The Effect of Blending Methods on the Properties of PLA/Gr Nanocomposites

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Abstract. Polymer nanocomposites based on polylactic acid (PLA) and graphene (Gr) were blended via melt blending and solution mixing. The properties of hardness and melt flow index (MFI) were investigated with variables of Gr loading from 0.5–2.0 wt.% and the effect of poly(ethylene glycol) (PEG) as plasticizer. The PLA/Gr nanocomposites exhibited higher hardness compared with neat PLA for both methods of nanocomposites preparation which were due to stiffness effect from nanofiller. The loading of PEG in the PLA nanocomposites resulted in the slightly decreasing of hardness. The hardness of PLA and PLA nanocomposites obtained from melt blending were higher than hardness from solution mixing where 2.0 wt.% Gr loading in PLA exhibited maximum value which was 83.1 Shore D. The significant improvement on the MFI could be seen with plasticizer loading compared to unfilled PEG in PLA blends obtained from both methods. Again, the MFI values of PLA/Gr showed from melt blending were higher than exhibited from solution blending method. The highest MFI was 70.6 g/10 min, obtained from 0.5 wt.% Gr loading in PLA/PEG/Gr nanocomposite. The morphology study from Field Emission Scanning Electron Microscopy (FESEM) analysis confirmed the interfacial interaction and homogeneity of Gr in PLA in order to enhance the hardness and MFI properties as discussed above.

1. Introduction
Non-biodegrability plastics grab major attention due to environmental problem. On the other hand, these petroleum-based polymers are finite. Therefore, a great interest in the study of an alternative and biodegradable polymers from other resources can be seen recently. Biodegradable polymers have been researched for several applications in engineering fields such as automotive, aerospace and aeronautics, as well as in biomedical sector, enhancing the autonomy and efficiency of the life cycle of components. Instead of these facts, polymers exhibit several disadvantages such as reduced mechanical properties, like tensile strength, toughness and fatigue resistance, promoting devices and components early failure.

Composites have provided an alternative to traditional engineering materials such as metals and woods. Instead assisting to overcome the short comings of the individual components, these materials provide additional strength and functionality to engineering materials. Basically, composite materials can be categorized as structural materials and functional materials. Structural materials focus on the improved mechanical performance which are designed to improve stiffness, strength and resistance to
deformation relative to traditional monolithic materials [1]. This means, functional materials take advantage of a materials response to heat, light, conductive properties and others [2].

Today, the production of nanocomposites is increasing drastically to support the worldwide demands. As an example, referring to market survey reports, the consumption of nanocomposites was 138,389 metric tons in 2011 with a net worth of around $920 million [3] and expected to rise at a compound annual growth rate (CAGR) of 26.7% in the period of 2016–2021, with a projected revenue of $5.3 billion [4]. One fact when considering on this, the market shares of polymer nanocomposites alone is expected to reach $11,549 million by 2022 [5]. These unstoppable technological development and innovative processing techniques, it promoted the production of new and high-performance nanocomposites.

Nanoscale fillers provide a particular excellence advantage of significant reinforcement at low loadings in exhibiting dramatic changes of mechanical and electrical properties due to their large surface area for a given volume. This processing specific area resulting in two or more times greater than that of micro or larger aspect fillers as reported by several studies [6]. Therefore, the end-product utilizing a similar loading of nanoscale filler is expected to possess properties that are improved three to four times the magnitude more than is found with microscale filler. One of the most intriguing properties of nanofiller is the minimal filler loading to polymer ratio required to provide optimum performance [7].

The relationship between the matrix and reinforcement phase is paramount to the overall performance of a matrix due to dispersion ability. The matrix is not only responsible for holding the reinforcement phases in the required direction, but also helps in protecting the reinforcement phase from environmental damage due to abrasion. Generally, it assists to improve toughness while improving compression strength among other supporting characteristics. Composites from biodegradable polymers become the important material, not only in optimization of components performance and production during life but also considering the degradation ability in waste disposal, due to environmental issue.

The quality of the interface between the nanofiller and matrix strongly affects the efficiency of properties enhancement. Dispersion and distribution of material in matrix is a great importance to maximize exploitation of nanomaterial properties. Low surface energy differences between nanofillers and matrix resins lead to better dispersion [8–10], opposed with high surface energy contributing to limitation of dispersion [11–12]. Aggregation of nanoparticles leads to stress build up in composites that contributes to material failure bringing to poor properties. Several studies mentioned a desirable dispersion for reinforcement is characterized by an individual nanoparticle fully surrounded by a polymer matrix [13–15].

In the relation of the processing properties, it is worth noting that addition of plasticizer into PLA can perform lubrication in improving filler dispersion and reducing matrix viscosity. In addition, plasticizer also aids in extruding the polymer at lower temperatures and can improve flexibility and reduce cracking tendencies of finished products.

In this study, a biodegradable polyester, poly(lactic acid) (PLA) as a matrix has been chosen to be modified with graphene material. The addition of this nanofiller was made by melt and solution blending. The prepared samples were then analysed to study their properties of hardness, melt flow index (MFI) and also Field Emission Scanning Electron Microscopy (FESEM) morphology.

2. Methodology
In this study, poly(lactic acid) (PLA), poly(ethylene glycol) (PEG) and graphene (Gr) were used as raw materials. PLA resin with grade 3251D was provided from NatureWorks®, UNIC TECHNOLOGY, China. Low molecular weight PEG was purchased from Merk KgaA, Darmstadt, Germany. Gr nanoplatelets with Grade M was supplied by XG sciences Inc. (Lansing, MI, USA). Table 1 shows the properties of PLA, PEG and Gr.
Table 1: Properties of materials

|                          | PLA                          | PEG                          | Gr                          |
|--------------------------|------------------------------|------------------------------|-----------------------------|
| Physical state           | Solid granules               | Liquid                       | Solid                       |
| Clarity                  | Transparent                  | Transparent                  | Opaque                      |
| Melting point            | 155–170 °C                   | 5 °C                         | 3,725–5,726 °C              |
| Glass transition         | 55–60 °C                     | -                            | -                           |
| Melt Flow Rate           | 35 g/10 min (190 °C),        | -                            | -                           |
| Formula                  | (C₃H₄O₂)n                    | HO(C₂H₄O)ₙH                  | C                           |
| Formula weight           | 72.06 g/mol                  | 400 g/mol                    | -                           |
| Surface area             | -                            | -                            | 120–150 m²/g                |

Two series of PLA nanocomposites were prepared by melt and solution blending: PLA/Gr and PLA/PEG/Gr nanocomposites. In melt blending method, prior to the blending, the PLA and graphene nanofiller were vacuum dried at 60 °C for overnight. Afterwards, they were melt-blended via an internal mixer operated at 180 °C for both front and back screw. The speed was set between 3–5 rpm. PLA was fed into internal mixer and became molten followed by addition of Gr till homogenous blending were obtained. The weight ratios of PLA nanocomposites prepared were 99.5/0.5 wt.%, 99.0/1.0 wt.%, 98.5/1.5 wt.% and 98.0/2.0 wt.%. For PLA/PEG/Gr nanocomposites, the 5 wt.% PEG was loaded in molten PLA followed by addition of graphene in order to study the effect of plasticizer on properties of nanocomposites. Figure 1 shows the samples prepared from melt blending. The composites obtained were molded into sheets 1 mm in thickness by hot press equipment at 170 °C for 10 min with pressure of 110 kg/cm², followed by cooling at room temperature. The prepared sheets were used for further characterization.

Figure 1: Samples prepared by melt blending method; (a) Neat PLA; (b) PLA nanocomposite

The second method of mixing was done by using chloroform (CHCl₃) as mutual solvent. Due to less toxic and easy get rid from PLA blend compares to other organic solvent such as DMF and NMP, CHCl₃ was chosen as mutual solvent in dispersion of Gr [16–17]. 1 g of PLA was completely dissolved in 20 g of chloroform at 45 °C. The graphene nanofiller was dispersed in chloroform with amount 0.2 mg/mL. The PLA solution was mixed with Gr nanofiller dispersion at certain ratio in Teflon bottle and stirred for 4 h at 40 °C to obtain homogenous PLA/Gr-based solution. Another 10 min sonication was proceeded to maintain the stability, the mixed solution was poured into petri dish and evaporated in fume hood to obtain the film as shown in Figure 2. Finally, the film was dried at 60 °C under vacuum conditions for 24 hrs to remove the residue solvent completely. PLA was mixed with graphene-based nanofillers of weight ratios 99.5/0.5 wt.% , 99.0/1.0 wt.% , 98.5/1.5 wt. % and 98.0/2.0 wt.% respectively. For PLA/PEG nanocomposites series, the 5 wt.% PEG was added in well-dispersed PLA solution followed by addition of Gr.
The hardness properties measurement of sample was carried out following the ASTM D standard on a Shore Durometer Type D, TH210. The testing was run at ambient atmosphere. In this experiment, each samples were tested for three times in order to obtain the average of the hardness. In hardness testing, the samples were put in the flat surface. The Shore Durometer was pressed enclosed to the sample and after 15 s, the result was obtained.

The MFI testing of PLA and PLA nanocomposites was carried out by Melt Flow Rate (MFR) tester, DYNISCO 4002 based on ISO 1133 and ASTM D1238 standards under fixed load of 2.16 kg. The temperature at 190 °C was applied for samples during the test. Three readings were taken for each sample and the average of MFI was calculated.

3. Results and Discussion
Figure 3 shows the values of all samples and the trends based on graphene loading. As compared with unfilled PEG nanocomposites, the neat PLA gave the lowest hardness value which is 77.6 Shore D obtained from melt blending and 69.0 Shore D from solution mixing. The Shore D hardness of PLA increased upon addition of graphene attributes to the increased stiffness of nanocomposites. As known, the PLA is one of the brittle material contributes to high hardness value. The application of PEG as plasticizer would decreases the hardness in all nanocomposites because the interaction of molecular chain is weakened by the insertion of the plasticizer. When comparing the values from both methods, the hardness exhibited from melt blending were higher than values from solution blending.
The dispersion quality of neat PLA and PLA nanocomposites was verified from Melt Flow Index (MFI) as plotted in Figure 4. The neat PLA from melt blending was 39.4 g/10 min of melt flow rate and 36.1 g/10 min from solution mixing. Obviously, in presence and absence of PEG, the loading of graphene up to 2 wt.% decreased the rate of flowability. The reason for this is the dispersion of nanofiller within the polymer matrix, as depicted in hardness result. An interconnected network of graphene increases the viscosity of polymer. The agglomeration after the continual loading of nanofiller destructs the ability to obtain good dispersion during processing, hence a failure to achieve good mechanical properties. Yet, the PEG raised the MFI value compared with unfilled PEG nanocomposites. The presence of hydroxyl group from PEG structure assists in filler dispersion in obtaining good interfacial adhesion between Gr and PLA matrix.

Figure 4: MFI trend of neat PLA and PLA nanocomposites

Figure 5 shows the micrographs of PLA nanocomposites. The Gr was not well-dispersed in PLA matrix since the filler spots are observed in Figure 5 (a) obtained from melt blending and the pores could be seen from Figure 5 (c) obtained from solution blending method. The pore existence could affect the performance of properties of the nanocomposites due to lack interfacial interaction between PLA and Gr nanofiller. This explains the lower results of hardness and MFI viewed from solution blending when compared with values from melt blending method. Obviously, from Figure 5 (b) and (d), the addition of PEG increases the dispersion between PLA and graphene by giving smooth surface. It caused by stronger interfacial interaction between the Gr sheets and the polymer matrix. The matrix wrapped the wrinkled layer of Gr, so no boundary between nanofiller and matrix is observed.
4. Conclusions
In this study, the PLA/Gr and PLA/PEG/Gr were successfully prepared by using two methods, melt and solution blending. The effect of graphene loading up to 2.0 wt.% were studied with presence and absent of plasticizer. The nanocomposites obtained from melt blending showed higher hardness and MFI values compared with nanocomposites from solution blending. The PEG slightly reduced the hardness values but dramatically increased the MFI values for both methods of blending. FESEM analysis confirmed the fracture surface of nanocomposites and smooth interfacial interaction between Gr and PLA contributed to high hardness and melt flow index.

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References
[1] Lionel W C J 2017 Processing and characterization of nanocomposites prepared by high torque melt mixing Doctoral dissertation, Clark Atlanta University. Retrieved from http://digitalcommons.auctr.edu/cauetds/86/
[2] Wang R-M, Zheng S-R and Zheng, Y G 2011 Polymer matrix composites and technology Beijing: Woodhead Publishing
[3] McWilliams A 2018 Nanocomposites, nanoparticles, nanoclays and nanotubes: Global markets to 2022 Retrieved from https://www.bccresearch.com/market-research/nanotechnology #NAN021H
[4] Allied Market Research 2018 World Nanocomposites Market – Opportunities and Forecasts, 2017–2023," Retrieved from https://www.alliedmarketresearch.com/nanocomposites-market 2017
[5] Allied Market Research 2018 Polymer Nanocomposites Market by Type (Carbon Nanotubes, Nanoclays, Metal Oxide, Ceramics), Application (Construction, Automotive, Electrical & Electronics, Packaging) - Global Opportunity Analysis and Industry Forecast, 2014-2022," Retrieved from https://www.alliedmarketresearch.com/polymer-nanocomposites-market
[6] Sahakaro K 2018 3 - Mechanism of reinforcement using nanofillers in rubber nanocomposites BT - progress in rubber nanocomposites, In S. Thomas and H. J. Maria (Eds.)," Woodhead Publishing Series in Composites Science and Engineering, United Kingdom, UK, Woodhead Publishing, p 81
[7] Kim H, Abdala A A and Macosko C W 2010 Graphene/polymer nanocomposites," Macromol. 43 6515
[8] Rivière P 2017 Unmodified multi-wall carbon nanotubes in polylactic acid for electrically conductive injection-moulded composites," J. Therm. Comp. Mater. 30 1615
[9] Chen G, Li A, Liu H, Huang S, Zhang Z, Liu W and Wang Z 2018 Mechanical and dynamic properties of resin blend and composite systems: A molecular dynamics study Compos. Struct. 190 160
[10] Alam A, Wan C and McNally T 2017 Surface amination of carbon nanoparticles for modification of epoxy resins: plasma-treatment vs. wet-chemistry approach Eur. Polym. J. vol. 87 422
[11] Akindoyo J O, Beg M D H, Ghazali S, Heim H P and Feldmann M 2017 Effects of surface modification on dispersion, mechanical, thermal and dynamic mechanical properties of injection molded PLA-hydroxyapatite composites Compos. Part A: Appl. Sci. Manuf. 103 96
[12] Tomić M, Đunjić B, Nikolić M S, Maletaškić J, Pavlović V B, Bajat J and Djonlagić J 2018 Dispersion efficiency of montmorillonites in epoxy nanocomposites using solution intercalation and direct mixing methods Appl. Clay Sci. 154 52
[13] Rallini M and Kenny J M 2017 3 - Nanofillers in Polymers BT. In C. F. J.-G. and Kenny J M (Ed.), Modification of Polymer Properties, United Kingdom, UK: William Andrew Publishing pp 47
[14] Cyras V P, D’Amico D A and Manfredi L B 2018 Chapter 10 - Crystallization Behavior of Polymer Nanocomposites BT - Crystallization in Multiphase Polymer Systems Elsevier 2018 pp 269
[15] Norazlina H and Kamal Y 2015 Graphene modifications in polylactic acid nanocomposites: a review Polym. Bul. 72 931
[16] Xianye L, Yinghong X, Anne B, Marc L and Jianfei, C 2013 Preparation of Polylactide/graphene Composites from Liquid-phase Exfoliated Graphite Sheets Polym. Compos. 35 396
[17] Yoon J T, Jeong G, Lee S C and Min B G 2009 Influences of Poly(lactic acid)-grafted Carbon Nanotube on Thermal, Mechanical, and Electrical Properties of Poly(lactic acid) Polym. Adv. Techno. 20 631