Bio-Based Diblock Copolymers Prepared from Poly(lactic acid) and Natural Rubber

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ABSTRACT: New bio-based diblock copolymers were synthesized from poly(lactic acid) (PLA) and natural rubber (NR). NR polymer chains were modified to obtain hydroxyl telechelic natural rubber oligomers (HTNR). Condensation polymerization between PLA and HTNR was performed at 110°C during 24 or 48 h. The molecular weight of PLA and HTNR and the molar ratio PLA : HTNR were varied. The new ester linkage in the diblock copolymers was determined by ^{1}H-NMR. The molecular weight of the diblock copolymers determined from SEC agreed with that expected from calculation. The thermal behavior and degradation temperature were determined by DSC and TGA, respectively. The diblock copolymers were used as a toughening agent of PLA and as a compatibilizer of the PLA/NR blend. PLA blended with the diblock copolymer showed higher impact strength, which was comparable to the one of a PLA/NR blend. The former blend showed smaller dispersed particles as showed by SEM images, indicating the increase in miscibility in the blend due to the PLA block. The compatibilization was effective in the blends containing ∼10 wt % of rubber. At a higher rubber content (>10 wt %), coalescence of the NR and diblock copolymer was responsible of the larger rubber diameter in the blends, which causes a decrease of the impact strength. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41426.

INTRODUCTION

Poly(lactic acid) or polylactide (PLA) is a well-known bio-based polymer. The ester linkage in its chemical structure allows PLA to be biodegradable although its biodegradation rate is relatively slow compared to some other biodegradable polymers.[1,2] Nevertheless, PLA is widely used in plastic applications and there are many research groups that have worked to try to improve its toughness and flexibility because PLA is a brittle polymer. The commercial product Ecovio®—a completely biodegradable plastic is one example of a successful modification of PLA. This product is the blend poly(lactide)/poly(butylene adipate-*co*-terephthalate). There was an attempt to improve the toughness of PLA by blending it with natural rubber (NR) or modified NR. It was found that the optimum content of NR was ∼10 wt %.[3–7] The modified NR was in that case a graft copolymer such as NR grafted with poly(vinyl acetate),[3] NR grafted with poly (methyl methacrylate)[4] and NR grafted with glycidyl methacrylate.[7] These modified NR copolymers were used to increase the compatibility of the PLA/NR blend. Mastication of NR in a two-roll mill was also another technique that was used

to improve the compatibility of this blend.[3,4] A common method for increasing the compatibility of a polymer blend is the addition of a diblock copolymer. Therefore, a PLA-NR diblock copolymer could be a promising compatibilizer of the PLA/NR blend or perhaps a toughening agent.

On the basis of our knowledge, there has been no previous publication on the synthesis of a PLA-NR diblock copolymer. The PLA-based diblock copolymers have included PLA-poly(ethylene glycol),[8–18] PLA-poly(ethylene oxide),[19–23] PLA-PS,[24,25] and PLA-poly(para-phenylenevinylene).[26] NR has been chemically modified to obtain a hydroxyl terminated liquid rubber (a hydroxyl telechelic natural rubber, HTNR). Only two publications have reported the synthesis of HTNR-based diblock copolymers, i.e., HTNR-poly(butyl acrylate)[27] and HTNR-poly(propylene oxide) diblock copolymers.[28]

The objectives of the present study were to synthesize linear PLA-NR diblock copolymers and investigate the effect of their addition on the impact strength of PLA and PLA/NR blends. One of the features of these diblock copolymers obtained from PLA and HTNR is that they are completely bio-based because
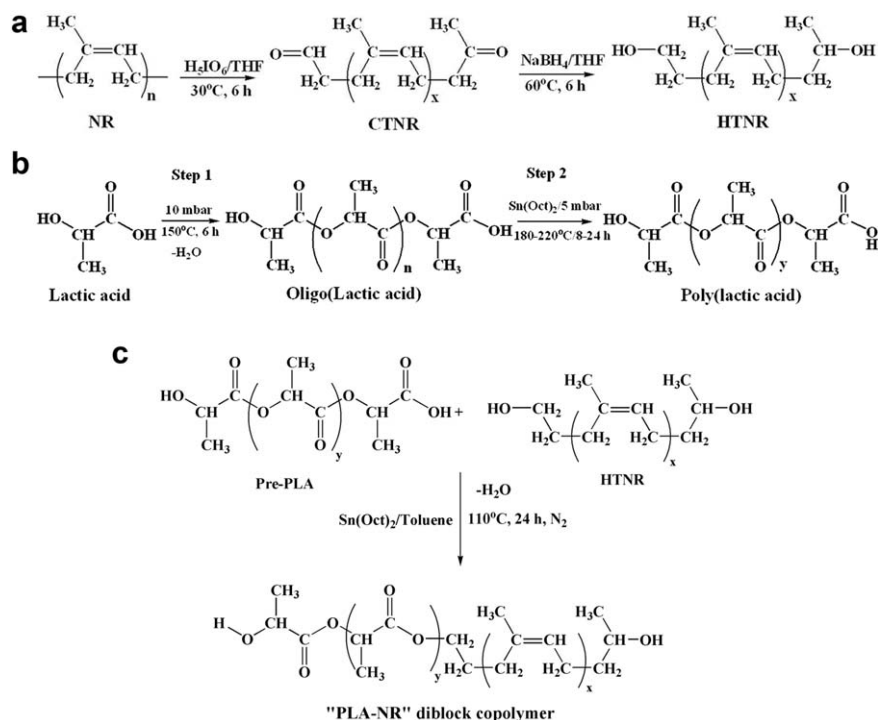
Figure 1. Schematic diagram of the synthesis methods: (a) HTNR; (b) PLA; and (c) PLA-NR diblock copolymer.

both NR and PLA are from renewable resources. The diblock copolymers were characterized in terms of their chemical structure, molecular weight and thermal properties. They were used as a compatibilizer of the PLA/NR blend and as a toughening agent for PLA.

EXPERIMENTAL

Materials

The constant viscosity grade natural rubber (CV60) used for the synthesis of the diblock copolymers was obtained from Hutchinson (France) and that for the preparation of polymer blends was obtained from Jana Concentrated Latex (Thailand). Its Mooney viscosity was 60. The 90% aqueous solution of $L(+)$-lactic acid (LLA) and sodium borohydride (NaBH$_4$) were from ACROS ORGANICS, USA. Tin (II) octanoate (Sn(Oct)$_2$) and periodic acid (H$_5$IO$_6$) were purchased from SIGMA-ALDRICH, USA. All chemicals were AR grade and all solvents were purified before use. Poly(lactic acid) (2002D) was produced by Nature Works, USA.

Synthesis of the Carbonyl Telechelic Natural Rubber (CTNR) Oligomers

NR was dissolved in tetrahydrofuran (0.6 M) at 30°C for 12 h. The periodic acid was suspended in tetrahydrofuran (0.4 M) and slowly added into the NR solution. The reaction was performed at 30°C for 6 h. The product was filtered from the solution and residual tetrahydrofuran was evaporated at 40°C and 350 mbar. The obtained CTNR was dissolved in dichloromethane, and washed twice with a mixture of saturated sodium bicarbonate solution and saturated sodium chloride solution (50% in volume each), followed by a mixture of 70% in volume sodium thiosulfate solution (20 wt %) and 30% volume

saturated sodium chloride solution. Anhydrous magnesium sulfate was added to remove water from the CTNR solution. Finally, the CTNR solution was filtered and dried under vacuum at 40°C. The CTNR from every batch was characterized by ^{1}H NMR and SEC to determine the chemical structure and molecular weight, respectively. The molecular weight of CTNR was controlled by the concentration of the periodic acid. CTNR was synthesized according to the previous works[29–31] and had various molecular weights.

Synthesis of the Hydroxyl Telechelic Natural Rubber (HTNR) Oligomers

HTNR was obtained from the reaction between CTNR and sodium borohydride in a tetrahydrofuran medium at 60°C for 6 h. The molar ratio between CTNR and sodium borohydride was 10 : 1. CTNR was dissolved in tetrahydrofuran (0.4 M) and slowly dropped in the sodium borohydride dissolved in tetrahydrofuran (0.5 M). The HTNR solution was washed with saturated NaCl and the residual water was removed by anhydrous magnesium sulfate. Finally HTNR was dried under reduced pressure at 40°C. The chemical structure and the molecular weight of HTNR were investigated by using ^{1}H NMR and SEC, respectively. Figure 1(a) shows a schematic diagram for the synthesis of HTNR. The molecular weight of HTNR depended on the molecular weight of CTNR according to the methodology described in previous works.[29–33]

Synthesis of the Poly(lactic acid) (PLA)

The PLA was synthesized according to Figure 1(b). The lactic acid was dehydrated at 150°C by stepwise vacuum using the following conditions: an atmospheric pressure for 2 h, 100 mbar and 10 mbar for another 4 h each. Then 0.5% of tin catalyst was added into the reactor. The polymerization reaction was
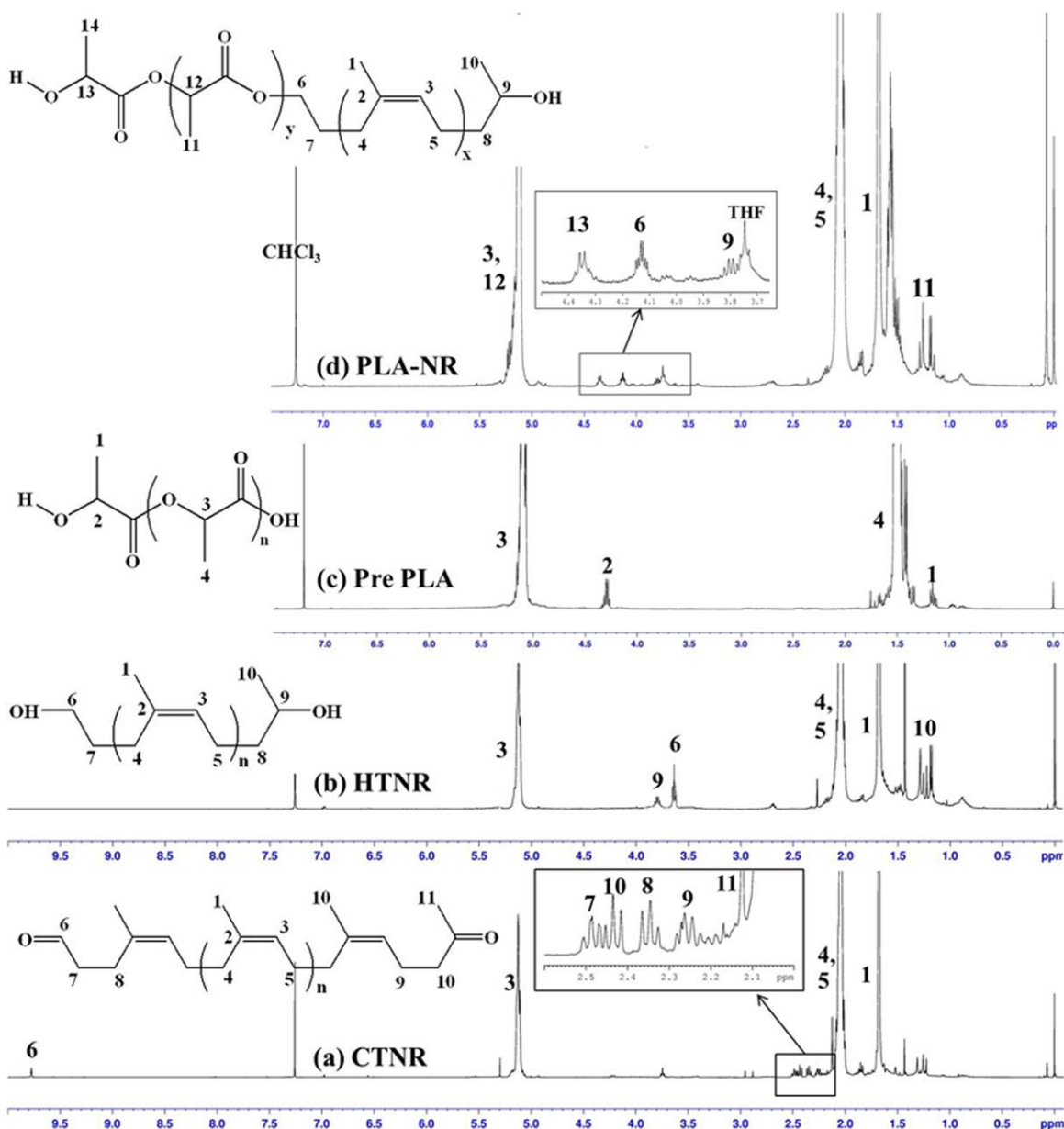
Figure 2. The ^{1}H NMR spectra: (a) CTNR; (b) HTNR; (c) PLA; and (d) PLA-NR diblock copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carried out at a pressure of 5 mbar between 180 and 200°C for 8–16 h.[34,35] The final products were purified by dissolving in dichloromethane and precipitating in methanol in order to remove the traces of any lactide as a byproduct generated from the depolymerization process. The purified PLA was dried in a vacuum oven for 24 h at 40°C and investigated by ^{1}H NMR and SEC.

Synthesis of the PLA-NR Diblock Copolymers

The PLA and HTNR were dissolved in toluene in a nitrogen atmosphere at 110°C and 0.5 wt % of tin catalyst based on HTNR and PLA total weight was added. The reaction was maintained at 110°C for 24 h in an atmosphere of nitrogen. The obtained product was dissolved in dichloromethane,

precipitated in ethanol and vacuum dried at 25°C for 24 h. The chemical structure and the molecular weight of all final products were investigated using ^{1}H NMR and SEC techniques, respectively. Figure 1(c) shows a schematic diagram of the synthesis method.

Preparation and Testing of the Polymer Blends

The diblock copolymers as a solid polymer and natural rubber were cut into small pieces before mixing with dried PLA pellets. Mechanical blending was performed using a twin screw extruder (Prism®TSE16TC, Thermo Electron Corporation, USA). The screw temperature was 120 and 160°C for the feed and mixing zones, and the die temperature was 160°C. It was necessary to carried out a double extrusion in order to obtain homogeneous

Table I. The Chemical Shift Assignment of HTNR, PLA, and Diblock Copolymer

HTNR		PLA		PLA-NR	
—C=C**H**—	5.1 (H$_3$)	—C**H**— (repeating unit)	5.2 (H$_3$)	—C**H**— (PLA)	5.2 (H$_{12}$)
—**CH**OH	3.8 (H$_9$)	—C**H**— (end group)	4.4 (H$_2$)	—C=C**H**— (HTNR)	5.2 (H$_3$)
—**CH$_2$**OH	3.6 (H$_6$)	—C**H$_3$** (repeating unit)	1.5 (H$_4$)	—C**H**, —C**H$_3$** (chain end of PLA)	4.4 (H$_{13}$), 1.2 (H$_{14}$)
—**CH$_2$**—	2.0 (H$_4$ and H$_5$)	—C**H$_3$** (end group)	1.2 (H$_1$)	—C=O—O**CH$_2$**— (PLA-HTNR)	4.1 (H$_6$)
—**CH$_3$**	1.7 (H$_1$)			—**CH**OH (HTNR)	3.8 (H$_9$)
				—**CH$_2$**—, —**CH$_3$** (HTNR)	2.0 (H$_{4,5}$), 1.6 (H$_1$)
				—**CH$_3$** (main chain of PLA)	1.5 (H$_{11}$)
				—**CH$_3$CH**OH (HTNR)	1.2 (H$_{10}$)

polymer blends. The screw speed of blending was 150 and 190 rpm for the first and the second extrusion, respectively. The blends were compressed at 160°C to obtain a 2 mm-thick sheet.

The impact resistance was determined according to ASTM D256 by using a Zwick® 5102 (Zwick Roell, Germany). The notched Izod impact strength was performed. Eight to ten specimens were tested for every sample at room temperature (25°C).

Characterization

The ^{1}H NMR spectra were obtained using a Bruker® Avance 400 spectrometer (400 MHz) using deuterated chloroform as a solvent. The molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) (Spectra SYS-TEM® AS 1000). The mobile phase was tetrahydrofuran at a flow rate of 1 mL min^{-1} and the column temperature was 40°C. Thermal properties were examined over the temperature range of −80–200°C using a differential scanning calorimeter (TA Instrument® DSC Q100). To have a similar thermal history for each sample, the thermogram from the second heating scan was compared. The heating and cooling rate was 10 and −10°C min^{-1}, respectively. Thermal degradation was investigated using a themogravimetric analyzer (TA Instrument® TGA Q500). Samples of ∼10 mg were heated at 10°C min^{-1} from 30 to 600°C under a dry nitrogen gas flow rate of 90 mL min$_{-1}$. The blend morphology was observed with a scanning electron microscope (JEOL® 5800LV) (JEOL, Japan). The freeze fractured surfaces were coated with gold before observation. The number averaged diameter of the rubber phase was calculated from 300 rubber particles.

RESULTS AND DISCUSSION

Characterization of the Chemical Structure of the Synthesized Starting Materials

NR derived oligomers and PLA structures were characterized by ^{1}H NMR and SEC. The ^{1}H NMR spectra of CTNR, HTNR, and PLA are shown in Figure 2. The chemical shift assignment is listed in Table I.[29–38] CTNR and HTNR showed the characteristic peaks of NR at 5.1, 2.0, and 1.7 ppm, which were assigned to the methine proton (—C=C**H**—), methylene proton (—**CH$_2$**—) and methyl proton (—**CH$_3$**), respectively. CTNR showed new peaks at 9.8 ppm (—**CH**=O), 2.4 ppm (CH$_3$C=OCH$_2$—), and 2.1 ppm (CH$_3$C=OCH$_2$—) that corresponded to the new groups at the chain ends. HTNR did not show any signal at 9.8 ppm that belonged to the proton of the
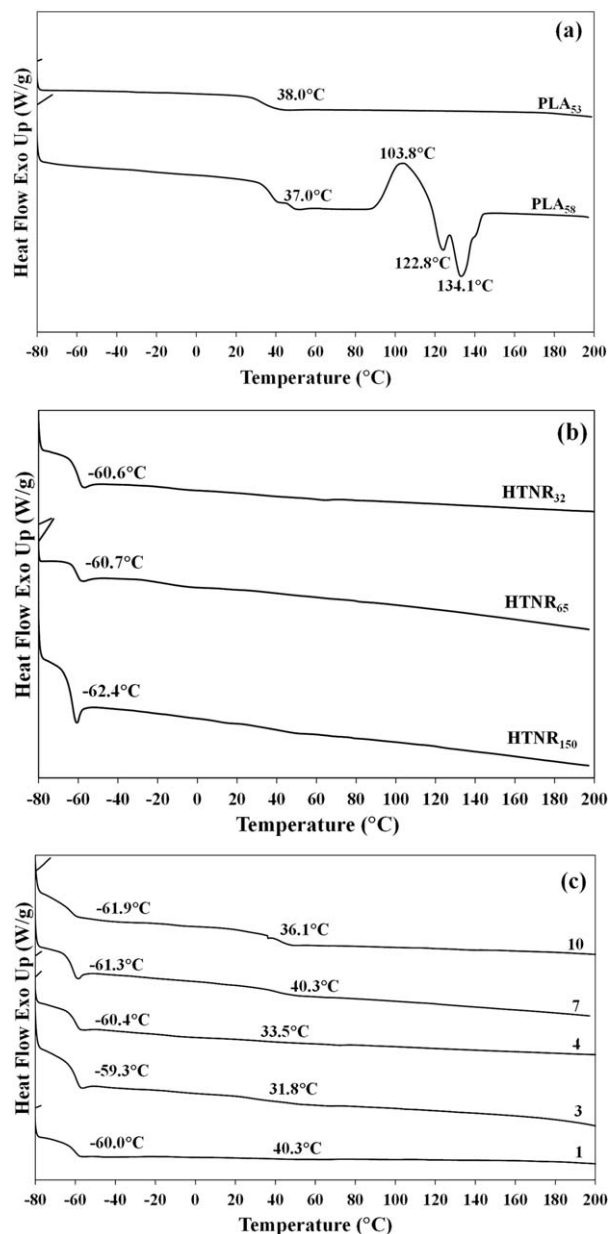

Figure 3. DSC thermograms from the second heating scan: (a) PLA with different molecular weights: 5300 and 5800; (b) HTNR with different molecular weights: 3200, 6500, and 15,000; and (c) diblock copolymers.

Table II. Reaction Conditions and Molecular Weight of Starting Materials and Diblock Copolymers

Sample	PLA:HTNR mole ratio	Reaction time (h)	M_n (g mol^{-1})		Diblock copolymer			
			prePLA	HTNR	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	$M_{n\text{-cal}}$ (g mol^{-1})
1	2 : 1	24	5300	3200	8800	11,300	1.28	8500
2	2 : 1	48	5300	3200	8900	11,300	1.27	8500
3	1 : 1	24	5300	3200	8200	12,100	1.48	8500
4	1 : 2	24	5300	3200	8400	12,300	1.46	8500
5	1 : 2	48	5300	3200	8700	12,900	1.48	8500
6	2 : 1	24	5800	3200	9000	13,600	1.51	9000
7	2 : 1	24	5800	6500	11,300	30,600	2.71	12,300
8	2 : 1	24	5800	15,000	23,000	62,700	2.73	20,800
9	2 : 1	48	5800	15,000	22,800	66,570	2.92	20,800
10	1 : 1	24	5800	15,000	20,800	45,300	2.18	20,800

aldehyde end group. New signals related to the presence of the hydroxyl end groups in HTNR were observed at 3.6 and 3.8 ppm. The formation of the PLA was verified by the ^{1}H NMR spectrum [shown in Figure 2(c)], which differed from that of the lactic acid interpreted by Esoartero et al., 1996.[37]

The molecular weights of prepared PLA samples were determined using SEC method. The PLA was synthesized from a direct condensation polymerization of lactic acid. This technique provided low molecular weight PLA compared to ring opening polymerization of lactide. The PLA samples with molecular weights (M_n) of 5300 and 5800 g mol^{-1} were selected as precursor for copolymer preparation, and their polydispersity index (PDI) were 1.30 and 1.87, respectively. Both PLA were solid and showed different morphology [Figure 3(a)]. The lower molecular weight PLA (PLA$_{53}$) was amorphous whereas the higher molecular weight one (PLA$_{58}$) showed a cold crystallization temperature (T_{cc}) and a double melting peak. The amorphous nature of PLA$_{53}$ and the crystalline nature of the PLA$_{58}$ were observed in both the first and second heating scan. To remove the effect of the thermal history of samples, the DSC thermograms from the second heating scan were discussed. Both PLA samples showed a relatively low glass transition temperature ($\sim$37–38°C) compared to the general commercial PLA ($\sim$70°C) due to their lower molecular weight. Although PLA$_{58}$ showed the melting temperature at $\sim$134°C, it was completely dissolved in toluene at 110°C during the condensation copolymerization. PLA could be either amorphous or semicrystalline polymer. The crystalline nature of PLA is dependent on the stereoisomers used, the molecular weight, the molecular weight distribution, the heating/cooling rate, and the nucleating agent or other components. The semicrystalline PLA has so low crystallization rate that it may not show melting temperature in the second heating scan. The molecular weight of the PLA$_{58}$ is high enough for cold crystallization that affected on its crystallization behavior, resulting in the double melting peak. This double endotherm in the DSC trace is common for polyester which shows cold crystallization peak. On the basis of our previous works, the double melting peak in PLA was found.[3,4]

The molecular weights (M_n) of the prepared HTNR samples were 3200, 6500, and 15,000 g mol^{-1}, and their PDI were 1.66, 2.18, and 2.88, respectively. The lowest molecular weight HTNR (HTNR$_{32}$) was an extremely viscous liquid, the higher molecular weight one (HTNR$_{65}$) became a semi-solid, whereas the highest molecular weight HTNR (HTNR$_{150}$) was a solid. Although their molecular weights were significantly different, their T_gs were in the same range: −61 to −62°C [Figure 3(b)].

Characterization of the Chemical Structure of PLA-NR Diblock Copolymers

Diblock copolymers with various molecular weights were prepared and a fairly high molecular weight (>8000) was our target in order to use them as compatibilizers for the PLA/NR blend and toughening agents for the PLA. The copolymerization conditions were varied including the mole ratio of PLA : HTNR, the reaction time and the molecular weight of the starting materials (Table II). The diblock copolymers were used as a toughening agent of PLA; therefore, the rubber block (HTNR) should have higher molecular weight than the plastic block (PLA) in order to provide the higher toughness in the blend. In this point, the high molecular weight of HTNR was preferred. However, a difficulty of synthesizing high molecular weight HTNR found in the interpretation of the ^{1}H-NMR spectrum because the high number of repeating isoprene units causes low signals for the protons that confirm the presence of the hydroxyl end groups, at the point that it was not possible to observe them. For this reason, the maximum M_n of the synthesized HTNR in the present study was 20,000.

Every PLA-NR diblock copolymer was investigated by ^{1}H NMR and SEC. The ^{1}H NMR spectrum of the diblock copolymer is represented in Figure 2(d) and the chemical shift assignment is listed in Table I. The peak at 5.2 ppm was assigned to the —C=CH— proton of NR (proton 3) and the —CH— proton of PLA (proton 12). The main characteristics of the PLA were 4.4 ppm (proton 13) and 1.5 ppm (proton 11), and those of the HTNR were 1.6 ppm (proton 1) and 3.80 ppm (proton 9). The condensation reaction between the OH groups of HTNR and
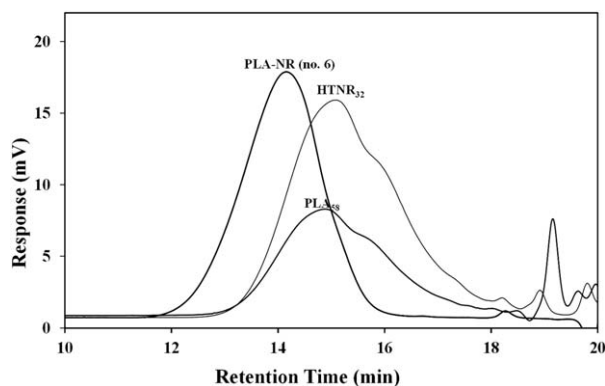
Figure 4. SEC chromatograms of the PLA$_{58}$, HTNR$_{32}$ and the PLA-NR diblock copolymer (no. 6).

COOH groups of PLA led to a new ester linkage. As a result, a new peak of the methylene proton at 4.1 ppm (proton 6) was evident in the resulting diblock copolymer. This methylene proton has been also observed in the PLA-PEO diblock copolymers.[17–19] The —CH— proton in the α position of the hydroxyl endgroup (—CHOH) at 3.80 ppm (proton 9) was observed, which indicated that only one chain end of HTNR had reacted and contributed to the formation of the diblock copolymer.

The SEC chromatograms of the starting materials and the diblock copolymer are shown in Figure 4. The PLA-NR block copolymer had a molecular weight corresponding to the sum of the M_n of the parent oligomers. A uni-modal curve was observed in the diblock copolymer and indicated a high purity. The molecular weight (M_n and M_w) and PDI of the obtained diblock copolymers are listed in Table II. The $M_{n\text{-}cal}$ was derived from a summation of the M_n of the starting materials in terms of a 1 : 1 mole ratio, and that was in the same range as that measured by SEC. This indicated that all conditions provided a diblock copolymer, even though the mole ratio of PLA : NR was 2 : 1 or 1 : 2. PLA could still be able to self condensate and this would increase the molecular weight in comparison to the expected one. However, we have no evidence of the occurring of this side reaction and the results from the ^{1}H NMR and SEC verified the formation of the diblock copolymers. The reaction temperature was found to be crucial. Only one chain-end of HTNR was active at the reaction temperature of 110°C. As shown in Figure 1(c), the opposite chain-end was more bulky due to the presence of CH$_3$ that caused a steric hindrance at a relatively low reaction temperature. We demonstrated that a tri-block copolymer could by formed by increasing the temperature to 170°C, when the mole ratio of PLA : NR was 2 : 1.[39]

All diblock copolymers showed a uni-modal molecular weight distribution curve similar to that in Figure 4 and their PDI (shown in Table II) was classified into two levels: (1) 1.27–1.51 and (2) 2.18–2.92. Both starting blocks, PLA and HTNR, are polydispersed polymers, so a narrow distribution of masses for the final diblock could not be expected. Moreover the PDI increases with molar mass for HTNR; this is due to the fact that it is difficult to control the oxidative degradation of polyisoprene chains when a molar mass higher than 10,000 g mol^{-1} is targeted. The reason is that the first step, for the synthesis of

the carbonyl oligomers, the amount of periodic acid to add to obtain high masses is so small in comparison to the overall volume of solution of natural rubber in THF that it is very difficult to have a homogeneous dissolution of periodic acid. Therefore, what probably happens is that there are different concentrations in different regions of the reactor and consequently the polyisoprene chains are cut into oligomers of various sizes.

In the present study, all starting materials and diblock copolymers were well purified after synthesis and were proven by the ^{1}H NMR spectra and SEC chromatograms of the samples before and after purification. No impurities were observed after purification. Thus, it was evident that the diblock copolymer from the PLA and HTNR had been successfully generated.

Thermal Properties of the Diblock Copolymers

The DSC thermograms of some of the diblock copolymers are shown in Figure 3(c) and the glass transition temperatures (T_g) recorded from the second heating scan of all diblock copolymers are listed in Table III. All diblock copolymers showed two T_gs, owing to the HTNR (T_{g1}) and the PLA (T_{g2}). The T_g of the HTNR block in the diblock copolymers was in the same range as in the starting material (-62°C to -60°C) while the T_g of the PLA block showed some differences in each sample (32–40°C). The high T_g (48°C) of the sample no. 6 may be due to its crystalline structure observed in the first and second heating scan as described below. Generally, the morphology of the diblock copolymers was strongly dependent on the morphology of their starting materials. For examples, samples no. 1–5 were amorphous because they were synthesized from the amorphous PLA (PLA$_{53}$) and amorphous HTNR; samples no. 6 and 7 showed the melting temperature at ~136°C in the first heating scan due to the crystalline nature of PLA$_{58}$. The sample no. 7 did not show a melting peak in the second heating scan because of the effect of the higher molecular weight of the HTNR. This was observed also in the samples no. 8–10, which became amorphous although they consisted of PLA$_{58}$. The longer molecules

Table III. Glass Transition Temperatures and Thermal Degradation Temperatures of PLA-NR Diblock Copolymers

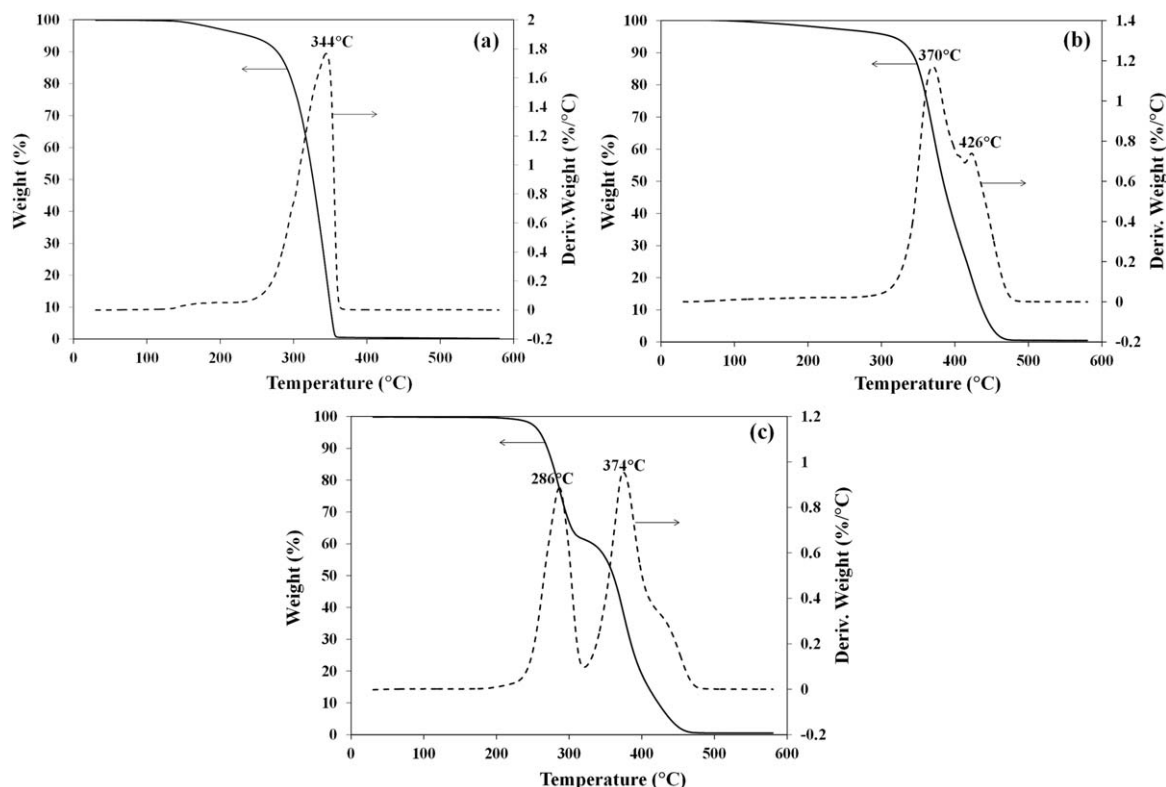| Sample	Transition temperature (°C)		Degradation temperature (°C)	
	T_{g1}	T_{g2}	T_{d1}	T_{d2}
1	−60.0	40.3	241	370
2	−59.5	32.8	244	371
3	−59.3	31.8	242	369
4	−60.4	33.5	232	371
5	−59.0	32.4	231	370
6	−61.0	48.7	287	374
7	−61.3	40.3	261	376
8	−62.4	40.0	258	373
9	−61.6	38.9	261	372
10	−61.9	36.1	260	376

Figure 5. TGA and DTG thermograms: (a) PLA_{58}, (b) $HTNR_{32}$, and (c) PLA-NR diblock copolymer (no. 10).

in the higher M_n HTNR (6500 and 15000 g mol^{-1}) may contribute to more chain entanglement that restricted the crystallization process of the PLA molecules. It could be concluded that only the sample no. 6 was a semi-crystalline polymer based on the second heating scan. The highest T_g of the diblock copolymer containing PLA_{58} and $HTNR_{32}$ (the sample no. 6) was attributed to the presence of crystallinity.

The TGA thermograms of the polymers are shown in Figure 5. The thermal degradation behavior of the PLA (PLA_{58}) exhibited one-stage degradation at 344°C whereas the $HTNR_{150}$ showed the first degradation stage at 370°C and the second stage at 426°C. The diblock copolymer (no. 10) showed two stages of thermal degradation, 287°C (T_{d1}) and 374°C (T_{d2}), belonging to the PLA and the HTNR, respectively. The PLA showed a relatively lower thermal degradation than the HTNR, particularly for the PLA_{53} that showed T_d at 266°C (data not shown). In contrast, the thermal degradation temperature of all HTNRs was in the same range. PLA was more sensitive to thermal degradation than HTNR because the hydrolysis at high temperature is common to polyesters, including PLA, and induces chain scission responsible of a lower resistance to thermal degradation. The thermal degradation temperatures of all diblock copolymers are tabulated in Table III. Noticeably, the thermal degradation temperature of the PLA block in the diblock copolymers was lower than that of the starting material. This may be due to partial depolymerization of the PLA during copolymerization; in fact the formation of lactide was observed during the copolymerization as it was found in the diblock copolymer crude product before purification. Again, the TGA

results also substantiated the formation of the PLA-NR diblock copolymer. The thermal degradation temperature of each block depended upon the starting materials. All diblock copolymers showed a similar thermal degradation temperature of the HTNR block (T_{d2}), ~369–376°C. The thermal degradation temperature of the PLA block (T_{d1}) was classified into three groups. Group 1 was the lowest T_{d1}, ~231–244°C (samples no. 1–5). This group arose from the amorphous and low M_n starting materials. Group 2 (samples no. 7–10) consisted of crystalline PLA and amorphous and high M_n HTNR. This group showed higher T_{d2} values, ~258–261°C. The last group (sample no. 6) showed the highest T_{d2}, ~287°C due to the crystallinity in PLA_{58}.

The Impact Strength and Morphology of Polymer Blends
After optimization of the initial reaction conditions, new diblock copolymers were synthesized (as shown in Table IV) for the preparation of the rubber toughened PLA. These new diblock copolymers were also identified by ^{1}H NMR and SEC. The M_n determined from the SEC coincided with that from the calculation. The M_n of PLA and HTNR were used for sample nomenclature of the diblock copolymers in this section. For example, $P_{60}N_{120}$ was the diblock copolymer containing PLA with M_n of 6000 g mol^{-1} and HTNR with M_n of 12,000 g mol^{-1}.

Two sets of polymer blends were investigated. The first set was PLA containing ≤10 wt % rubber that included the NR and PLA-NR diblock copolymers. The second set was the PLA/NR blend having the PLA-NR diblock copolymer as the

Table IV. Number Averaged Molecular Weight of the Diblock Copolymers for Polymer Blending

Sample	M_n of precursor (g mol^{-1})		Block copolymer			
	Pre PLA	HTNR	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	M_{n-cal} (g mol^{-1})
$P_{60}N_{120}$	6000	12,000	19,350	50,700	2.62	18,000
$P_{35}N_{150}$	3500	15,000	17,560	41,270	2.35	18,500
$P_{60}N_{150}$	6000	15,000	21,030	44,790	2.13	21,000
$P_{60}N_{200}$	6000	20,000	24,083	63,819	2.65	26,000

compatibilizer and these blends contained 90 wt % PLA, 10 wt % NR, and 2.5–15 pph (parts per hundred of polymers) diblock copolymer. The notched Izod impact strengths of all the blends are shown in Figure 6. It was interesting that the diblock copolymers could be used as a toughening agent as found in the 90/0/10 blend, which was the blend between 90 wt % PLA, and 10 wt % PLA-NR diblock copolymer [Figure 6(a)]. All blends containing diblock copolymers showed higher impact strength than PLA alone. It should be noted that the comparison of the impact strength between the PLA and the blends was carried out under a similar thermal history. In this case, PLA was extruded in a similar manner to the blends. The impact strength increased almost twice in the blends containing $P_{60}N_{150}$ and $P_{60}N_{200}$. The other two diblock copolymers, $P_{60}N_{120}$ and $P_{35}N_{150}$, conferred a lower impact strength than

the former blends. The results indicated that a high molecular weight of each block was required. Although the maximum impact strength obtained from the PLA/PLA-NR blend was 5.63 kJ m^{-2} this was lower than the PLA containing 10 wt % NR (6.44 kJ m^{-2})[2]; however, the PLA-NR diblock copolymer showed synergy to the PLA. First, the PLA/PLA-NR blend had less rubber content than the PLA/NR blend by ~50% because the mole ratio of the PLA : NR in the diblock copolymer was 1 : 1. Second, the M_n of the PLA-NR (15,000 g mol^{-1}) was much lower than that for the NR ($\sim10^5-10^6$ g mol^{-1}). This was due to the effect of the PLA block that promoted the miscibility of the PLA/PLA-NR blend as observed from the SEM micrograph [Figure 7(a)] showing tiny holes that corresponded to the particles of the PLA-NR diblock copolymer. The average diameters of the diblock copolymers in the PLA/PLA-NR blends
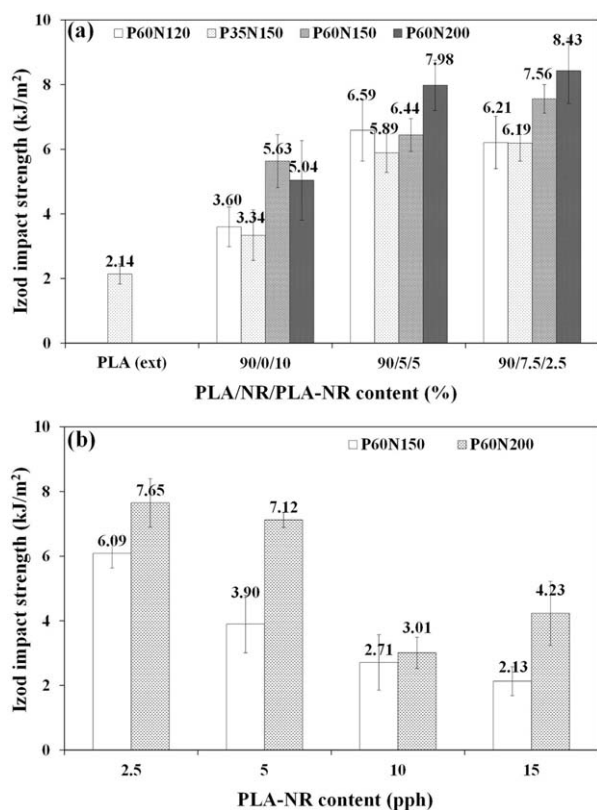

Figure 6. The effect of the diblock copolymers on the notched izod impact strength of the blends: (a) the blends containing ≤10 wt % rubber and (b) the blends containing >10 wt % rubber.
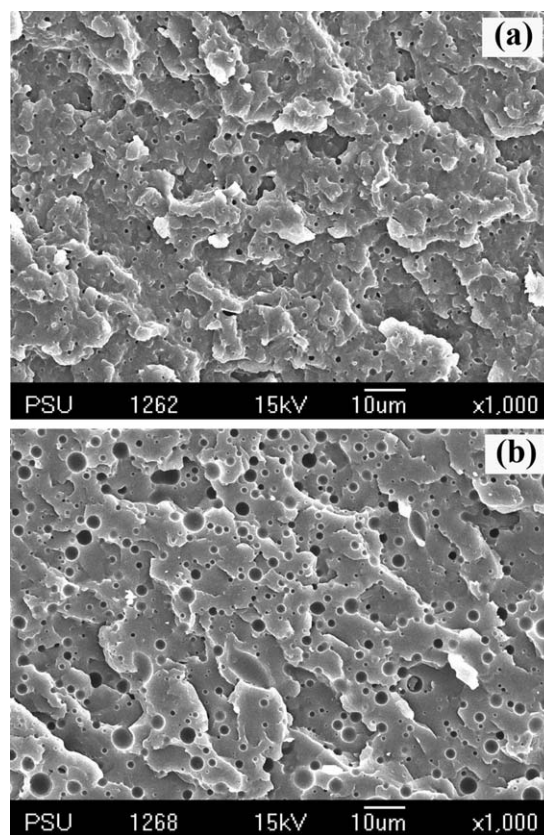

Figure 7. SEM micrographs of the PLA/NR/PLA-NR blends containing P60R120: (a) 90/0/10 and (b) 90/7.5/2.5.

Table V. Average Diameter of Rubber Particles in the Blends Containing ≤10 wt % Rubber

Diblock copolymer	Rubber particle diameter (µm)		
	90/0/10	90/5/5	90/7.5/2.5
$P_{60}N_{120}$	1.25 ± 0.32	2.50 ± 0.89	2.50 ± 0.95
$P_{35}N_{150}$	1.79 ± 0.87	2.61 ± 1.16	2.52 ± 1.00
$P_{60}N_{150}$	1.41 ± 0.27	2.44 ± 0.83	2.27 ± 1.11
$P_{60}N_{200}$	1.75 ± 1.13	2.13 ± 0.95	2.20 ± 1.13

are listed in Table V. Their average diameter was in the range of 1.4–1.8 µm while the average diameter of the NR particles in the PLA/NR blend was 2.5 µm.[4]

It was mentioned previously that the actual rubber content in the PLA/PLA-NR blend was relatively low; thus a mixture of NR and a PLA-NR diblock copolymer was employed to prepare the blend containing 10 wt % rubber. Synergistic behavior was observable in the PLA/NR/PLA-NR blends in which the impact strengths of the PLA/NR/PLA-NR blends (90/5/5 and 90/7.5/2.5) were higher than those of the PLA/PLA-NR blends (90/0/10) [Figure 6(a)]. The higher NR content tended to provide the higher impact strength and the $P_{60}N_{200}$ gave the highest impact strength, particularly in the 90/7.5/2.5 blend (8.43 kJ m^{-2}). Furthermore, some PLA/NR/PLA-NR blends showed a higher impact strength than that of the PLA/NR blend (6.44 kJ m^{-2}).[2] This indicated that the diblock copolymer could act as the compatibilizer for the PLA/NR blend. Figure 7(b) is the SEM micrograph of the PLA/NR/PLA-NR (90/7.5/2.5) blend showing spherical rubber particles in the blend, and Table V shows the average diameters of the rubber in the PLA/NR/PLA-NR blends. The impact strength of the PLA/NR/PLA-NR blends seemed to relate to the rubber particle diameter. The lower diameter tended to provide the higher impact strength.

The results showed that the combination of NR and PLA-NR diblock copolymer was more preferable than the single rubber but the average diameters of the rubber particles in the PLA/NR/PLA-NR blends were larger than those of the PLA/PLA-NR blends. From this point of view, the smaller particles were not necessary and the particle size should not be the only criterion used to control the impact strength of the blends. The presence of NR resulted in more rubber characteristics and the presence of the PLA-NR diblock copolymer resulted in a higher miscibil-

ity. These may be responsible of the higher impact strength of this blend although it did show larger particle sizes. The above experiments showed promising results of the PLA/NR/PLA-NR blends containing 10 wt % rubber (NR and PLA-NR) which indicated that both NR and diblock copolymer were a good toughening agent for PLA.

The effect of a higher content for the diblock copolymer was determined in order to investigate the compatibilization effect of the diblock copolymer. The blends consisted of >10 wt % rubber and its composition was maintained at 90 wt % PLA and 10 wt % NR, and the diblock copolymer was added at between 2.5 and 15 pph. The diblock copolymers with a relatively high molecular weight were employed. The notched Izod impact strengths are shown in Figure 6(b). The strength of the blends tended to decrease with the higher content of the diblock copolymer, and the higher molecular weight of the diblock copolymer provided the higher impact strength. Table VI provides the average particle diameter of these blends. The type of diblock copolymer had a slight effect on the rubber particle diameter. Noticeably, the rubber particle seemed to increase as the PLA-NR diblock copolymer content increased, and particle diameters of more than 3 µm was too large as it showed a drop in the impact strength.

CONCLUSIONS

Novel bio-based PLA-NR diblock copolymers were successfully synthesized from poly(lactic acid) (PLA) and hydroxyl telechelic natural rubber oligomers (HTNR) by the condensation reaction between the functional endgroups of PLA and HTNR. The optimal reaction conditions for the diblock copolymer synthesis were 110°C for 24 h, and the PLA:HTNR mole ratio was 1 : 1. The presence of new ester linkages in the diblock copolymers was verified by the ^{1}H NMR spectrum. The number-average molecular weight of the diblock copolymer obtained from SEC agreed with that determined from calculation. Two glass transition temperatures assigned to PLA and HTNR blocks were observed from DSC traces. TGA thermograms also substantiated the presence of the diblock copolymers, two thermal degradation temperatures were observed. The diblock copolymers acted as a toughening agent for PLA and as a compatibilizer for the PLA/NR blend. The diblock copolymers increased the impact strength of the PLA by approximately >200%. The maximum impact strength of the blends appeared in the PLA/NR/diblock (90/7.5/2.5) blend and was higher than that of the PLA/NR blend. The compatibilization effect became less effective when the diblock copolymer content was further increased.

Table VI. The Average Diameter of Rubber Particle in the Blends Containing >10 wt % Rubber

PLA/NR/PLA-NR	Rubber particle diameter (µm)	
	$P_{60}N_{150}$	$P_{60}N_{200}$
90/10/2.5	2.53 ± 1.07	2.22 ± 1.35
90/10/5	2.78 ± 1.78	2.52 ± 1.39
90/10/10	3.53 ± 1.97	3.36 ± 2.09
90/10/15	3.78 ± 2.31	3.45 ± 2.05

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