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# Mechanical and Thermal Properties of Polylactic Acid/Liquid Epoxidized Natural Rubber Blends

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Polylactic acid (PLA) is a potential polymer to be used in various applications due to biodegradable and biocompatible characteristics. However, its brittle nature limits the usage of PLA. In order to improve the brittleness of PLA, liquid epoxidized natural rubber (LENR) was incorporated with PLA. The objective of this study is to investigate the effect of LENR as toughening agent on rigid PLA matrix in term of mechanical and thermal properties. Polylactic acid/liquid epoxidized natural rubber (PLA/LENR) blends were prepared by melt blending method using Brabender internal mixer with temperature 160 °C, mixing speed of 60 rpm and molded into test samples by compression molding. The LENR content was varied from 0, 5, 10, 15 and 20 wt%. It was found that the addition of LENR increased the impact strength of PLA.10 wt% of LENR showed the optimum impact strength which was 86.05 J/m. However, tensile strength and tensile modulus decreased slightly with increasing of LENR content. The morphology of PLA/LENR blends showed a good dispersion of LENR on PLA matrix at 10 wt% LENR. The differential scanning calorimeter (DSC) showed a gradual drop in melting temperature ($T_m$) as well as glass transition temperature ($T_g$) as LENR content increased.

## 1. Introduction

Plastic materials have been used widely in many applications including packaging, electrical appliances, automotive and construction materials due to its properties such as light weight, easy to fabricate, low cost and comparatively cheap to produce in mass quantities. However, main issue regarding the use of plastic is the environmental problem. According to Lee and Hong (2014), most plastics are not biodegradable because it is based on synthetic polymer made from crude oil. Thus, plastic waste will create a massive quantity of waste on the landfills.

Polymer from natural resources has been used as a way to minimize the environmental problem. This kind of polymer will break down into natural by products such as gases carbon dioxide ($CO_2$) and nitrogen ($N_2$), biomass, inorganic salts and water. Polylactic acid (PLA) is a natural-based polymer that has a great potential to take over petroleum-based polymers due to its properties which are biocompatible and environmental friendly (Rashid et al., 2019). However, there are some negative aspects which restrain its usage in certain applications as it is very brittle, poor in toughness, has low heat deflection temperature and expensive (Basri et al., 2019).

Nowadays, most of the researchers focused on the way to modify the brittle nature of PLA in order to increase its toughness and allow it to be used in high impact applications. One way is by blending PLA with rubbery material that has lower modulus than PLA itself (Taib et al., 2012). Rubbery material is usually added into the brittle polymer to increase its flexibility and impact strength. Epoxidized natural rubber (ENR) are recent material used as a toughening agent for plastic. ENR is a chemically modified structure of cis-1,4-polyisoprene rubber. Abdullah et al. (2019) reported that the addition of 10 wt% ENR in PLA matrix increased its impact strength due to the excellent interaction between PLA and ENR.

Liquid epoxidized natural rubber (LENR) is a degraded structure of ENR which has lower molecular weight and shorter chain because of the chain scission of polyisoprene backbone. LENR is useful as compatibilizers,

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plasticizers and as an adhesive (Ibrahim et al., 2014). Compared to ENR, LENR has more advantages for the production of numerous products as it requires less energy and easy to process. Besides, LENR can be modified easily because of lower molecular weight. Other than that, the presence of reactive groups in the structure of LENR provide place for the probability of chemical functionalisation (Hasan et al., 2019). Nampitch and Megaraphan (2010) reported the possible reaction between OH group in PLA structure and epoxide group in ENR structure which can form a hydrogen bonding when PLA was blended with ENR helps to improve the toughness of PLA. Most studies used LENR compared to ENR due to its properties which has shorter chain (Mohammad et al., 2018) and relatively lower molecular weight (Darji et al., 2018). Besides, LENR reveals unique physical and mechanical properties for instance its sticky appearance, high elasticity and resilience. These are the important factors in improving the toughness and flexibility of the composites or polymer blends. Kargarzadeh et al. (2014) reported that unsaturated polyester resin (UPR) which modified with LENR showed positive improvement for its mechanical properties in contrast to liquid natural rubber-unsaturated polyester resin (LNR-UPR) due to the good interaction between UPR and LENR. In another study, Ahmad et al. (2015) added LENR in epoxy matrix. The strain at break of the system increased with respect to the alteration of the ductility but the tensile modulus decreased.

The objective of this work is to study the effect of LENR as toughening agent on mechanical, thermal and morphological properties of PLA. To date, extensive studies have been reported on blending of PLA with NR (Hajba and Tabi, 2017), ENR (Abdullah et al., 2019), liquid natural rubber (LNR) (Shahdan et al., 2016) and other impact modifier (Phruksaphithak and Noomhorm, 2012). However, research on PLA/LENR blends is still limited and require further exploration.

## 2. Experimental

### 2.1 Materials

Polylactic acid (PLA) with grade 3052D supplied by Innovative Pultrusion Sdn. Bhd., Malaysia was used as matrix in this study. It has density of 1.24 g/cm$^3$. The liquid epoxidized natural rubber (LENR) with molecular weight (Mw) of ~90 000 g/mol was used as a toughening agent and was supplied by Malaysia Rubber Board, Malaysia.

### 2.2 Sample preparation

The melt blending method was used to prepare the blend samples. Brabender internal mixer with the speed of 60 rpm was used with mixing temperature of 160 ℃ for 6 min. PLA resin was dried overnight in the oven at 40 ℃ to remove the residual water content prior to blending. PLA and LENR content were varied according to the Table 1. The samples prepared were P100, P95LE5, P90LE10, P85LE15 and P80LE20 which indicate 100 wt% PLA, 95 wt% PLA and 5 wt% LENR, 90 wt% PLA and 10 wt% LENR, 85 wt% PLA and 15 wt% LENR and 80 wt% PLA and 20 wt% LENR. After blending, the compound were moulded into sheets of 3 mm and 1 mm by hot pressing at 160 ℃ with the pressure of 110 kg/cm$^2$. The preheating, full compression and cooling times for 3 mm thickness were 10 min, 5 min and 20 min while for 1 mm thickness were 5 min, 3 min and 10 min. The moulded sheets were cut according to the dimension for testing.

*Table 1: Formulation of the samples*

| Samples | PLA (wt%) | LENR (wt%) |
|---|---|---|
| P100 | 100 | 0 |
| P95LE5 | 95 | 5 |
| P90LE10 | 90 | 10 |
| P85LE15 | 85 | 15 |
| P80LE20 | 80 | 20 |

### 2.3 Testing and characterization

The izod impact test was carried out by using ZwickRoell pendulum impact testing machine at ambient temperature. The testing was performed according to ASTM D256 by using specimen with rectangular shape and dimension of 65 mm x 12.7 mm x 3 mm. The impact strength value was recorded from the average of five samples.

The tensile strength was measured by using material testing machine brand ZwickRoell. The test was performed at ambient temperature according to ASTM D638 with 5 mm min$^{-1}$ speed and 500 N load. The average value of five samples were recorded.

The dispersion of LENR in PLA matrix was studied by using field emission scanning electron microscope (FESEM) brand Hitachi from Japan. The samples used were from the impact fracture and were coated with platinum to avoid electrostatic charging during examination.

Perkin-Elmer differential scanning calorimetry (DSC) was used to study the thermal behavior of the PLA/LENR blends. About 6-10 mg of each sample was used. The sample was heated from 0 until 250 ℃ and cooled down from 250 to 0 ℃ and then heated again to 250 ℃ at a heating rate of 5 ℃/min. First heating and cooling process were done to remove the thermal history of the system. The results from second heating were taken for discussion. The percentage crystallinity, $X_c$ was calculated using Eq(1);

$$\%\ Crystallinity, X_c = \frac{\Delta H_m}{\Delta H^{\circ}_m} \times \frac{100}{w} \tag{1}$$

From Eq(1), $\Delta H_m$ indicate melting enthalpy; $\Delta H_m^{o}$ is melting enthalpy for 100% crystalline PLA. The value is taken as 93.1 J/g (Wahit et al., 2015) while w symbolized the weight fraction of PLA present in the blends.

## 3. Result and discussion

### 3.1 Impact properties

The impact strength of PLA/LENR blends was shown in Figure 1. It can be seen that the impact strength of the blend increased up to 86.05 J/m with the addition of 10 wt% LENR as compared to pure PLA which was 40.88 J/m. The presence of LENR in PLA matrix helps to absorb the energy when load is applied during the test. In this condition, LENR acted as an impact modifier to enhance the toughness and ductility of PLA. Good interaction between PLA and LENR can lower the interfacial energy presence in the interfacial region and will produce the better dispersion of LENR in PLA matrix. As a result, the stress transfer will be improved as well as impact strength. However, the optimum impact strength was showed at 10 wt% of LENR. Further addition of LENR decreased the impact strength. At this stage, the addition of LENR could be functioning as plasticizer instead of compatibilizer. Thus, after 10 wt% of optimum concentration, LENR in the PLA matrix phase no longer promote any interaction, instead increases the ratio of the short LENR chains over the PLA chains which resulted in decreasing of overall viscosity for the PLA/LENR phase due to the plasticisation effect. Another factor could be as the amount of LENR increased above the optimum concentration, the agglomeration of LENR might happen thus affecting interfacial adhesion between rubber and matrix (Rosli et al., 2016). From Figure 3b and 3c, the distribution and size of particles in 90 wt% PLA was smoother compared to 80 wt% PLA, thus increase the amount of force absorbs before deformation resulting in higher impact strength. However, the overall impact strength at 15 and 20 wt% LENR are still higher compared to PLA alone.

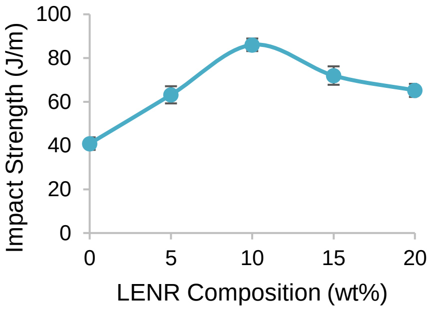
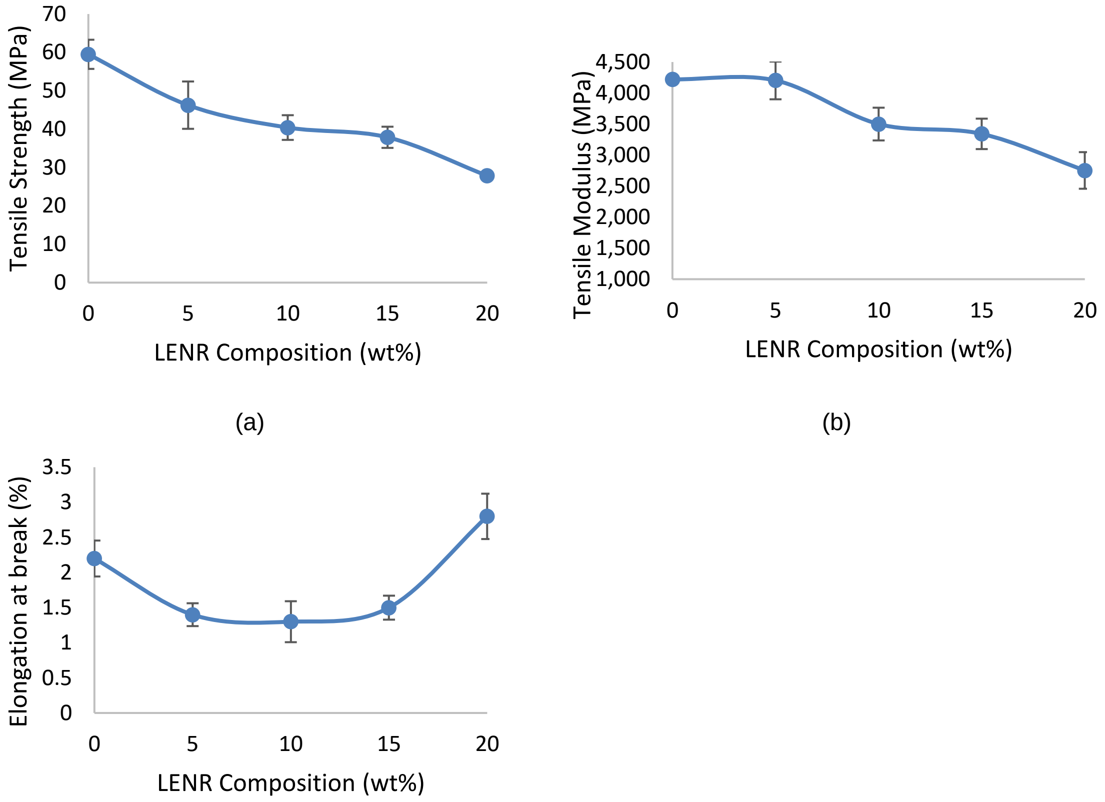


*Figure 1: The impact strength of PLA/LENR blends at various LENR content.*

### 3.2 Tensile properties

Figure 2 shows the tensile strength, tensile modulus and elongation at break of PLA/LENR blends. Tensile strength and tensile modulus decreased with increasing LENR value. According to Taib et al. (2012), this observation is expected as the value of tensile modulus and tensile strength of LENR are lower than PLA thus lowering the overall tensile modulus and tensile strength of the blends. Besides, the presence of LENR in PLA could also act as stress concentrator resulting in lower stress value than pure PLA. Whilst, the addition of 5 and 10 wt% of LENR was found to decrease the elongation at break of the blends prior to the increase of the elongation at break at 15 and 20 wt% of LENR. Similar observation was reported by Pongtanayut et al. (2013) where the elongation at break of PLA decrease with the addition of 10 and 20 wt% of ENR but increased with the addition of 30 wt% of ENR. They concluded that the ability of PLA to elongate depends on the dispersion and distribution size of rubber particle. The capability of rubber to elongate also cause by another factors like type of rubber, mechanical properties of the matrix, distribution of the rubber and the size of rubber dispersion on the matrix phase (Hasan et al., 2019). Abdullah and Mohamad (2018) found that the elongation at break of PLA/ENR blends dropped with the addition of 10, 20 and 30 wt% of ENR due to the interaction between PLA and ENR that formed crosslinks in the blend. In this study, the reduction in elongation at break at low percentage of LENR is suggested due to the dispersion of rubber particle on PLA matrix. The 5 and 10 wt% of LENR were not enough to increase the elongation at break due to very small amount of rubber particle. The sudden increase in elongation at break at 20 wt% of LENR can be related to the presence of extensive shear whitening in the specimens after tensile test. This can be proved by FESEM analysis of impact fracture where the whitening shear effect can be clearly seen in Figure 3c.



(a)

(b)

(c)

*Figure 2: (a) Tensile strength, (b) tensile modulus and (c) elongation at break of PLA/LENR blends at various LENR content.*

### 3.3 Morphological study

The morphological studies for impact fractured surfaces for PLA/LENR blends were examined by FESEM micrograph as showed in Figure 3.

The fractured surface of pure PLA was shown in Figure 3a. As can be seen, the fractured surface was smooth and does not shown any visible toughening effect. This smooth surface is normally associated with polymers that has brittle characteristic. The addition of LENR increase the surface roughness of PLA. Figure 3b and 3c show the ductile fractured with toughening effect when PLA was incorporated with LENR. This can be related as the addition of LENR increase the ductility and toughness of PLA matrix. It can be seen that the fractured surface of 90 wt% PLA and 10 wt% LENR was smoother compared to fractured surface of 80 wt% PLA and 20 wt% LENR. Thus, it can be related that the good dispersion of LENR in PLA matrix contributed to the highest impact strength of 90 wt% PLA and 10 wt% LENR blends.

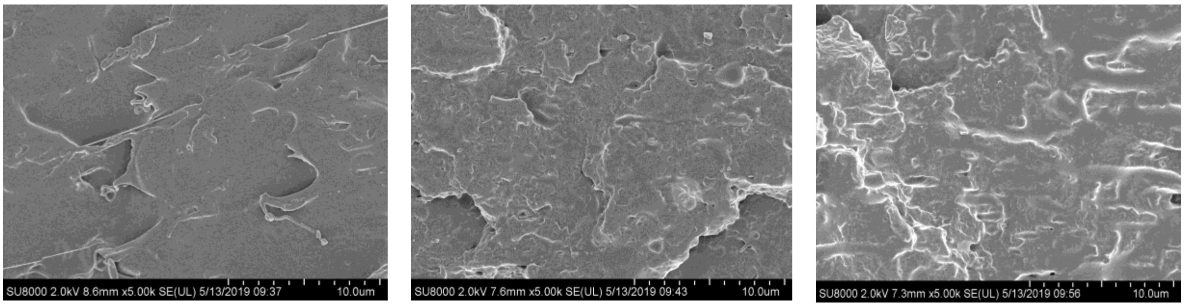

(a) (b) (c)

*Figure 3: The FESEM images of (a) 100 wt% PLA (b) 90 wt% PLA and 10 wt% LENR and (c) 80 wt% PLA and 20 wt% LENR.Thermal analysis*

Glass transition temperature ($T_g$), melting temperature ($T_m$) and crystallinity percentage of PLA ($X_c$) from differential scanning calorimetry (DSC) analysis for PLA and PLA/LENR blends were tabulated in Table 2. From the DSC result, PLA and PLA/LENR blends showed the $T_g$ between 55 to 60 ℃, $T_m$ around 156 to 158 ℃ and $X_c$ between 27 to 32%. $T_g$ value decreased with increasing of LENR content. According to Rosli et al. (2016), decreasing in $T_g$ value of PLA/LENR blends might be due to the capability of LENR to decrease the brittleness of PLA and lower molecular weight of LENR which contains lots of chain ends. In this study, the addition of LENR which act as plasticizer somehow soften the PLA matric thus decrease the overall $T_g$ of the blends. Sample of 90 wt% PLA and 10 wt% LENR showed the higher percent of crystallinity. This indicate that the blend of the sample was more compatible compared to other samples. The higher the percentage of crystallinity, the better the compatibility between the blends (Pongtanayut et al., 2013). This can be proven by the impact properties of 90 wt% PLA and 10 wt% LENR blends which has the highest impact strength than other composition.

*Table 2: Thermal characteristic of PLA/LENR blends*

| Sample | $T_g$ (℃) | $T_m$ (℃) | $X_c$ (%) PLA |
|---|---|---|---|
| P100 | 60.07 | 158.52 | 27.33 |
| P95LE5 | 58.91 | 158.44 | 31.39 |
| P90LE10 | 58.06 | 157.61 | 34.20 |
| P85LE15 | 59.73 | 157.51 | 32.32 |
| P80LE20 | 55.63 | 156.79 | 32.06 |

## 4. Conclusion

As a conclusion, PLA/LENR was successfully blended to improve the toughness of PLA. Impact strength of PLA increased to 86.05 J/m with the addition of 10 wt% LENR compared to pure PLA which was 40.88 J/m. This is due to the presence of LENR which acts as a toughening agent for PLA matrix to absorb more energy when the load is applied to the sample. Tensile strength and modulus of PLA/LENR blends decreased with increasing of LENR content due to the properties of LENR which has lower modulus than PLA. Elongation at break also decreased up to 10 wt% LENR, however the value increased as the LENR content increased to 15 and 20 wt%. The PLA/LENR blends morphology showed a good dispersion at 10 wt% of LENR compared to 20 wt% of LENR content which consistent with finding from impact strength. The DSC result showed increment in the percentage of crystallinity in PLA/LENR blends as LENR content increased up to 10 wt% while the melting and glass transition temperature decreased.

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