

Reinforcement of graphene nanoplatelets on plasticized poly(lactic acid) nanocomposites: Mechanical, thermal, morphology, and antibacterial properties

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ABSTRACT: Plasticized poly(lactic acid) (PLA)-based nanocomposites filled with graphene nanoplatelets (xGnP) and containing poly(ethylene glycol) (PEG) and epoxidized palm oil (EPO) with ratio 2 : 1 (2P : 1E) as hybrid plasticizer were prepared by melt blending method. The key objective is to take advantage of plasticization to increase the material ductility while preserving valuable stiffness, strength, and toughness via addition of xGnP. The tensile modulus of PLA/2P : 1E/0.1 wt % xGnP was substantially improved (30%) with strength and elasticity maintained, as compared to plasticized PLA. TGA analysis revealed that the xGnP was capable of acting as barrier to reduce thermal diffusion across the plasticized PLA matrix, and thus enhanced thermal stability of the plasticized PLA. Incorporation of xGnP also enhanced antimicrobial activity of nanocomposites toward *Escherichia coli*, *Salmonella typhimurium*, *Staphylococcus aureus*, and *Listeria monocytogenes*. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41652.

KEYWORDS: mechanical properties; morphology; polyesters; properties and characterization; thermogravimetric analysis (TGA)

Received 13 June 2014; accepted 17 October 2014

DOI: 10.1002/app.41652

INTRODUCTION

Poly(lactic acid) (PLA) has received great attention in the scientific community recently due to its biodegradability and based on natural resources. PLA offers a possible alternative to the traditional non-biodegradable polymers such as polyethylene and polypropylene especially when their recycling is difficult or not economical. However, some of its disadvantages such as relatively poor mechanical properties and gas barrier, slow crystallization rate, and low thermal stability have limited its wider applications. Therefore, polymer blending and nanocomposites preparation have often been employed to modify the physical properties of PLA in order to extend the practical applications.

Many efforts have been made in particular to improve PLA's toughness and ductility. Polymer blending with plasticizers is commonly used to enhance the flexibility and ductility of glassy PLA. Many types of plasticizers for PLA have been studied, such as epoxidized palm oils (EPOs),¹ poly(ethylene glycol)

(PEG),² poly(propylene glycol),³ citrate esters,⁴ oligomeric malonate esteramides,⁵ polyglycerol esters,⁶ poly(1,3-butylene adipate),⁷ glucosemonoesters,⁸ oligomeric lactic acid,⁹ partial fatty acid ester,⁸ and glycerol.⁹ Recently, a new way of plasticizing PLA with hybrid plasticizers has been developed to improve the ductility of PLA. Hybrid plasticizer consists of two or more plasticizers incorporated into a single polymer matrix. By producing a hybrid plasticizer, the advantages of one type of plasticizer could complement with what are lacking in the other plasticizer. As a consequence, a balance in performance could be achieved through a proper material design. PEG and EPO were used as hybrid plasticizers to plasticize PLA in Chieng *et al.*'s study. Addition of the hybrid plasticizer to PLA shows a significant improvement of 12,402% in elongation at break, compared to neat PLA, even with respect to individually plasticized PLA. This synergic plasticization effect of hybrid plasticizer may be due to high miscibility between PEG and EPO and both act as co-plasticizers to each other. From the calculated solubility

Table I. Properties of PLA and PEG Used in this Study

Materials	M^n (g/mol)	T^m (°C)	T^g (°C)	Chemical formula
Poly(lactic acid), PLA, 4042D	66,000	150	63	
Poly(ethylene glycol), PEG	200	-65	-41	

parameter of 2 : 1 (wt/wt) of PEG and EPO hybrid plasticizers, it was close to that of PLA, which indicated that they should be miscible and an efficient plasticizer for PLA.

However, the plasticization of PLA always accompanied by a drastic drop in material stiffness that is out of line with some applications such as in automotive applications. Consequently, reinforcing nanofillers are employed to form nanocomposites. Here, the key objective is to take advantage of plasticization to increase the material ductility while preserving valuable stiffness, strength, and toughness via addition of nanofiller. Various nano-reinforcement filler, such as layered silicate clay,¹⁰ carbon nanotubes,¹¹ and layered double hydroxide¹² are being developed and extensively studied. However, the discovery of new nanomaterial graphene by Geim in year 2004¹³ attracted worldwide interest among researchers. Graphene, which is fabricated from natural graphite can also be used as a potential alternative nano-reinforcement to both clay and carbon nanotubes. Graphene combines layered structure of clays with superior mechanical and thermal properties of carbon nanotubes, which can provide excellent functional properties enhancements.¹⁴

The current work is focused on the effect of graphene nanoplatelets (xGnP) in a PLA matrix plasticized by PEG and EPO hybrid plasticizers. The combination of polymer plasticization and nanocomposite concepts represents a progressive approach to meet the increasingly high requirement of the properties of materials for different applications.

EXPERIMENTAL

Materials

PLA Natureworks grade 4042D (95.8% L-lactide, 4.2% D-lactide), number average molecular mass, $M_n = 183,000$ g/mol, was purchased from Natureworks LLC. Low molecular weight PEG ($M_n = 200$ g/mol) was purchased from Sigma-Aldrich. Their properties are listed in Table I. EPO was obtained from pilot plant in Advanced Oleochemical Technology Division (AOTD) of Malaysia Palm Oil Board (MPOB), Malaysia. The characteristics of the EPO obtained are listed in Table II. Graphene nanoplatelets, trade name xGnP®, Grade M, was supplied by XG Sciences (Lansing, MI). Each particle consists of several sheet of graphene with an average thickness of ~6–8 nm, average diameter of 15 microns.

Preparation of PLA/Hybrid Plasticizer/xGnP Nanocomposites

The PLA/hybrid plasticizer blend were prepared by melt blending technique using Brabender internal mixer with 50 rpm of the rotor speed, at 170°C for 10 min. EPO was added after 5

min blending of PLA with PEG. The weight ratio of PEG to EPO studied was fixed at 2 : 1 (2P : 1E). The xGnP content was varied between 0.1 wt % and 1.0 wt %. The blends obtained were then molded into sheets of 1 mm in thickness by hot pressing at 165°C for 10 min with pressure of 110 kg/cm², followed by cooling to room temperature. The sheets were used for further characterization.

Characterizations

Tensile Properties Measurement. Tensile properties test were carried out by using Instron 4302 series IX. The samples were cut into dumb-bell shape as described in ASTM D638 (type V) standard. Load of 1.0 kN was applied at constant crosshead speed of 10 mm/min at room temperature. Tensile strength, tensile modulus, and elongation at break were evaluated from the stress–strain data. Each sample included seven tested replicates to obtain a reliable mean and standard deviation.

Thermal Properties. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 7 TGA analyzer with scan range from 35° to 800° at a constant heating rate of 10 °C/min and continuous nitrogen flow. The thermal degradation temperature taking into account were the temperature at onset (T_{onset}), the temperature of maximum weight loss (T_{max}), and temperature at 50% weight loss (T_{50}).

Morphology. The fracture surfaces of tensile failed sample were studied under a JEOL scanning electron microscopy (SEM) instrument JSM-6400 (Japan) at an accelerating voltage of 30 kV. The fractured surfaces were coated with a thin layer of gold prior to observation. Transmission electron microscopy (TEM)

Table II. Properties of EPO

Sample composition	Epoxidized palm oil (EPO)
Oxygen oxirane content (%)	3.2309
Acid value (mg KOH/g sample)	0.4287
Iodine value (g I ₂ /100 g sample)	0.6371
Moisture content	0.08
pH	5–6
Chemical structure	

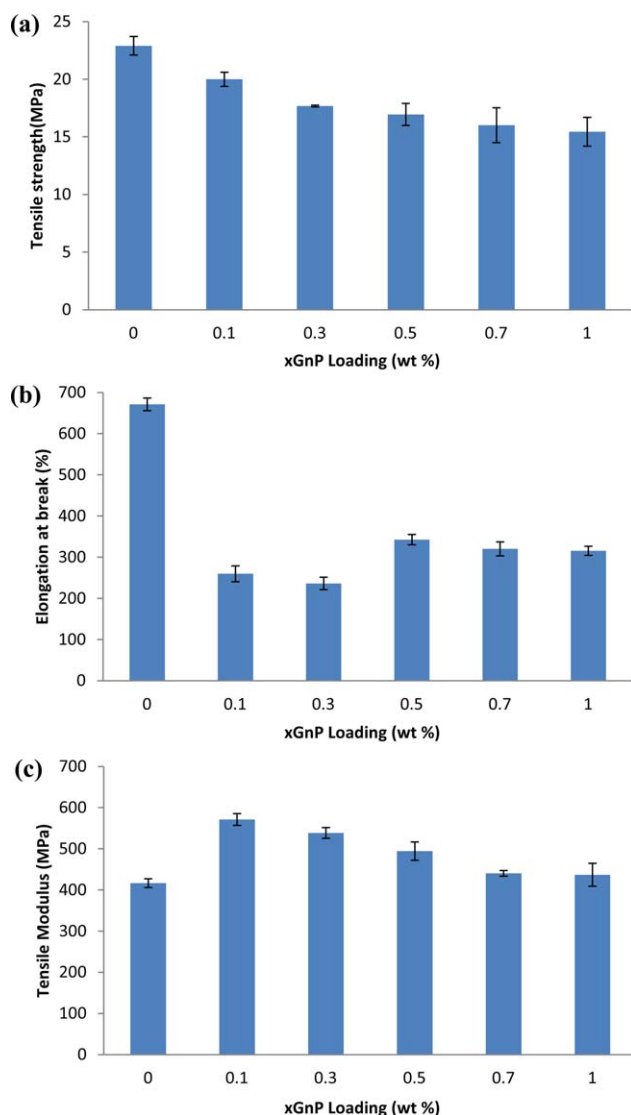


Figure 1. Effect of xGnP loading on (a) tensile strength, (b) elongation at break, and (c) tensile modulus of PLA/2P : 1E/xGnP nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

image were obtained using a Hitachi H-7100 TEM operated at an accelerating voltage of 100 kV to observe the nanocomposites. All samples were ultrathin-sectioned using a microtome equipped with a diamond knife.

Antibacterial Properties. Antibacterial properties of the samples were tested as described in ISO 22196 “measurement of antibacterial activity on plastics and other non-porous surface.” The samples were cut into $(10 \pm 2) \text{ mm} \times (10 \pm 2) \text{ mm}$. A thin film ($18 \text{ mm} \times 18 \text{ mm}$) was used to enable the test inoculums contact with the sample. The sample and thin film were sterilized by immersing in 70% ethanol in water for 1 h. After 1 h, the sample and thin film were left to dry in laminar flow.

Each test specimen was placed into a separate sterile Petri dish with the test surface uppermost. Ten microliters of the inoculum was pipette onto the test surface. The inoculum was covered

with the thin film and gently pressed down on the film so that the test inoculums spread to the edges. The Petri dishes containing the inoculated sample were incubated at 37°C for 24 h. After the incubation, the bacteria on the sample were recovered by adding 10 mL of tryptic soy broth (TSB) and vortex, followed by 10-fold serial dilutions. After the dilution, 0.1 mL of each dilution was inoculated on Tryptic Soy Agar (TSA, Merck, Germany) by spread plate method and incubated at 37°C for 24 h. The number of colonies on the agar were counted and recorded.

RESULTS AND DISCUSSION

Tensile Properties

The tensile properties of PLA plasticized with PEG and EPO with ratio 2 : 1 (PLA/2P : 1E) and their nanocomposites as a function of xGnP loading are shown in Figure 1. It can be seen that tensile strength and elongation at break of PLA/2P : 1E all decreased, respectively, with incorporation of xGnP into the polymer matrix. The addition of a nanofiller to a thermoplastic matrix, even if plasticized, usually decreases significantly the elongation at break as can be observed in Figure 1(b). As seen in Figure 1(b), the elongation at break measurement does not show a well-defined dependence on loading, but seem not to be considerably affected by filler addition. This is not a determinant fact, since for many applications only the properties at the yield point, and not at the fracture limit, are relevant for the performance of the material. On average, the tensile modulus [Figure 1(c)] for the hybrid plasticized PLA/xGnP nanocomposites was about 10% greater than that of hybrid plasticized PLA. PLA/2P : 1E with 0.1 wt % xGnP loading showed the highest tensile modulus (571.3 MPa) among the nanocomposites.

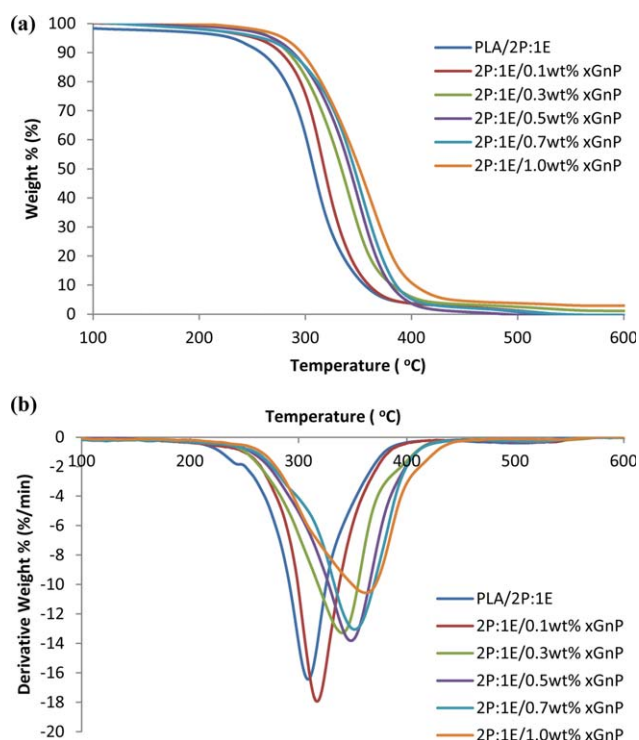


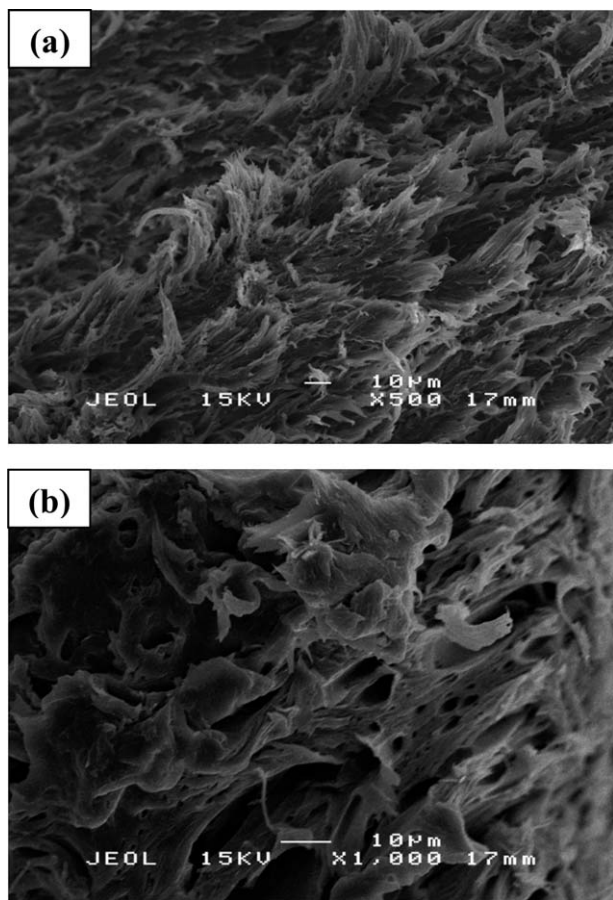
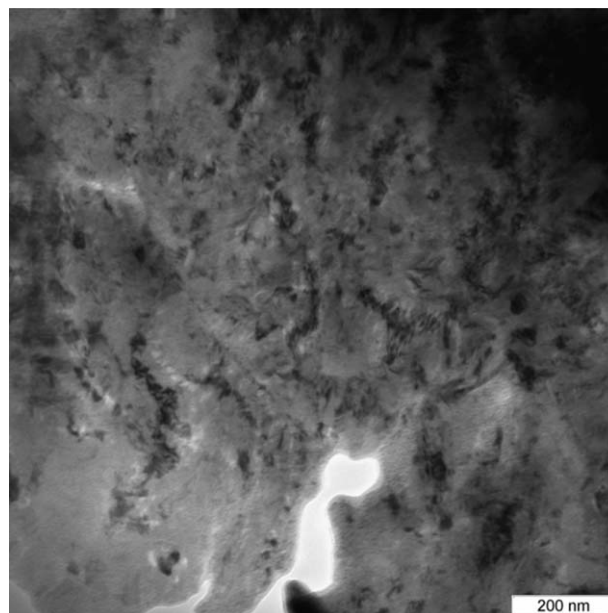
Figure 2. (a) TG and (b) DTG thermograms of PLA/2P : 1E and PLA/2P : 1E/xGnP nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Characteristic Temperature of PLA/2P : 1E and PLA/2P : 1E/xGnP Nanocomposites

Samples	T_{onset}	T_{50}	T_{max}
PLA/2P : 1E	231.6	307.8	310.6
PLA/2P : 1E/0.1 wt % xGnP	255.5	317.9	314.0
PLA/2P : 1E/0.3 wt % xGnP	261.1	334.0	341.8
PLA/2P : 1E/0.5 wt % xGnP	252.6	341.9	343.8
PLA/2P : 1E/0.7 wt % xGnP	257.8	351.1	347.5
PLA/2P : 1E/1.0 wt % xGnP	268.2	346.2	361.6

Thermogravimetric Analysis

The thermograms of PLA/2P : 1E and PLA/2P : 1E/xGnP nanocomposites are shown in Figure 2. As can be seen from Figure 2, the onset temperature (T_{onset}), 50% loss temperature (T_{50}), and maximum decomposition temperature (T_{max}) of the PLA/2P : 1E/xGnP nanocomposites are higher than those of PLA/2P : 1E, especially T_{max} is enhanced by about 50°C depending on the xGnP loading. The T_{onset} , T_{50} , and T_{max} of the samples are summarized in Table III. The T_{onset} and T_{50} increased as the xGnP loading increased. The incorporation of 1.0 wt % xGnP leads to the shift of the T_{onset} and T_{50} of PLA/2P : 1E from 231.6°C and 307.8°C to 268.2°C and 346.2°C, respectively. This

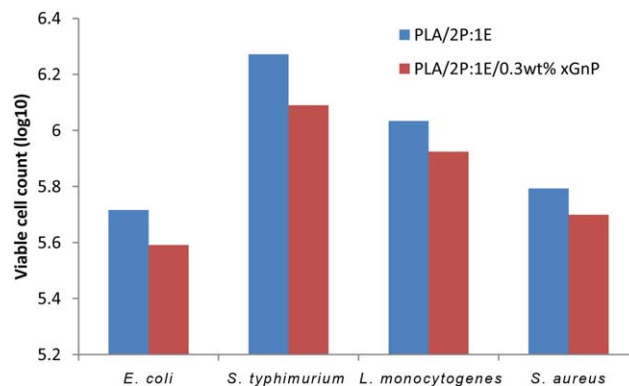
**Figure 3.** SEM images of (a) PLA/2P : 1E and (b) PLA/2P : 1E/0.3 wt % xGnP nanocomposites.**Figure 4.** TEM image of PLA/2P : 1E/0.3 wt % xGnP nanocomposite.

result shows that the introduction of xGnP nanofiller into plasticized PLA system can enhance the thermal stability due to the presence of inorganic graphene sheets in the fabricated nanocomposites. The enhanced thermal stability probably involves a mechanism in which the formation of a physical barrier by the accumulation of xGnP sheets at the surface and promotion of charring provides reduction of heat release rate (HRR) and flammable gases to the flame.¹⁵

Figure 2(b) shows derivative thermogravimetric (DTG) thermograms, in which the peak point gives the temperature that causes main weight losses during decomposing process. The incorporation of 1.0 wt % xGnP leads to the shift of the maximum decomposition temperature (T_{max}) of PLA/2P : 1E from 310.6°C to 361.6°C. These results continued to support the conclusion that the xGnP can act as a barrier to reduce the diffusion of the heat in polymer matrices.

Scanning Electron Microscopy

It is well known that the brittle nature of PLA could be observed by a smooth fracture surface without any visible

**Figure 5.** Antibacterial activity of PLA/2P:1E and PLA/2P : 1E/0.3 wt % xGnP nanocomposite against selected bacteria. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plastic deformation. For PLA/2P : 1E in Figure 3(a), it can be seen that the hybrid plasticizer was brought into and tuned brittle PLA matrix, with fibrous structure and relative rough fracture surface.

Although the graphene sheets at the fracture surface of the nanocomposites are not easily distinguishable, even from high magnification of SEM image due to sample instability when large magnifications are attempted, we may reasonably conclude that the fluctuant edge structure can be interpreted as the protruded xGnP sheets, indicating that the graphene sheet embedded in the matrix are crumpled and wrinkled, or even folded as shown in PLA/2P : 1E/0.3 wt % xGnP nanocomposite [Figure 3(b)].

Transmission Electron Microscopy

The TEM micrograph of PLA/2P : 1E with 0.3 wt % xGnP is shown in Figure 4. The dark area is the xGnP and bright area is the matrix. The figure shows that xGnP was uniformly dispersed in the plasticized PLA matrix. xGnP platelets and small aggregates can be identified. Besides that, there is percolated network formed that can be observed as a result of the xGnP–xGnP and xGnP–matrix interaction. This xGnP–xGnP and xGnP–matrix interaction contributed to the enhanced tensile properties especially in elongation at break compared to others xGnP loading.

Antibacterial Test

The antibacterial ability of plasticized PLA/xGnP nanocomposites against four selected bacteria was investigated by viable cell colony count method. Four different food pathogenic bacteria including two Gram negative bacteria (*Escherichia coli* and *Salmonella typhimurium*) and two Gram positive bacteria (*Staphylococcus aureus* and *Listeria monocytogenes*) were used in this study. *E. coli* and *S. typhimurium* are common Gram-negative bacteria that can cause disease in humans and animals.

The results of antibacterial test are illustrated in Figure 5. As can be seen from the figure, the plasticized PLA/xGnP nanocomposites show antimicrobial activity toward all four types of bacteria. The plasticized PLA/xGnP nanocomposites show significant lower viable cell count compared to the plasticized PLA. The introduction of xGnP reduces the probability that the bacteria will colonize on implant surface.^{16,17} Furthermore, high aspect ratio of xGnP dispersed in polymer matrix created protective barriers which slow down the diffusion of micro-organism into polymer matrix. Nanocomposite antimicrobial systems are particularly effective, because of the high aspect ratio and enhanced surface reactivity of the nanosized antimicrobial agent such as graphene, making them able to inactivate micro-organisms more effectively than their micro- or macroscale counterpart.¹⁸

CONCLUSIONS

The combination of xGnPs and PLA plasticized with hybrid plasticizer can give nanocomposites with a well balanced

mechanical behavior. Regarding the influence of xGnP incorporated into PLA matrix, the tensile modulus was substantially improved with strength and elasticity maintained, as compared with PLA/2P : 1E blend. TGA analysis revealed that the xGnP was capable of acting as barrier to reduce thermal diffusion across the plasticized PLA matrix, and thus enhanced thermal stability of the plasticized PLA. Incorporation of xGnP also enhanced antimicrobial activity of nanocomposites toward *E. coli*, *S. typhimurium*, *S. aureus*, and *L. monocytogenes*. This will further widen the application of PLA nanocomposites such as in medical, packaging industry and etc.

ACKNOWLEDGMENTS

The authors would like to thank the Exploratory Research Grant Scheme (ERGS/1/11/STG/UPM/02/5) from Ministry of Higher Education (MOHE), Malaysia for their financial support.

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