

Poly(L-lactic acid)/deproteinized natural rubber blends with enhanced compatibility

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Abstract: PLLA-g-LMWNR (LMWNR – low molecular weight natural rubber) was used as a compatibilizer (1–3 wt %) of poly(L-lactic acid)/deproteinized natural rubber (PLLA/DPNR) blend (95/5 w/w). The LMWNR was prepared using TiO₂/ZnO (9 : 1 w/w) and H₂O₂ as co-catalyst. The obtained LMWNR was grafted with 0–12 wt % maleic anhydride (LMWNR-g-MA) and then with PLLA (PLLA-g-LMWNR). A significant improvement in the mechanical properties of the PLLA/DPNR blend was found in the blend that contained 3 wt % PLLA-g-LMWNR. Scanning electron microscopy showed a decrease in the pore diameter from 5.44 to 1.56 μm. The thermal analysis of PLLA/DPNR blends showed that the T_g value of PLLA phase shifted from 63.1 to 61.4°C. These results confirmed that PLLA-g-LMWNR can enhance the compatibility of the PLLA/DPNR blend.

Keywords: compatibility, PLLA, DPNR, low molecular weight, natural rubber, grafting.

Mieszaniny poli(kwas L-mlekowy)/zdeprotonowany kauczuk naturalny o zwiększonej kompatybilności

Streszczenie: PLLA-g-LMWNR (LMWNR – kauczuk naturalny o małym ciężarze cząsteczkowym) stosowano jako kompatybilizator (1–3% mas.) mieszaniny PLLA/DPNR [poli(L-kwas mlekowy)/zdeprotonowany kauczuk naturalny] (95/5 w/w). LMWNR otrzymano z DPNR przy użyciu TiO₂/ZnO (9 : 1 w/w) i H₂O₂ jako kokatalizatora, a następnie szczepiono bezwodnikiem maleinowym w ilości 0–12% mas. (LMWNR-g-MA). PLLA-g-LMWNR uzyskano w wyniku szczepienia PLLA z LMWNR-g-MA. Stwierdzono poprawę właściwości mechanicznych mieszaniny PLLA/DPNR zawierającej 3% mas. PLLA-g-LMWNR. Metodą SEM wykazano zmniejszenie średnicy porów z 5,44 do 1,56 μm. Wartość temperatury zeszklenia T_g fazy PLLA mieszaniny PLLA/DPNR, wyznaczona metodą analizy termicznej, zmniejszyła się z 63,1 do 61,4°C. Uzyskane wyniki potwierdziły, że dodatek PLLA-g-LMWNR zwiększa kompatybilność mieszaniny PLLA/DPNR.

Słowa kluczowe: kompatybilność, PLLA, DPNR, kauczuk naturalny o małym ciężarze cząsteczkowym, szczepienie.

The blending process of two materials, *e.g.* poly(L-lactic acid) (PLLA) and deproteinized natural rubber (DPNR), which have totally different properties, can produce an

immiscible blend that mostly leads to incompatibility issues [1, 2]. An immiscible blend can be obtained due to the differences in polarity of the materials, here PLLA and DPNR. As a consequence, numerous studies have been conducted to enhance the properties of PLLA/DPNR blends by incorporating several kinds of additive, *i.e.* compatibilizer and natural fibers. However, the use of MA (maleic anhydride) grafted polymer, epoxidized natural rubber, acrylated natural rubber, and liquid natural rubber as compatibilizers, as well as natural fibers, *i.e.* cellulosic based products, cannot overcome those compatibility issues [2–7].

Several previous studies were performed to obtain a graft of PLLA-g-DPNR by a direct process in the presence of catalyst. The earliest study of PLLA-g-DPNR was prepared using low molecular weight PLLA and ribbed, smoked natural rubber that had been grafted with MA without any catalyst added to the system [8]. This study was followed by others with an improved method in

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which the catalyst 4-dimethylaminopyridine (DMAP) and tin octoate (TO) was added to the system [3, 9, 10]. Instead of using a solvent system, grafted PLLA-g-DPNR without grafted MA was also prepared through a melt-blending technique in the presence of dicumyl peroxide (DCP) and Irganox 1010 [11, 12].

The grafted PLLA with low molecular weight deproteinized natural rubber and its effect on the mechanical, morphology, and thermal properties of the PLLA/DPNR blends has not been evaluated. Low molecular weight natural rubber (LMWNR) has a shorter chain than untreated natural rubber, and this can increase the probability of the grafting reaction between PLLA and natural rubber. As an assumption, the direct effect will result in the improvement of the grafting degree of PLLA-g-DPNR, and the compatibility of PLLA/DPNR blends. Thus, the objective of this study was to evaluate and determine the role of PLLA-g-LMWNR as a compatibilizer for PLLA/DPNR blends [95/5 w/w]. The compatibilized PLLA/DPNR blends were compared with the uncompatibilized and maleated PLLA/DPNR blends.

EXPERIMENTAL PART

Materials

Poly(L-lactic acid) (PLLA) 4032D was produced by Natureworks® LLC (Minnetonka, Minnesota). The catalyst of 4-dimethylaminopyridine (DMAP, $C_7H_{10}N_2$), the monomer of maleic anhydride (MA, $C_4H_2O_3$), dicumyl peroxide (DCP, $C_{18}H_{22}O_2$), zinc oxide (ZnO), sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$) and hydrogen peroxide (H_2O_2) were purchased from Sigma Aldrich (Singapore). High ammonia natural rubber latex (HANR, dry rubber content = 60.0%) was obtained from a rubber plantation in Thanh Hoa Province, Vietnam. Titanium dioxide (TiO_2) was obtained from our previous study [13].

Preparation of low molecular weight deproteinized natural rubber (LMWNR) latex

The obtained DPNR prepared using the Kawahara method [14] was treated in a photocatalytic chamber in the presence of 2 phr (parts per hundred resin) of SDS, 0.8 phr of TiO_2/ZnO (9 : 1 w/w) and 10 phr of H_2O_2 30 wt %. The photocatalytic treatment was performed for 48 h. Centrifugation was performed at the end of the process to separate out the undissolved material. The obtained latex was dried at a temperature of 60°C until a constant weight was obtained.

Preparation of maleic anhydride grafted natural rubber (LMWNR-g-MA)

The obtained dried LMWNR was dissolved in toluene (1 g : 10 cm³) at a temperature of 80°C and mixed at 600 rpm. The solution of MA was added drop wise into the LMWNR

solution over 10 min after adding 2 wt % DCP, the amount of loaded MA was varied, *i.e.* 0–12.0 wt %, depending on the final formulation. After two hours, the grafting reaction was stopped by the addition of a small drop of water. The separation of the grafted natural rubber was performed by precipitation into a mixture of acetone/methanol. The obtained product was labeled as LMWNR-g-MA-1, LMWNR-g-MA-3, LMWNR-g-MA-12 (the number at the end of the labeled product notes the MA content of the grafted product).

Preparation of poly(L-lactic acid) grafted natural rubber (PLLA-g-LMWNR)

The grafted PLLA-g-LMWNR was prepared using a solvent system, toluene, at 120°C for 24 h with mixing at 600 rpm. The ratio of PLLA and LMWNR-g-MA was 1 : 1 (based on weight ratio), and 0.0380 mole of the N-catalyst. The obtained PLLA-g-LMWNR was placed in the fume hood to evaporate the toluene [9]. The obtained product was labeled as PLLA-g-LMWNR-1, PLLA-g-LMWNR-3, and PLLA-g-LMWNR-12 (the number at the end of the labeled product notes the MA content of the LMWNR used for preparing PLLA-g-LMWNR).

Preparation of PLLA/DPNR blends

The blends of PLLA/DPNR (Table 1) were prepared using a Labo Plastomil 4M150 (Toyoseiki) at 50 rpm, with maximum loading capacity of 35 g. The processing condition was set at 180°C with 15 minutes blending time. The blending process of PLLA, PLLA-g-LMWNR and DPNR was carried out by loading PLLA pellets into the chamber. After 6 minutes, the PLLA was molten, then PLLA-g-LMWNR and DPNR were added for another 9 minutes, and the blending process was stopped when the torque value showed a constant value [15].

Methods of testing

- The functional groups of the rubber samples, before and after treatment, were determined using a FT-IR-6300 (Jasco Inc., Japan).
- The weight-average molecular weight (M_w) of the low molecular weight natural rubber was determined using a Viscotek multi-detector gel permeation chromatograph (GPC, Malvern, UK), the measurement was carried out at 30°C using tetrahydrofuran (THF) as the mobile phase and polyisoprene as the internal standard.
- The mechanical properties (tensile strength, Young's modulus, and elongation at break) of compatibilized and uncompatibilized PLLA/DPNR blends were evaluated using a Strograph VG5E (Toyoseiki, Japan) equipped with a 5 kN load cell at a speed of 10 mm/min.
- The hardness properties of PLLA/DPNR blends were determined using a durometer GS-709N Type A (Teclock, Japan) equipped with a 1 kg load cell.

Table 1. The formulation of PLLA/DPNR blends

PLLA wt %	DPNR wt %	PLLA-g-LMWNR* wt %	Code
*from LMWNR-g-MA 1%			
94.05	4.95	1.00	1% PLLA/DPNR/PLLA-LMWNR-1
93.10	4.90	2.00	2% PLLA/DPNR/PLLA-LMWNR-1
92.15	4.85	3.00	3% PLLA/DPNR/PLLA-LMWNR-1
*from LMWNR-g-MA 3%			
94.05	4.95	1.00	1% PLLA/DPNR/PLLA-LMWNR-3
93.10	4.90	2.00	2% PLLA/DPNR/PLLA-LMWNR-3
92.15	4.85	3.00	3% PLLA/DPNR/PLLA-LMWNR-3
*from LMWNR-g-MA 12%			
94.05	4.95	1.00	1% PLLA/DPNR/PLLA-LMWNR-12
93.10	4.90	2.00	2% PLLA/DPNR/PLLA-LMWNR-12
92.15	4.85	3.00	3% PLLA/DPNR/PLLA-LMWNR-12

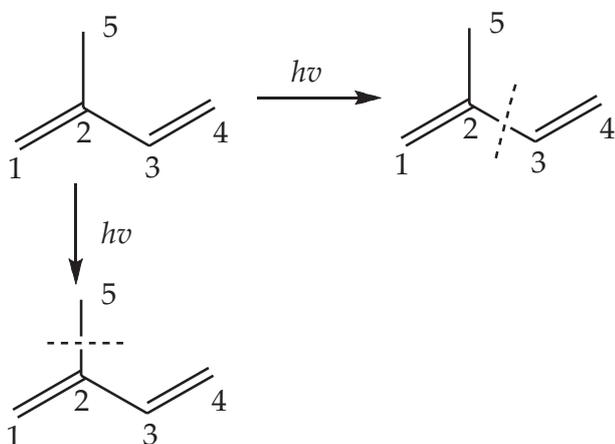
– The morphological analysis of the fractured surface of specimens was captured using a scanning electron microscope Nova NanoSEM 450 (Nova, USA).

– The thermal properties of the blends were examined using a DTG-60 Shimadzu with temperature ranging from 30–600°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Photodegradation of deproteinized natural rubber

The photocatalysis of deproteinized natural rubber latex using a composite of TiO₂/ZnO, and the presence of H₂O₂ showed a satisfactory result for the reduction of the natural rubber molecular weight. The presence of UV light during photocatalysis caused photon migration that generated holes and electrons on the surfaces of the photocatalyst materials. The photodegradation of DPNR in the presence of TiO₂/ZnO composite and H₂O₂ can be considered as the photolysis of C₁-C₂ and C₃-C₄ carbon-carbon bonds, or the case of C₂-C₅ (Scheme A), which then causes direct cleavage of the DPNR.



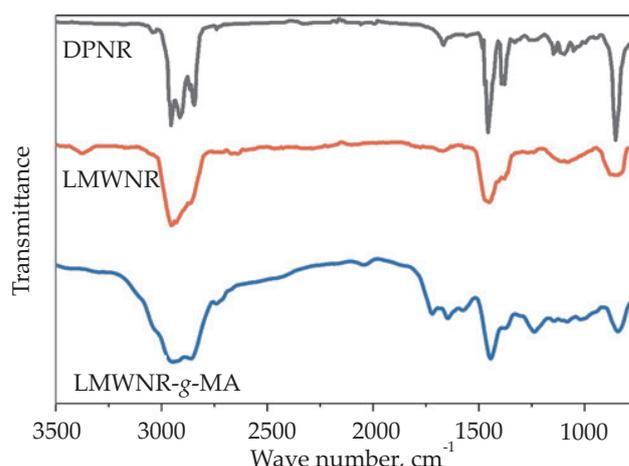
Scheme A

Table 2 shows the molecular weight of deproteinized natural rubber before and after photocatalysis. In the presence of composite TiO₂/ZnO, the molecular weight of deproteinized natural rubber was reduced to 15.8 · 10³ kDa with a polydispersity of 3.6. Generally, both FT-IR spectra of DPNR and LMWNR (Fig. 1) showed a quite similar pattern.

Table 2. Molecular weight of deproteinized natural rubber

Sample	M_n 10 ³ · kDa	Polydispersity	Gel content %	C=C band area
DPNR	549.30	7.50	19.2	0.7956
LMWNR	15.80	3.60	0.49	0.7626

There was a depletion and increase in some bands indicating the breaking of chains. Due to the similarity of these spectra, the observation was based on the difference of band areas (Table 2). The bands for the C=C and C=O bonds from both spectra were used as references because changes of these peaks have been found after degradation. In Table 2, the band area of C=C of LMWNR had a lower value than the signals in DPNR.

**Fig. 1.** FT-IR spectra of DPNR and modified DPNR

Modification of LMWNR through a grafting process

The modification of LMWNR was performed through a grafting process using 1.0–12.0 wt % of MA in the presence of DCP as an initiator. The presence of the MA group in the LMWNR was confirmed by the presence of an additional peak around 1700 cm^{-1} attributed to the C=O stretching vibration of MA. The grafting degree had a linear correlation and slightly increased within the amount of MA that was added during the reaction (Fig. 2). A similar result was also obtained in several studies that prepared polymer grafted MA [5, 16, 17].

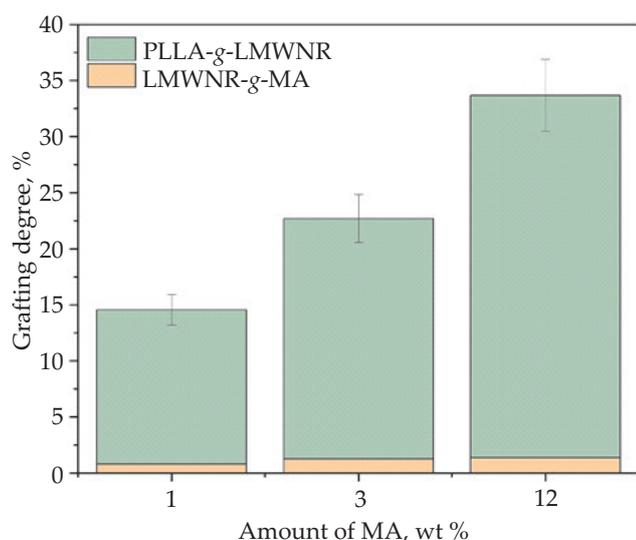


Fig. 2. Grafting degree of LMWNR-MA and PLLA-LMWNR

The esterification of LMWNR-g-MA and PLLA was performed at a ratio of 1 : 1 with the presence of N-catalyst. In LMWNR-g-MA, the IR spectra show absorbance bands at 1778 and 1853 cm^{-1} , which correspond to the symmetric and asymmetric anhydride ring C=O vibrations, respectively. Thereafter, PLLA was grafted onto LMWNR-g-MA in toluene solvent at a temperature of 120°C . The complete grafting was proved by FT-IR. As seen, the IR absorption band at 1853 cm^{-1} , corresponding to the anhydride moiety, disappears (see Fig. 1). The increase of PLLA-g-LMWNR's grafting degree showed a linear correlation to the content of MA in LMWNR-g-MA.

Characteristics of PLLA/DPNR blends in the presence of PLLA-g-LMWNR

The effect of PLLA-g-LMWNR as a compatibilizer on the mechanical properties of PLLA/DPNR blends can be seen in Fig. 3.

The addition of PLLA-g-LMWNR to PLLA/DPNR (95/5) blends significantly increase the toughness value. The toughness value was determined from the value of area under the strain *vs.* stress curve that was obtained during tensile testing. The highest toughness value was obtained in the presence of 3.0 wt % PLLA-g-LMWNR, which was prepared from LMWNR that contained 3.0 wt % MA. The improvement of toughness value by the presence of PLLA-g-LMWNR can be explained as the effect of a bridge structure [15]. A phase separation was observed in the PLLA/DPNR blend without the addition of any PLLA-g-LMWNR (Fig. 4a), which is shown with spherical pores of varied diameter. This kind of morphology is commonly obtained in a blend that is not compatible [18–21]. Table 3 shows the summarized data of the DPNR's spherical pores. In the case of PLLA/DPNR without any compatibilizer, the diameter and diameter distribution (σ) parameters were $5.44\text{ }\mu\text{m}$ and 1.99, respectively. After the addition of compatibilizer, PLLA-g-LMWNR, the PLLA/DPNR blends exhibited little homogeneity in the morphology of the fracture surface. Significant changes were observed in the diameter and diameter distribution parameter of spherical pores, *e.g.* 1.56 – $2.27\text{ }\mu\text{m}$ and 0.76 – 1.41 , respectively.

A decrease of the pore size after the addition of compatibilizer was also observed in several previous studies [9, 10, 22]. This also has a direct effect on the improvement of the mechanical properties of blends. The tensile, Young's modulus and elongation at break of PLLA/DPNR blends that were compatibilized in the presence of PLLA-g-LMWNR showed a significant improvement. This result was quite different from the previous study that used PLLA-g-DPNR as the compatibilizer. In that study, the mechanical properties of compatibilized PLLA/DPNR blends had a similar value with the uncompatibilized blends and cavities found after mechanical testing. The formation of these cavities on the blend surface confirmed that the interaction of natural rubber itself

Table 3. Diameter of spherical pores and their distribution parameter

Sample	Diameter, μm	Diameter distribution
PLLA/DPNR	5.44	1.99
3% PLLA/DPNR/PLLA-LMWNR-1	2.15	1.13
3% PLLA/DPNR/PLLA-LMWNR-3	1.56	0.76
3% PLLA/DPNR/PLLA-LMWNR-12	2.27	1.41

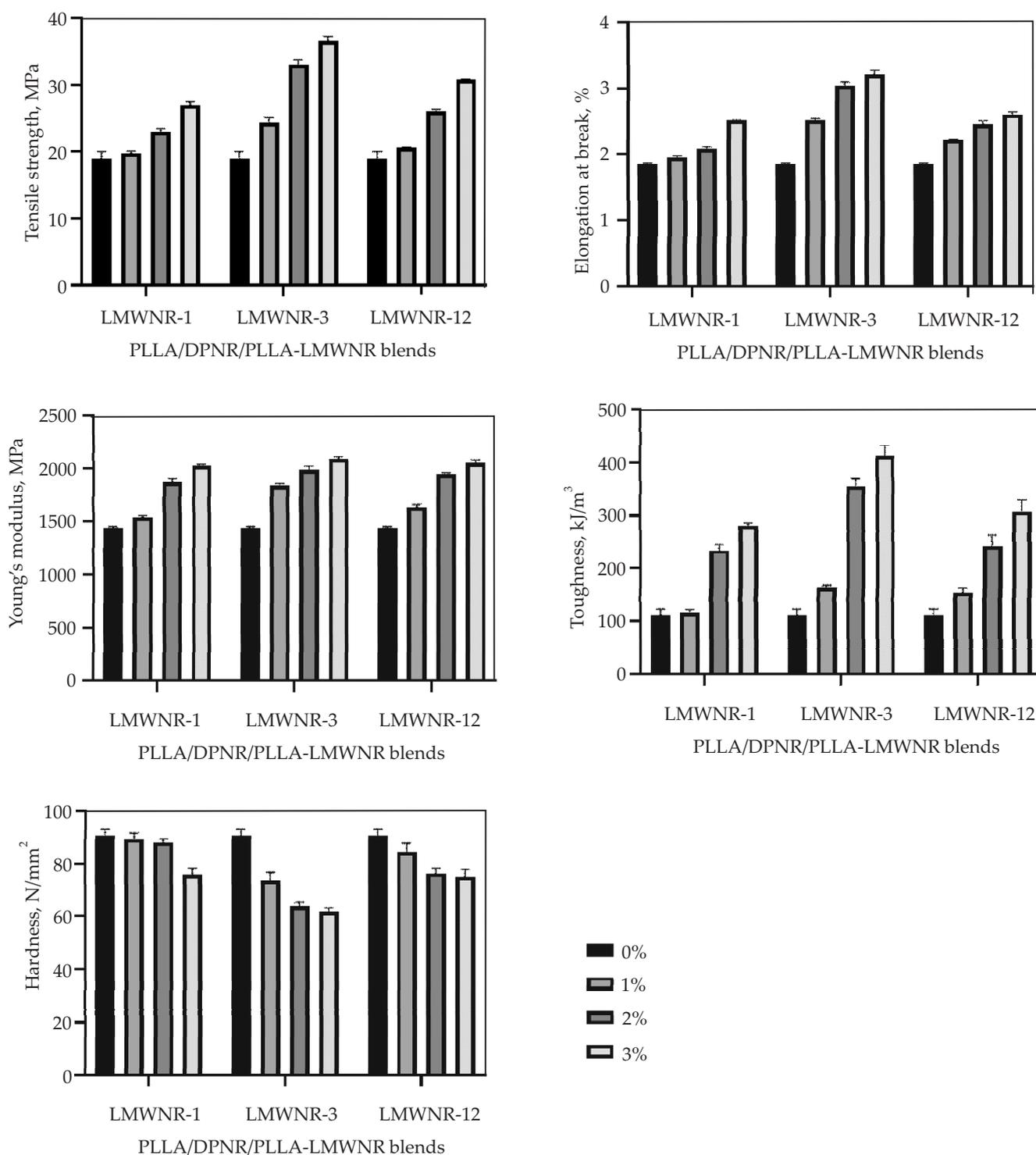


Fig. 3. Mechanical properties of PLLA/DPNR blends

and the compatibilizer in these blends were not enough to act as an absorber for reducing the stress obtained from the load during testing. This implied that the use of PLLA-g-LMWNR was more effective than PLLA-g-DPNR to enhance the compatibility of PLLA/DPNR blends.

The thermal properties of PLLA, PLLA/DPNR and the blends that were compatibilized with PLLA-g-LMWNR are comparatively summarized in Fig. 5 and Table 4.

The addition of PLLA-g-LMWNR into the PLLA/DPNR blends increased the decomposition temperature to

349°C and 366°C. This result proved that the addition of PLLA-g-LMWNR could enhance the thermal stability of PLLA/DPNR blends; this data also showed a linear result to the morphological property of the blends, PLLA-g-LMWNR also could improve the homogeneity between the PLLA and DPNR phases. The T_g values of the PLLA phases in the compatibilized PLLA_g/DPNR blends shifted to the left position or lower value. This kind of shift was also observed in other compatibilized blends, *i.e.* PLLA/NR [9], PP/CNR [15], LLDPE/Nylon-6

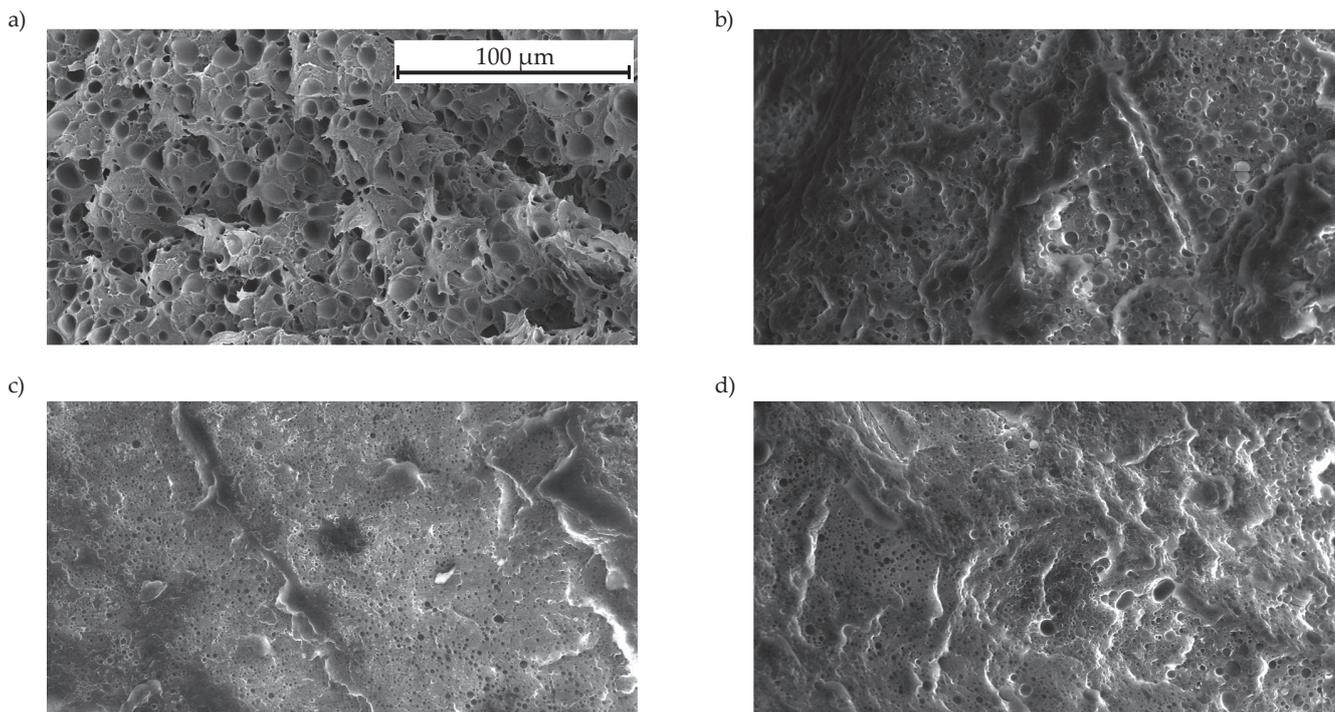


Fig. 4. Fracture surface morphology of: a) PLLA/DPNR, b) 3% PLLA/DPNR/PLLA-LMWNR-1, c) 3% PLLA/DPNR/PLLA-LMWNR-3, d) 3% PLLA/DPNR/PLLA-LMWNR-12

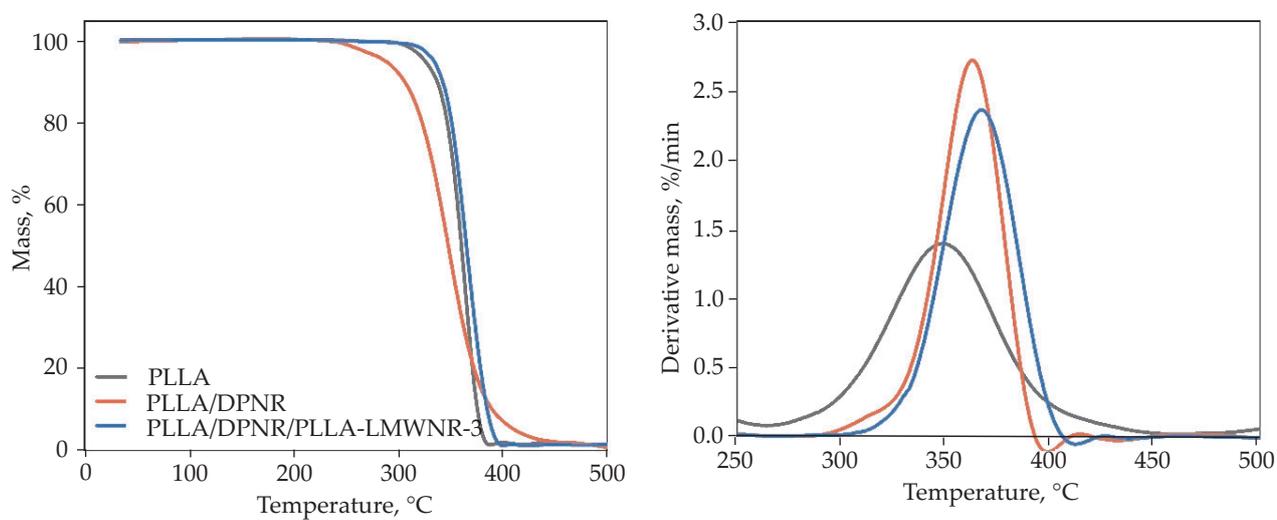


Fig. 5. TGA and DTG curves of PLLA blends

Table 4. Thermal stability of PLLA blends

Sample	T_{max} , °C	T_g of PLLA phase, °C
PLLA	362.63	63.51
PLLA/DPNR	349.69	63.14
3% PLLA/DPNR/PLLA-LMWNR-3	366.33	61.40

[23], and PLLA/PBAT/PLLA [24] that also indicated that the addition of PLLA-g-LMWNR as compatibilizer could induce the formation of a miscible blend between PLLA and DPNR.

CONCLUSIONS

The PLLA-g-LMWNR-3 that we prepared from LMWNR, which has 3 wt % of MA content (LMWNR-g-MA 3%), was able to improve the mechanical properties of PLLA/DPNR blends, including tensile strength, Young's modulus, elongation at break, and toughness, but the hardness was decreased as the PLLA-g-LMWNR amount added to the blends increased. The SEM images confirmed the positive effect of the incorporation of compatibilizer, the spherical pore size of natural rubber was found to be smaller, indicating a better dispersion of DPNR in the PLLA matrix. The addition of PLLA-g-LMWNR into the PLLA/DPNR blends gave a slight reduction of T_g for the PLLA phase. It can be assumed that the presence of compatibilizer induced the formation of a miscible blend between PLLA and DPNR.

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