

## ***Melt Blends of Poly(lactic acid)/Natural Rubber and Liquid Epoxidised Natural Rubber***

MOHD BIJARIMI<sup>\*,\*\*#</sup>, SAHRIM AHMAD<sup>\*</sup> AND ROZAIDI RASID<sup>\*</sup>

*Although poly(lactic acid) (PLA) is among widely used biodegradable polymers, it has limited applications due to its inherent brittleness, low elongation at break and toughness. Blending with natural rubber (NR) and epoxidised natural rubber (ENR) seems to be a promising alternative, as both materials are derived from renewable resources. Natural rubber was melt-blended with poly(lactic acid) in an internal mixer, Haake Rheomix, with a rotor speed of 50 r.p.m. at 180°C. Liquid epoxidised natural rubber (LENR) was used as a compatibiliser in the binary blending system of thermoplastic natural rubber (TPNR). Results indicate that the mixing torque value and stabilisation torque value in LENR blends are lower than in blends without the compatibiliser. Various compositions of natural rubber, epoxidised natural rubber and compatibiliser were investigated with respect to the stress-strain behaviour. It was found that the addition of LENR compatibiliser improved the stress at break and Young's modulus in the blend system of 40/60 PLA/rubber compositions. The increase in stress at break and Young's modulus were associated with the ability of LENR to compatibilise the PLA/NR binary blends.*

**Keywords:** PLA; natural rubber; blend; ENR; compatibiliser

At present, most development work on plastic materials has been focused on the application of biodegradable materials, especially poly(lactic acid)(PLA). PLA is gaining popularity due to its renewability and comparable properties with petroleum-based polymers<sup>1</sup>. Similar to PLA, natural rubber is derived from renewable sources and can be processed using the most conventional polymer processing equipment. PLA is a brittle thermoplastic with high strength and modulus<sup>2</sup>, while NR is ductile with a lower strength and modulus. In view of their complementary properties, blending

PLA with NR is a good choice to improve the properties of PLA, such as toughness and elongation at break without compromising its biodegradability. In contrast, the epoxidised natural rubber (ENR) is a chemically modified form of the *cis*-1,4-polyisoprene rubber with epoxide groups randomly situated along the polymer backbone<sup>3</sup>. The incorporation of ENR into rubber blends offers many advantages, such as improved processability, stiffness, resilience as well as excellent oil resistance, reduced air permeability, good damping and wet grip performance<sup>4,5</sup>.

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\* School of Applied Physics, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, Bangi Selangor, Malaysia.

\*\* Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Kuantan, Malaysia.

# Corresponding author (e-mail: bijarimi@ump.edu.my)

The use of rubbery materials such as ethylene-propylene copolymer, ethylene-acrylic rubber, acrylonitrile-butadiene rubber (NBR) and polyisoprene for PLA toughening modification was demonstrated by Ishida and co-workers<sup>6</sup>. In this study, they have shown that toughening was achieved when PLA was blended with NBR due to smaller particle size in the blends as reflected on the Izod impact test results. The morphology analysis also confirmed that the interfacial tension between PLA phase and NBR was the lowest, suggesting that rubber with high polarity is more suitable for toughening. Similar works for PLA toughening by natural rubber and epoxidised natural rubber were investigated and reported by Bitinis *et al.*<sup>7</sup>, Jaratrotkamjorn *et al.*<sup>8</sup> and Zhang *et al.*<sup>9</sup> However, most of the works reported are based on the PLA-rich composition. In our earlier publication<sup>10</sup> we have shown that the liquid natural rubber was successfully used as a compatibiliser in the PLA/ENR blend system. As far as the authors are aware, the blend of PLA/NR with liquid epoxidised natural rubber (LENR) especially on the rubber-rich composition has not been reported elsewhere. The biodegradable thermoplastic natural rubber (TPNR) based on rubber-rich compositions is another class of material that does not require any chemical crosslink and can be readily recycled. The success of TPNR based on linear low density and high-density polyethylene and propylene has long been established and reported in the literature<sup>11–19</sup>. The aim of this paper is to report the process and mechanical properties of PLA/NR with LENR blends.

## EXPERIMENTAL

### Materials

Polylactic acid of Natureworks Ingeo™ Biopolymer 3251D grade thermoplastic resin supplied by Unic Technology Ltd., China

was used in this study. It has a density of 1.24 g/cm<sup>3</sup> and melt flow index of 30 – 40 g/10 minutes. (190°C/2.16 kg) and melting temperature between 160 – 170°C. Natural rubber of SMR L grade and epoxidised natural rubber (ENR50) were obtained from the Malaysian Rubber Board. Other chemicals were used as received. The LENR was prepared *via* a photo degradation technique in our laboratory as described by previous publications<sup>11,14</sup>.

### Equipment and Method

The compositions of PLA, NR, ENR or LENR compatibiliser were varied as listed in Table 1. Initially, ENR was incorporated into the PLA directly without any LENR compatibiliser. For the evaluation of LENR compatibiliser, the composition of PLA was fixed at 40% while the amounts of NR, ENR or LENR were varied. Comparison was made when ENR was substituted with LENR in the PLA/NR binary blend system. All melt blends were prepared in a laboratory mixer (Haake Rheomix 600p) at 180°C with a capacity of 69 cm<sup>3</sup>. The batch weight of 60 g was held constant for all the variants experimented. Blending was carried out with a rotor speed of 50 r.p.m. for 15 minutes. The NR was initially softened for 60 s and subsequently, liquid ENR was incorporated for another 120 seconds. Finally, the PLA resin was added to the mixture and mixing was continued for another 12 minutes. The blend was removed from the internal mixer and then moulded at 180°C under 45 MPa of pressure for 13 min using a hot press to produce a sheet measuring 150 mm width × 125 mm length × 1 mm thickness.

### Stress-strain Analysis

All compositions of blends were tested and compared in terms of their mechanical

TABLE 1. COMPOSITIONS OF PLA/NR, PLA/NR/ENR AND PLA/NR/LENR BLENDS

Sample	PLA, %	NR, %	ENR, %	LENR, %
PLA/NR	50	50	-	-
PLA/ENR	20	-	80	-
	30	-	70	-
	40	-	60	-
	50	-	50	-
	60	-	40	-
	70	-	30	-
PLA/NR/ENR	40	55	5	-
	40	55	-	5
	40	50	10	-
	40	50	-	10
	40	45	15	-
	40	45	-	15

properties. The tensile test was carried out according to *ASTM D638* using a Testometric tensile tester under ambient conditions with crosshead speeds of 50 mm min<sup>-1</sup>. At least five samples were tested for each case and the average value was taken as the result for determining stress at peak, strain at break as well as Young's modulus.

### Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) morphology characterisation provides an insight into the distribution of the rubbery impact modifiers in a polymer matrix, distribution of components in binary blends, the effect of interfacial addition to the particle size, the crystalline phase and dispersion/agglomeration of particles as well as particle size<sup>20</sup>. SEM was performed on small pieces of the fractured specimens after the tensile test using a LEO 1450 VP scanning electron microscope (LEO Electron Microscopy Ltd., UK). Prior to the microscopic observation, the fractured surfaces were sputter coated with a thin layer of gold.

## RESULTS AND DISCUSSION

### Comparison Between NR and ENR

It is known that PLA, NR and ENR are not miscible and incompatible due to the difference in chemical structures. The blend of PLA and NR exhibits a clear incompatibility due to the non-polar part of NR as shown in *Figure 1*. In this case, the PLA was melt blended with NR at 50PLA/50NR composition. However, due to the poor interfacial adhesion between the PLA and NR, it was not possible to further characterise the mechanical properties. In contrast, the direct melt blending between PLA and ENR was found to be promising due to the polarity of both materials. Moreover, the compatibility of a rubber with other polymers can be related to its solubility parameters. Previous studies by Gelling<sup>21</sup> has reported the solubility parameters of NR and ENR50 to be 16.7MPa<sup>1/2</sup> and 18.2MPa<sup>1/2</sup> respectively. On the other hand, a higher value of the PLA solubility parameters at 20.5–21.05 MPa<sup>1/2</sup> were found in the literature<sup>22,23</sup>. When there is a large difference in solubility parameters between the two polymers, there is

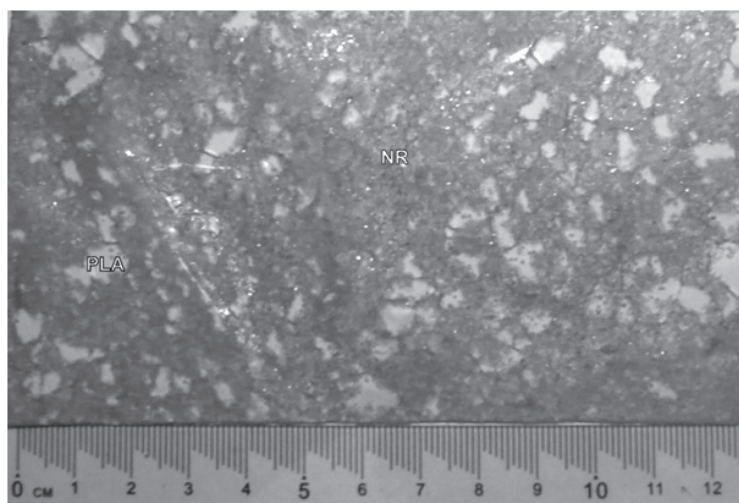


Figure 1. Photograph of the compression moulded sheet showing a clear phase separation between PLA domain and NR for 50PLA/50NR blend.

high interfacial tension and phase sizes will be large<sup>24</sup>. As such, in any case, PLA will not be compatible with NR and/or ENR chemically.

### Torque Measurements During Mixing

*Effect of Polymer Ratio.* The mixing torque measures the twisting force required to rotate its blades at a fixed rotor speed as a function of time during mixing. Torque produced by the resistance of a material to shearing action is an indirect indicator of shear stress and the rotor speed is an indirect indicator of shear rate. Figure 2 shows the representative torque values plotted as a function of mixing time for 30PLA/70ENR, 50PLA/50ENR and 70PLA/30ENR, respectively. The results show that the initial torque values increased with increasing ENR contents. The increase in mixing torque with the increase in rubber content is due to the higher viscosity of ENR phase compared to PLA. A similar phenomenon was observed by other researchers where they

found that the mixing torque increases with rubber content in NR/PS blend<sup>25,26</sup>.

*Effect of LENR Compatibiliser.* It is known that the mixing torque, mixing energy and temperature are related to blending properties. Properties of a blend vary with the different ratio of polymer melt viscosities and processing conditions. Figure 3 shows the mixing torque recorded for 40PLA/50NR/10ENR and 40PLA/50NR/10LENR blend systems. The 40PLA/50NR/10LENR blend recorded a much lower torque compared to the blend without LENR, *i.e.* at 4.7 Nm and 14.1Nm, respectively. This can be attributed to the lower molecular weight of LENR that was able to reduce the mixing torque and thus responsible for the reduction of shear stress acting on the blend. It was also observed that the torque of 40PLA/50NR/10LENR blend stabilised at around 5 min as compared to 8 min for blend without LENR. The influence of such effects on the tensile properties of the blends will be discussed in the following sections.

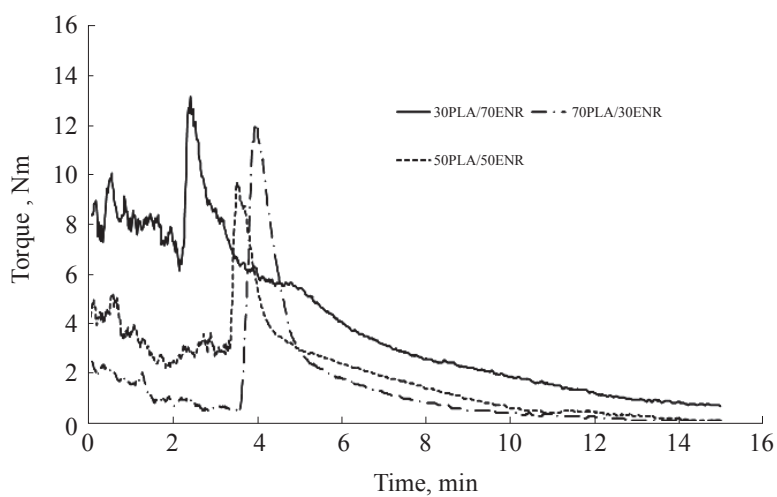


Figure 2. Representative torque values plotted as a function of mixing time for 30PLA/70ENR, 50PLA/50ENR and 70PLA/30ENR blends.

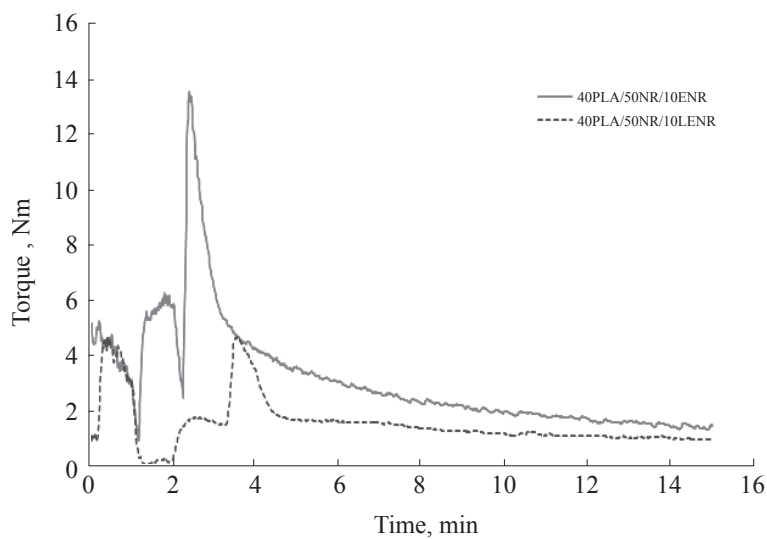


Figure 3. Torque is plotted as a function of mixing time for 40PLA/50NR/10ENR and 40PLA/50NR/10LENR blends.

Figure 4 shows the mixing energy-temperature was plotted as a function of mixing time for 40PLA/50NR/10ENR and 40PLA/50NR/10LENR blend systems. The temperature profile showed a different characteristic for both blends. It was observed that the initial and intermediate temperatures decreased after the addition of the material then stabilised at 180°C. The stabilisation of temperature was expected due to the internal temperature controller in the internal mixer itself. Nevertheless, the mixing energy is much higher for blends without a compatibiliser, *i.e.* 40PLA/50NR/10ENR. The blend with LENR for 40PLA/50NR/10LENR was found to have lower energies and reached a plateau at around 8 min, indicating that the final viscosity of the mixture had already stabilised (Figure 3).

### Stress-strain Properties

*Effect of Polymer Ratio.* Load-displacement curves of the samples for different ratios of PLA and ENR are given in Figure 5. The effects of ENR composition in the PLA blends on deformation of the samples under an applied load are clearly evident from these curves. The load at peak shows a decreasing trend when the amount of PLA was reduced. This can be explained due to the presence of low modulus of ENR, which directly influenced the stress-strain properties of the blend. The stress-strain curves as illustrated in Figure 6 showed that the blends changed from brittle to ductile failure with the addition of ENR. Previous studies have reported similar findings on the PLA/rubber blend systems<sup>7,9</sup>.

*Effect of LENR compatibiliser.* In general, all compositions containing LENR showed an improvement in the stress at break. However, the highest stress at break was noted for the blend with 10% LENR, as shown in Figure 7. The remarkable improvement of stress at break is 56% higher than the blend without the LENR

compatibiliser. It was also observed that the stress at break reduced when the composition of LENR was increased by another 5%, *i.e.* at 15%. This was not surprising as the addition of LENR was thought to be functioning as plasticiser instead of compatibiliser. After the optimum concentration of 10%, the LENR in the NR phase does not promote interaction, instead increases the ratio of the short polyisoprene polymer over the normal NR polymer resulting in an overall viscosity drop for the NR phase due to the plasticisation effect.

The elongation at break for all blends with different concentrations of LENR is shown in Figure 8. It was observed that the addition of LENR decreased the strain at break gradually from 5 – 15% of LENR concentration. However, a twofold increase of Young's modulus was noted for the blend containing 10% LENR as depicted in Figure 9. The remarkable increment of stress at break and Young's modulus is primarily attributed to the contribution of the LENR compatibiliser in the 40PLA/50NR binary blend. The morphology of the tensile fractured specimen for the 40PLA/50NR/10ENR and 40PLA/50NR/10LENR was observed by scanning electron microscopy (SEM). The SEM micrographs of the tensile fractured specimens for both uncompatibilised and LENR compatibilised blends are depicted in Figures 10a and b. It was observed that the PLA and NR/ENR phases were separated due to immiscibility of PLA/rubber blend system. This is consistent with previous reports where the PLA/NR blends are completely immiscible and the NR domains are dispersed in the PLA matrix<sup>27</sup>. Nevertheless, morphology of the LENR compatibilised blend showed a smaller diameter of voids as compared to the uncompatibilised blend system. This can be explained by the fact that LENR, having a lower molecular weight and lower viscosity, contributed to the particle diameter in the blend.

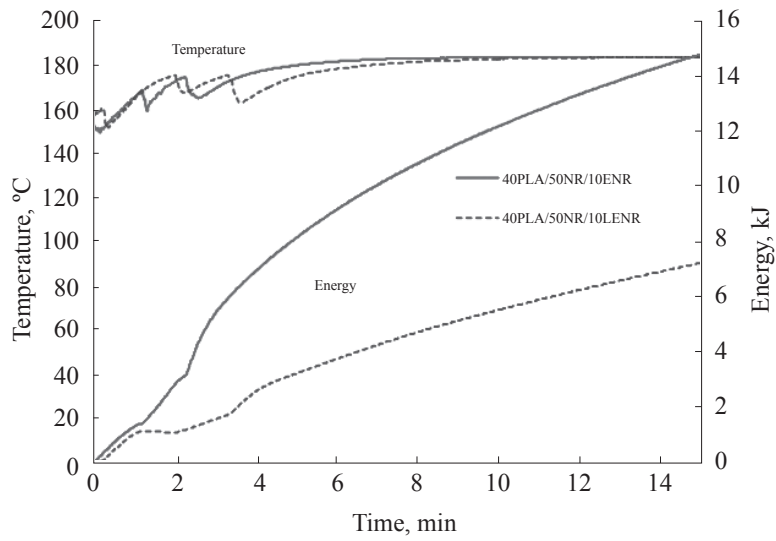


Figure 4. Mixing energy-temperature values are plotted as a function of mixing time for 40PLA/50NR/10ENR and 40PLA/50NR/10LENR blends.

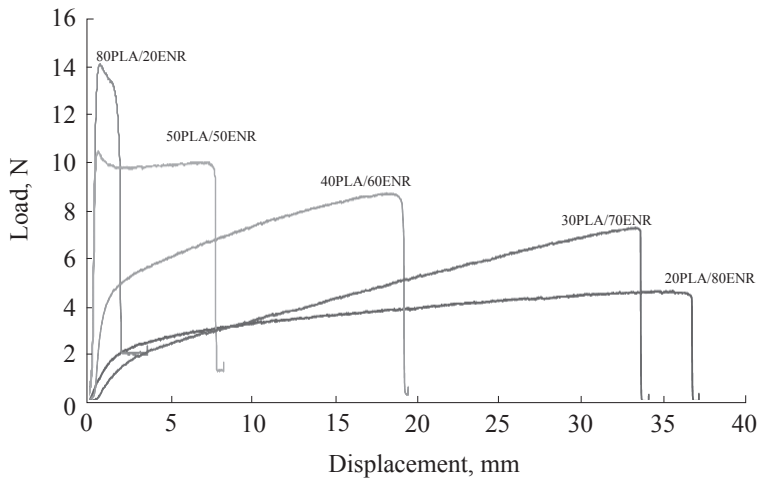


Figure 5. Load-displacement curves are plotted as a function of polymer ratio.

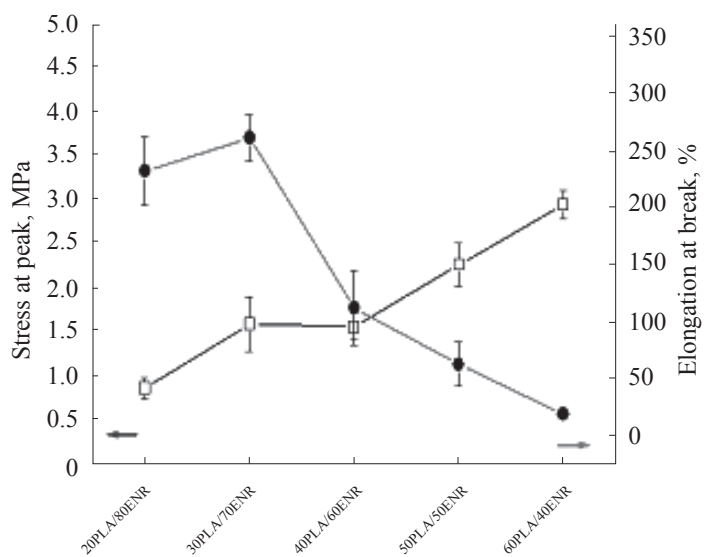


Figure 6. Stress-strain values are plotted as a function of polymer ratio.

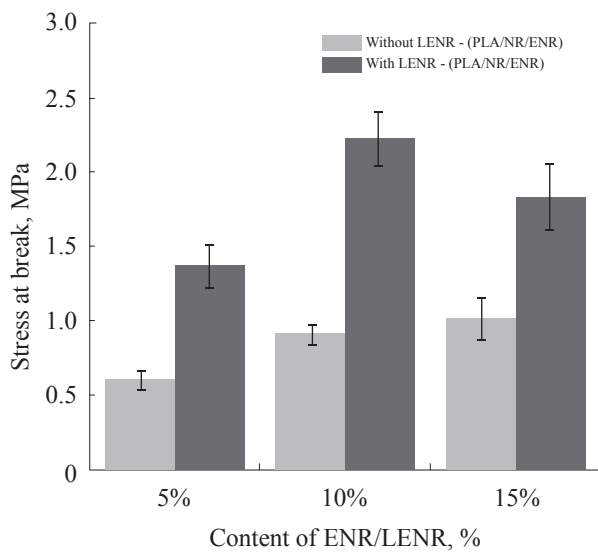


Figure 7. Stress at break values are plotted as a function of polymer ratio for blends with and without LENR.



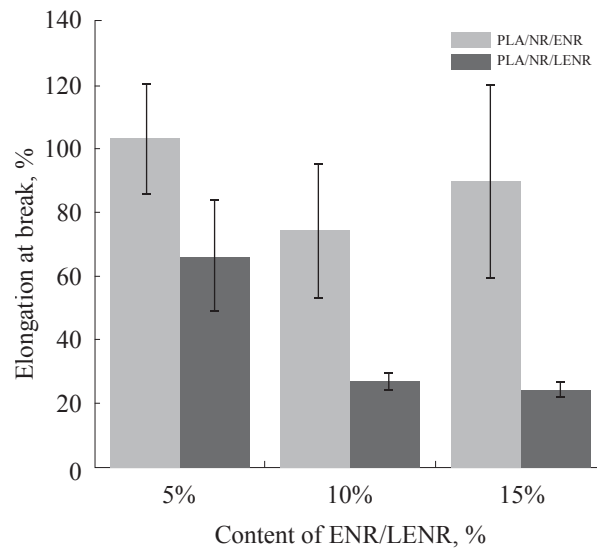


Figure 8. Elongation at break values are plotted as a function of polymer ratio for blends with and without LENR.

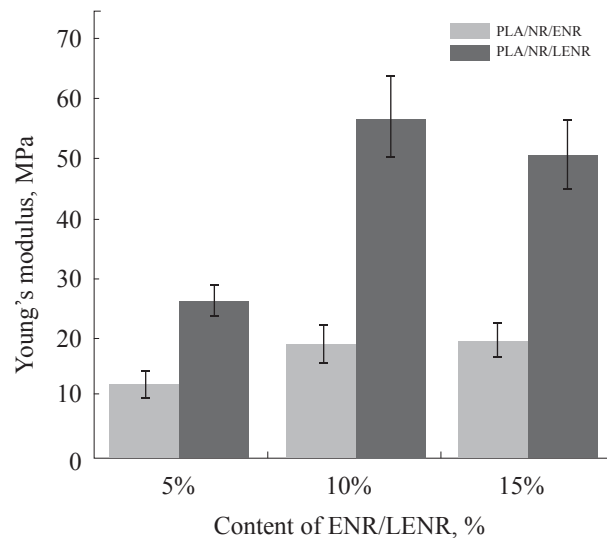


Figure 9. Young's modulus values are plotted as a function of polymer ratio for blends with and without LENR.

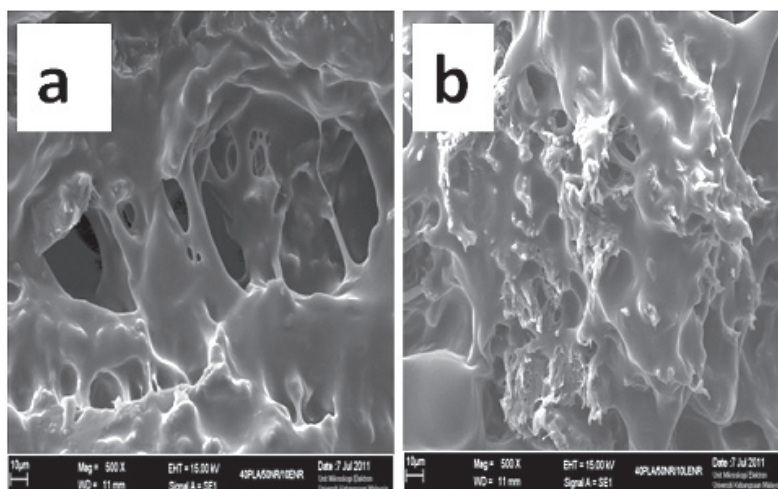


Figure 10. Scanning electron microscopy (SEM) of the tensile fractured specimens for (a) 40PLA/50NR/10ENR and (b) 40PLA/50NR/10LENR blends.

It is worth noting that in the work of Jaratrotkamjorn *et al.*, they have suggested that the masticated NR was better in toughening the PLA primarily due to molecular weight and viscosity which played a key role in determining the morphology of the PLA/NR and PLA/ENR blend systems<sup>8</sup>.

## CONCLUSION

In this study, a novel approach for toughening of PLA/NR and LENR is reported. LENR was used as a compatibiliser in the binary blending system of TPNR. The results show that the stress-strain properties change gradually with increasing rubber composition in the blend. It was found that the addition of LENR compatibiliser improved the stress at break and Young's modulus in the blend system of 40/60 PLA/rubber compositions. The improvement in the mechanical properties might be related with the ability of lower molecular weight of LENR in compatibilising the PLA/NR blends.

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