

Mechanical and Thermal Properties of Polylactic Acid/Liquid Epoxidized Natural Rubber/Graphene Oxide Composites

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Poly(lactic acid) (PLA) is one of the biodegradable polymer that is widely used in many applications to replace petroleum-based polymer. Despite the advantages of PLA, its disadvantages such as poor toughness and brittleness restrict the usage of PLA. The purpose of this study is to improve the properties of PLA by blending with liquid epoxidized natural rubber (LENR) and graphene oxide (GO). Two different samples were prepared which were PLA/LENR/GO and PLA/GO grafted LENR (PLA/GO-g-LENR) composites. GO-g-LENR was prepared by using grafting method. The materials were blended by using Brabender internal mixer with rotor speed of 60 rpm at 160 °C. The GO content was varied from 1, 3 and 5 phr while the composition of LENR was fixed at 10 wt%. After blending, the compound was compressed into a plate under hot pressing machine then was cut according to ASTM D256 for characterization. The properties of the composites were investigated in term of mechanical, thermal and morphological aspects. Fourier transform infrared (FTIR) analysis was used to confirm the efficiency of grafting method. The addition of 1 phr GO using GO-g-LENR into PLA composite showed the highest impact strength which is 96.02 J/m while 1 phr GO without grafting increased the impact strength from 86.05 J/m to 91.42 J/m. Thermal analysis study by TGA indicated that addition of GO into the composite system has improved its thermal stability. Morphological study revealed that 1 phr GO has better dispersion in PLA/LENR matrix compared to 3 phr GO.

1. Introduction

Plastics play an important role in our daily life due to their advantages such as light in weight, flexibility, durability, chemical resistance and low cost of production. The applications of plastics are worldwide in many engineering fields including automotive, medical, construction, aerospace and electrical (Idumah and Nwuzor, 2019). Majority of plastics are made from monomers which is derived from petroleum such as propylene and ethylene. These type of plastics are non-biodegradable and will create environmental problems. The amount of plastics on the landfills increased from 26.03 Mt in 2015 to 26.97 Mt in 2018. This waste also can be found in ocean resulted in contamination of the freshwater system and affected the habitats of aquatic life (Geyer et al., 2017). Realizing this situation, researchers have developed polymer that can easily degraded or biodegradable which is made from natural resources. According to Anuar et al. (2017), Poly(lactic acid) (PLA) is one of the biodegradable polymers that commonly used to replace petroleum-based polymer. There are some drawbacks of PLA which limits its usage in certain applications. PLA has poor mechanical properties and very brittle which make it quite difficult in term of processing. To improve the processability, mechanical properties and reduce the brittleness of PLA, addition of toughening agent and nanofiller is one of the solutions (Mohamad et al., 2018). Epoxidized natural rubber (ENR) is a chemically modified form of natural rubber (NR), commonly used as toughening agent for PLA. Compared to NR, ENR is a polar molecule which is more compatible and has good interfacial interaction with polar PLA. Addition of ENR into PLA matrix had improved the impact strength of PLA/ENR blends (Tessanan and Phinyocheep, 2020). High molecular weight of ENR can limit its processability and solubility. The liquid form of ENR which is liquid epoxidized natural rubber (LENR) is a good candidate to replace ENR due to its lower molecular weight and the presence of epoxy group in the structure (Salehuddin et al., 2020). LENR can be produced by chemical degradation, photooxidation or mechanical milling method

(Rooshenass et al., 2016). Bijarimi et al. (2014) reported that addition of LENR as compatibilizer in thermoplastic natural rubber (TPNR) system has improved the stress at break and Young's modulus of the blend.

Nanofiller is added to the polymer to further improve its mechanical and thermal properties. Graphene oxide (GO) has recently attracted interests of many researchers as nanofillers due to its incredible properties in terms of mechanical, thermal and electrical. In contrast with graphene, the molecular structure of GO which consists of many functional groups such as epoxide, carbonyls, hydroxyls and carboxyls has made GO a hydrophilic material resulting in strong physical interactions with polymers. Incorporation of GO into PLA blends at low content has successfully improved the mechanical and thermal properties of PLA nanocomposites (Mazlan et al., 2020). Conventional mixing method of preparing composites has caused aggregation of GO due to its high specific surface area and produce poor dispersion of GO in the rubber matrix (Yin et al., 2019). Modification of GO surface can be an option to prevent this problem.

This paper focused on modification of GO by grafting with LENR to produce GO-g-LENR as toughening agent and nanofiller for PLA. The objective of this research is to compare the efficiency of grafted PLA/GO-g-LENR and ungrafted PLA/LENR/GO composites in terms of mechanical and thermal properties.

2. Experimental

2.1 Materials

The matrix used in this study was Ingeo™ Biopolymer 3052D Polylactic acid (PLA) produced by NatureWorks LLC. The specific gravity, melting temperature (T_m) and glass transition temperature (T_g) of PLA are 1.24 g/cm³, 155 - 160 °C and 55 - 60 °C. Liquid epoxidized natural rubber (LENR) with molecular weight (M_w) of 38,669 g/mol was supplied by Malaysian Rubber Board, Malaysia. Graphene oxide (GO) powder used as nanofiller is UGOX™ United Graphene Oxide (Graphite Generated Nanomaterials) supplied by United Nanotech Innovations Private Limited, India. It has purity of 99 % with average thickness of 0.8-2.0 nm and lateral dimensions of 5-10 μ m.

2.2 Preparation of GO-g-LENR

GO and LENR were dissolved in chloroform separately. Both solutions were mixed together and undergo reaction under nitrogen atmosphere for three hours. After that, the sample solution was centrifuged at 5000 rpm for 15 min to separate between grafted and ungrafted part (dissolve in the solvent). The sample was dried in an oven at 40 °C for 24 h to remove excess solvent.

2.3 Preparation of nanocomposites

The samples were prepared by using melt mixing method in a Brabender internal mixer 50 EHT with speed of 60 rpm at 160 °C. PLA and GO were dried in the oven at 40 °C for 24 h before blending. Formulation of materials were shown in Table 1. The composition of PLA and LENR were fixed at 90 wt% and 10 wt% based on previous study by Syed Mustafa et al. (2020) which showed the maximum impact strength is at this ratio. GO content was varied at 1, 3 and 5 phr. After blending, the compound was compressed by compression moulding machine under pressure of 110 kg/cm² at 160 °C and cut according to dimension for testing. The preheating, compression and cooling times were 10 min, 5 min and 20 min.

Table 1: Formulation of samples

Samples	PLA (wt%)	LENR (wt%)	GO (phr)
PLA/LENR/1GO	90	10	1
PLA/LENR/3GO	90	10	3
PLA/LENR/5GO	90	10	5
PLA/1GO-g-LENR	90	10	1
PLA/3GO-g-LENR	90	10	3
PLA/5GO-g-LENR	90	10	5

2.4 Sample characterization

Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups present in GO, LENR and GO-g-LENR. The impact properties were studied by a using ZwickRoell HIT pendulum impact tester machine at room temperature according to ASTM D256. Five samples with dimension of 65 mm x 12.7 mm x 3 mm were notched and tested for impact properties. Thermal stability of nanocomposites was analysed by thermogravimetric analysis (TGA) using a Perkin Elmer TGA-7 thermal analyser at a heating rate of 10 °C/min and temperature range from 25 °C to 900 °C. The weight loss of the samples was measured as a function of

temperature. The impact fractured of PLA composite was examined using field emission scanning electron microscope (FESEM) brand Hitachi.

3. Results and discussion

3.1 Fourier transform infrared analysis

Figure 1 shows the FTIR spectra of GO, LENR and GO-g-LENR. The absorption band of GO appeared at $3,420\text{ cm}^{-1}$ indicate the stretching vibration of hydroxyl ($-\text{OH}$) broad peak. Other peaks which appear at $1,615\text{ cm}^{-1}$, $1,200\text{ cm}^{-1}$ and $1,056\text{ cm}^{-1}$ are corresponding to $\text{C}=\text{C}$ in aromatic ring, $\text{C}-\text{OH}$ group and $\text{C}-\text{O}$ stretching vibrations. Khalili, (2017) also reported on assignment of GO peak in their FTIR results. Important peaks of LENR can be observed at $1,246\text{ cm}^{-1}$ and 875 cm^{-1} as presented in Figure 1. These peaks related to symmetric and asymmetric stretch of epoxide ring. For LENR spectrum, only slight OH stretching can be detected around $3,200 - 3,600\text{ cm}^{-1}$. This is due to the epoxidation occurrence where some cleavage of oxirane turned into diols (Shafinaz et al., 2019). For GO-g-LENR spectra, the new peaks between $3,200$ and $3,600\text{ cm}^{-1}$ are combined spectrum of two components which indicated that LENR was successfully incorporates with GO sheets. This can be proved by the appearance of peak at $1,414\text{ cm}^{-1}$ which indicates methyl/methylene deformation which quite similar with the findings by Kotal et al. (2016) in their research. Peak that appeared at $2,922\text{ cm}^{-1}$ indicates methyl stretches. This is due to the presence of LENR in GO-g-LENR structure. In addition, grafting of LENR into GO was confirmed when the intensity of $\text{C}=\text{C}$ band at 758 cm^{-1} of LENR spectra was reduced compared to FTIR spectra of GO-g-LENR.

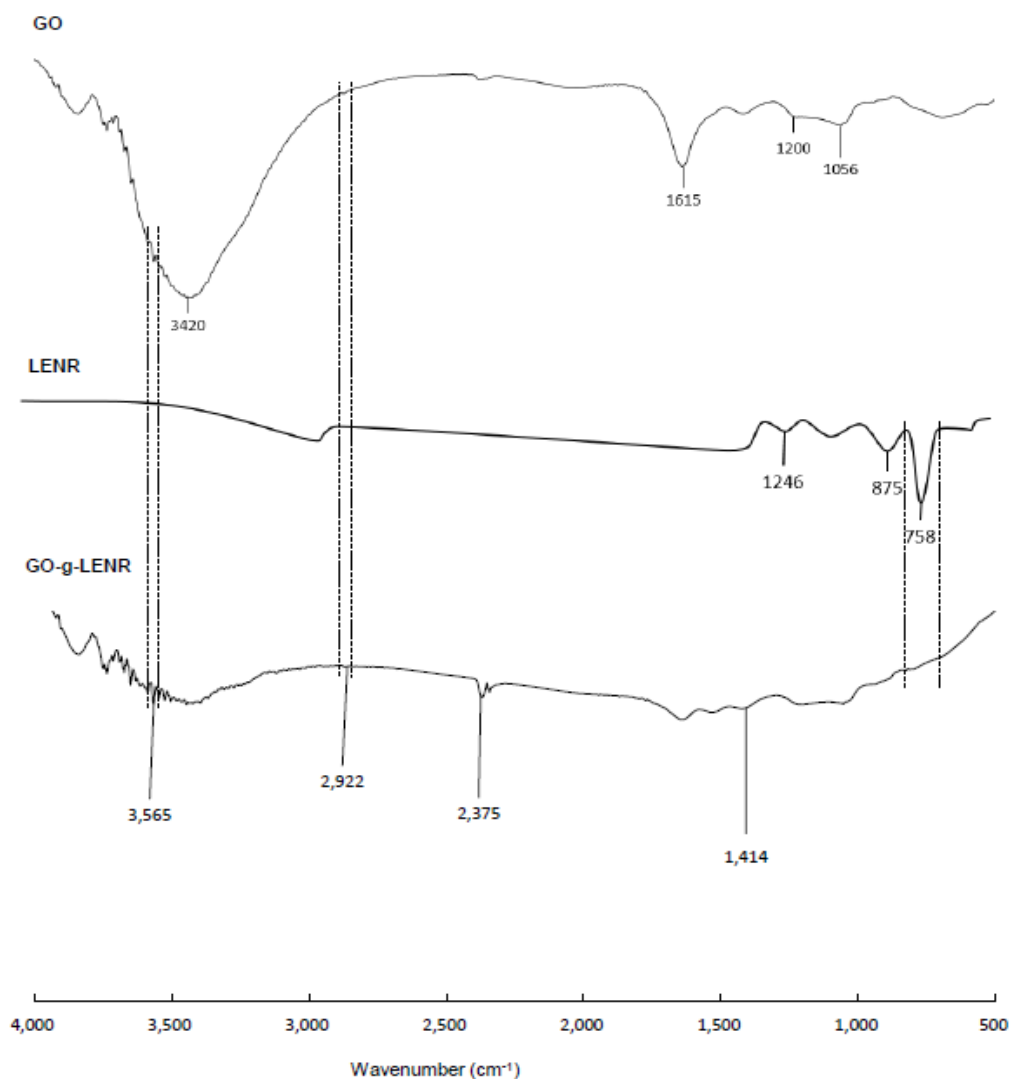


Figure 1: FTIR spectrum of GO, LENR and GO-g-LENR

3.2 Impact properties

Impact strength is the ability of materials to absorb energy at fracture when exposed to sudden impact (Megahed et al., 2019). Figure 2 shows the impact strength for PLA/LENR, PLA/LENR/GO and PLA/GO-g-LENR composites. The impact strength for PLA and LENR without GO at 10 wt% LENR is 86.05 J/m (Syed Mustafa et al., 2020). Addition of 1 phr GO into the polymer system increased the impact strength for both samples (PLA/LENR/GO and PLA/GO-g-LENR) to 91.32 J/m and 96.02 J/m. The dispersion of nano size GO play important roles in increment of impact strength. Mohamad et al. (2018) reported that the good distribution of graphene in PLA/NR/graphene composite had produced a smaller size of rubber particles which prevent the rubber particles from coalesces. When GO particles are well dispersed in the matrix, it could form a bond and bridges the cracks during the fracture resulting in enhancement of toughness (Huang et al., 2018). The presence of grafted GO/LENR also proven better compatibility between the matrix and the filler thus improve the impact property.

Further addition of GO at 3 and 5 phr reduced the impact strength. This observation might due to the agglomeration and stacking of GO particles in polymer matrix which reduce the efficiency of load transfer from PLA/LENR matrix to GO nanofiller (Abdullah et al., 2019). Excess filler particles tend to agglomerate at the interface and causes the main crack to propagate along the composite interface. Similar observation was also reported by Yin et al., (2019). It is noted that the impact strength of PLA/GO-g-LENR was higher compared to PLA/LENR/GO composite at all GO loading.

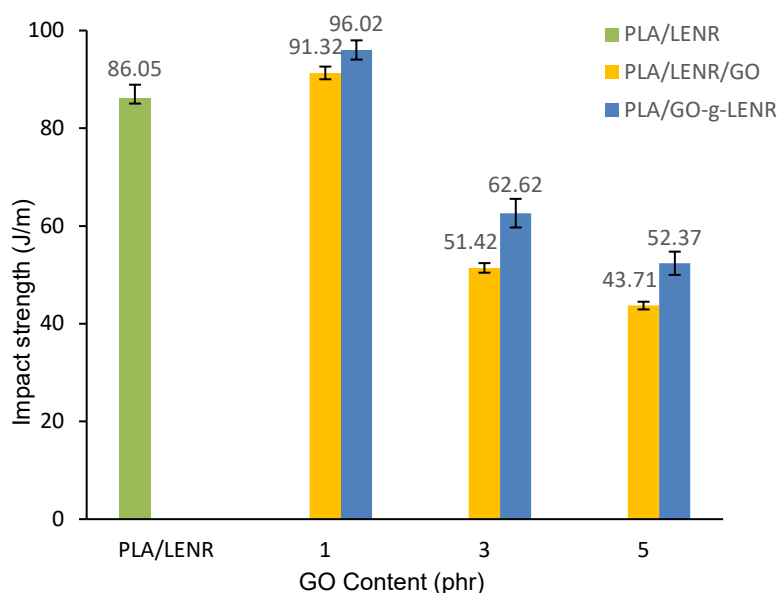


Figure 2: Impact strength of PLA/LENR, PLA/LENR/GO and PLA/GO-g-LENR

3.3 Thermal analysis

Figure 3 shows the weight loss for (a) ungrafted and (b) grafted composites at different GO loading. As can be seen from Figure 3(a) and (b), increasing amount of GO in the composites had shifted the TGA curve to higher temperature. The degradation temperature occurring at 60% weight loss (T_{60}) of PLA/LENR/GO composite changed from 300.2 °C to 323.8 °C as the GO content increased from 1 phr to 5 phr. This is due to the thermal stability properties of GO that presented in composite. According to Abdullah et al. (2019), graphene acted as a shield to hinder the diffusion of volatile decomposition products. Another study also reported that addition of graphene into the polymer system had improved the thermal stability of composites (Bijarimi et al., 2018). T_{60} for PLA/1GO-g-LENR is 329.11 °C. The temperature increased up to 333.11 °C with addition of 5 phr GO. This is might due to the interaction between GO-g-LENR with PLA which causes the increment in the concentration of the entanglement point that increased the outward diffusion of thermal energy until certain point and delayed the alkyl oxygen cleavage. Hence, thermal stability of the PLA/GO-g-LENR composites is improved (Miao et al., 2018). Compared to other samples, PLA/5GO-g-LENR composite has the highest residue mass at 800 °C which is 13% showing the stability of the grafted part of the composites.

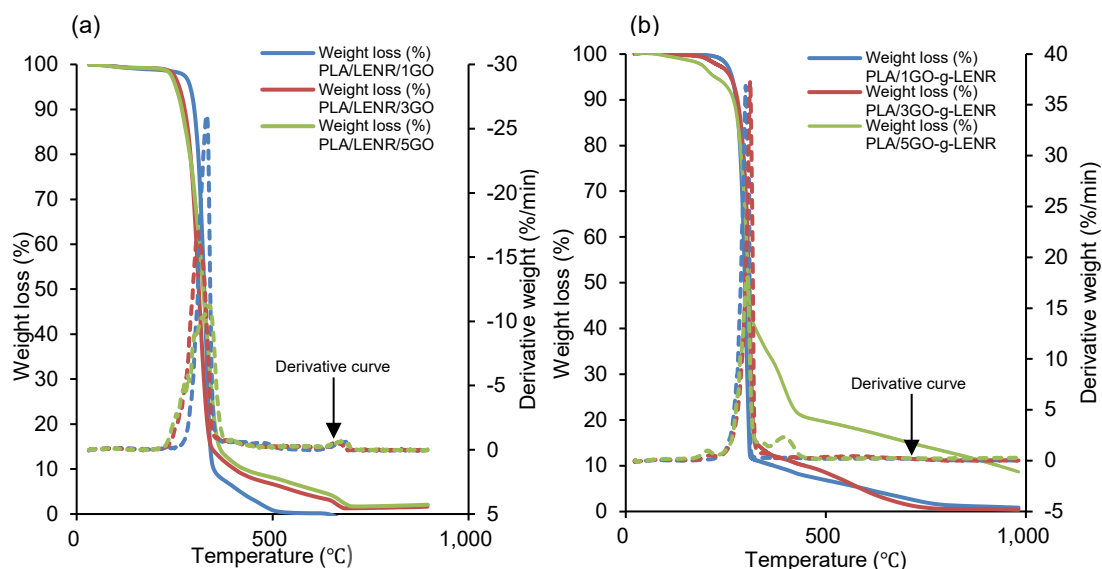


Figure 3: TGA curve of (a) ungrafted composite (b) grafted composite

3.4 Morphological analysis

Figure 4 shows the impact fractured surface of PLA/LENR with 1GO and 3GO content. The rough surface of PLA/LENR/1GO (Figure 4(a)) shows the presence of uniform distribution of GO in the composite. PLA/LENR/3GO (Figure 4(b)) on the other hand shows crack propagation for fracture surface which might due to the agglomeration of GO resulted in decrement in load transfer and impact strength of PLA composite (Abdullah et al., 2019).

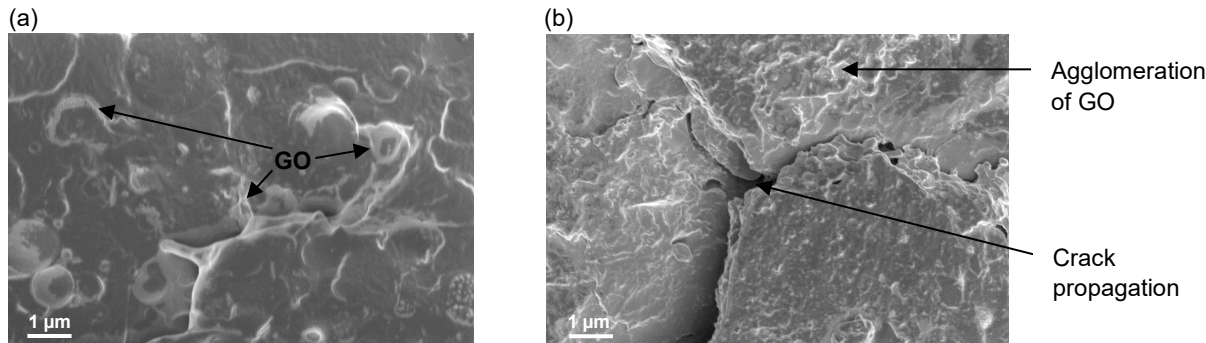


Figure 4: FESEM micrograph of (a) PLA/LENR/1GO and (b) PLA/LENR/3GO

4. Conclusion

PLA composites was successfully prepared by blending PLA with LENR and GO. GO-g-LENR was produced by using grafting method. The appearance of new peaks from FTIR analysis has confirmed the effectiveness of grafting mechanism of GO and LENR. Incorporation of 1 phr GO-g-LENR with PLA increased the impact strength of the composite to 96.02 J/m. This value was higher than blending of PLA with ungrafted LENR and GO. Further addition of GO reduced the impact strength of the composites which might due to agglomeration of GO in the matrix as can be seen from FESEM analysis. Addition of 1 phr GO in the PLA/LENR system was found to be optimum to increase the toughness of the composites. The thermal stability of the composites improved with the addition of GO as shown by increasing of degradation temperature in TGA analysis. Significant improvement was observed for the composites with grafted GO. In conclusion, the incorporation of grafted GO in the composites displayed higher improvement in comparison to the ungrafted composites which proven good compatibility between the matrix and filler. The improvement in the mechanical and thermal properties of PLA composites can be further enhance by incorporation of compatibilizer for the grafting of GO and LENR.

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