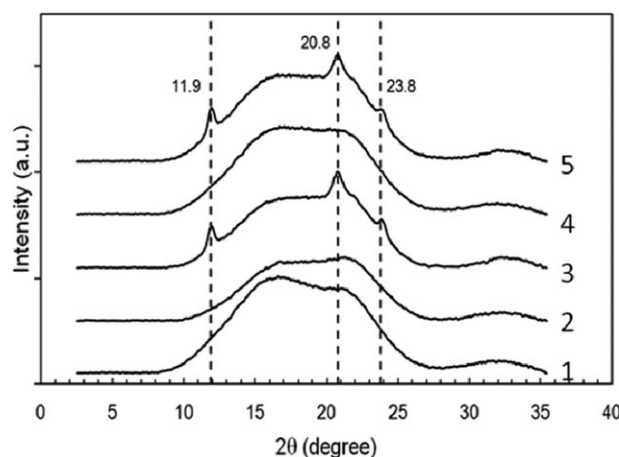


Figure 3. WAXS for the neat PLA, melt blended and compression molded samples. The curves have been offset for clarity. Sample labels follow Table III.

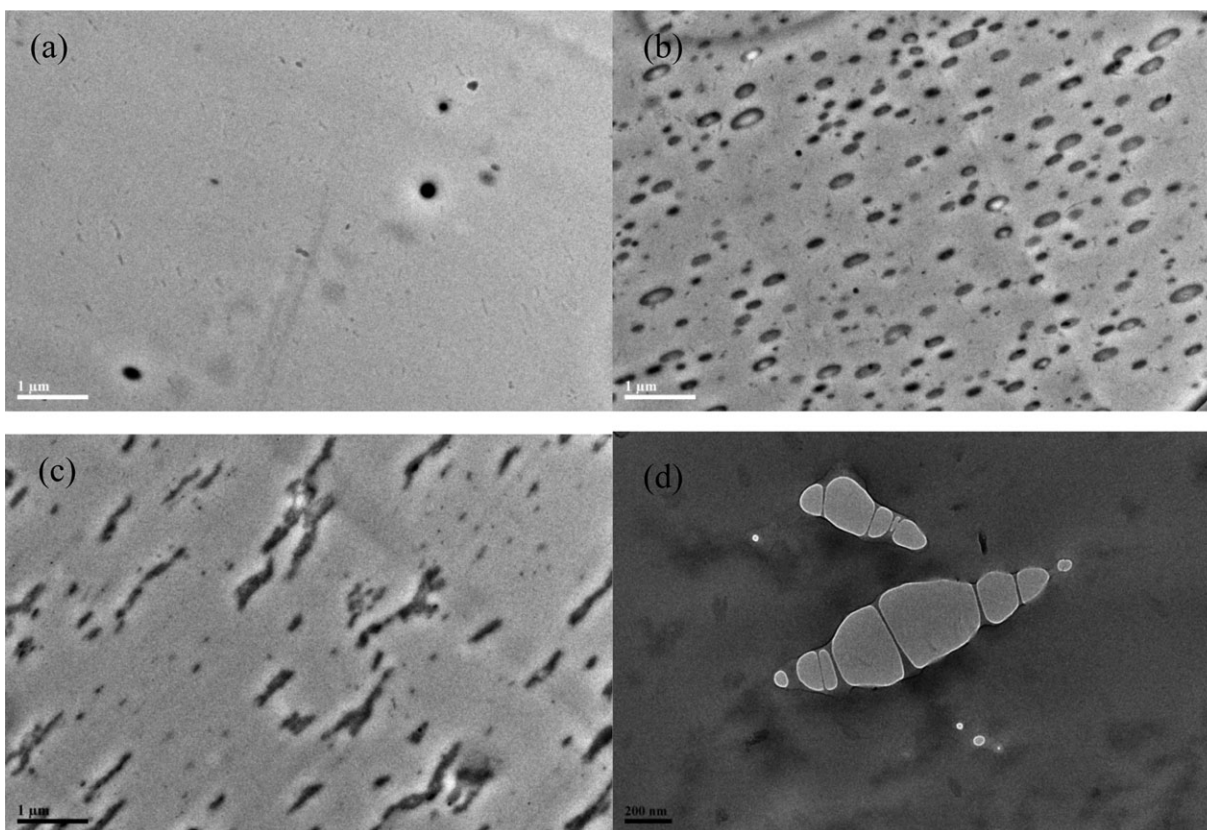


Figure 4. TEM micrograph of PLA/PBA-g-PLA blends. (a) PLLA NatureWork 3051D; (b) PLLA3051D+10 wt % PBA-g-PLLA4; (c) PLLA3051D+10 wt % PBA-g-PDLA4 before tensile testing; (d) PLLA3051D+10 wt % PBA-g-PDLA4 after tensile test.

Figure 4 are TEM images of PLLA control (a), PLLA + 10 wt % PBA-g-PLLA4 (b), PLLA + 10 wt % PBA-g-PDLA4 (before tensile testing) (c) and PBA-g-PDLA4 (after tensile testing) (d), respectively. For neat PLLA, nothing can be seen due to single phase. For the blends, phase separation microstructures are visible, in which PBA particles are dispersed in PLLA matrix, but images b and c are very different. Dispersed sea-island morphology in Figure 4(b) suggests very low interfacial adhesion between the PBA-g-PLLA4 and matrix PLLA. Figure 4(c) shows rubber particles have much higher aspect ratio, indicating a better interfacial adhesion between PBA-g-PDLA4 and matrix PLLA. The morphological difference possibly results from the preferentially formed stereocomplex between pendant PDLA in graft copolymer and matrix PLLA (as stereocomplex has greater crystallization rate than that of homopolymer), which traps the soft PBA segments within the amorphous regions of the crystalline lamellae of the PLLA matrix. After tensile test, crazes were developed in the sample of PLA+10 wt% PBA-g-PDLA4 (middle part of the dog bone tensile bars turned white) as shown in Figure 4(d).

CONCLUSIONS

A series of PBA-g-PLLA and PBA-g-PDLA graft copolymers of varying compositions were prepared by the combination of ring opening polymerization and free radical polymerization and characterized by NMR and GPC. The synthesized PBA-g-PLA copolymers were used to toughen brittle PLLA. Tensile tests show that great increase of elongation at break was obtained when commer-

cial PLLA was blended with 10 wt % of graft copolymer with PBA-g-PDLA; when PLLA was blended with 10 wt % of PBA-g-PLLA, the elongation at break only increases slightly. It is believed that the formation of stereocomplex between PLLA and PDLA, which increases interfacial adhesion between the phase-separated PLLA and PBA domains, plays a significant role in the toughening of PLLA. The hypothesis was confirmed by DSC, XRD, and TEM techniques. The results also show that the branch length of the graft copolymer (M_n of PLA) has some influence on the resultant toughening. TEM images show the different microstructures between PLLA blended with PBA-g-PDLA and PLLA with PBA-g-PLLA. Our study demonstrates that PBA-g-PDLA graft copolymers we synthesized are promising PLLA toughness modifiers. Studies on optimizing the structures of the PBA-g-PLA copolymers (modifying PLA chain length, by grafting from method etc.) and promoting the PLLA/PDLA complex formation at the interface by isothermal crystallization are currently undergoing.

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