

SYNTHESIS OF NATURAL RUBBER- BASED TOUGHENING AGENTS FOR POLY(LACTIC ACID)

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Abstract

Two types of modified natural rubber (NR) which are a low molecular weight hydroxyl terminated NR (HTNR) and its triblock copolymer with poly(lactic acid) (PLA), were synthesized and applied as toughening agents for PLA. The HTNR was achieved by depolymerization and hydroxylation using an ultraviolet radiation reaction. The HTNR with a hydroxyl functionality of 1.77 ± 0.21 had a number-average molecular weight ($\bar{M}_n$) of 28000 g/mol. Triblock copolymers of HTNR with 2 different low molecular weight PLA, PLA1 ($\bar{M}_n \approx 3000$) and PLA2 ($\bar{M}_n \approx 9700$ g/mol), were prepared by direct condensation polymerization. The formation of triblock copolymers was confirmed by nuclear magnetic resonance spectroscopy, ^1H -NMR and ^{13}C -NMR. The toughening efficiency of the HTNR and its triblock copolymer on the mechanical and morphological properties for PLA was evaluated. The amount of NR, HTNR, and block copolymer in the blend was 10 percent by weight (%wt). The PLA/HTNR blend showed the highest impact strength and elongation at break. Compared to other blends, the PLA/PLA2-NR-PLA2 triblock copolymer blend showed the highest tensile strength. However, the value was still lower than that of neat PLA.

Keywords: Poly(lactic acid), hydroxyl terminated natural rubber, block copolymer, toughening agent

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Introduction

Poly(lactic acid) (PLA) is one of the biodegradable thermoplastic aliphatic polyesters, a green alternative to petrochemical commodity plastics. PLA is a growing alternative for agricultural products, disposable packaging, etc. However, the main drawbacks of PLA that has limited its application are high brittleness and low heat distortion temperature. Many researchers have tried to overcome the brittleness drawback by blending PLA with a plasticizer, such as ductile synthetic polymers and elastomers. The use of natural rubber (NR) as a toughening agent for brittle plastics such as PLA has become an attractive field of study due to its elasticity, renewability, and biodegradability. The more interesting point of NR is the high production yield of NR in Thailand which was about 4,000,000 metric tons in 2012-2014 (Thailand Board of Investment, 2016). The toughness of PLA was mostly found to have the highest increase with the addition of 10 percent by weight (%wt) NR. However, the tensile strength of the blend was significantly decreased (Bitinis *et al.*, 2011; Pongtanayut *et al.*, 2013; Xu *et al.*, 2014). This was attributed to a poor compatibility between PLA and NR. The molecular weight of NR was also high and resulted in large NR particles and low interfacial adhesion with the PLA matrix. To get higher toughness while maintaining the tensile strength of PLA, modification of the polymer interface in the PLA/NR blends should be applied. Interfacial adhesion between PLA and the NR phase in the PLA/NR blends was achieved by grafting NR, a non-polar polymer, with more polar monomers, such as glycidyl methacrylate, vinyl acetate, and butyl acrylate (Zhang *et al.*, 2011; Juntuek *et al.*, 2012; Pongtanayut *et al.*, 2013; Xu *et al.*, 2014). The addition of a variety of block thermoplastic elastomers based on PLA into the PLA matrix was also another approach that has been published (Cohn and Hotovely, 2005; Fernández *et al.*, 2012; Lee *et al.*, 2017). Copolymerization of PLA can be conducted either through polycondensation of lactic acid with other monomers and polymer segments or ring-opening copolymerization of lactic acid (LA)

with other cyclic monomers and polymer segments (Auras *et al.*, 2010). For example, PLA-block-poly(ϵ -caprolactone) (PCL)-block-PLA was synthesized by ring-opening polymerization (ROP) of successively added ϵ -caprolactone and DL-lactide in the presence of ethylene glycol, using zinc powder as the catalyst (Liu Zhang, 2011). Rathi *et al.* (2012) synthesized triblock copolymer of PDLA-block-PEG-block-PDLA by ROP and used it as a toughening agent for poly(L-lactic acid) (PLLA). Chumeka *et al.* (2015) and Chumeka *et al.* (2014) synthesized PLA-block-NR and PLA-block-NR-block-PLA and used them as compatibilizers and as toughening agents for PLA. They generated carbonyl telechelic natural rubber by oxidative chain cleavage reaction and further chemical modification of the carbonyl end-group to hydroxyl telechelic natural rubber and used it as a precursor.

In this work, hydroxyl terminated liquid natural rubber (HTNR) was obtained from photochemical degradation of natural rubber, as reported by Ravindran *et al.* (1988). HTNR was then copolymerized with low molecular weight poly(lactic acid) via condensation polymerization. The more polar low molecular weight HTNR and its block copolymer with PLA are expected to improve the compatibility between PLA and NR. Consequently, the impact strength of PLA/HTNR and PLA/triblock copolymer blends is further improved, whereas tensile strength of the blends is higher than that of the PLA/unmodified NR blend. From many research works, 10%wt NR and modified NR was found to be the optimum content that gave the highest impact strength for PLA (Juntuek *et al.*, 2012; Pongtanayut *et al.*, 2013; Srisuwan *et al.*, 2015). Therefore, in this study, the amount of NR, HTNR, and triblock copolymer in the blends was fixed at 10%wt.

Materials and Methods

Materials

Natural crumb rubber (STR 5L) was purchased from Pee Jae Rubber Co., Ltd.,

Chumphon, Thailand. Hydrogen peroxide, methanol, hydroquinone, and toluene were purchased from Carlo Erba Reagents S.A.S., Val de Reuil, France. L-(+)-Lactic acid as a 80% solution in water and Tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) were purchased from Sigma-Aldrich Corporation, St. Louis, MO, USA. Toluene, dichloromethane, and methanol were purchased from Acros Organics, Pittsburgh, PA, USA. A commercial grade of poly(lactic acid) (PLA 4043D) was purchased from NatureWorks LLC, Minnetonka, MN, USA.

The Preparation of Hydroxyl Terminated Natural Rubber (HTNR)

Natural crumb rubber was masticated for 30 min at 50°C using a 2-roll mill mixer and then dissolved in toluene with a ratio of 1 gram (g):10 milliliter (ml) in the photochemical reactor. Hydrogen peroxide with a ratio of 0.5 ml:1g of masticated natural rubber was added. The solution mixture was homogenized by the addition of 1.5 ml methanol:1 g of masticated natural rubber. A 500W high pressure mercury vapor lamp was placed in the reaction box. After 54 h of irradiation time, hydroquinone (0.02%wt/v of the reaction mixture) was added to the reaction mixture. The HTNR product was separated and washed with methanol and dried at 60°C (Ravindran *et al.*, 1998).

Synthesis of Low Molecular Weight poly (lactic acid) (pre-PLA)

Two different low molecular weight PLAs (pre-PLA) were synthesized using condensation polymerization of lactic acid. A 80% aqueous solution of lactic acid was added into a round-bottom flask equipped with a mechanical stirrer and condenser and connected to a vacuum line with a pressure sensor. After the lactic acid was dehydrated for 2 h at 130°C, the reaction temperature was

raised to 170°C. The amount of the initiator, reaction step, and reaction time for each step are shown in Table 1. The obtained pre-PLA was precipitated in methanol and dried at 40°C to a constant weight.

Synthesis of PLA-NR-PLA Triblock Copolymers

The HTNR was firstly dissolved in toluene with a ratio of 0.0025 mol:1 liter of toluene, followed by the addition of the pre-PLA. The molar ratio of the pre-PLA and HTNR was 2:1. After the reaction temperature was raised to 170°C, 0.5%wt of $\text{Sn}(\text{Oct})_2$ was added into the solution mixture. The reaction was carried out for 24 h and then the toluene was removed. The obtained product was dissolved in dichloromethane and precipitated in an excess of distilled ethanol. Finally, the obtained product was dried in a vacuum oven at 40°C until the weight was constant. The synthetic block copolymers from PLA1 and PLA2 were coded as PLA1-NR-PLA1 and PLA2-NR-PLA2, respectively.

Preparation of Polymer Blends

A master batch of PLA and the HTNR blend was prepared by a film casting solution using chloroform as a solvent. One hundred g HTNR was dissolved in chloroform with a ratio of 1 g:10 ml of chloroform. Next, 100 g PLA was added into the HTNR solution and stirred until the PLA was already dissolved and showed a homogenous phase. After that, the solution mixture was dried at 40°C to a constant weight. The HTNR master batch was blended with the PLA by melt blending in a HAAKE Rheomix, 3000p internal mixer (Thermo Fisher Scientific, Waltham, MA, USA), at 170°C with a rotor speed of 60 rpm for 10 min. PLA/PLA-NR-PLA triblock copolymer blends was prepared similar to the PLA/HTNR blend. The test

Table 1. The synthesis condition for pre-PLA

Pre-PLA	Lactic acid (ml)	1 st step		2 nd step	
		$\text{Sn}(\text{Oct})_2$ (v/v%)	Reaction time (h)	$\text{Sn}(\text{Oct})_2$ (v/v%)	Reaction time (h)
PLA1	50	0.2	24	-	-
PLA2	50	0.2	24	0.1	18

specimens were molded by compression molding (LabTech LP20-B, LabTech Engineering Co., Ltd., Samutprakarn, Thailand) at 170°C for 10 min.

Materials Characterization

Chemical Structure and Molecular Weight of HTNR and Block Copolymer

The hydroxyl number of HTNR was estimated according to ASTM D4274-16 (ASTM, 2016). The molecular weight of the HTNR, PLA, and PLA-NR-PLA triblock copolymer was characterized by gel permeable chromatography (GPC) (Agilent 1200 series, Agilent Technologies, Santa Clara, CA, USA) using chloroform as a solvent with a flow rate of 0.5 ml/min. The calibration curve was generated from polystyrene standard (polyscience). The chemical structure of the PLA-NR-PLA triblock copolymer was determined using ¹H-NMR, ¹³C-NMR, nuclear magnetic resonance (NMR) (Varian model Inova 300 NMR spectrometer, Varian Inc., Palo Alto, CA, USA) at 25°C and 500 MHz. CDCl₃ and TMS were used as a solvent and an internal standard, respectively.

Mechanical Properties of the Blends

The unnotched Izod impact test was performed according to ASTM D256-10 (ASTM, 2018) using an impact testing machine (CEAST 9050, Instron, Norwood, MA, USA). Tensile properties were obtained according to ASTM D638-14 (ASTM, 2014) using an Instron universal testing machine (UTM, model 5565, Instron, Norwood, MA, USA) with a load cell of 5 kN and crosshead speed of 10 mm/min.

Morphological Properties of the Blends

The morphologies of the PLA, PLA/NR, PLA/HTNR, PLA/PLA1-NR-PLA1, and PLA/PLA2-NR-PLA2 blends were characterized using a scanning electron microscope (SEM, model JSM-6010LV, JEOL Ltd., Tokyo, Japan) with an acceleration voltage of 10 kV. All specimens were coated with gold prior to examination. The diameter of the rubber particles in all blends was measured from SEM micrographs of freeze-fractured surface

specimens. Two hundred particles were used to calculate the average particle diameter (Wu *et al.*, 2010). The number-average particle diameter was calculated using Equation (1).

The number-average particle diameter

$$(d_n) = \frac{\sum_{i=1}^{200} n_i d_i}{\sum_{i=1}^{200} n_i} \quad (1)$$

where:

n_i = the number of particles with diameter d_i
 d_i = the diameter of particles

Results and Discussion

HTNR Characteristics

The production yield of HTNR was calculated as follows:

$$\% \text{yield} = \frac{\text{gram of HTNR product (g)}}{\text{gram of NR material (g)}} \times 100 \quad (2)$$

The yield of HTNR prepared from photochemical reaction was calculated from 3 batches, and the average %yield of HTNR was 91.1±3.9%. The obtained results showed a high production yield of HTNR from the photochemical degradation reaction.

The hydroxyl group of HTNR was esterified with a solution of phthalic anhydride in pyridine under reflux condition at 115±2°C. The excess reagent was titrated with a standard sodium hydroxide solution. The hydroxyl number, mg KOH/g, and functionality of the sample was calculated according to ASTM D4274-16 (ASTM, 2016) as follows:

$$\text{Hydroxyl number} = [(B - A)N \times 56.1]/W \quad (3)$$

where:

A = NaOH required for titration of the sample, ml,

B = NaOH required for titration of the blank, ml,

N = normality of the NaOH, and

W = sample used, g.

The functionality of the HTNR was calculated from the hydroxyl number using the following formula:

$$F = \frac{\bar{M}_n \times \text{Hydroxyl number}}{56100} \quad (4)$$

where:

$\bar{M}_n$ = the number-average molecular weight (g/mol) of the sample

F = functionality, the number of the OH group/mol, and

56100 = equivalent weight of KOH, in milligrams.

From the calculation, the hydroxyl value estimated for the HTNR was 3.55 ± 0.42 mg KOH/g of sample which gave a functionality of 1.77 ± 0.21 . This indicated that approximately 2 hydroxyl groups per molecules of HTNR were generated.

Molecular Weight and Molecular Weight Distribution of the HTNR, pre-PLA, and PLA-NR-PLA Triblock Copolymers

The molecular weights of the HTNR, pre-PLA, and PLA-NR-PLA triblock copolymer are listed in Table 2. It was found that $\bar{M}_n$ of triblock copolymer from the GPC results agreed with the prediction from $\bar{M}_n$ of pre-PLA and HTNR with a molar ratio of 2:1 ($\bar{M}_{ncal}$).

Chemical Structure of the HTNR and PLA-NR- PLA Triblock Copolymer.

The ^1H -NMR spectrum of the HTNR, masticated NR, and NR are shown in Figure 1. The signal of the unsaturated methine proton ($-\text{C}=\text{CH}-$) of the HTNR appeared at 5.12 ppm (H3). The peaks at 2.04 ppm (H1, H4) and 1.68 ppm (H5) corresponded to the methylene proton ($-\text{CH}_2-$), and methyl proton ($-\text{CH}_3$), respectively.

New peak signals at 3.2 ppm (H12) and 3.4 ppm (H11) belonged to the methylene proton ($-\text{CH}_2-$) adjacent to the hydroxyl group which related to the presence of the hydroxyl end groups in the HTNR. Moreover, the HTNR product also had an epoxide group which was a peak that appeared at 2.68 ppm (H8) (Auras *et al.*, 2010). The ^{13}C -NMR spectra of the HTNR, masticated NR, and NR are shown in Figure 2. The signal at 23.6 ppm (C5) corresponded to methyl carbon ($-\text{CH}_3$). The peak signals at 26.0

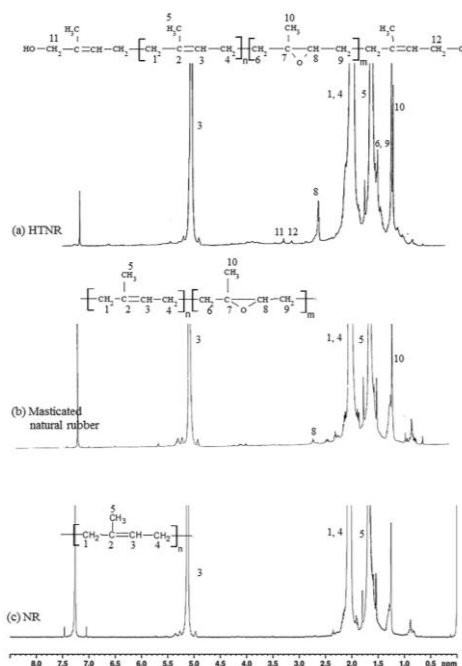


Figure 1. ^1H -NMR spectrum of (a) HTNR, (b) masticated NR, and (c) NR

Table 2. Molecular weight and molecular weight distribution of HTNR, pre-PLA, and PLA-NR-PLA triblock copolymers

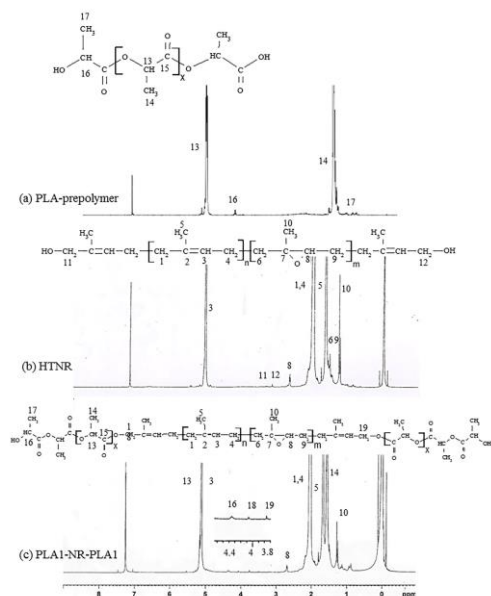
Samples	Molecular weight			Polydispersity index (PDI)
	$\bar{M}_n$ (g/mol)	$\bar{M}_{ncal}$ (g/mol)	$\bar{M}_w$ (g/mol)	
HTNR	28003	-	98030	3.50
PLA1	3091	-	4388	1.42
PLA2	9696	-	23968	2.47
PLA1- NR-PLA1	34681	34180	62476	1.80
PLA2-NR-PLA2	48487	47392	116097	2.39

(-CH₃), respectively. The chemical shift at 69.2 ppm (C18) and 68 ppm (C19) belonged to the ester link between the HTNR and pre-PLA. The disappearances of the chemical shift of the hydroxyl group in the pre-PLA at 60 ppm (C12) and 62 ppm (C11) confirmed the condensation reaction between the OH group of the HTNR and the COOH group of the pre-PLA leading to a new ester linkage in the PLA-NR-PLA triblock copolymer. The ¹H-NMR spectrum and ¹³C-NMR spectrum of the PLA1-NR-PLA1 and PLA2-NR-PLA2 are shown in Figures 6 and 7, respectively. The spectrum of PLA1-NR-PLA1 and PLA2-NR-PLA2 are similar in the chemical shifts of the protons and the carbons are in the same ranges, but some peak signals of PLA2-NR-PLA2 in the ¹³C-NMR spectrum did not clearly appear as PLA1-NR-PLA1 due to the higher molecular weight of PLA2-NR-PLA2 (Table 2).

Mechanical Properties of Polymer Blends

Figure 8 shows the impact strength of the PLA, PLA/NR, PLA/HTNR and PLA/PLA-NR-PLA blends at 10%wt of rubber. The

impact strength of the blends was higher than that of neat PLA. This was because the NR, HTNR, and PLA-NR-PLA phase absorbed and dissipated the crack energy produced and prevented the abrupt breaking of the specimen. The maximum impact strength of 67.78±12.10



kJ/m^2 which was about 4 times higher than that of neat PLA was found in the blend containing 10%wt HTNR. The impact strength of PLA/HTNR was also higher than PLA/NR which was $65.35 \pm 2.85 \text{ kJ/m}^2$. This suggested that the occurrence of the hydroxyl group and low molecular weight of HTNR tended to improve compatibility with PLA. In addition, the OH groups of HTNR probably reacted with the carboxyl group of PLA (Rosli *et al.*, 2016). Therefore, interfacial adhesion between the HTNR and PLA phase was increased. The impact strength of $41.91 \pm 6.68 \text{ kJ/m}^2$ was found for the PLA/PLA1-NR-PLA1 blend

which was about 2.3 times higher than that of neat PLA. PLA/PLA2-NR-PLA2 showed the impact strength of $46.42 \pm 8.45 \text{ kJ/m}^2$ which was about 2.5 times higher than neat PLA. However, the impact strength of both PLA/PLA1-NR-PLA1 and PLA/PLA2-NR-PLA2 was lower than the PLA/NR and PLA/HTNR blends. This was because the actual rubber content in the PLA/PLA1-NR-PLA1 and PLA/PLA2-NR-PLA2 blends was 8.07%wt and 5.78%wt, respectively. In addition, the size of the triblock copolymer particles in the PLA/triblock copolymer blends was too small to efficiently absorb energy compared to the size of the HTNR particle in the PLA/HTNR blend (Table 4). The impact strength of the PLA/PLA2-NR-PLA2 blend was higher than PLA/PLA1-NR-PLA1 blend, although the rubber content in the PLA/PLA2-NR-PLA2 blend was lower than the PLA/PLA1-NR-PLA1 blend. The longer chain of PLA in PLA2-NR-PLA2 could lead to higher entanglement with the PLA matrix.

The tensile stress-strain curves of the neat PLA, PLA/NR, PLA/HTNR, and PLA/PLA-NR-PLA blends are plotted in Figure 9. Neat PLA showed brittle fracture behavior whereas the PLA/NR, PLA/HTNR, and PLA/PLA-NR-PLA blends exhibited higher elongation before failure. The mechanical properties of all blends are also listed in Table 3. From the results summarized in Table 3, PLA had a tensile strength and modulus values of 61.47 MPa and 0.68 GPa, respectively, whereas the elongation at break is only 12.91%. The tensile strength

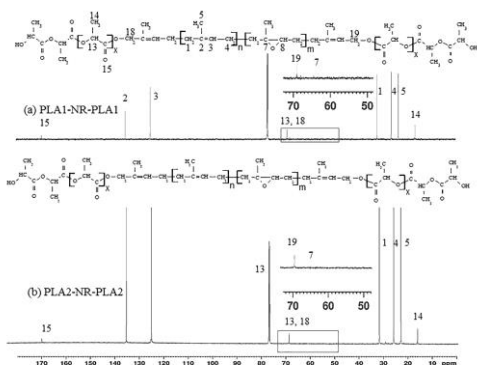


Figure 7. ^{13}C -NMR spectrum of PLA-NR-PLA triblock copolymer, (a) PLA1-NR-PLA1 and (b) PLA2-NR-PLA2

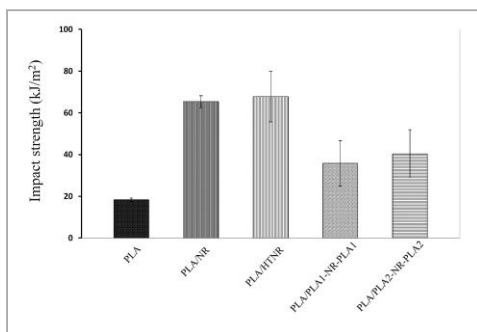


Figure 8. Unnotched impact strength of PLA, PLA/NR, PLA/HTNR, PLA/PLA1-NR-PLA1, and PLA/PLA2-NR-PLA2 blends at 10%wt of rubber

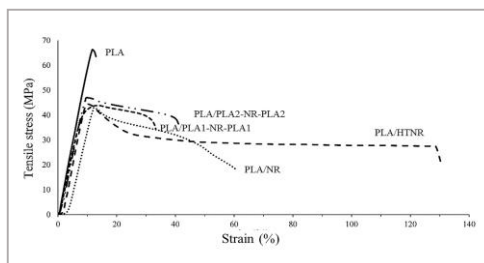


Figure 9. Stress-strain curves of PLA, PLA/NR, PLA/HTNR, and PLA/PLA-NR-PLA triblock copolymer blends at 10%wt rubber

and tensile modulus of all blends were lower than neat PLA whereas the elongation at break was highly increased. The tensile strength and elongation at break of the PLA/HTNR blend were higher than the PLA/NR blend due to better interfacial adhesion. The PLA/HTNR blend showed the highest elongation at break which was obviously improved to 127.23% that was about 2 times higher than the PLA/NR blend. For the PLA/triblock copolymer blends, the tensile strength and tensile modulus of the PLA/PLA1-NR-PLA1 and PLA/PLA2-NR-PLA2 blends were higher than the PLA/NR blend. For the PLA/PLA1-NR-PLA1 and PLA/PLA2-NR-PLA2 blends, the higher molecular weight of the PLA end block in PLA/PLA2-NR-PLA2 led to a higher tensile strength and tensile modulus. The elongation at break of the PLA/triblock copolymer blends was lower than the PLA/NR and PLA/HTNR blends. This could be attributed to too small rubbery particles and a lower rubber content present in the PLA/triblock copolymer blends (Table 4).

The impact strength of the PLA/PLA-NR-PLA triblock copolymer and PLA/NR blends at 10%wt rubber was also studied by Chumeka *et al.* (2014). Similarly, it was found that the impact strength of the blend containing

triblock copolymer with a short PLA ($\bar{M}_n = 3500$ g/mol) end block was lower than the PLA/NR blend. However, when the $\bar{M}_n$ of the NR and PLA block was respectively increased to 20000 g/mol and 6000 g/mol, the impact strength was close to the PLA/NR blend. This was different from the present work. The triblock copolymer with a longer PLA chain end ($\bar{M}_n = 9700$ g/mol) in this work was more compatible with the PLA matrix leading to small rubber particles which was not efficient in energy absorption (see rubber particle size in Table 4). Consequently, the impact strength of the PLA/PLA2-NR-PLA2 blend was lower than the PLA/NR blend.

Morphological Properties of Polymer Blends

SEM micrographs of the freeze-fractured surfaces of the PLA, PLA/HTNR, and PLA/PLA-NR-PLA blends and the average particle diameter of the HTNR particles in the blends are shown in Figure 10 and Table 4, respectively. The blends showed good dispersion of rubbery particles in the PLA matrix. The size of the HTNR, PLA1-NR-PLA1, and PLA2-NR-PLA2 particles in the blends was 0.92 μm , 0.34 μm , and 0.22 μm , respectively. This could be

Table 3. Tensile strength, modulus, elongation at break, and impact strength of the blends

Samples	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)	Impact strength (kJ/m ²)
PLA	61.47±3.69	0.68±0.03	12.91±1.00	18.41±1.49
PLA/NR	42.60±0.64	0.55±0.02	60.54±13.00	65.35±2.85
PLA/HTNR	44.46±1.08	0.54±0.02	127.23±6.00	67.78±12.10
PLA/PLA1-NR-PLA1	43.09±1.29	0.57±0.02	36.53±5.90	41.91±6.68
PLA/PLA2-NR-PLA2	46.79±1.14	0.58±0.02	41.89±18.59	46.42±8.45

Table 4. Diameters of HTNR and PLA-NR-PLA particles in the blends

Samples	Number average particle diameter (μm)	Minimum particle diameter (μm)	Maximum particle diameter (μm)
PLA/NR	2.02±0.68	0.45	4.25
PLA/HTNR	0.92±0.71	0.30	3.40
PLA/PLA1-NR-PLA1	0.34±0.09	0.13	0.70
PLA/PLA2-NR-PLA2	0.22±0.05	0.11	0.29

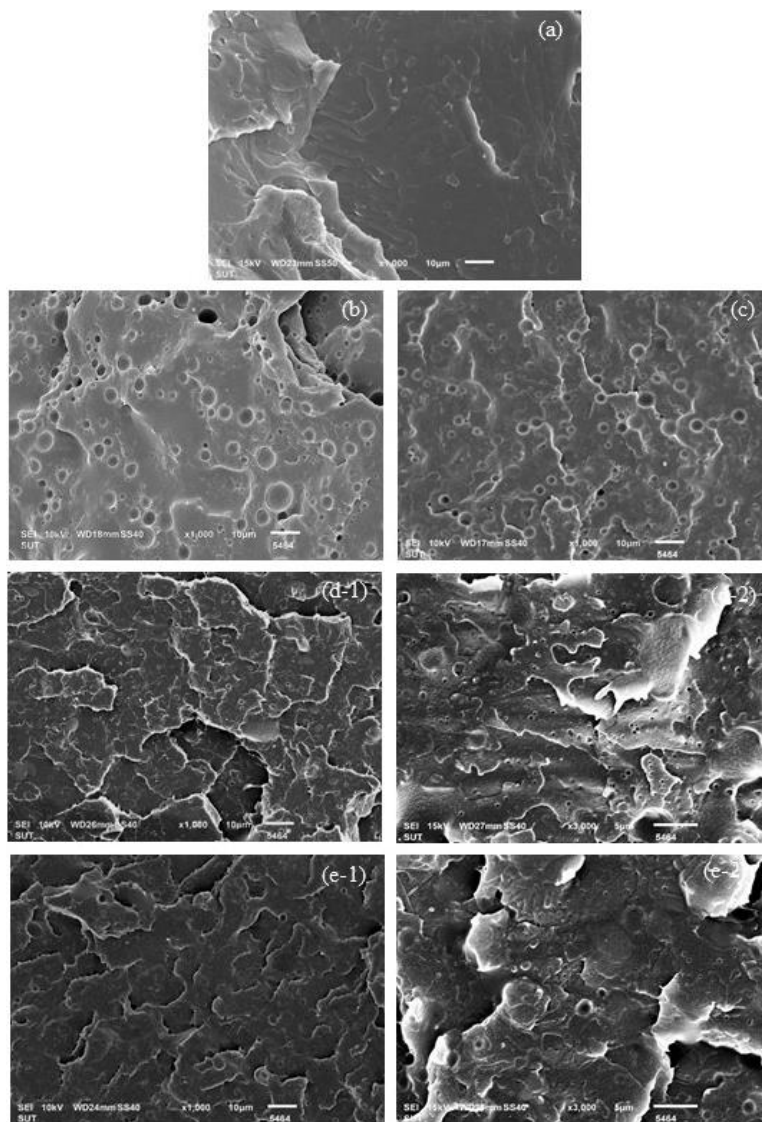


Figure 10. SEM micrographs of freeze-fractured surface of (a) PLA, (b) PLA/NR (1000x), (c) PLA/HTNR (1000x), (d-1) PLA/PLA1-NR-PLA1 (1000x), (d-2) PLA/PLA1-NR-PLA1 (3000x), (e-1) PLA/PLA2-NR-PLA2 (1000x), and (e-2) PLA/PLA2-NR-PLA2 (3000x)

attributed to more compatibility between the PLA matrix and triblock copolymer. However, the blend which had the lowest dispersed particles did not show the highest impact

strength. This might be because the dispersed particles were too small to absorb or dissipate the crack energy produced (Chumeka *et al.*, 2015).

Conclusions

Two types of NR-based toughening agent for PLA including HTNR and its block copolymer with PLA were synthesized. HTNR was prepared by photochemical degradation reaction with a production yield of 91%. The hydroxyl value estimated for the HTNR was 3.55 ± 0.42 mg KOH/g of the sample which gave a hydroxyl functionality of 1.77 ± 0.21 . The PLA-NR-PLA triblock copolymers were prepared by the reaction between the low molecular weight PLA ($\bar{M}_n$ of 3000 and 9700 g/mol) and HTNR using $\text{Sn}(\text{Oct})_2$ as a catalyst. The $\bar{M}_n$ of the obtained PLA-NR-PLA copolymers were 34681 g/mol and 48487 g/mol, respectively, which was related to $\bar{M}_n$ of the pre-PLA and HTNR with a molar ratio of 2:1. Evidence for the triblock copolymer formation was shown by the results from both the ^1H -NMR and ^{13}C -NMR characterization. The toughening efficiency of the HTNR and triblock copolymer was compared with unmodified NR. It was found to be in the following order: HTNR > NR > PLA2-NR-PLA2 > PLA1-NR-PLA1. The impact strength and elongation at break of the PLA/HTNR blend were 67.78 ± 12.10 kJ/m² and 127.23 ± 6.0 %, respectively. Compared to other blends, the PLA/PLA2-NR-PLA2 blend showed the highest tensile strength (46.79 ± 1.16 MPa) and tensile modulus (0.58 ± 0.02 GPa).

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