Toughness Enhancement of Poly(lactic acid) by Melt Blending with Natural Rubber

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ABSTRACT: Rubber toughened poly(lactic acid) (PLA) was prepared by blending with natural rubber (NR)-based polymers. The blends contained 10 wt % of rubber and melt blended with a twin screw extruder. Enhancement of impact strength of PLA was primarily concerned. This study was focused on the effect of rubber polarity, rubber viscosity and molecular weight on mechanical properties of the blends. Three types of rubbers were used: NR, epoxidized natural rubber (ENR25 and ENR50), and natural rubber grafted with poly(methyl methacrylate) (NR-g-PMMA). Effect of viscosity and molecular weight of NR, rubber mastication with a two-roll mill was investigated. It was found that all blends showed higher impact strength than PLA and NR became the best toughening agent. Viscosity and molecular weight of NR decreased with increasing number of mastication. Impact strength of PLA/NR blends increased after applying NR mastication due to appropriate particle size. DMTA and DSC characterization were determined as well. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5027–5036, 2012

Key words: biodegradable polymer; epoxidized natural rubber; impact resistance; natural rubber; poly(lactic acid); renewable resource

INTRODUCTION

Polylactide or poly(lactic acid) (PLA) is a well-known biodegradable polymer. Advantages and disadvantages of PLA have been summarized by Rasal et al.[1] PLA is an eco-friendly and biocompatible bioplastic. PLA can be processed by conventional processing methods such as extrusion, tubular blown film, injection molding, and thermoforming. One of the significant drawbacks of PLA is poor toughness. This limits the applications of PLA in order to replace the conventional thermoplastics. Toughening PLA has been reviewed by Anderson et al.[2] There are many methods for increasing toughness of PLA, including controlled stereochemistry of PLA, addition of plasticizers and other polymers. Rubber toughened PLA can be classified into two types: blending with nonbiodegradable polymers and blending with biodegradable polymers. Typically, the impact strength is an indicator of toughness whereas the elongation at break indicates ductility of materials. The impact strength of PLA increases when blending with polycaprolactone, polyurethane, caprolactone/trimethyl carbonate copolymer, caprolactone/lactide diblock copolymer, poly(butylene adipate-co-terepthalate), poly(butylenes succinate), and acrylonitrile–butadiene–styrene terpolymer.[1–9] Linear low-density polyethylene and styrene–ethylene–butylene–styrene triblock copolymer can improve impact strength as well.[10,11]

Natural rubber (NR) is an eco-friendly rubber and derived from a renewable resource. NR should be a good toughening agent due to its high molecular weight and very low glass transition temperature ($\sim -70^{\circ}C$). Based on our knowledge, there is little publication reporting a polymer blend between PLA and NR. Considering chemical structure of NR and PLA, chemical-modified NR may provide more miscibility than the virgin NR. It has been reported that the toughness of the PLA/NR blend was improved by adding the natural rubber grafted with glycidyl methacrylate (NR-g-GMA).[12] There are many factors affecting the toughness of the rubber toughened plastics. For instance, the blends should have high interfacial adhesion between the plastic matrix and the dispersed phase (the rubber particles) and the melt viscosity of both polymers should not be much different. Furthermore, mechanical properties of all polymer blends are strongly dependent on blending method and sample preparation. Although the rubber toughened plastics are not a miscible blend, but it is required to have low surface tension in the
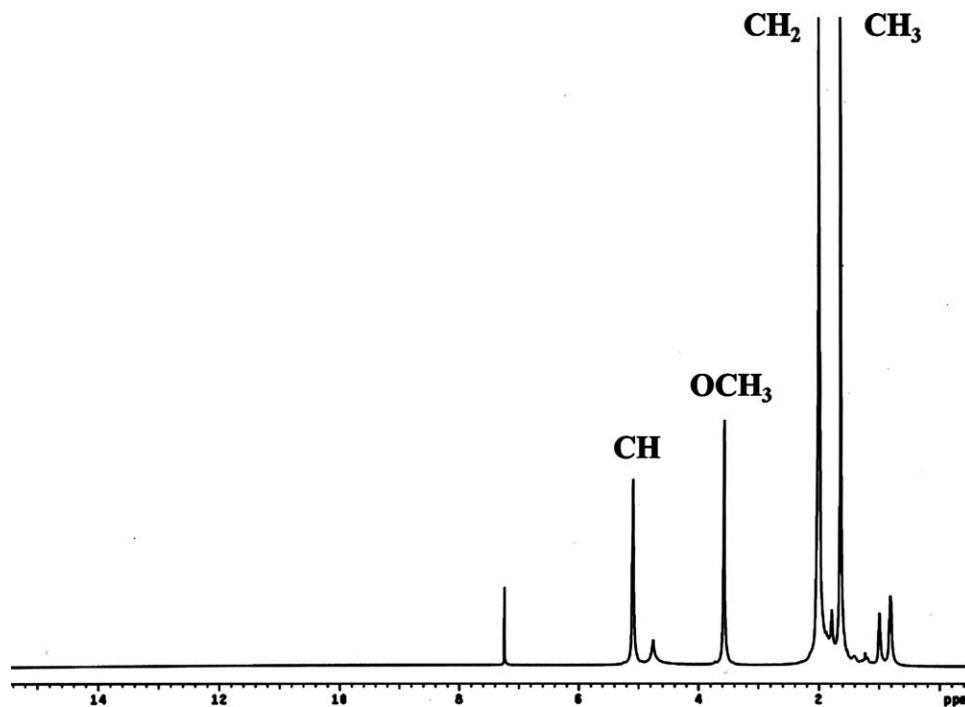
Figure 1 ^{1}H-NMR spectrum of the NR-*g*-PMMA containing 35% grafted PMMA (G35).

blends in order to obtain the appropriate rubber particle diameter. It is believed that the PLA blended with poly(methyl methacrylate) could be a miscible blend.[13–15] Therefore, using NR-*g*-PMMA as a compatibilizer should increase the toughness of the PLA/NR blend, which was one of our assumptions. NR-*g*-PMMA is not a new polymer and it has been studied for more than 10 years.[16–23] It also has been reported that cumene hydroperoxide (CHP)/tetraethylene pentamine (TEPA) is the most effective redox initiator. As a result, this study selected this system to synthesize the NR-*g*-PMMA because the new method of graft copolymerization was not the objective of this study. Another assumption was that the lower molecular weight of NR should show the smaller particle diameter in the blend. Basically, NR is a high molecular weight polymer. Mastication of NR by using a two-roll mill is a typical method in order to decrease its molecular weight. Polarity of rubber should be concerned for preparation the rubber toughened PLA. Consequently, it was interesting to compare the commercialized epoxidized NR with NR.

The aims of this study were to determine the effect of NR-*g*-PMMA, viscosity of NR and type of rubber (NR and ENR) on mechanical properties, particularly the impact strength, of the rubber toughened PLA. Although there are many publications about toughened PLA, but it is difficult to compare among those results and this study. Because there are several parameters that significantly affect mechanical properties including PLA grade, type of rubber, rubber content, blending method (equipment and condition), specimen preparation, and testing condition. Therefore, there is no attempt to make a comparison between this study and those publications.

EXPERIMENTAL

Materials

All polymers used are commercial grade. PLA Ingeo® 2002D produced by Natureworks LLC. It contains ∼ 96.0% of L-lactide configuration and ∼ 4.0% of D-lactide configuration. NR, STR5 CV60, was produced by Jana Concentrated Latex Co.,

TABLE I
Characteristics of Synthesized NR-*g*-PMMA

Sample code	Conversion (%)	Free NR (%)	Free PMMA (%)	Grafting efficiency (%)	Grafted PMMA (wt %)
G35	83.99	2.31	28.07	79.70	35.42
G5	93.17	5.18	0.84	94.02	4.67

TABLE II
Tensile Properties of PLA and the Blends Containing Different NR-Based Rubbers

Sample	E (MPa)	σ_y (MPa)	σ_b (MPa)	ε_b (%)
PLA	1638 ± 39	62.08 ± 0.48	61.88 ± 0.48	5.44 ± 0.19
10% NR	1309 ± 122	39.89 ± 3.90	32.16 ± 4.47	7.26 ± 1.20
10% G5	1319 ± 29	35 ± 1	31.50 ± 3.05	4.61 ± 0.79
10% G35	1375 ± 152	–	26.42 ± 4.50	2.90 ± 0.30
10% ENR25	1382 ± 27	–	19.30 ± 0.40	2.31 ± 0.08
10% ENR50	1360 ± 46	–	17.80 ± 4.60	2.25 ± 0.33
5% NR + 5% G5	1298 ± 26	36.48 ± 1.22	34.20 ± 1.91	5.40 ± 0.84
5% NR + 5% G35	1331 ± 51	41.13 ± 0.35	35.06 ± 2.54	6.86 ± 1.95

Songkla, Thailand. Epoxyprene® 25 (ENR25) and Epoxyprene® 50 (ENR50) were produced by Meuang Mai Guttri (Thailand) Co., Suratthani, Thailand. Their degree of epoxidation was 25 and 50 mol %, respectively. Antioxidant of the rubber (Wingstay® L) was added during blending. High ammonium concentrated NR latex was produced by Jana Concentrated Latex Co., Thailand. Methyl methacrylate (99% purification, Sigma–Aldrich) was used as a monomer for graft copolymerization. Sodium hydroxide (Ajax Finechem) and calcium chloride (Ajax Finechem) were used for MMA purification and dehydration processes. CHP (Fluka) and TEPA (Fluka) were a redox initiator. The 37 wt % potassium laurate aqueous solution acted as a stabilizer of latex and was prepared from potassium hydroxide (Lab-scan Asia) and lauric acid (QReCä).

NR-g-PMMA copolymerization

NR-g-PMMA was copolymerized and determined grafting efficiency according to Kalkornsurapranee et al.[21] Methyl methacrylate was purified by 10% (w/v) sodium hydroxide aqueous solution, washed with distilled water until MMA was neutral, and dehydrated by using anhydrous sodium sulfate. The mixture containing latex, TEPA, potassium laurate, and water was stirred for 30 min at 50°C under nitrogen gas. Then, solution of MMA and CHP was added drop-wise within 1 h. The mixture was then left for 2 h. Graft copolymer was coagulated with 10% (w/w) calcium chloride solution, then washed and dried at 40°C for 48 h. Prior to determine the grafted PMMA content, PMMA homopolymer and free NR were eliminated by Soxhlet extraction using acetone at 60°C for 24 h and petroleum ether at 40°C for 24 h for extraction of free PMMA and free NR, respectively. Percentage of grafted PMMA in the NR-g-PMMA was evaluated by the ^{1}H-NMR (Varian INOVA, 500 Hz) using deuterated chloroform as a solvent.

Polymer blend preparation

Melt blending was performed in a twin screw extruder, Prism® TSE16TC, at 160°C and the screw speed of 190 rpm. NR was mixed with the antioxidant (1 phr of Wingstay® L) prior to blending with PLA. The NR-g-PMMA was used as received, without extraction of free PMMA and free NR. The blends consisted of 10 wt % rubber. Compression molding was carried out at 160°C for 9 min to obtain a 2-mm thick sheet. The blends were kept in a desiccator before testing. Rubber mastication was done by using a two-roll mill. It was controlled by a number of passing such as 20–240 passes.

Mechanical properties testing

Tensile properties, flexural properties (three-point bending), and impact resistance were carried out according to ASTM D412, ASTM D790, and ASTM D256, respectively. Eight specimens were used for every sample. Testing speed was 5 mm/min and 1.3 mm/min for tensile properties and flexural properties, respectively. Impact strength was investigated by using v-notched and un-notched specimens. Both Izod and Charpy test modes were applied.

Blend characterization

Molecular weight of polymers was determined with a gel permeation chromatography (SHIMADZU LC-20AD-230V) by using refractive index detector. Three runs were applied for every sample and reported in terms of an average value and a standard deviation. Perkin Elmer®DSC7 was used for measurement of thermal properties at a heating scan of 10°C/min from 20°C to 200°C. After the first heating scan the sample was cooled at a cooling rate of −100°C/min and then heated again. DSC thermograms were recorded from both the first heating scan and the second heating scan. The heat of fusion of pure crystalline PLLA (ΔH_C) is 93 J/g.[5,24] Dynamic mechanical thermal analysis was investigated by using
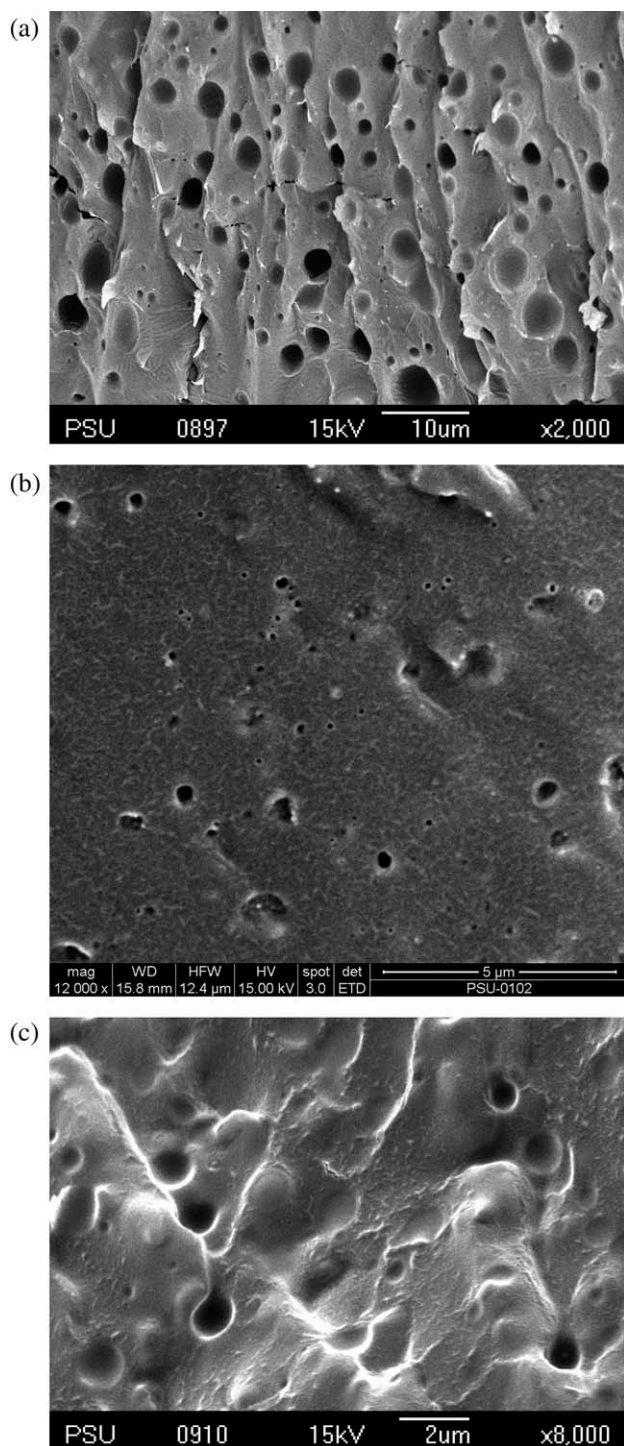
(a)

(b)

(c)

Figure 2 SEM micrographs of freeze fractured surfaces of the blends: (a) 10% NR, (b) 10% NR-*g*-PMMA (G35), and (c) 10% ENR25.

Rheometric Scientific DMTA V under the following condition: frequent 1 Hz, heating rate 3°C/min, strain control 0.01%, and dual cantilever mode. Mooney viscosity of NR was examined by using Alpha Technology Rheometer MV2000. Testing was performed by using a large rotor at 100°C and the

specimen was warmed for 1 min and tested for 4 min, as called ML(1 + 4). Scanning electron micrographs were recorded by using JEOL®JSM5800LV and Quanta®400 FEI. All specimens were immersed in liquid nitrogen for 4 h and immediately fractured prior to coating with gold.

RESULTS AND DISCUSSION

Graft copolymerization

Two different grafted PMMA contents were synthesized, coded as G5 and G35 according to percentage of grafted PMMA. Figure 1 represents the ^{1}H-NMR spectrum of the sample (G35) after Soxhlet extraction of both free NR and free PMMA. The main characteristic peaks confirming the grafting of PMMA on NR backbone are 3.5 ppm (OCH$_3$ protons of PMMA) and 5.1 ppm (C=CH$_2$ protons of NR).[20,21] Table I shows details of the derived NR-*g*-PMMA, determined according to Kalkornsuprapranee.[21] It is common to obtain higher free PMMA (homopolymer) when using higher MMA content.[18,21] Therefore, G35, containing 35% grafted PMMA, showed higher PMMA homopolymer during graft copolymerization than G5. Percentage of conversion and grafting efficiency were high, 80–90%.

Effect of chemical modification on mechanical properties

Tensile properties of the blends containing NR, ENR, and NR-*g*-PMMA were compared as shown in Table II. Obviously, these rubbers decreased the Young's modulus (E), the yield stress (σ_y), and the tensile strength (σ_b) of PLA. Furthermore, the addition of NR-*g*-PMMA and ENR did not improve the elongation at break of PLA. In general, addition of a soft polymer, e.g., rubber, into the plastic matrix causes deterioration in modulus and strength of that blend. The Young's modulus of the blends containing NR-*g*-PMMA and ENR seemed to be higher than that of PLA/NR blend. This may attributed from the presence on PMMA and epoxide ring due to their higher rigidity than the purely flexible chains in NR. The yield stress of PLA dropped largely when blended with 10% of NR and G5. No yielding appeared in the blends containing 10% of G35, ENR25, and ENR50 and these blends became more brittle than PLA. This should be due to their rigidity as well. The lower stress at break in these blends may relate to their lower ductility. NR gave higher tensile strength and ductility than ENR; although ENR should be more compatible to PLA than NR because ENR is more polar which, theoretically, provides more miscibility providing smaller particle size of ENR in the blends

TABLE III
Flexural Properties of PLA and the Blends Containing Different NR-Based Rubbers Tested at a Speed of 1.3 mm/min

Sample	E (MPa)	σ_{max} (MPa)	ε_b (%)
PLA	3739 ± 107	101.34 ± 5.41	4.42 ± 0.52
10% NR		Unbroken	
10% G5	3056 ± 99	52.00 ± 0.60	2.40 ± 0.24
10% G35	3162 ± 158	32.90 ± 4.30	1.20 ± 0.15
10% ENR25	2884 ± 98	22.00 ± 1.80	0.87 ± 0.06
10% ENR50	2804 ± 144	20.40 ± 3.50	0.83 ± 0.10

[Fig. 2(c)]. G5 and G35 should be used as a compatibilizer rather than used as a second polymer in the blends as demonstrated in Table II. They increased the yield stress, the tensile strength and the elongation at break of the blends after adding 5% NR-*g*-PMMA in the blends containing 5% NR. This result indicated the effect of PMMA which agreed with our assumption in enhancing compatibility of the PLA/NR blend.

Three-point bending was applied to determine flexural properties of the blends. The addition of ENR and NR-*g*-PMMA reduced flexural properties of PLA. Flexural modulus, flexural strength, and flexural strain of these blends were much lower than PLA (Table III). In contrast, the blend consisted of NR did not break under the same testing condition, indicating higher flexibility.

Impact resistance was tested by Izod and Charpy test mode with notched and un-notched specimens. Impact strength of the notched specimens may not relate to that of the un-notched ones. The tip of the v-notched specimen is a stress concentrator bringing about fracture at this position. On the other hand, a crack in the un-notched specimen will start at any point in the specimen that behaves as a stress concentrator. Basically the rubber particles in a rubber toughened polymer will be a craze starter or crack initiator. As a result, fracture in the un-notched specimen can occur randomly in the test samples. It is common to obtain higher impact strength in the un-notched specimen because the v-shaped notch generates high stress concentration. Table IV represents the impact strength of PLA and the blends. The notched impact strength was lower than the un-notched impact strength in both Izod and Charpy test modes. It can also be seen that the Izod impact strength was different from the Charpy impact strength. As the testing method of both modes is not similar; therefore, it is not necessary to compare results between both modes. Moreover, it was not the objective of this study to identify the origin of this difference. Tai et al.[25] and Rogers and Plumtree[26] have found the difference between Izod impact strength and Charpy impact strength. Regarding to the Izod impact test, NR and G5 acted as a toughening agent of PLA, whereas G35, ENR25, and ENR50 decreased the impact strength of PLA. For Charpy test mode, NR, G5, and G35 enhanced impact strength of PLA in both un-notched and notched specimens. Meanwhile, ENR25 showed good promising only in the un-notched specimens and ENR50 showed inferiority. G35 acted as a compatibilizer for the PLA/NR blend, similarly to the tensile testing. The ternary blend (PLA/NR/G35) exhibited increases in un-notched Izod and Charpy impact strength. Generally speaking, it was successful to enhance the toughness of PLA by using NR, ENR25, and NR-*g*-PMMA. PMMA content in NR-*g*-PMMA revealed significant effect in the impact strength and morphology of the blends. The lower content (G5) could be used as a toughening agent but the higher content (G35) was suitable for compatibilization as displayed in the PLA/NR/G35 blend. It should be noted that the PLA/NR/G35 blend had less NR content than the binary blend (PLA/NR).

The results of impact test agreed with both test results described earlier. NR became the best toughening agent compared with NR-*g*-PMMA and ENR. At this stage, it is not so clear as to the exact cause for the observed highest mechanical properties from NR. This result was unique because polarity of rubber did not play an important role in mechanical

TABLE IV
Impact Strength and Particle Diameter of the Blends Containing Different NR-Based Rubbers

Sample	Izod impact strength (kJ/m^2)		Charpy impact strength (kJ/m^2)		Average particle Diameter (μm)
	Un-notched	Notched	Un-notched	Notched	
PLA	19.55 ± 2.67	2.85 ± 0.66	19.24 ± 5.22	2.54 ± 0.55	–
10% NR	Unbroken	6.36 ± 0.36	30.16 ± 5.90	4.29 ± 0.54	2.50 ± 1.16
10% G5	Unbroken	5.46 ± 0.65	24.87 ± 5.93	3.67 ± 0.61	0.25 ± 0.17
10% G35	9.42 ± 2.99	2.25 ± 0.77	22.39 ± 5.83	3.49 ± 0.80	0.08 ± 0.02
10% ENR25	7.96 ± 1.75	3.14 ± 0.36	23.10 ± 6.67	2.55 ± 0.88	0.45 ± 0.03
10% ENR50	9.18 ± 3.00	2.26 ± 0.66	12.57 ± 1.36	1.17 ± 0.19	0.14 ± 0.09
5% NR + 5% G5	16.29 ± 3.33	3.78 ± 0.48	13.19 ± 3.05	2.72 ± 0.63	1.23 ± 0.82
5% NR + 5% G35	29.21 ± 4.08	5.41 ± 0.85	26.33 ± 3.41	4.10 ± 0.45	0.10 ± 0.06

TABLE V
Molecular Weight of the Different Rubbers Used

Rubber	M_n (g/mol)	M_w (g/mol)
NR	1,485,000 ± 32,000	2,702,000 ± 42,000
G5	230,000 ± 8000	849,000 ± 30,000
G35	157,000 ± 12,000	618,000 ± 5000
ENR25	309,000 ± 4200	780,000 ± 12,000
ENR50	181,000 ± 15,600	558,000 ± 11,000

Average value ± standard deviation.

properties of the blends. Molecular weight of these rubbers was determined and revealed in Table V. It was shown that chemical modification of NR decreases its molecular weight and the more modification the more reduction in molecular weight. It may be expected that higher molecular weight of NR attributes to higher mechanical properties of the blends. This hypothesis did not coincide with the results in the following section. Another key factor should be considered which was diameter of rubber particles in the blends (Table IV). All blends displayed relatively spherical rubber particles (Fig. 2). In the binary blends, the average particle diameter of NR was largest (2.50 μm), whereas NR-g-PMMA and ENR showed submicron size. The smaller size of the chemical-modified NR indicated higher miscibility than virgin NR. However, the lower molecular weight of these rubbers might affect the particle size as well because of lower viscosity. It was assumed that particle size of NR-g-PMMA and ENR is too small for acting as a good toughening agent. Moreover, NR-g-PMMA and ENR have more structural rigidity than NR.

Effect of rubber mastication on mechanical properties

The effect of mastication of NR on tensile properties shows in Figure 3. Compared with the un-masticated NR, the Young's modulus slightly increased when number of mastication was 20–100 passes, then the value slightly dropped when increased number of mastication. Mastication of NR insignificantly affected on the yield stress but tended to decrease the tensile strength of the blends. The advantage of rubber mastication appeared in the elongation at break which increased as increasing number of mastication from 20 to 100. Further increase of the number of mastication decreased this property but it still higher than that of PLA. Practically, the number of mastication between 60 and 100 seemed to be most appropriate for improvement tensile properties by increasing tensile toughness of the PLA/NR blend. Moreover, rubber mastication gave better tensile properties of the blends than rubber modification.
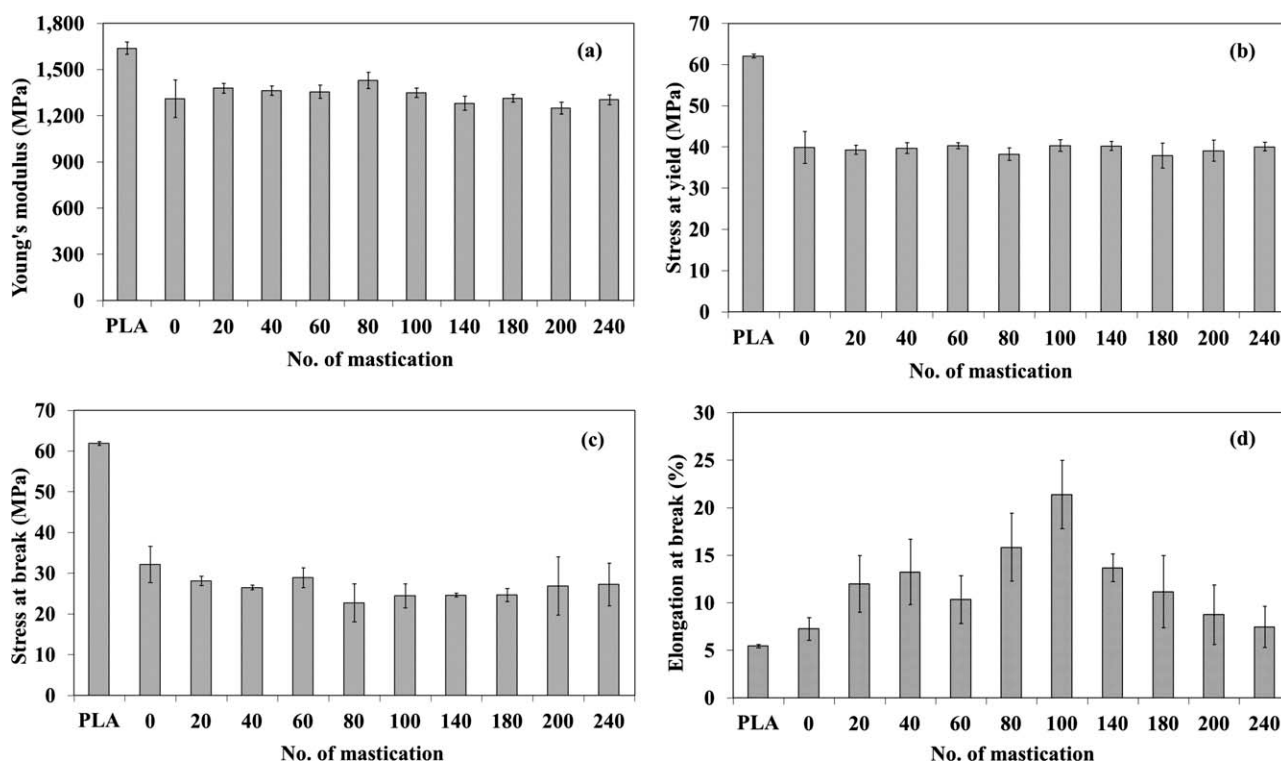

Figure 3 Effect of rubber mastication on the tensile properties of the PLA/NR blends: (a) Young's modulus, (b) yield stress, (c) stress at break, and (d) elongation at break.
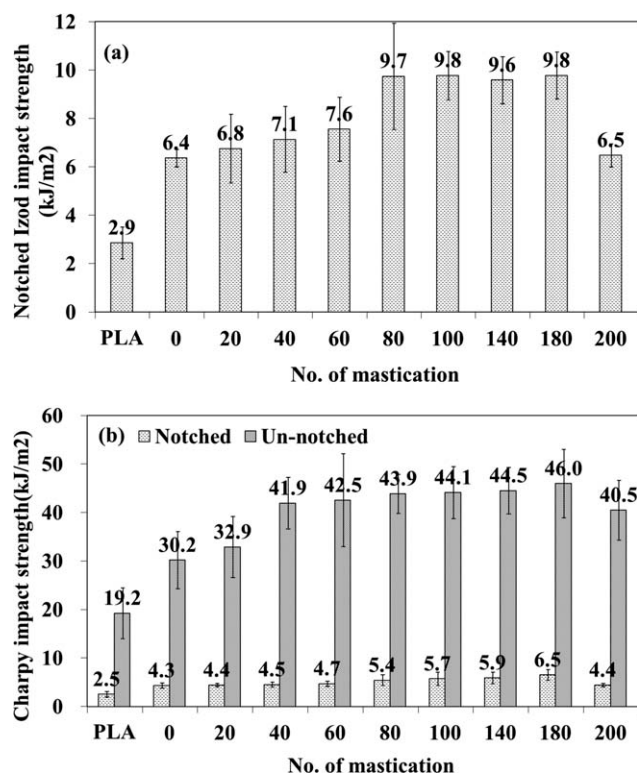
Figure 4 Effect of rubber mastication on the impact strength of the PLA/NR blends: (a) Izod testing and (b) Charpy testing.

High flexibility of the PLA/NR blends has been observed from three-point bending test. All samples did not break during testing even though the testing speed increased to 15 mm/min.

Rubber mastication significantly increased the impact strength of the blends (Fig. 4). All un-notched Izod specimens did not break, and the notched Izod specimens showed the enhanced impact strength, i.e., 50%, from 6.36 to 9.77 kJ/m^2. The suitable number of mastication for Izod impact strength was 80–180. The Charpy impact strength increased with increasing the number of rubber mas-
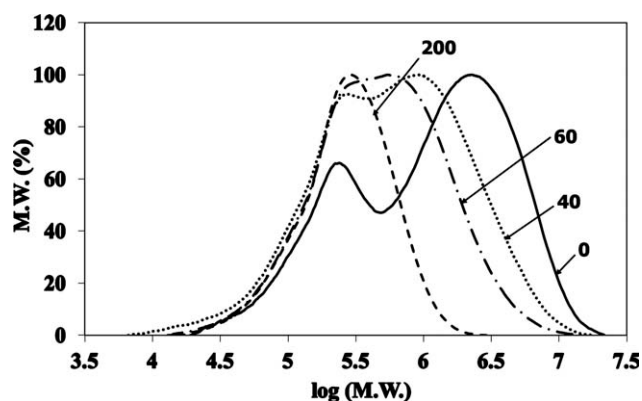

Figure 5 Effect of rubber mastication on the molecular weight of NR.

tication from 20 to 180. The optimal number of mastication was 80–180, similarly to the Izod test results. Beyond 180 passes, the Charpy impact resistance decreased.

As stated previously, viscosity and particle diameter are the key factors in the rubber toughened plastics. Certainly, chain scission of NR molecules occurs during mastication due to applied stress. Figure 5 shows molecular weight distribution of NR before and after mastication. Normally, molecular weight of NR is bimodal. It revealed that the higher molecular weight part was destroyed and the average molecular weight moved toward to the lower part. Molecular weight and Mooney viscosity of NR decreased with increasing number of mastication (Table VI). These attributed to reduction in NR particle size in the blends (Table VI). It is noticeable that NR particles reduced from 2.50 to 0.62 μm after mastication at 180 passes. Lower particle diameter, e.g., 0.56 and 0.47 μm, was not favorable for impact resistance of the PLA/NR blend. The optimal NR diameter should be $\sim$ 0.5–1.0 μm.

Blend characterization

The objectives of these experiments were to investigate miscibility of the blends whether changes in the glass transition temperature (T_g) occurring or not and observe the effect of rubber on thermal properties of PLA. Transition behavior of the blends was evaluated by DMTA and DSC. Figure 6 shows tan δ of PLA and the blends and transition temperatures are listed in Table VII. The NR-140 was NR masticated at 140 passes. All blends revealed two transition temperatures in the temperature range of 40–140°C. The lower temperature represents T_g of PLA. The higher transition temperature, assigned as T_H, did not appear in PLA [Fig. 6(c)]. Unfortunately, this study was unable to characterize the unvulcanized rubber under this condition. T_g of PLA changed insignificantly after blending with these rubbers. This result substantiated a characteristic of an immiscible blend in these blends. The lower surface tension in the blends containing ENR and NR-g-PMMA as confirmed by very small particle diameter seemed to not relate to T_g. At the present time, it is unable to explain the effect of the second transition temperature (T_H) because its existence was not relevant to mechanical properties, particularly the impact strength.

DSC thermograms of PLA and the blends are demonstrated in Figure 7 and thermal properties are listed in Table VIII. Thermal history dominated degree of crystallinity and melting temperature of PLA. Crystallization of PLA significantly decreased from 42.6% to 14.9% after compression molding. Its T_m also reduced from 151°C to 147°C. PLA did not

TABLE VI
Characteristics of Masticated NR

| No. of mastication	M_n (g/mol)	M_w (g/mol)	ML(1 + 4) at 100°C	Average diameter (μm)
0	1,485,000 ± 32,000	2,702,000 ± 42,000	56.62	2.50 ± 1.16
20	1,200,000 ± 30,800	2,169,000 ± 31,000	50.57	1.88 ± 0.94
40	992,000 ± 24,000	1,668,000 ± 3,600	44.76	1.76 ± 0.63
60	225,000 ± 7000	705,000 ± 6500	41.82	1.48 ± 0.61
80	210,000 ± 14,000	538,000 ± 9400	34.34	1.28 ± 0.54
100	202,000 ± 5000	468,000 ± 1000	26.35	0.95 ± 0.44
140	189,000 ± 1500	389,300 ± 3000	17.20	0.86 ± 0.74
180	176,000 ± 2700	343,400 ± 4400	11.82	0.62 ± 0.41
200	168,000 ± 1400	319,400 ± 5000	10.59	0.56 ± 0.49
240	158,000 ± 3800	271,000 ± 4500	6.88	0.47 ± 0.28
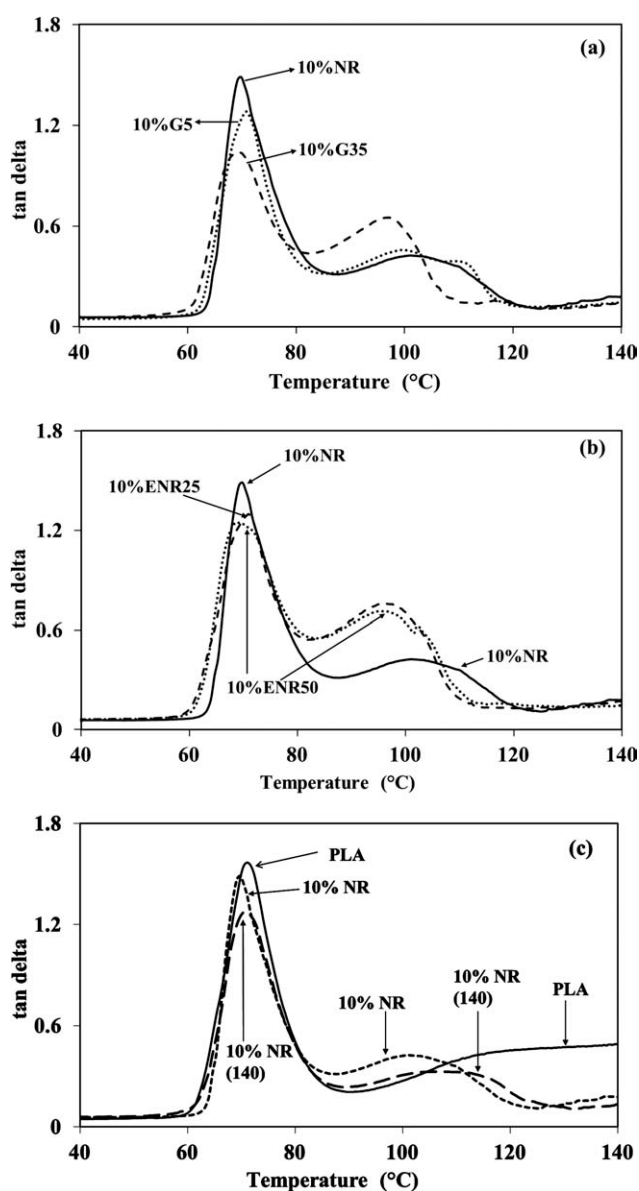
Figure 6 The tan δ vs. temperature obtained from the DMTA of PLA and the blends including 10% NR, 10% G5, 10% G35, 10% ENR25, 10% ENR50, and 10% NR masticated for 140 passes.

show cold crystallization. All the blends performed similar thermal behavior as displayed in Figure 8. They showed over-shoot glass transition, cold crystallization and multiple melting peaks. T_g of PLA in the blends was approximately $58 \pm 2°C$ whereas T_g of virgin PLA and compression molded PLA was 58.9 and 57.9°C, respectively. No significant change in T_g was observed. There was no simple correlation between the cold crystallization temperature (T_{cc}) and the blend components. T_{cc} of PLA in the blends was in the range of 101–113°C. The presence of cold crystallization of PLA in the blends could be explained into two aspects. First, it implied that the rubber acted as a nucleating agent. Second, molecular weight of PLA decreased after blending and the relatively short chains of PLA were able to crystallize during heating above T_g, likewise other polyesters. T_m of PLA in the blend was about $144\pm1°C$ and lower than the pure PLA, indicating a decrease in molecular weight. Double melting phenomenon in polymers has been published for a long period of time.[27–29] There was no an attempt to identify the origin of the double melting peak because the double melting peak of PLA in the blends disappeared after the second heating scan. Both PLA pellet and PLA compression molded sheet could be classified as a semicrystalline polymer. For a polymer showing cold crystallization, the original crystallization determined from the heating scan must calculate from the

TABLE VII
Transition Temperature of PLA and the Blends Determined from DMTA

Sample	T_g (°C)	T_H (°C)
PLA	71.2	–
10% NR	69.8	101.5
10% NR-140	71.2	109.6
10% ENR25	71.1	96.9
10% ENR50	68.6	96.8
10% G5	70.7	100.2
10% G35	69.3	97.6
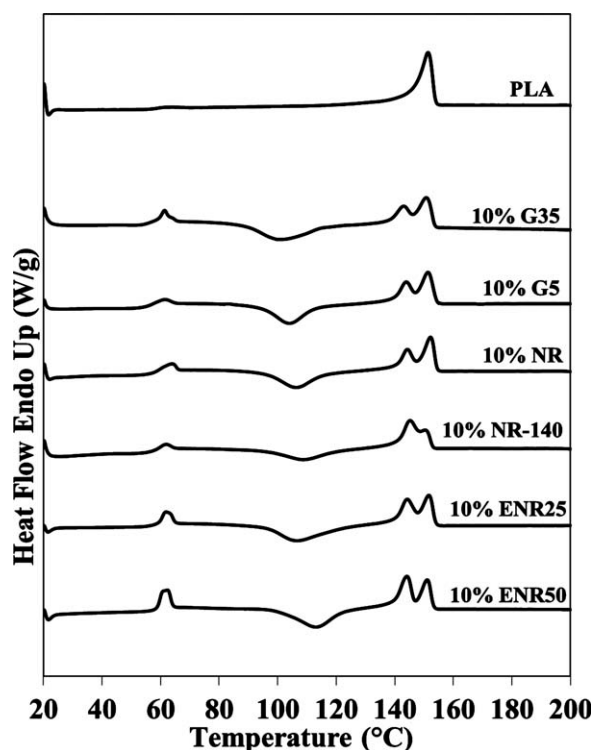
Figure 7 DSC thermograms of PLA and the blends recorded from the first heating scan.

Figure 8 Typical DSC thermograms recorded from the first heating scan of the blend containing 10% NR.

Another aspect on crystallization should be concerned, neglecting the original crystallization concept. The apparent crystallinity (X_{C2}) was determined, regardless the duration of crystallization. In this point of view, all blends showed higher degree of crystallinity (X_{C2}) as shown in Table VIII. This behavior was noticed in the second heating scan which did not show here. Without rubber, PLA did not show cold crystallization resulting in lower apparent crystallinity.

CONCLUSIONS

Rubber mastication method was more effective than chemical modification method in order to raise the toughness of PLA in this study. NR seemed to be the best toughening agent than ENR and NR-*g*-PMMA and the masticated NR was better than the virgin NR. This indicated that molecular weight and viscosity of rubber played a major role in the mechanical properties and morphology of the blends. The appropriate particle diameter was very important and perhaps more important than rubber polarity. The tiny particles of ENR and NR-*g*-PMMA in the blends designated higher miscibility to PLA than virgin NR. But these particles may be too small to

difference between ΔH_m and ΔH_{cc} because there is new crystallization in the sample during heating. For that reason, PLA in the blends became amorphous due to little degree of crystallinity ($X_{C1} \leq 4\%$). The amorphous PLA showing cold crystallization and melting peak has been reported by Degirmenbasi et al.[24] as well. In the second heating scan, PLA pellet and PLA sheet became amorphous, no melting peak was observed in the pellet, whereas the sheet showed 2% of crystallinity. The blends exhibited T_{cc} at higher temperature, e.g., 124–128°C and one single melting peak. PLA in the blends was amorphous due to little degree of crystallinity ($< 1\%$).
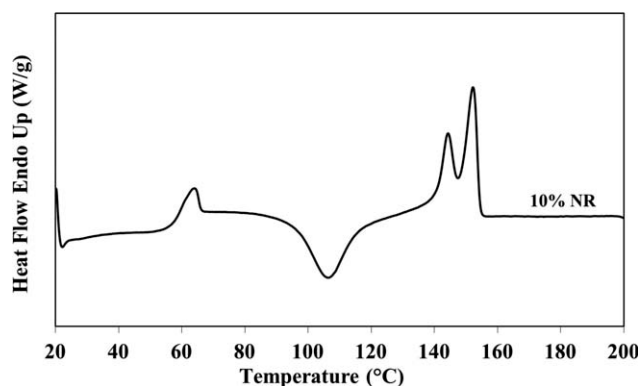
TABLE VIII
Thermal Transition Temperature of PLA and the Blends Obtained from the First Heating Scan of DSC

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc}	ΔH_m	X_{C1} (%)	X_{C2} (%)
PLA pellet	58.9	–	151.3	–	39.6	42.6	42.6
PLA sheet	57.9	–	147.0	–	13.7	14.7	14.7
10% NR	60.7	106.3	144.3, 152.2	28.6	29.7	1.2	31.9
10% NR-140	58.0	108.8	145.2, 150.3	23.2	26.6	3.7	28.6
10% ENR25	59.4	106.5	144.3, 151.7	32.5	32.3	0.2	34.7
10% ENR50	60.4	113.0	144.2, 151.0	29.3	32.7	3.7	35.2
10% G5	56.0	104.0	143.8, 151.3	30.7	31.0	0.3	33.3
10% G35	58.7	100.8	143.0, 150.8	32.2	32.2	0	34.6

$X_{C1} = [(\Delta H_m - \Delta H_{cc}) \times 100]/93$ and $X_{C2} = [\Delta H_m \times 100]/93$.

promote toughening and they were also more structural rigidity than NR.

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