Properties Enhancement of Polylactic Acid Biocomposite

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Natural rubber toughened by polylactic acid/graphene (PLA/NR/GR) biocomposite was prepared by two different processes known as the in-situ melt mixing process (conventional) and the integration of latex compounding masterbatch and melt mixing process. These two processes were employed to compare the state of graphene dispersion and distribution in the biocomposite. Good dispersion and distribution of nanographene is a key factor that can enhance or change the properties of the nanocomposite. The objectives of this work are to evaluate the effect of different processes and graphene content on the mechanical, and morphological of PLA/NR/GR biocomposites. The composition of PLA/NR blend was fixed at 80/20 wt% and the graphene content was varied from 0.1 - 0.4 parts per hundred (phr). The integration process produced the PLA/NR/GR nanocomposite with better mechanical properties compared with the conventional process due to a better state of GR dispersion in the nanocomposite. The tensile strength was slightly improved at lower GR content indicating that GR is effective in increasing strength of toughened PLA nanocomposite. NR improved the impact strength of PLA biocomposites with a sacrifice of tensile strength. The results also revealed that the PLA/NR blend was reinforced and toughened simultaneously by GR, which is extraordinary as compared with many reported nanofiller-reinforced PLA composites. The simultaneous improvement in both strength and toughness could be attributed to the homogeneous dispersion of GR in PLA/NR matrix. The integration process had given a promising method to homogeneously dispersed GR in the polymer matrix which in turn can become a successful method for producing graphene nanocomposite.

1. Introduction

Plastics are widely used around the world for various applications due to their advantages such as lightweight, low-cost, easy to process and good mechanical properties. The difficulties in waste management arise as plastics take a longer time to degrade and cannot degrade properly. This adversely affects the environmental, economic and ecological system. One of the solutions to tackle the waste management problem is by using the environmentally friendly polymers that is biodegradable (Zurina et al., 2017). Polylactic acid (PLA) is one of the materials that derived from the biomass such as sugar and starch, which exhibits high physical and mechanical properties, combined with excellent biodegradability and biocompatibility properties. The brittleness and low toughness of PLA usually limit their usage in most of the applications. In order to modify the drawback, natural rubber (NR) is blended with PLA and the rubber particles behave as toughening agent and enhance the fracture energy absorption of the brittle polymers and ultimately improve toughness (Pongtanayut et al., 2013). Graphene (GR) is sort of an encouraging nanofiller for the polymer, resulting in high strength and effective loads transfer (Pinto et al., 2016). The introduction of GR into polymer produces irreversible agglomeration and challenges the properties improvement (Jiang et al., 2013), thus necessary action must be met. Based on the previous report, the latex compounding method introduced was capable to reduce the incompatibility between the filler and polymer and exhibited better dispersion and improves the properties (Tkalya et al., 2010). The latex compounding method reduces the agglomeration of the filler and result in good dispersion in the polymer matrix. It is expected that the latex compounding method could improve the dispersion of the GR in the PLA/NR/GR nanocomposites and improve the mechanical properties of the nanocomposites.

2. Experimental

2.1 Materials

Polylactic acid with the Injection Grade NatureWorks@PLA Polymer 3051D was purchased from Nature Network USA. The natural rubber latex was supplied by Getahindus (M) Sdn. Bhd. Malaysia, GR nanoplatelets Grade-M with average particle diameters of 5 - 25 microns were purchased from XG Sciences Inc. Calcium chloride which used as a coagulant agent was purchased from Merck KGaA.

2.2 Experimental Procedure

PLA was dried in the oven at 60 °C for 24 h before the melt mixing process. GR/NR latex dispersion was prepared by the addition of GR with different loading (0.1 - 0.4 parts per hundred (phr)) into the NR latex with the mechanical stirrer at 150 rpm for 30 min. GR/ NR latex was coagulated by calcium chloride to form the GR/ NR masterbatch. The masterbatch was rolled by two roll mills and dried in the oven at 100 °C for 24 h. The PLA/NR/GR was prepared by melt mixing process by the twin screw extruder with a temperature range of 130 - 160 °C and a speed of 25 rpm by incorporating PLA and GR/ NR masterbatches as latex compounding method and incorporating PLA/ NR and GR as an in-situ method. The compound was pelletised by using the pelletiser. The pellet of the compound was compressed by the compression moulding machine with the temperature range of 150 - 170 °C. The tensile properties of PLA/NR/GR biocomposites were measured by using Instron Universal Testing Machine Model 5582. The machine speed was set at 10 mm/min and the sample was prepared in the dumb bell shape as ASTM D638. The Izod impact test was carried out according to ASTM D256 with the unnotched sample dimensions of (about 64 mm x 12.7 mm x 3.2 mm). The impact fracture morphology of PLA/NR/GR nanocomposites was analysed by using scanning electron microscopy (SEM).

3. Results and discussion

3.1 Morphology

To understand the results of the mechanical properties of PLA/NR/graphene nanocomposites, the FESEM and SEM micrographs of the nanocomposites are analysed by using the impact fracture sample during the mechanical testing. The nanocomposites were prepared at a different loading of graphene by two different methods which are in-situ melt mixingmethod and integration method (latex compounding +in siti melt mixing). Figure 1 shows the SEM micrograph of impact fracture surfaces of PLA/NR/graphene nanocomposites for both methods.

As can be seen, all the PLA/NR/graphene nanocomposites show phase separated morphology between NR and PLA matrix where the rubber particles dispersedly occurred as small droplets in PLA matrix because the non- polar NR was immiscible with the polar PLA (Zhang et al., 2013). Furthermore, the rough fracture surface of PLA/NR/graphene (Figure 1) indicates the ductile fracture behaviour which can be related to the increase in toughness and elongation at break of the nanocomposites. It is clearly seen that as the graphene loading increases, the rubber particles in the PLA matrix is decreasing in size and becomes smaller for both methods. The rubber particles in integrationmethod show smaller rubber particles size compared with in-situ melt mixing method. This is due to the excellent interaction between graphene and latex during latex compounding which prevent the rubber particle coalesces. It proves that latex compounding method is capable to reduce the agglomeration while increases the dispersion of graphene in the matrix (Jiang et al., 2007). 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.

Figure 2 shows the agglomeration of graphene at 0.4 phr graphene loading. Formation of aggregates is a common feature in the polymer nanocomposites. The higher loading of filler may affect the dispersion and distribution of graphene into the polymer matrix. This shows that the dispersion of graphene dependent on the affinity between the polymer and particles and also the processing method. These agglomerations of graphene may reduce the mechanical properties of the nanocomposites. Similar to the researches by Gui et al., (2016), the agitation of silica in the matrix improves the dispersion of silica in the SBR latex in the preparation of silica/SBR masterbatches compare to the traditional dry blending and leads to the superior properties of the composites. Latex compounding method gives a much finer and more uniform of dispersion of graphite nanosheets in NBR, and the interface between the graphite sheets and NBR is greatly improved (Yang et al. 2007). In this study, it also proves that the latex compounding method of producing masterbatches leads to more uniform dispersion of graphene in the matrix than the in- situ melt mixing method of producing PLA/NR/graphene nanocomposites.
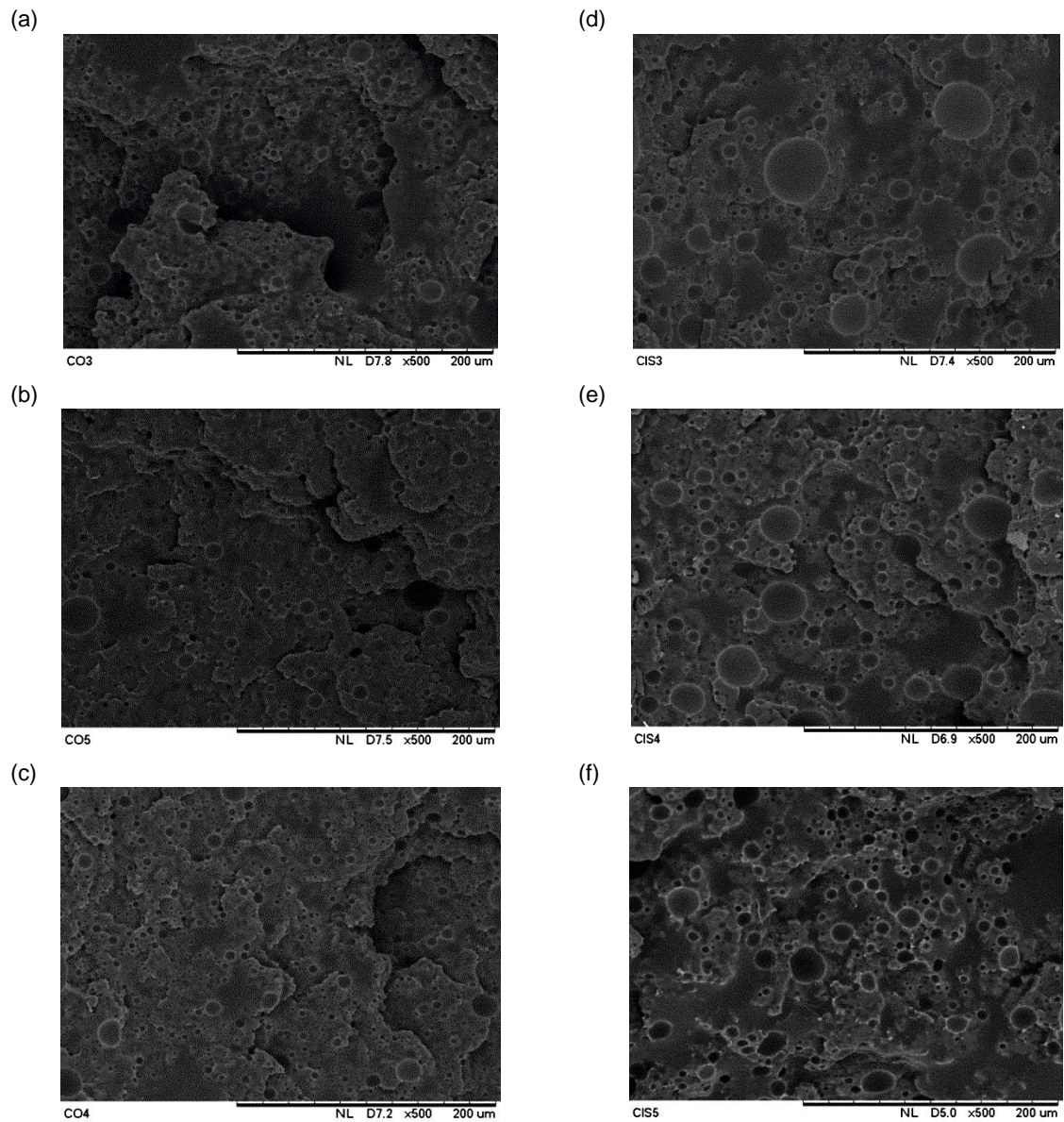
(a)

(d)

(b)

(e)

(c)

(f)

Figure 1: SEM micrograph of impact fracture surface for PLA/NR/GR nanocomposites by latex compounding method at different graphene loading (a) 0.2 phr (b) 0.3 phr (c) 0.4 phr and by in-situ method (d) 0.2 phr (e) 0.3 phr (f) 0.4 phr
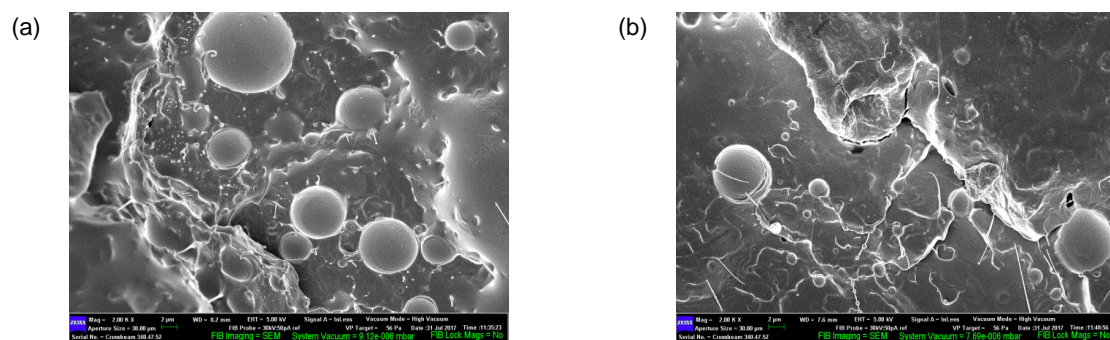
(a)

(b)

Figure 2: FESEM impact fracture of integration method with a) 0.3 phr and b) 0.4 phr of graphene loading

3.2 Mechanical properties

The tensile strength, tensile modulus and elongation at break of PLA/NR/GR biocomposites are presented in Figure 3, 4 and 5.
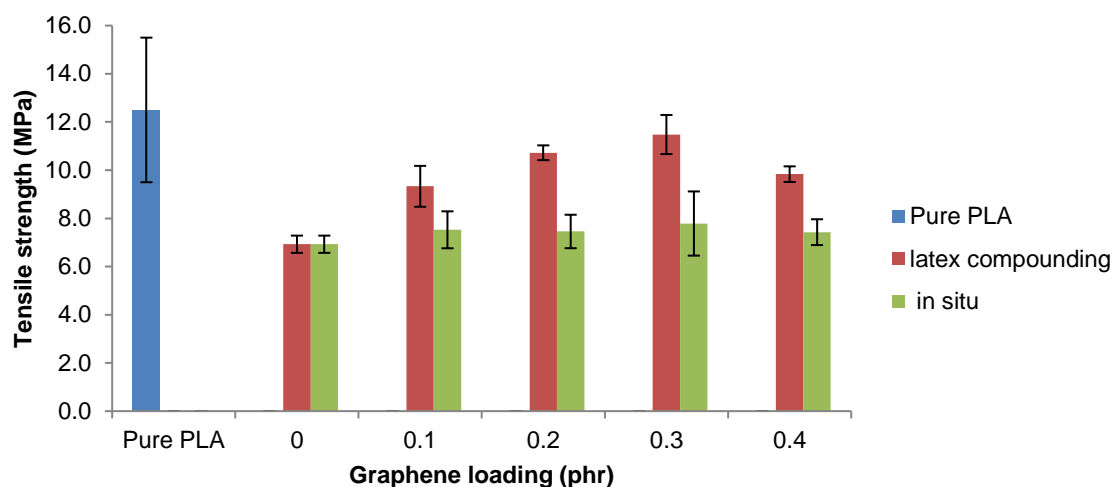

Figure 3: Tensile strength of PLA, PLA/NR/GR biocomposite as a function of graphene loading

Figure 3 shows that tensile strength of the pure PLA is 12.5MPa. The tensile strength of the nanocomposites decreased to 6.926 MPa as 20 wt% of NR is added in the PLA matrix. Generally, it is expected that the introduction of the soft material such as rubber reduces the strength and improve the toughness of the nanocomposites. This result is consistent with the finding from the previous research by Bitinis et al, (2011) which reported that the rubber phase lowered the strength. The reduction of tensile strength compare to tensile strength of the pure PLA was due to the result of the rubbery nature of NR (Juntuek et al., 2012).

In the case of integration method, it recorded the increase of tensile strength as the graphene loading is increased, respectively. The 0.3 phr of graphene is considered as its optimum graphene loading, as the PLA/NR/graphene nanocomposite of 0.3 phr graphene has the highest tensile strength compared to other samples. The results show the optimum graphene loading can increase the compatibility between the PLA and NR. This might be due to the good dispersion of the graphene in the PLA/NR matrix (Figure 2a) and hindered the agglomeration to occur thus giving the higher tensile strength. The lower amount of graphene can easily dispersed in the nanocomposites thus giving the improvement in the polymer matrix- filler interfacial bonding. Similar finding was reported by Zhang et al., (2015), in their study on poly (lactic acid) nanocomposite films reinforced with alkylated graphene nanosheets. However, the increase in tensile strength had dropped as it reached optimum value. Moreover, as the filler loading exceed the optimum value, the agglomerations occur (Figure 2b) and mechanical properties start to deteriorate.

For the in-situ method, there is a slight increase in tensile strength with the addition of graphene. No significant changes were observed as graphene loading is increased. The result showed that the tensile strength of the nanocomposites with different loading of graphene is quite similar in the whole range proportion, increasing by about 8.66% and 12.42 % respectively. This might be because of graphene is not well dispersed in the PLA/NR compound due to mixing method of the nanofillers. The different tensile properties of PLA/NR/graphene naocomposites can be attributed to the different dispersion quality of graphene. Potts et al., (2012) has found that compounding methods could pose a significant effect on the morphology and properties of natural rubber/reduce graphene oxide nanocomposite. They found that co-coagulating a stable RG-O suspension with NR latex afforded a weblike morphology consisting of platelet networks between the latex particles, while two-roll mill processing broke down this structure, yielding a homogeneous and improved dispersion. In general, it can be concluded that 0.3 phr graphene nanofiller is considered the optimum amount of filler in the nanocomposites and capable to increase the strength of the toughened PLA using the integration method
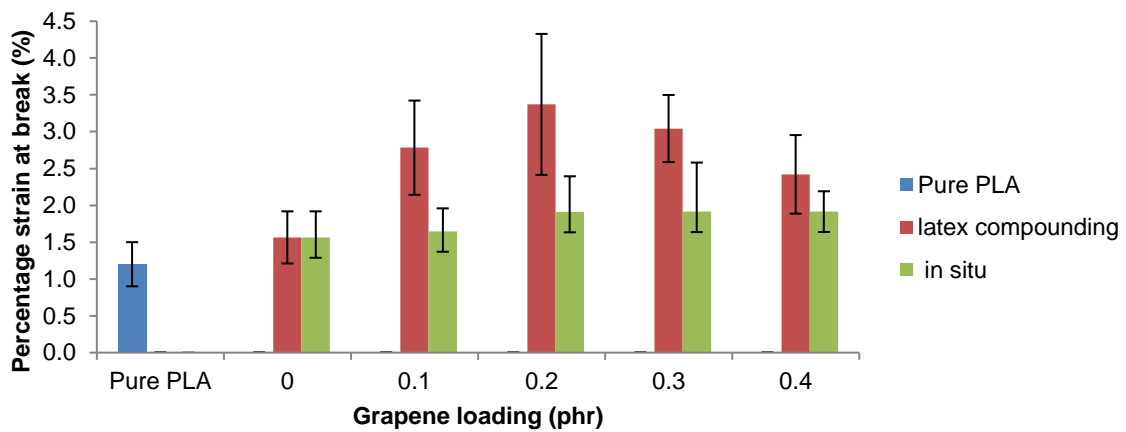
Figure 4: Percentage strain at break of PLA/NR/GR biocomposites as function of graphene loading

The percentage of strain at break of PLA/NR/GR biocomposites is presented in Figure 4. The percentage strain at break of pure PLA is increased as 20 wt% of rubber content is introduced in the PLA matrix. This is similarly reported in the previous study (Pongtanayut et al., 2013), the addition of NR into the PLA matrix possesses higher elongation. The NR content overcomes the rigidity and brittleness of the PLA by improving the flexibility and softness of the blends. As the graphene loading increased, the percentage strain at break of the biocomposite is also increased up to 0.2 phr of graphene. The increment for integration method is obviously seen compared with the in-situ method. It may be due to a good graphene dispersion and distribution in the composite with integration method. The loading of graphene which exceeds these optimum amounts (0.2 phr) leads to decrease of the percentage strain at break.

Impact resistance was tested by Izod test mode with unnotched specimens. The impact strength of PLA and PLA/NR/GR biocomposites were presented in Figure 5. Neat PLA had an impact strength of 96.081 J/m. An improvement of impact strength or toughness was reported as PLA blended with NR and the amount approximately doubles at the addition of 0.3 phr of graphene in the blend by integration method. The blend of rubber with the PLA significantly affects the impact strength which acts as a toughening agent (Zhang et al., 2013). As the graphene loading increased, the impact strength for the blends was also increased. This can be obviously seen as the integration method and only a slight increment for in-situ mixing method. As shown in Figure 2 the dispersion of graphene in the blend also affected the toughness of blends besides its tensile behaviour. The blend of 0.3 phr graphene by integration method gives the maximum impact strength. Adding the amount of graphene does significantly improve the impact strength of the biocomposites but at the higher loading, the toughness dropped.
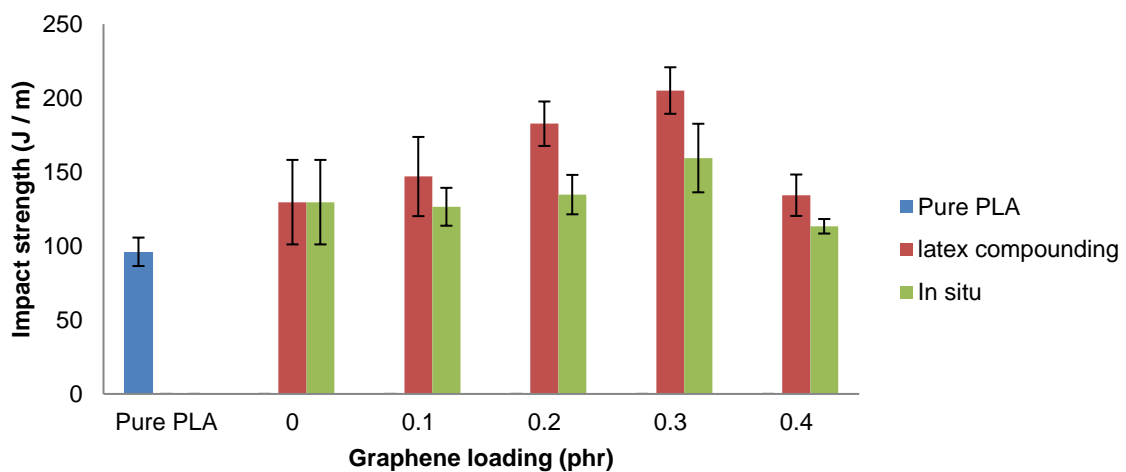

Figure 5: Impact strength of PLA/NR/GR biocomposites as function of graphene loading

4. Conclusion

Toughened PLA was successfully prepared by incorporating NR latex in the blends. The addition of the rubber content in the PLA increases the ductility and toughness of the PLA and overcome its brittleness property. There was an improvement in the tensile strength, elongation at break and impact strength of the biocomposite with the addition of graphene and the optimum loading is 0.3 phr. The incorporation of natural rubber and graphene into PLA matrix via integration method have given the synergistic effect in toughness and strength of PLA nanocomposite. The integration method was found to be feasible to be used in the production of toughened PLA graphene biocomposite/nanocomposites.

Acknowledgments

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