Thermal and Toughness Enhancement of Poly (Lactic Acid) Bio-Nanocomposites

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Bio-nanocomposites based on poly (lactic acid)/epoxidized natural rubber (PLA/ENR) blends containing graphene (G) nanofiller were prepared by melt compounding using nano-single screw extruder with a screw speed of 60 rpm, and followed by compression molding. The ENR and graphene loading was varied from 0-30 wt% and 0.5-2.0 phr. The objectives of this work are to investigate the effect of ENR and graphene loading on PLA matrix on the thermal, morphology and toughness properties. The TGA curve of PLA/ENR and PLA/ENR/G bio-nanocomposites shows a single step of thermal degradation. As increasing the loading of graphene, degradation temperature (T_{deg}) was increase where graphene act to slow down the rate of degradation. The PLA/ENR blends showed a co-continuous morphology while PLA/ENR/G bio-nanocomposites revealed a good dispersion of graphene in a PLA/ENR matrix at 1 phr of graphene loading. The optimum impact strength was recorded at 10 wt% of the ENR loading which is 104.6 J/m for the PLA/ENR system. In the case of PLA/ENR/G system, the optimum impact strength was recorded at 1 phr of graphene which is 219.5 J/m. The thermal and toughness enhancement of PLA/ENR/G bio-nanocomposites will diversify the future application of this bio-nanocomposites.

1. Introduction

The bio-based polymer known as a biodegradable polymer which the properties such as mass, molecular weight, and strength of the material may degrade with time when scavenge by a microorganism and produced by-products such as carbon dioxide, water, inorganic compounds or biomass. The bio-based polymer has a positive effect on the environment where the sustainability can be improved and it considers as environmental friendly material (Cinelli et al., 2017). The bionanocomposite is a nanocomposite material that consists of bio-based polymers with a combination of nano-sized reinforcements to produce composites with improved properties by varying stiffness, permeability, crystallinity, thermal stability, biodegradability, and biocompatibility.

Poly (lactic acid) (PLA) is one of the promising biodegradable and commercially material on the market of bio-based polymer that has potential to replace the engineering plastics in food packaging, automotive parts and medical devices. PLA is a biodegradable aliphatic polyester that produced via fermentation of the carbohydrate from the renewable agriculture sources (Aghjeh et al., 2015). From the mechanical properties, PLA is highly transparent that behaves as glassy and brittle material that exhibits high tensile strength of 30 to 50 MPa with an elongation at break between 1% and 7% depends on its molecular weight (Yang et al., 2015). However, the limitation of the PLA to replace engineering plastics is brittleness. poor toughness and low thermal stability (Xu et al., 2016). Incorporation of nano-fillers such as graphene (G) into the PLA matrix can enhance the mechanical properties, thermal stability and crystalline behaviour of PLA even at lower filler loading.

Graphene is a single layer of carbon material consisting of two-dimensional sheet with a hexagonal packed lattice structure. It is extremely stiff and exhibits very high thermal conductivity. Graphene shows several unique properties such as tensile strength of 130 GPa, high Young's modulus (~1.0 TPa), large theoretical specific surface area (2,630 m^2g^{-1}), and good thermal conductivity (~5,000 Wm^{-1} K^{-1}) (Bouakaz et al., 2015). Several studies have been demonstrated that graphene has high reinforcing efficiency in the PLA matrix.

Norazlina and Kamal (2015) have found that PLA/graphene has created good thermal stability by decreasing the diffusion pathway of the degradation of by-products such as acidic species, metallic ions or residual products. The tensile strength of the poly (lactic acid)/graphene nanoplatelets (PLA/GNP) has no much different as compared to neat PLA which reported and proved by Pinto et al. (2015). Based on the Zhang et al. (2018), they reported that the incorporation of only 0.2 wt% functionalized graphene oxide into PLA resulting an extraordinarily 26.6-fold increase in elongation at break relative to PLA without sacrificing strengths. On the other hand, graphene/elastomer nanocomposites have been reported by some publications. According to the She et al. (2014), they found that as the graphene loading increases in the ENR matrix, the tensile strength of the composites will be increases while the elongation at break will be lower due to the reinforcing of the graphene in the ENR matrix. Yaragalla et al. (2015) reported on ENR/graphene nanocomposite where the graphene content was fixed at 2 % w/w. The morphology of the ENR/graphene was observed by using TEM and showed the homogeneous phase between ENR and graphene since the graphene sheet fully exfoliated throughout the ENR matrix and the particle size is small. Thus, the nanocomposite shows a good compatibility between the component in the system.

To overcome the brittleness of PLA, the addition of the elastomeric material or impact modifier could be a good idea. The epoxidized natural rubber (ENR) has been used as an interfacial compatibilizer, toughening agent and polymeric compatibilizer since ENR has high impact strength and excellent resistance to puncture and tear. The ENR is the elastomeric material that has been modified from the natural rubber, NR consists of the double functionality of crosslinking which are an epoxy group and double bond that makes ENR is a polar material (Ahmad et al., 2016). Pongtanayut et al. (2013) stated that there is partially compatibility between PLA and ENR at 20 wt% of rubber composition where ENR act as stress concentrators that enhance the fracture energy absorption of brittle PLA and resulting in improving the toughness of the PLA. According to Zhang et al. (2013), they reported that the impact strength and elongation at break of 20 wt% ENR50/PLA and ENR20/PLA were increased as compared to pure PLA and this is due to the good interfacial adhesion between PLA and ENR. In addition, Akbari et al. (2014) reported that the addition of 20 wt% of ENR into the PLA/talc composites, improved the impact strength due to the ENR enhancing the mobility of the PLA chains. The properties of PLA/ENR blend was again reported in this study in order to gather the control data using the same processing parameter with PLA/ENR/G bio-nanocomposite.

This work has interest in toughening PLA which focused on incorporated of ENR and graphene nanofiller to improve the toughness and thermal stability since there is no report on the plastic/elastomer/graphene nanocomposite and toughening properties are rarely analysed in detailed. The objectives of this work are to investigate the effect of ENR and graphene loading on PLA matrix on the thermal, morphology and toughness properties.

2. Experimental

2.1 Materials

The poly (lactic acid) (PLA) grade 3052D supplied by Innovative Pultrusion Sdn. Bhd., Malaysia was selected for use in this study. The epoxidized natural rubber (ENR), grade "Epoxyprene 50" with 50% epoxidization level was supplied by Malaysia Rubber Board, Malaysia. No commercial modifier was added to the rubber. The nanofiller used was graphene multilayer (G) with a diameter of ~5µm and thickness of 2 to 10nm from Innovative Pultrusion Sdn. Bhd., Malaysia.

2.2 Sample preparation

The PLA/ENR/G bio-nanocomposites were prepared according to the formulation on Table 1.

Table 1: The formulation of the bio-nanocomposites

Samples	PLA (wt%)	ENR (wt%)	Graphene (phr)
P90E10	90	10	-
P80E20	80	20	-
P70E30	70	30	-
P90E10/G0.5	90	10	0.5
P90E10/G1.0	90	10	1.0
P90E01/G1.5	90	10	1.5
P90E10/G2.0	90	10	2.0

The melt mixing was carried out by using nano-single screw extruder with a screw speed of 60 rpm. The barrel temperature profile adopted during mixing is 150°C to 170°C from the hopper to the die head and mixing time was 30 min. Prior to melt mixing process the PLA and graphene were dry overnight in the oven at 50°C to remove residual water content. The ENR was undergoing mastication process by using two-roll mill and then was cut into small pieces. The ENR and graphene content was varied from 10 to 30 wt% and 0.5 to 2.0 phr. Then, the composites were moulded into sheets of 3 mm in thickness by hot pressing at 170°C with the pressure of 110 kg/cm^2. The preheating, compression molding and cooling times were 6 min, 3 min and 5 min.

2.3 Testing and characterization

The Izod impact test was carried out by using impact testing machine and the samples were tested at ambient temperature. The testing was performed according to ASTM D256 and the impact strength value was recorded. The samples used for the testing was a rectangular shape with a dimension of 65 mm × 12.7 mm × 3 mm.

Scanning electron microscope (SEM) was used to study the dispersion of the ENR in toughened PLA matrix. The SEM was performed by using SEM Philips ZL40. The samples used was from the impact fracture. The other method used to study the dispersion and distribution of the graphene in toughened PLA matrix was field emission scanning electron microscope (FESEM) by using JOEL machine from Japan. The FESEM can be used to obtain the image of the surface at the nanoscale. To avoid the electrostatic charging during the examination, the samples were coated with platinum.

The thermogravimetric analysis (TGA) was investigated the thermal stability of the samples. The weight loss of the samples was measured as a function of temperature. The TGA was performed by using Perkin Elmer TGA-7 thermal analyser. The heating rate used was 10°C/min and the temperature range used was from room temperature to 900°C.

3. Results and discussion

3.1 Impact properties

Figure 1 shows the impact strength of the PLA/ENR blends and PLA/ENR/G bio-nanocomposites. As can be seen in Figure 1a, the impact strength increases up to 104.6 J/m as compared to pure PLA, 72.6 J/m when incorporated with 10 wt% of ENR. The results are different from the studies by Akbari et al. (2014) which reported that the optimum value of the impact strength is at 20 wt% of ENR loading. More energy can be absorbed when the load is applied during the test with the presence of the ENR in the PLA matrix. Thus, the impact strength of pure PLA has been increased. This was attributed to the good interaction between PLA and ENR which may reduce their interfacial energy in the interfacial region where it can create the finer dispersion of ENR domain and improving the stress transfer thus increased the impact strength. Figure 2a shows the finer dispersion of ENR domain in PLA/ENR blend. Epoxidized natural rubber can absorb more energy when the load transfers from PLA matrix to ENR particles and create multiple crack propagations at the surrounding of ENR particles at a high impact speed (Zhang et al., 2013).
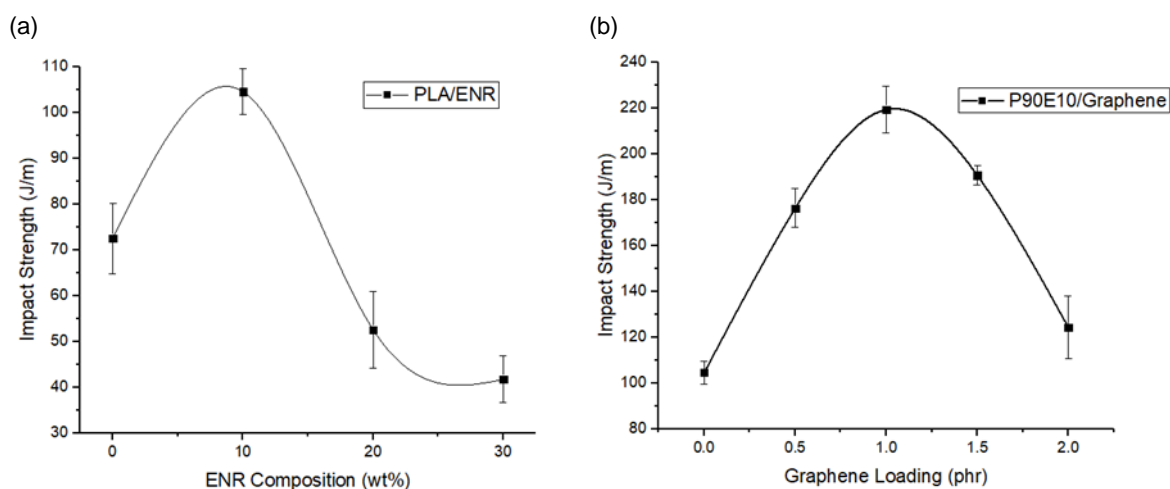
(a)   (b)

Figure 1 : The impact strength of (a) PLA/ENR blends (b) P90E10/Graphene bio-nanocomposites.

The incorporation of ENR had already improved the toughness of PLA, besides graphene is another factor contributing to the improvement of toughness. The 10 wt% of ENR loading was chosen to be used in the PLA/ENR/G bio-nanocomposites based on the optimum impact strength. Figure 1b shows that the impact strength increases almost 2 times at 1 phr of graphene loading which was 219.5 J/m as compared to P90E10 which was 104.6 J/m. This is due to the good dispersion of graphene in the PLA/ENR matrix and the nanoparticle sizes of graphene as can be observed in Figure 2d - e. Zurina et al. (2018) reported that the good dispersion of graphene in PLA/Natural rubber/graphene nanocomposite had produced a smaller rubber particles size. The good dispersion of graphene prevents the rubber particle coalesces. The reduction in rubber particles also known to contribute to the increment of the toughness of the nanocomposites since the smaller rubber particle will give a better interfacial interaction between rubber and matrix thus facilitate the stress transfer in the nanocomposites. In addition, when graphene sheets are well dispersing throughout the matrix, it could form a bridge and bond the cracks during fracture and thus favoured enhancing toughness (Huang et al., 2018). Increasing in graphene loading up to 2 phr, the impact strength was decreased to 124.3 J/m and may be due to the agglomeration and stacking of graphene Figure 2f – g and resulting in the reducing load transfer efficiency from the PLA/ENR matrix to graphene nano-filler.

3.2 Morphological study

The morphology of impact fractured surfaces of PLA/ENR blends and PLA/ENR/G bio-nanocomposites were examine by SEM and FESEM micrograph shows in Figure 2. The ENR phase was selectively etched using toluene in order to explore the phase structure and morphology of the blend.
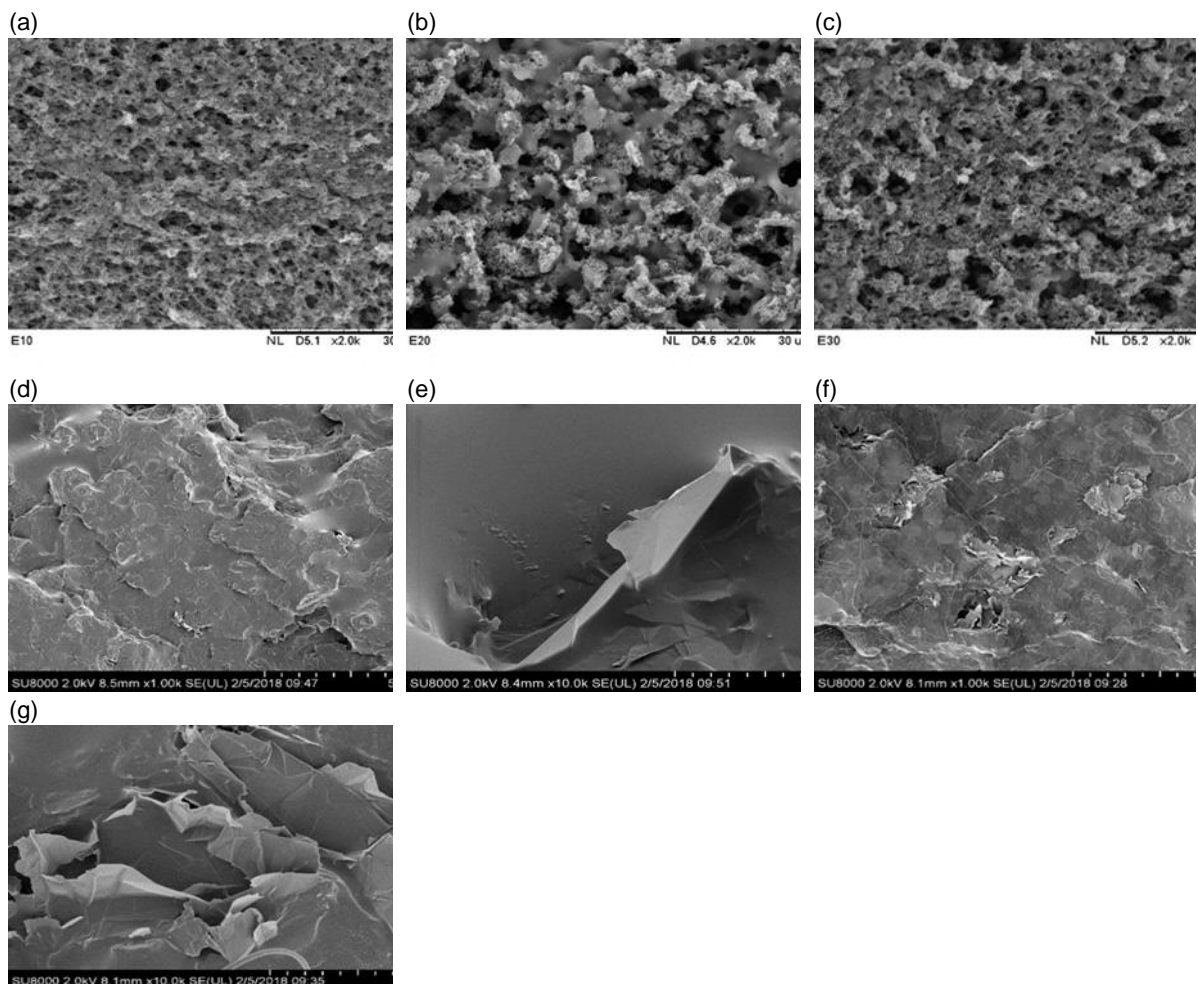

Figure 2: The SEM images of (a) P90E10 (b) P80E20 and (c) P70E30 and FESEM micrographs of (d) & (e) P90E10/G1.0 and (f) & (g) P90E10/G2.0.

The PLA/ENR blends (Figure 2a - c) showed a co-continuous morphology with a coarse surface. This can be considered a partially compatible between ENR particles and PLA matrix. The continuous structure of ENR increased the molecular entanglement and network structure that lead to the increase of the impact strength. During the fracture process, the fracture crack ran along the interface between the PLA matrix and ENR particles which resulting the crack energy produced can be absorbed and dissipated by the ENR phase. From Figure 2a, the ENR with 10 wt% loading showed a finer dispersion as compared to 20 wt% and 30 wt% loading where the stress transfers improved and lead to the increasing the impact strength. The graphene in the P90E10/G1.0 nanocomposite (Figure 2d - e) was good and uniformly dispersed and resulting in good compatibility with PLA/ENR matrix and may restrict the movement of polymer chains due to the strong interaction between the nano-filler particles and polymer chains. Conversely, many agglomerations and stacking of graphene were observed in the P90E10/G2.0 nanocomposite (Figure 2f - g). This resulting in the decrement of mechanical properties, load transfer and energy absorption during the testing.

3.3 Thermal analysis

The initial degradation temperature (T_{onset}) and the final degradation temperature T_{deg} of PLA/ENR blend and bio-nanocomposites were determined from TGA curve in Figure 3. The TGA curves in Figure 3 shows that there was only one step of decomposition. The T_{onset} of pure PLA is 331.0 °C. The T_{onset} of PLA/ENR blend with 10 wt% of ENR content (P90E10) was reduced to 305.6 °C. The final degradation temperature (T_{deg}) of the P90E10 blend also reduced from 353.4°C to 331.5°C as compared to pure PLA. The decrement of the thermal stability of the PLA/ENR blend is due to the inferior thermal stability of elastomer ENR than PLA matrix (Zurina et al., 2005). It might also attribute from the presence of the hydroxyl group in ENR. Decomposition of the hydroxyl group in ENR molecules gave a by-product of hydroxyl volatile gas which can promote the chains scission reaction of PLA molecules (Pongtanayut et al., 2013). Incorporation of 2 phr graphene into the P90E10 blend, the T_{onset} and T_{deg} were improved to 316.0 °C and 340.2 °C compared with PLA/ENR blend. At 1 phr of graphene loading, the T_{onset} and T_{deg} values were lower than 2 phr of graphene loading which was 311.0°C and 336.3°C. The thermal stability of PLA/ENR/G bio-nanocomposite increased with increasing in graphene loading. Graphene is known as a thermally stable material. This is due to the graphene acts as an obstacle to hinder the diffusion of volatile decomposition products in the composites (Norazlina and Kamal, 2015). The previous researcher reported that the thermal degradation temperatures of PLA/Exfoliated graphene nanocomposites increased substantially with the increment of graphene content up to ~3 wt% (Il and Young, 2010).
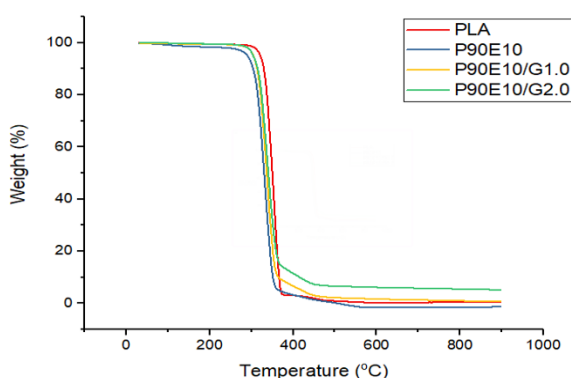

Figure 3 : The TGA curve of pure PLA, P90E10 blend, P90E10/G1.0 bio-nanocomposite and P90E10/G2.0 bio-nanocomposite.

4. Conclusion

It can be concluded that PLA/ENR blend gives the highest impact strength at 10 wt% of ENR loading which was 104.6 J/m and the highest impact strength of PLA/ENR/G bio-nanocomposite was recorded at 219.5 J/m. ENR acts as a toughening agent for PLA matrix where it has the capability to absorb more energy when the load is applied. Graphene gives a synergistic effect by further improving the toughness of the PLA/ENR/G bio-nanocomposite with a good compatibility with PLA/ENR matrix. The PLA/ENR blends show a co-continuous morphology with finer dispersion at 10 wt% of ENR while a good and uniform dispersion was observed at 1 pht graphene content. The thermal stability of PLA matrix decreases with the incorporation of ENR. The

degradation temperature was proportionally increased with increasing in graphene content. Graphene has enhanced the thermal stability of PLA/ENR/G bio-nanocomposite.

Acknowledgements

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