

Enhanced Impact Properties of Polylactide by Poly(lactide-*b*-butadiene-*b*-lactide) Triblock Copolymer

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Abstract: Polylactide (PLA) was copolymerized with polybutadiene (PBD) to improve its impact properties. Triblock copolymers of poly(lactide-*b*-butadiene-*b*-lactide) (PLBDL) were obtained by the ring opening polymerization of lactide using tin 2-ethylhexanoate (Sn(Oct)₂) and hydroxyl terminated polybutadiene (HTPBD) as a catalyst and macroinitiator, respectively. PLA and PLBDL were blended at 5, 10, and 15 wt% PLBDL. After blending, the samples exhibited a shift in the T_g of PLA, which means that PLBDL and PLA are compatible. The tensile strength and Young's modulus decreased with increasing PLBDL. On the other hand, the PLA/PLBDL blend containing 10 wt% PLBDL showed a 4 fold increase in impact strength. In addition, the elongation at break of the blend containing 10 wt% PLBDL was 467%, showing a 27 fold increase compared to neat PLA. This suggests that the PBD chains on the PLBDL backbone have a significant effect on the impact properties of PLA.

Keywords: impact strength, polylactide, polybutadiene, triblock copolymer.

Introduction

Polylactide (PLA) is a synthetic aliphatic polyester derived from renewable resources, such as corn, sugar beet and cassava,^{1,2} which can ultimately be degraded under composting conditions. PLA has unique properties, such as biodegradability, biocompatibility and good mechanical properties,^{3,4} and has been used in biomedical and food packaging applications.⁵⁻¹⁰ On the other hand, the PLA has some drawbacks, such as brittleness, low crystallization rate and low impact strength.¹¹ Therefore, it has limitations in applications as common plastic materials. Many studies have been attempted to improve the properties of PLA, particularly the impact properties, by blending with other polymers, such as rubber,¹² poly(ethylene glycol) (PEG),^{13,14} acrylonitrile-butadiene-styrene copolymer (ABS).¹⁵ The rubbery polybutadiene moiety can help increase the impact strength of PLA. Nevertheless, the immiscibility between these impact modifying additives and the PLA matrix is a major drawback. Hiltner *et al.*^{13,14} reported the phase separation of a blend composed of PLA and PEG. Although the PLA/PEG blend has desirable mechanical properties, the mechanical properties of this blend decrease with time due to phase separation. Therefore, for stable mechanical properties and improved interfacial interactions between two phases, the blends require agents, such as compatibilizers and block copolymers.¹⁶

Telechelic polybutadiene has functional groups at both termini on the chain and can be used in potential applications, such as pressure-sensitive adhesives, compatibilizers for polymer blends, and building blocks for segmented block copolymers.¹⁷ Therefore, hydroxy terminated polybutadiene (HTPBD), which is polymerized by ring opening metathesis polymerization (ROMP), can be used for the segment of the block copolymer. In addition, the high mobility of the non-crosslinking polybutadiene chain helps increase the impact strength.¹⁸

This study examined the reinforcing effects of a block copolymer composed of PLA and PBD on the impact strength of PLA. HTPBD was polymerized by ROMP and PLA was copolymerized at both termini of HTPBD by ring opening polymerization (ROP) using tin 2-ethylhexanoate. Subsequently, poly(lactide-*b*-butadiene-*b*-lactide) triblock copolymer (PLBDL) was blended with PLA. The addition of PLBDL in PLA improves the mechanical properties of PLA, particularly the impact strength.

Experimental

Materials. 1,5-Cyclooctadiene (COD, 98%) and sodium methoxide (NaOMe) were purchased from TCI, Japan. COD was freshly prepared prior to use by mixing with CaH₂ and distillation to remove moisture. *cis*-1,4-Diacetoxy-2-butene, first generation Grubbs' catalyst, L-lactide and tin 2-ethyl hexanoate (Sn(Oct)₂) were supplied by Aldrich Chemical

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Company, Inc., USA and used as received. Poly(lactide) (PLA) pellets for compounding were a kind gift from NatureWorks LLC, USA.

Preparation of Hydroxy Terminated Polybutadiene (HTPBD). The synthesis of hydroxyl-terminated polybutadiene (HTPBD) was reported by Grubbs *et al.*¹⁹ Purified COD (105.84 g, 0.98 mol) and *cis*-1,4-diacetoxy-2-butene (4 g, 23.27 mmol) were placed in a 3-neck round bottom flask with a mechanical stirrer under N₂. Grubbs' catalyst (0.16 g, 0.2 mmol in dichloromethane) was injected into the mixture through a septum. The mixture was stirred in an oil bath at 45–55 °C for 6 h. The light brown mixture was precipitated into acidic methanol (15 mL of 1 M HCl in 500 mL methanol) to quench the reaction and remove the unreacted monomer and catalyst. The obtained polymer was washed three times with methanol. The polymer was then dissolved in 120 mL anhydride THF. The acetoxy end chains were hydrolyzed by adding NaOMe (3.08 g, 0.06 mol in methanol) to the solution drop wise at 0 °C for 1 h with constant stirring for 6 h. The solution was precipitated in acidic methanol and washed with methanol/HCl, methanol/water and methanol to obtain hydroxyl end groups. The polymer was then dissolved in 1 liter of dichloromethane, isolated by rotary evaporation and subjected a high vacuum at room temperature.

Preparation of Poly(lactide-*b*-butadiene-*b*-lactide) Triblock Copolymer (PLBDL). HTPBD (17.5 g, 1.75 mmol) and L-lactide (15.12 g, 0.1 mol) were placed in a 3-neck round bottom flask and heated to 140 °C under N₂ until a clear mixture was obtained. Sn(Oct)₂ (0.34 mL, 1.05 mmol in 2 mL of toluene) was added *via* a septum. Polymerization was carried out for 1 h and the product was precipitated in *n*-hexane. The polymer was filtered and washed with methanol. PLBDL was dried overnight in a vacuum oven at 40 °C.

Preparation of PLA/PLBDL Blend. A series of PLA/PLBDL blends was prepared at PLA to PLBDL ratios of 95/5, 90/10 and 85/15 (wt%/wt%). For example, 5 wt% PLBDL in PLA/PLBDL blend was prepared by solution blending. PLA pellets (38 g) were dissolved in 750 mL of chloroform and PLBDL (2 g) was dissolved in 50 mL of chloroform. The solutions were mixed by stirring for 2 h and casted in a mold. The solvent was evaporated in a convection oven at 60 °C for 1 day and a vacuum oven at 60 °C for 2 days.

Characterization. The ¹H NMR spectra were obtained on a Varian Inova 400 at 400 MHz under ambient temperature, using chloroform-*d* and tetramethylsilane (TMS) as the corresponding solvent and internal chemical shift standard, respectively. The Fourier transform infrared (FTIR) spectra were obtained using a Bruker Equinox 55 spectrometer. The number-average molecular weight (*M_n*) of the polymer was measured by gel permeation chromatography (GPC) using a Water Breeze HPLC System. The tensile strength, Young's modulus and elongation at break were measured under uniaxial elongation at room temperature in

accordance with the ASTM D638 standards using a UTM from Hounsfield Test Equipment. Each sample had a dog-bone shape and the resulting value was an average of at least five measurements. The dynamic mechanical properties of the blends were investigated using a DMA (Q800, TA instruments). A frequency of 1 Hz and a 30 μm amplitude of dynamic deformation were used in Multi-stress-strain mode. The samples were heated from room temperature to 120 °C at a heating rate of 3 °C/min. A notched Izod test (Water 410 T50) of the blends was performed in accordance with the ASTM D256 standards at room temperature.

Results and Discussion

Characteristics of Poly(lactide-*b*-butadiene-*b*-lactide) Triblock Copolymer (PLBDL). The preparation of the HTPBD has been reported previously.¹⁹ Briefly, a neat mixture of COD and the simple allylic chain transfer agent together with a ruthenium metathesis catalyst were pre-

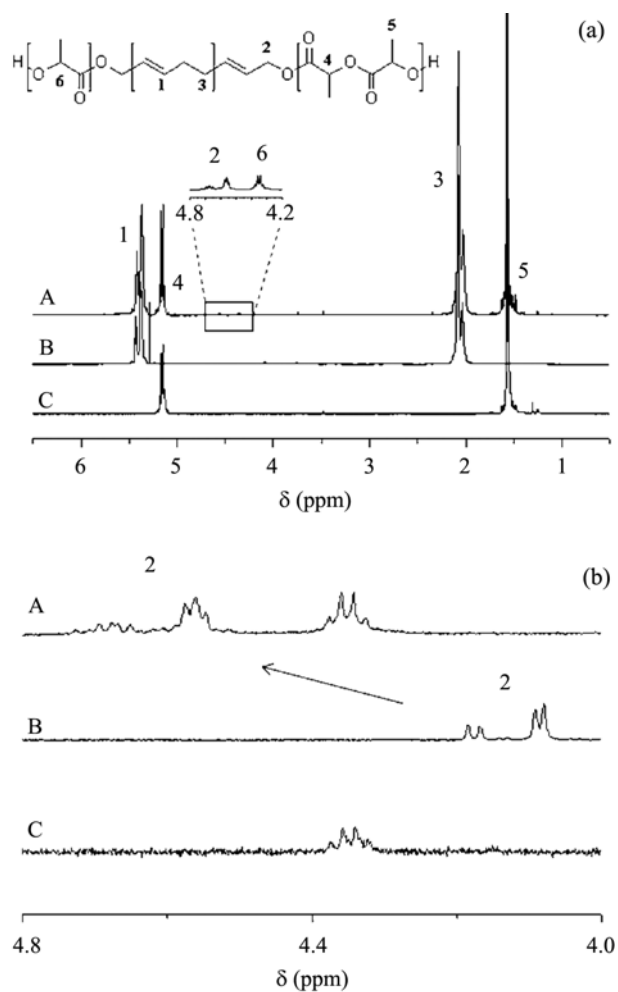


Figure 1. (a) ¹H NMR spectra (CDCl₃) of the PLA, HTPBD, and PLBDL. (b) expansion of the chemical shift region: PLBDL (A), HTPBD (B), and PLA (C).

pared. The Grubbs' catalyst is relatively stable in air, which allows easy handling. ^1H NMR spectroscopy of HTPBD (Figure 1a(B) shows the characteristic peaks at δ of H-3 (1.9-2.2 ppm), H-1 (5.0-5.7 ppm) and H-2 (4.09-4.18 ppm). H-2 is methyl proton at the end chain of HTPBD. HTPBD was applied as a macroinitiator for the ROP of lactide. Tin 2-ethyl hexanoate ($\text{Sn}(\text{Oct})_2$) was reported as an effective catalyst for ROP.²⁰ After copolymerization with lactide, the ^1H NMR spectrum of PLBDL (Figure 1a(A) showed the characteristic peaks for both lactide and butadiene, which is in contrast to the spectra of HTPBD and PLA (Figure 1a(B) and (C), respectively). On the other hand, it is difficult to confirm that the obtained spectrum was not a mixture of the two polymers. The expansion of the chemical shift region from δ of 4.0 to 4.8 ppm (Figure 1(b)) shows an upfield shift in the peak of the methylene proton (H-2) at the end chain of HTPBD at $\delta=4.56$ -4.67 ppm. This was attributed to the hydroxyl group of HTPBD acting as a nucleophile to open the ring of the lactide monomer and generate an ester bond to conjugate with the butadiene chain. The FTIR spectra of PLBDL (Figure 2) revealed the characteristic functional groups of both PLA and HTPBD. Figure 2(A) shows the alkene stretching peak of HTPBD at 1657 (*cis*) and 718 (*trans*) cm^{-1} . In addition, the carbonyl stretching peak of PLA appears at 1758 cm^{-1} . Quantitative analysis of ^1H NMR was used to determine the mole fraction of PLA in PLBDL by comparing the integral peak of the methyl proton of the lactide segment (H-5) and methylene proton (H-3) of the butadiene segment. The methylene proton (H-2) was applied as an internal standard. The calculation was performed

using the following equation

$$\text{mole fraction of PLA} = \frac{(I_{\text{H-5}}/3)/(I_{\text{H-2}}/2)}{(I_{\text{H-3}}/2)/(I_{\text{H-2}}/2)}$$

The mole fraction of PLA in PLBDL was 0.43. In addition, the molecular weight of HTPBD and PLBDL were measured by GPC, as shown in Table I.

Compatibility of the PLA/PLBDL Blend. In a binary system, the glass transition temperature (T_g) can be used to determine if the two polymers are compatible. In this study, DMA was used to confirm the effect of PLBDL on PLA. Figure 3 shows the relationship between temperature and storage modulus (E') (Figure 3(a) including $\tan \delta$ of the PLA/PLBDL blend (Figure 3(b)). At higher temperatures, E' increased with increasing PLBDL content. In addition,

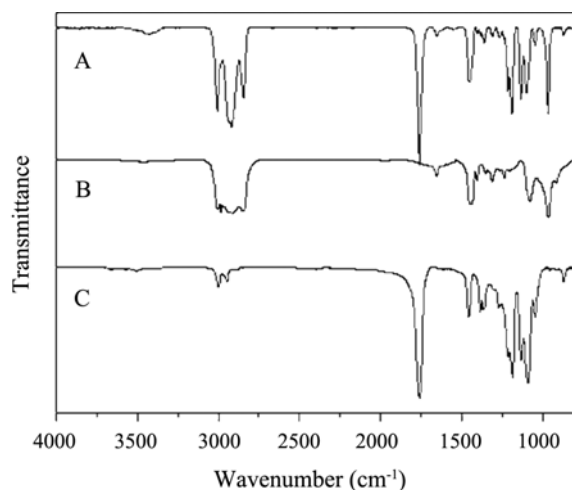


Figure 2. FTIR spectra of the PLA, HTPBD, and PLBDL: PLA (A), HTPBD (B), and PLBDL (C).

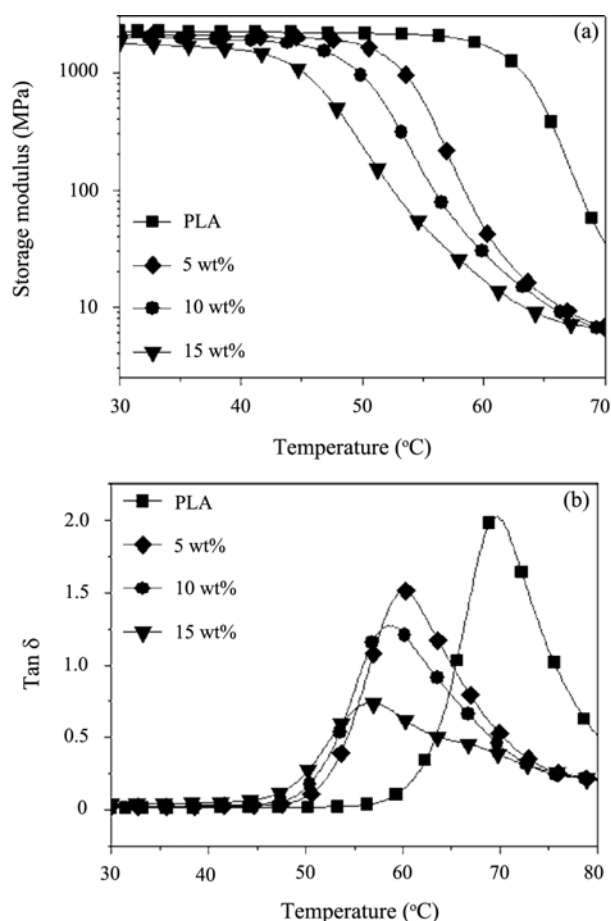


Figure 3. DMA data of the PLA/PLBDL blends with 5, 10, and 15 wt% of PLBDL: storage modulus of the blends (a) and $\tan \delta$ of the blends (b).

Table I. Polymerization of L-Lactide (in bulk at 140 °C) Using $\text{Sn}(\text{Oct})_2$ and HTPBD as the Coinitiators

Sample Name	Lactide/ $\text{Sn}(\text{Oct})_2$	Lactide/HTPBD	Yield (%)	M_n (g/mol)	PDI
HTPBD	-	-	-	10,130	1.83
PLBDL	100	60	-	20,204	1.69

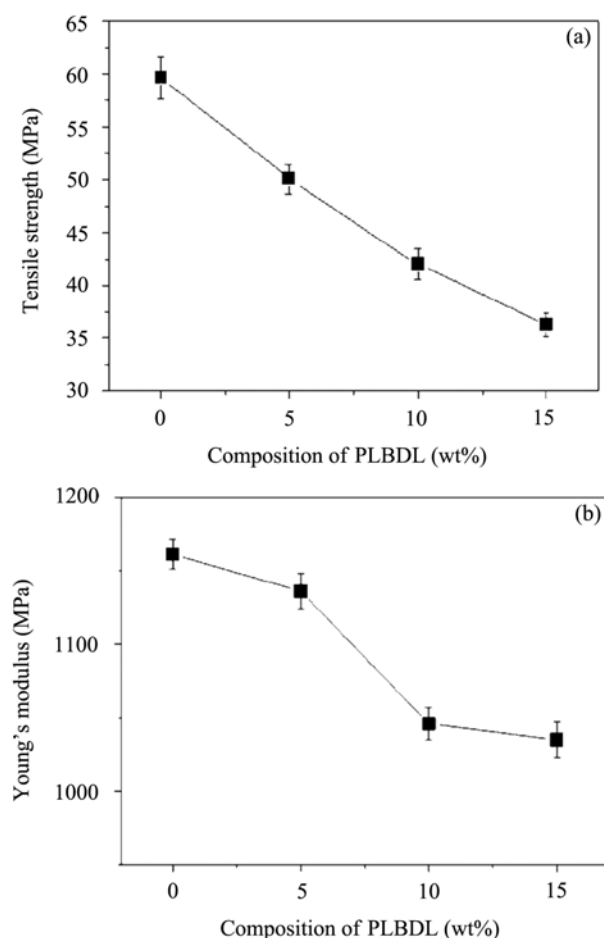


Figure 4. UTM data of the PLA/PLBDL blends with 5, 10, and 15 wt% PLBDL: tensile strength of the blends (a) and Young's modulus of the blends (b).

the peak of $\tan \delta$ which indicates the T_g of the materials, shifted toward a lower temperature with increasing PLBDL content. This highlights the compatibility between PLA and PLBDL due to the PLA segments on the PLBDL chain.

Mechanical Properties of PLA/PLBDL Blends. Figure 4 shows the tensile properties. When the PLBDL content was 10 wt%, the tensile strength (Figure 4(a)) and Young's modulus (Figure 4(b)) of the PLA/PLBDL blends were 30% and 10% lower, respectively, than neat PLA. The polymer chain has high mobility considering the structure of PLBDL, which has a polybutadiene segment as the softening part. This may enhance the relief for tensile stress. The elongation at break of the blend also supported the results of the tensile strength and Young's modulus as the increasing elongation of the PLA/PLBDL blend, containing 10 wt% PLBDL, to 467%. This indicates a 27 fold increase compared to neat PLA. These characteristics can be explained as the conventional behavior of the elongation at break of the plastic deformation zone as showing necking. Ishida *et al.*¹⁸ reported an increase in the elongation at break of the

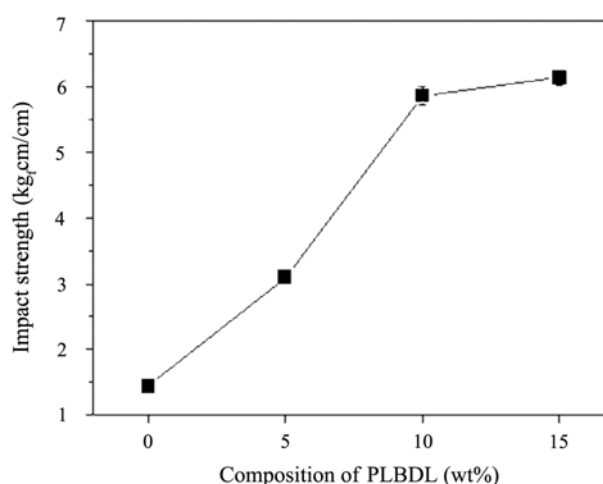


Figure 5. Impact strength of the PLA/PLBDL blends with 5, 10, and 15 wt% of PLBDL, as measured using a notched Izod test machine.

isoprene rubber/PLA blend. The acrylonitrile-butadiene rubber/PLA blend was affected by the chain mobility of the rubber compound.

Figure 5 shows the results of the Izod test of PLA and PLA/PLBDL blends. The impact strength was increased by the addition of PLBDL, which means that PLBDL performed as an impact modifier. Cohen *et al.*²¹ reported an increase in the impact strength of a polystyrene blend due to the presence of low molecular weight PBD. In addition, they reported that fracture propagation occurred through the PBD pools by examining the fractured surface. This suggests that the low molecular weight PBD had a significant and favorable effect on the toughness. The impact strength of the blend containing 10 wt% of PLBDL was 5.86 kg.cm/cm, which is approximately 4 times higher than the value for neat PLA. In addition, the impact strength of the PLA/PLBDL blend with 15 wt% PLBDL was increased to 6.14 kg.cm/cm. The change in impact strength until 10 wt% PLBDL was remarkable. On the other hand, the impact strength of the blend after adding 15 wt% PLBDL was increased slightly, which means that the optimal amount of PLBDL in PLA/PLBDL blend is 10 wt%.

Conclusions

PLBDL was prepared by combining ROMP and ROP. HTPBD and Sn(Oct)₂ were used as the macroinitiator and catalyst, respectively. The amount of PLA on the PLBDL chain was approximately 50%. The shift of the T_g of PLA to a lower temperature after blending with PLBDL confirmed that PLBDL and PLA have good compatibility. By blending PLA with 10 wt% PLBDL, the elongation at break of blend was increased 27 fold compared to neat PLA, but the tensile strength and Young's modulus of the blend was decreased

30% and 10%, respectively. Moreover, a 4 fold increase in the impact strength of PLA was achieved. Overall, PLBDL is a suitable impact modifier for PLA without additives.

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