

Original Article

Effect of maleic anhydride on mechanical properties and morphology of poly(lactic acid)/natural rubber blend

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Abstract

Natural rubber grafted with maleic anhydride (NR-g-MA) was synthesized in an internal mixer at different loadings of MA content. NR-g-MA was used as a rubber modifier of poly(lactic acid) (PLA) and a compatibilizer of PLA/NR blends. Polymer blends were prepared in a twin screw extruder. The grafting reaction of MA was analyzed by ¹H-NMR and FTIR. The percent of MA grafting was determined by the titration method and FTIR. The impact resistance and tensile properties were tested. NR-g-MA was a better impact modifier than NR. The PLA/NR-g-MA blends had greater impact strength and tensile properties than neat PLA and a PLA/NR blend. The significant effect of NR-g-MA as a compatibilizer appeared in the high ductility of the PLA/NR/NR-g-MA blends. Blend morphology was evaluated by SEM. The presence of MA in the polymer blends reduced the average particle diameter which suggested improved miscibility in the polymer blends. The α -transition temperature of the blends was determined by dynamic mechanical thermal analysis.

Keywords: graft copolymer, maleic anhydride, natural rubber, poly(lactic acid), reactive blend

1. Introduction

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester widely used in food packaging, agriculture, and household products. Like common polymers such as polystyrene and poly(ethylene terephthalate), PLA has a high tensile strength and modulus. However, poor toughness is a major drawback of PLA. In order to overcome this limitation, attempts have been made to reduce the brittleness of PLA by blending with natural rubber (NR). The characteristics of NR make it a good toughening agent for thermoplastics. The toughness of PLA was successfully improved by blending with NR and the impact strength of a PLA/NR blend was

increased by using masticated NR (Jaratrotkamjorn, Khao-kong, & Tanrattanakul, 2012). Theoretically, in order to obtain a compatible blend, the difference in melt viscosity between two polymers should not be too high because gross phase separation will be the result. NR is a high molecular weight polymer and its number average molecular weight (M_n) is ~1,000,000 g/mol, whereas the M_n of PLA is <200,000 g/mol. Mastication is a well-known method of reducing the molecular weight of NR. Therefore, mastication is used as a compatibilization method when blending PLA and NR which are generally immiscible owing to their chemical structure. Basically, rubber toughened polymer is not a miscible blend but it is expected to be a compatible blend. Consequently, compatibilization is essential in this blend. The mechanical properties of PLA/NR blends have been reported by other researchers (Bitinis, Verdejo, Cassagnau, & Lopez-Manchado, 2011; Suksut & Deeprasertkul, 2011; Zhang *et al.*, 2011; Pongtanayut, Thongpin, & Santawitee, 2013).

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NR latex is *cis*-1,4-polyisoprene containing a double bond in the repeating unit. A chemical reaction can occur easily via double bonds. This property has facilitated development of NR-based graft copolymers used as compatibilizers in PLA/NR blends. NR was grafted with poly(methyl methacrylate) (Jaratrotkamjorn *et al.*, 2012), with poly(vinyl acetate) (Chumeka, Tanrattanakul, Pilard, & Pasetto, 2013), with glycidyl methacrylate (Juntuek, Ruksakulpiwat, Chumsamrong, & Ruksakulpiwat, 2012), and with PLA (Mohammad, Arsad, Rahmat, Abdullah Sani, & Mohsin, 2016; Sookprasert & Hinchiranan, 2017).

Maleic anhydride (MA) is a useful reactive chemical widely used in reactive blending. During melt blending, an interfacial reaction occurs between MA and certain functional groups. NR grafted with MA (NR-*g*-MA) was developed and used in the compatibilization of NR and cassava starch (Nakason, Kaesaman, Homsin, & Kiatkamjornwong, 2001), and for a NR/acrylonitrile butadiene rubber blend (Afifi & El-Wakil, 2008). Also, NR-*g*-MA was blended with polypropylene (Nakason, Saiwari, & Kaesaman, 2006) and poly(methyl methacrylate) (Nakason, Saiwari, Tatun, & Kaesaman, 2006). The objective of this study was to determine the effect of MA content in NR-*g*-MA used as a toughening agent of PLA and as a compatibilizer in a PLA/NR blend. We expected that the NR-*g*-MA was more miscible and compatible to PLA than NR. The compatibility of the polymer blends was determined from the mechanical properties while increased miscibility was determined from rubber particle size and glass transition temperature.

2. Materials and Methods

2.1 Materials

PLA (Ingeo™ 4042D) was produced by Nature Works LLC. Natural rubber (STR5 CV60) was produced by Jana Concentrated Latex Co., Songkhla, Thailand. MA (99%) was purchased from Sigma-Aldrich. Wingstay® L was purchased from Kit Phaibun Chemistry Ltd. Toluene and acetone were purchased from Lab-Scan Asia Co., Ltd.

2.2 Synthesis of natural rubber grafted with maleic anhydride (NR-*g*-MA)

An amount of 300 g of NR was masticated in an internal mixer with a rotor speed of 60 rpm at 135 °C for 2 min. MA was then added and the mixing continued at 135 °C for 10 min. The MA content was 0.5 to 6 per hundred rubber (phr).

2.3 Polymer blend preparation

Melt blending of binary blends (PLA/NR and PLA/NR-*g*-MA) and ternary blends (PLA/NR/NR-*g*-MA) was carried out in a twin screw extruder (Prism® TSE16TC) at 170 °C with a screw speed of 150 rpm. PLA was dried at 105 °C for 24 h before use. The masticated NR, as described in a previous work (Jaratrotkamjorn *et al.*, 2012), and NR-*g*-MA (without purification) were mixed with 1 phr of Wingstay® L as an antioxidant before blending with PLA. The specimens were prepared by compression molding (Kao Tieh Go Tech Compression Machine) at 160 °C for 13 min to obtain a sheet

with a thickness of 2 mm. The polymer blend compositions and sample nomenclature are listed in Table 1.

Table 1. Compositions of PLA blends (PLA/NR, PLA/NR-*g*-MA and PLA/NR/NR-*g*-MA).

Sample	PLA (wt%)	NR (wt%)	NR- <i>g</i> -MA (wt%)		
			2 phr	4 phr	6 phr
PLA	100	-	-	-	-
10/0	90	10	-	-	-
0/10-2	90	-	10	-	-
0/10-4	90	-	-	10	-
0/10-6	90	-	-	-	10
5/5-2	90	5	5	-	-
5/5-4	90	5	-	5	-
5/5-6	90	5	-	-	5
10/5-2	90	10	5	-	-
10/5-4	90	10	-	5	-
10/5-6	90	10	-	-	5

PLA=poly(lactic acid), NR=natural rubber, NR-*g*-MA=natural rubber grafted with maleic anhydride, phr=parts per hundred rubber.

2.4 Characterization of NR-*g*-MA

A blend sample of 3 g was refluxed in 100 mL of toluene for 3 h and precipitated in an excess of acetone. The purified sample was dried at 40 °C until a constant weight was achieved. Samples were kept in a desiccator prior to use. The purified samples were analyzed using ¹H-NMR and FTIR in order to verify the grafting reaction. ¹H-NMR spectra were recorded on a Fourier transform NMR spectrometer (500 MHz, Varian®) using chloroform-*d* (CDCl₃) as the solvent. FTIR spectra were recorded on a Bruker® Tensor 27 spectrometer. The absorption bands were reported in the range of 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ for 128 scans. The percentage grafting of MA (%MA grafting) was determined from FTIR spectra and calculated according to equation (1), where S is the slope of the calibration curve, and A₁₇₈₃, A₁₇₂₀, and A₁₃₇₅ are the intensity area bands of C=O (succinic anhydride ring), C=O (succinic acid), and CH₃ (NR), respectively (Saelao & Phinyocheep, 2005). The calibration curve was obtained from a common titration method (titration of hydrolyzed NR-*g*-MA) and then evaluated the %MA grafting by calculating an intensity area band ratio of [(A₁₇₈₃ + A₁₇₂₀)/A₁₃₇₅] obtained from FTIR. NR with various amounts of MA (2–14 phr) was investigated.

$$\% \text{ MA grafting} = S \times [(A_{1783} + A_{1720}) / A_{1375}] \quad (1)$$

The M_n and weight average molecular weight (M_w) were determined at 40 °C by gel permeation chromatography on a Shimadzu Prominence system using tetrahydrofuran as the solvent. A polystyrene standard was used.

2.5 Mechanical properties test

Tensile properties were determined on a universal testing machine (Instron® 5569) in accordance with ASTM D412C at a testing speed of 5 mm/min. Six specimens were tested for each sample. The impact resistance was tested in

both Izod and Charpy mode following ASTM D256. Ten notched and un-notched specimens were tested for each sample.

2.6 Blend characterization

Dynamic mechanical thermal analysis (DMTA) was carried out on a Mettler-Toledo DMA 1 instrument in dual cantilever bending mode at a frequency of 1 Hz, strain control of 0.01%, ramp rate of 3 °C/min, and temperature range from 25 °C to 150 °C. The temperature accuracy was ± 0.5 °C. The morphology of the blends was observed using a QuantaV® 400 FEI scanning electron microscope. The freeze fractured surfaces were coated with gold.

3. Results and Discussion

3.1 Characterization of NR-g-MA

The sample nomenclature of the NR-g-MA is described in Table 2. In the ¹H-NMR spectrum of virgin NR, the characteristic peak assigned to the CH proton of NR appeared at 5.10 ppm (Figure 1). In the spectrum of natural rubber grafted with maleic anhydride using 4.0 phr of anhydride (NR-g-MA4.0) (Figure 1), a new characteristic peak, attributed to the CH₂ proton of the succinic anhydride ring, presented at 3.49 ppm (Sookprasert & Hinchiranan, 2015) (Figure 1). The FTIR analysis showed significant absorption bands of NR at 1665 and 834 cm⁻¹ which corresponded to C=C stretching and C=C-H bending vibrations, respectively (Figure 2). Two significant absorption bands assigned to the symmetric and asymmetric C=O stretching vibration of succinic anhydride ring were observed at 1783 and 1857 cm⁻¹, respectively (Nakason *et al.*, 2004; Saelao & Phinyocheep, 2005). These results confirmed the grafting reaction of MA onto the NR.

Table 2. Percentage grafting of MA in NR-g-MA and molecular weights of PLA, NR and NR-g-MA.

Sample	MA (phr)	MA grafting (%)	M_n (g/mol) ^a	M_w (g/mol) ^a
PLA	-	-	133,000	189,000
NR	-	-	1,452,000	2,702,000
masticated NR	-	-	426,000	647,000
NR-g-MA0.5	0.5	0.60	ND	ND
NR-g-MA1.0	1.0	1.10	ND	ND
NR-g-MA1.5	1.5	1.50	ND	ND
NR-g-MA2.0	2.0	1.51	137,900	325,883
NR-g-MA4.0	4.0	2.05	120,500	426,400
NR-g-MA6.0	6.0	3.08	163,400	430,500

^aDetermined by gel permeation chromatography and corrected by Benoit factor for polyisoprene (0.67) (Busnel, 1982).

MA=maleic anhydride, NR-g-MA=natural rubber grafted with maleic anhydride, PLA=poly(lactic acid), NR=natural rubber, M_n = number average molecular weight, M_w = weight average molecular weight, PLA=poly(lactic acid), NR=natural rubber, ND=not determined.

In order to determine the percentage grafting of MA onto the NR using FTIR, it was necessary to prepare a calibration curve. The intensity area band ratio of [(A₁₇₈₃ +

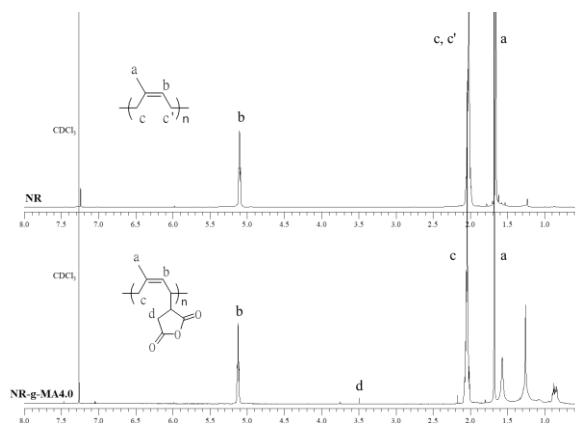


Figure 1. ¹H-NMR spectra of NR and NR-g-MA4.0.

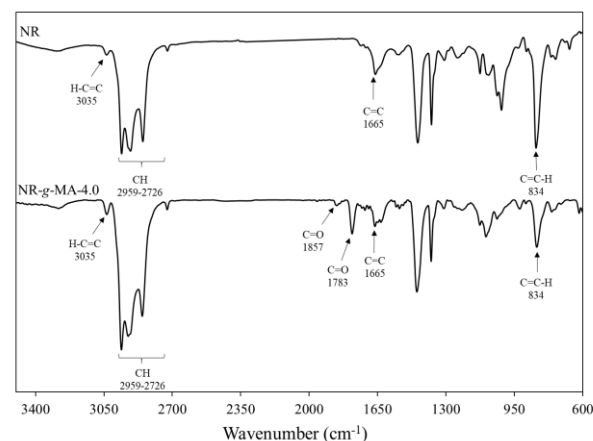


Figure 2. FTIR spectra of NR and NR-g-MA4.0.

$A_{1720}/(A_{1375})$] was determined for every sample. Data of the band ratio were plotted against MA content and a linear curve fit was evaluated. Figure 3 shows the calibration curve with a linear curve fit having an R² value of 0.9824 and a slope of 0.1071. This slope value was used in Equation 1. The %MA grafting values of NR-g-MA are listed in Table 2. At a high MA content (2.0–6.0 phr), the concentration of MA in the NR-g-MA was lower than the added concentration because non-grafted MA was removed during refluxing. It seemed that at a low MA content (0.5–1.0 phr), the calculated %MA grafting was slightly higher than the actual added content. This was probably due to an error of peak area integration because of tiny peaks caused by very small concentrations of MA. However, obtaining a low MA content was not the target of the present work.

The molecular weights of NR, masticated NR, and NR-g-MA are listed in Table 2. The molecular weight of masticated NR decreased considerably after mastication because of chain scissions in NR molecules. Our purpose was to reduce the molecular weight of NR in order to reduce the viscosity of NR. The molecular weight values of all NR-g-MA were lower than the masticated NR because different equipment was used. Mastication of virgin NR was carried out on a two-roll mill following the method of our previous work (Jaratrotkamjorn *et al.*, 2012) while NR-g-MA was synthesized in an internal mixer.

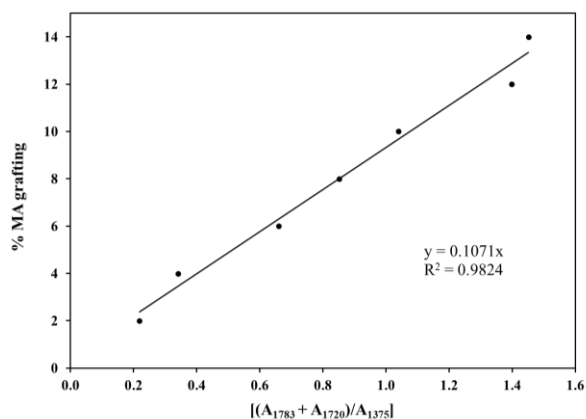


Figure 3. Calibration curve for calculation of Equation 1.

3.2 The mechanical properties of binary blends

Our previous work (Jaratrokamjorn *et al.*, 2012) indicated that 10% of masticated NR increased the toughness of PLA. Thus, this approach was employed in the present study. In the binary blends, two types of rubber (NR and NR-g-MA) were blended with PLA. NR-g-MA containing high MA content (2–6 phr) was selected for polymer blending. The impact strengths of the binary blends are shown in Table 3 and Figure 4. Both Izod and Charpy modes were tested on un-notched and V-notched specimens. The PLA/NR blend (10/0 sample) showed slightly higher impact strength than PLA. In contrast, the PLA/NR-g-MA blends (0/10-2 and 0/10-4 samples) showed much higher impact strength than neat PLA and the PLA/NR blend. The significant increase in the impact strength was observed in the un-notched Izod impact strength test in which the specimens remained unbroken. Additionally, the un-notched Charpy impact strength of the blend containing 10% of NR-g-MA2.0 (0/10-2 sample) was almost twice that of PLA. A higher MA content (NR-g-MA6.0) produced a decrease in the impact strength of the blend (0/10-6 sample) but it was still higher than the PLA. In conclusion, the positive effect of MA was strongly observed on the impact strength of the blends and NR-g-MA2.0 was the best impact modifier for PLA in this binary blend series.

The tensile properties of PLA and the binary blends are shown in Figure 5. The addition of 10% NR decreased all tensile properties of PLA. This is not unusual because, theoretically, the addition of softer polymers, such as an elastomer, would decrease the modulus and tensile strength of that polymer blend. The presence of MA increased the compatibility of the polymer blend. All PLA/NR-g-MA blends showed higher tensile properties, especially the modulus, than the PLA/NR blend. The PLA/NR-g-MA4.0 blend (0/10-4 sample) showed the highest modulus, which was also higher than the PLA. The other two blends containing MA showed a slightly lower modulus than PLA. It is known that unvulcanized NR or green NR is a low modulus polymer. The high moduli in the PLA/NR-g-MA blends can probably be attributed to the rigidity of the succinic anhydride ring in the structure of MA and MA may act as a compatibilizer in the blends. Another improved property was the elongation at break of the PLA/NR-g-MA2.0 (0/10-2 sample) which was higher than PLA.

The morphology of the polymer blends was determined from SEM micrographs (Figure 6). All polymer blends were immiscible, showing spherical particles of rubber as a dispersed phase. The average diameter of the NR-g-MA particles (1.63–1.88 μm) was smaller than the NR particles (2.14 μm) (Table 3). The average diameters of NR-g-MA particles based on MA content were ranked in the following order: 6MA > 2MA > 4MA. The larger particle diameter of NR-g-MA6.0 was possibly due to coalescence of the rubber particles or gelation or both during melt blending caused by the presence of non-grafted MA. The smaller particle diameter of NR-g-MA indicated an increase in miscibility of the polymer blends, which contributed to increased compatibility. It is well established that MA changes to succinic anhydride after grafting on polymer molecules. Theoretically, the terminal end groups of OH and COOH of polymers are able to react with the succinic anhydride as shown in Scheme 1 which results in a new graft copolymer which acted as a compatibilizer located at the interface between the continuous phase and dispersed particles. In this study, we believed that the MA grafting of NR was done through thermal grafting via an ene mechanism. This was a reason for the enhancement of the impact strength and the tensile properties of the PLA/NR-g-MA blends.

Table 3. Impact strength and average diameter of rubber particle of the blends.

Sample	Izod impact strength (kJ/m ²)		Charpy impact strength (kJ/m ²)		Average particle diameter (μm)
	Un-notched	Notched	Un-notched	Notched	
PLA	20.67±2.79	4.67±0.44	27.20±3.22	2.36±0.19	-
10/0	31.18±0.53	4.73±0.61	27.15±2.00	3.00±0.80	2.14±0.79
0/10-2	Unbroken	7.66±0.90	52.30±3.84	4.56±0.27	1.76±0.80
0/10-4	Unbroken	6.15±0.71	33.77±2.90	3.70±0.37	1.63±1.12
0/10-6	26.36±0.21	4.88±0.65	27.63±1.99	3.42±0.16	1.88±1.70
5/5-2	Unbroken	9.28±0.95	52.47±3.98	4.89±0.45	1.33±0.65
5/5-4	Unbroken	10.10±0.94	53.71±8.29	4.63±0.32	1.25±0.54
5/5-6	35.61±7.19	6.56±0.89	35.97±2.62	3.59±0.38	1.80±1.23
10/5-2	Unbroken	7.52±1.03	31.45±2.31	4.61±0.21	1.68±1.00
10/5-4	Unbroken	9.19±1.03	43.54±4.53	4.39±0.32	1.67±0.85
10/5-6	37.79±4.47	8.36±0.91	30.84±5.37	4.30±0.46	2.08±1.35

PLA=poly(lactic acid).

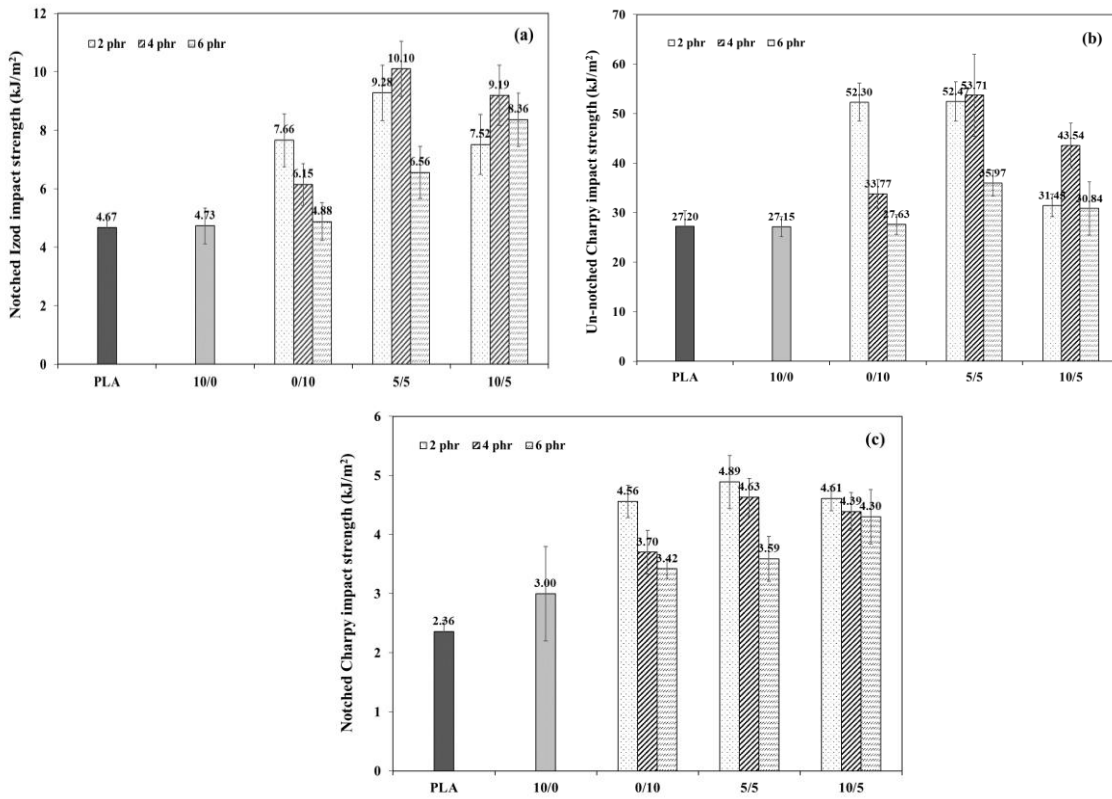


Figure 4. Impact strength of binary and ternary blends: (a) Notched Izod testing, (b) Un-notched Charpy testing, and (c) Notched Charpy testing.

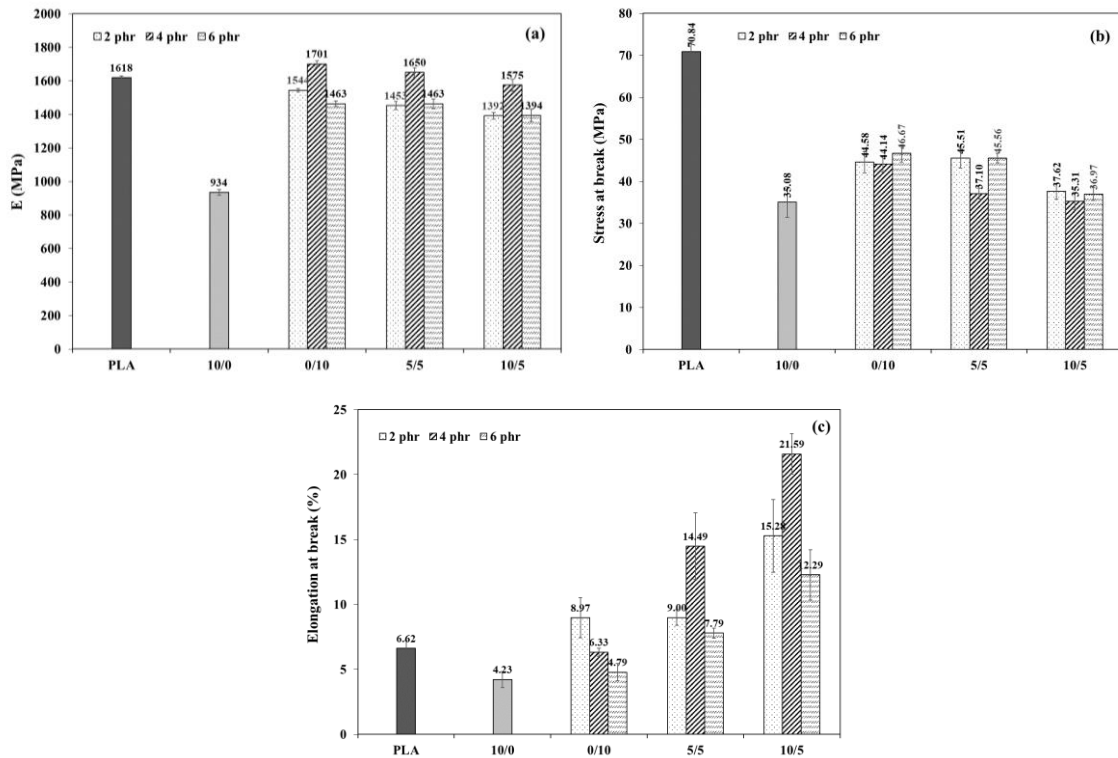


Figure 5. Tensile properties of binary and ternary blends: (a) Modulus, (b) Stress at break, and (c) Elongation at break.

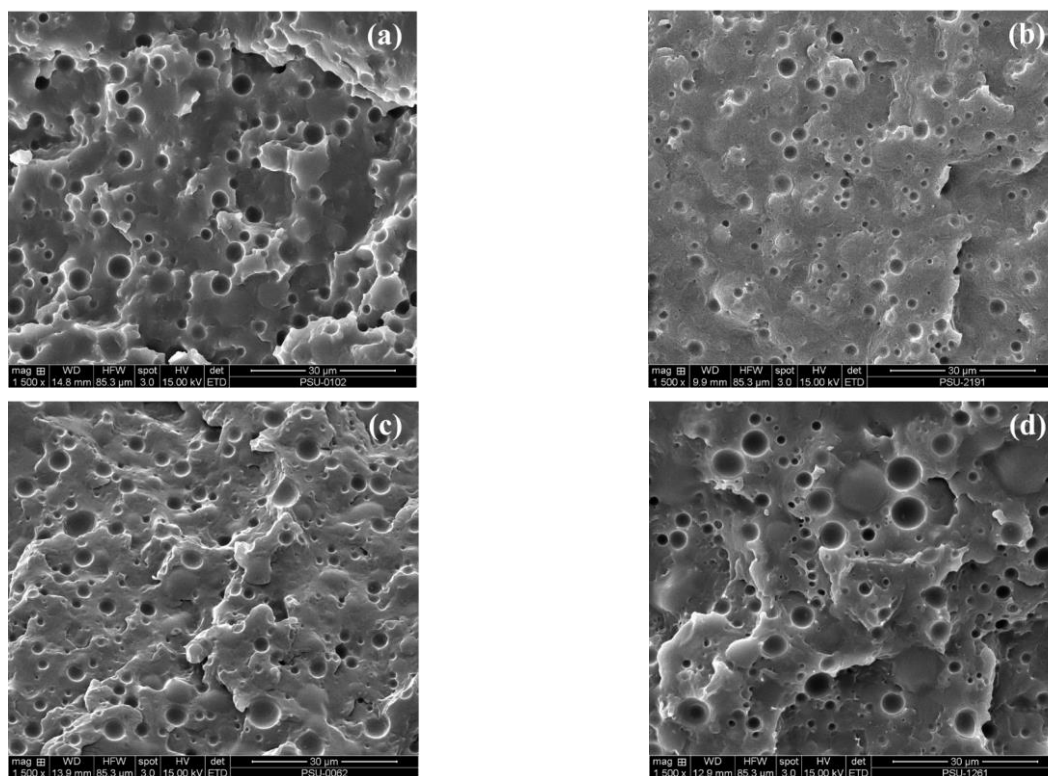
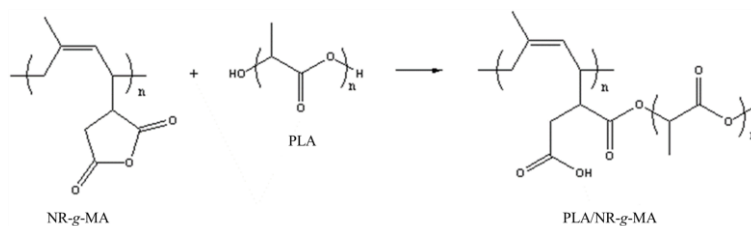


Figure 6. SEM micrographs of freeze fracture surfaces of the blends: (a) 10/0, (b) 0/10-2, (c) 0/10-4, and (d) 0/10-6.



Scheme 1. Proposed mechanism of compatibilization in PLA/NR blend.

3.3 Mechanical properties of ternary blends

The effect of NR-*g*-MA as a compatibilizer of the PLA/NR blend was investigated. The difference between NR and NR-*g*-MA used for blending was not only the presence of MA but also the molecular weight (Table 2). Therefore, ternary blends (PLA/NR/NR-*g*-MA) were prepared (Table 1). Their impact strengths are shown in Table 3 and Figure 4. All impact strengths of all ternary blends were higher than the PLA. Regarding MA content, the synergistic behavior in the ternary blends was derived from the content of NR-*g*-MA 2.0 and NR-*g*-MA4.0. The un-notched Izod impact specimens of the 5/5-2, 5/5-4, 10/5-2, and 10/5-4 samples were not broken nor were the 0/10-2 and 0/10-4 samples. The impact strengths of 5/5-2 and 5/5-4 samples were in the same range for all test modes and were little different from those of the 0/10-2 sample. A higher MA content in the polymer blends (5/5-6 and 10/5-6 samples) showed a decrease in the impact strength which was similar to that observed in the binary blend. But the impact strength of the 5/5-6 sample was higher than the 0/10-6

binary blend sample. Regarding rubber content, the last three blends in Table 1 and 3 consisted of 15% rubber. It appeared that only the 10/5-6 sample showed a higher impact strength than either of the binary blends (0/10-6 and 5/5-6 samples) whereas the others (10/5-2 and 10/5-4 samples) showed lower impact strengths than the 5/5-2 and 5/5-4 samples. This suggested that higher rubber content did not improve the impact strength of the present polymer blends.

The highest impact strengths shown in the 5/5-2 and 5/5-4 samples were possibly related to the average particle diameter (Table 3). The average rubber particle diameters of the 5/5-2, 5/5-4, 10/5-2, and 10/5-4 samples were 1.33, 1.25, 1.68, and 1.67 μm , respectively. The larger average particle diameters in the 10/5-2 and 10/5-4 samples were not unexpected because they contained higher rubber content (15%). It appeared that the smaller diameter particles produced higher impact strength. The average rubber particle diameter became larger when higher MA content was used (NR-*g*-MA6.0). The average rubber particle diameters of the 5/5-6 and 10/5-6 samples were 1.80 and 2.08 μm , respectively. As stated,

particle coalescence or gel formation or both may occur during melt blending and may have caused the lower impact strength in the 5/5-6 and 10/5-6 samples. The experimental data indicated that the optimal average particle diameter was in the range of 1.25–1.76 μm .

The positive effect of MA appeared in the elongation at break (Figure 5c). All ternary blends showed higher elongation at break than the PLA and binary blends. NR-g-MA4.0 provided the highest ductility. The elongation at break increased >2 fold and >3 fold in the 5/5-4 and 10/5-4 samples, respectively. At the same MA content, higher rubber content produced higher elongation at break. NR-g-MA4.0 also exhibited the highest modulus (Figure 5a) and the lowest tensile strength (Figure 5b) which was similar to the binary blends. The moduli and tensile strengths of the ternary blends were in the same range as those of the binary blends, and were higher than the PLA/NR blend.

The average particle diameters obtained from the SEM micrographs showed the effect of MA or NR-g-MA on blend morphology (Figure 6). For example, the average diameter of the PLA/NR blend decreased from 2.14 μm to 1.67 μm after adding 5% NR-g-MA4.0 (10/5-4 sample) (Table 3). This result indicated that NR-g-MA4.0 acted as an emulsifier by reducing interfacial adhesion between the PLA matrix and the dispersed NR phase. Consequently, the interfacial adhesion between both phases increased which enhanced the impact strength and elongation at break. In order to substantiate this effect, some samples were selected to investigate the α -transition temperature of the PLA matrix using DMTA. The loss tangent ($\tan \delta$) as a function of the PLA temperature and the polymer blends is represented in Figure 7. The α -transition temperature is equivalent to the glass transition temperature (T_g). The T_g of the PLA, 10/0, 10/5-4, and 0/10-4 appeared at 64.1, 63.9, 62.4, and 61.5 $^{\circ}\text{C}$, respectively, which indicated that the T_g of PLA in the polymer blends containing NR-g-MA4.0 shifted toward lower temperatures. A significant decrease in the T_g of the PLA matrix verified the effect of MA in the polymer blends. It is a result of reactive blending.

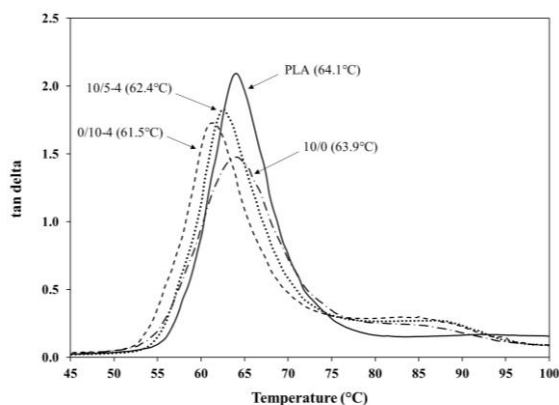


Figure 7. $\tan \delta$ versus temperature of PLA and PLA blends.

4. Conclusions

The effects of MA content in NR-g-MA on the impact strength and ductility of PLA and PLA/NR blends were determined. NR-g-MA containing 2, 4, and 6 phr of MA

was used as a toughening polymer for PLA and as a compatibilizer for PLA/NR blends. NR-g-MA was a better impact modifier than NR. Polymer blends containing NR-g-MA exhibited higher impact strength and tensile properties than PLA and the blend containing no NR-g-MA. The MA content in NR-g-MA showed a strong effect on the toughness and ductility of the polymer blends. NR-g-MA also acted as a good compatibilizer. It played an important emulsifying role which decreased rubber particle size. The α -transition temperature of PLA decreased significantly in the blends containing NR-g-MA which indicated a reactive blend. The optimal content of MA for NR-g-MA was 4.0 phr since it provided both the highest impact strength and elongation at break.

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