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The production and properties of polylactide (PLA) nanocomposites filled with graphene oxide (XGO)

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Graphene and its derivatives are today one of the latest and hottest research topics. This is due to their exceptional mechanical, electrical, thermal and optical properties, high surface area-to-volume ratio, and unique crystal structure. Therefore, many applications, for instance, electronic devices, composites and nanomedicine, are expected. This research aims to study the mechanical and thermal properties of poly(lactic acid)/graphene oxide (PLA/XGO) nanocomposites. The polymer nanocomposites were successfully prepared by solution processing in conjunction with compression molding at various contents of XGO from 0-1.0 wt%. The structure, mechanical properties and thermal stability of the composite materials have been investigated by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), mechanical test, and thermogravimetric analysis. The results obtained from those different studies revealed that PLA and XGO could mix with each other homogeneously. A uniform dispersion of filler in the matrix existed when the XGO content was less than 0.7 wt%. Mechanical properties of biopolymer were greatly improved by the addition of a small amount of XGO (0.5 wt%). The nanocomposites have potential application as packing materials.

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1. Introduction

Graphene, a two-dimensional sheet of sp^2-hybridized carbon system, has been a highlighted material in the past few years due to its exceptional properties [1,2]. Many applications of graphenes, such as nanoscale molecular electronics, sensing devices, membranes for gas separation and hydrogen storage, have been reported [3-5]. The major fabrication methods of graphene include micromechanical cleavage, chemical vapour deposition (CVD) and the oxidation, exfoliation and reduction of graphite. The third method uses graphite oxide (GO) to synthesis graphene oxide (XGO), creating a far higher yield [6].

Of major engineering materials, polymers have seen the rapidest increase in applications owing to their ease of fabrication and high specific strength. However, the properties of most polymers need improvement by using additives, which leads to development of composites and nanocomposites [7,8]. In particular, the use of inorganic nanomaterials as fillers in the preparation of polymer/inorganic composites has attracted increasing interest owing to their unique properties and numerous potential applications in the automotive, aerospace, construction and electronic industries. The superior properties of graphene and its derivatives compared to polymers are also reflected in polymer composites. Polymer/XGO nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared to the neat polymer [9].

Among the biopolymers, poly(lactic acid) (PLA) has been paid more attention academically and commercially [10]. PLA is one of the most promising biodegradable polymers with a good transparency, high mechanical properties, and good biocompatibilities. It has excellent processibility with relatively low melting temperature (T_m), and has thermal and chemical resistance. It is a thermoplastic, aliphatic polyester and bio-renewable polymer that can be prepared by both direct condensation of lactic acid and ring-opening polymerisation of lactide [11].

The properties of filler reinforced composites mainly depend upon the nature of filler, matrix and filler/matrix adhesion. Therefore, the objectives of this study are to fabricate PLA/XGO nanocomposites and to investigate the effect of filler content on the mechanical and thermal properties of the green composites.

2. Experimental details

2.1 Materials

PLA pellet (Ingeo^{TM} Biopolymer 3052D, NatureWorks LLC, USA) was used as a thermoplastic matrix. Graphite (fine powder extra pure) and hydrochloric acid (HCl) 37% were purchased from Merck Ltd., Germany. Sulfuric acid (H_2SO_4) 98% Grade AR was purchased from RCI Labscan Ltd., Thailand. Potassium permanganate ($KMnO_4$) was purchased from Ajax

Finechem PTY Ltd., Australia. Hydrogen peroxide (H_2O_2) 30-32% Grade AR was purchased from QReC Chemical Co. Ltd., Thailand. All other chemicals used were analytical grade reagents.

2.2 Preparation of GO, XGO and PLA/XGO nanocomposites

GO was synthesized from graphite powder by modified Hummer's method [12]. 5.0 g of graphite powder was first added into 180 ml concentrated H_2SO_4 and 20 ml phosphoric acid (H_3PO_4) at room temperature. Under stirring, the mixture was cooled to 5 °C using an ice bath, and the temperature of the mixture was kept to be below 5 °C for 30 min. $KMnO_4$ (15.0 g) was then added gradually under stirring and cooling for 1 h. Thereafter, the mixture was gently heated so that the temperature of the mixture reached 35 °C. 400 ml distilled water was added into the mixture, stirred at 80 °C for 1 h. After that, 30 ml of 30% H_2O_2 was added to the mixture to reduce the residual $KMnO_4$. The solid was filtered, washed with 5% HCl aqueous solution (800 ml) to remove metal ions and with distilled water until the pH were 6. The resulting GO was dried at 45 °C for 24 h. Aqueous colloids of XGO were prepared by dispersing 1.0 g GO into 500 ml of distilled water by ultrasonication and centrifugation for 2 h to remove any unexfoliated GO. The XGO was dried at 45 °C for 24 h [13]. The polymer nanocomposites were successfully prepared by solution processing in conjunction with compression molding at various contents of XGO from 0-1.0 wt%.

2.3 Materials characterization

The structure, mechanical properties and thermal stability of the composite materials have been investigated by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), mechanical test, and thermogravimetric analysis.

3. Results and discussion

3.1 Characterization of graphite, GO and XGO

The XRD patterns of graphite, GO, and XGO are shown in Fig. 1. Pristine graphite has a strong and sharp diffraction peak at $2\theta = 26.4°$, corresponding to the highly organized layer structure with an interlayer distance of 0.34 nm along the (002) orientation [13,14]. After the chemical oxidation and exfoliation into XGO, however, the (002) peak is shift to lower angle at $2\theta = 10.3°$, indicating an increase in d-spacing from 0.34 nm to 0.86 nm. An increased interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into carbon layer structure [15].

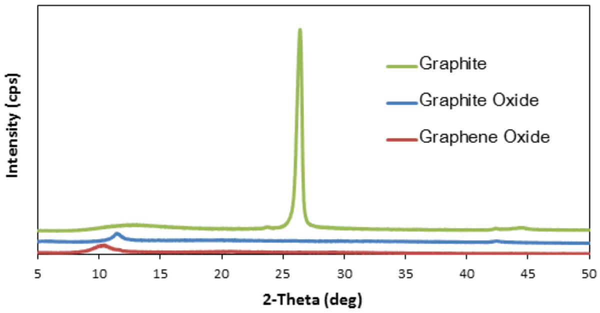

Fig. 1. XRD patterns of graphite, GO, and XGO.

The FTIR spectra of graphite, GO and XGO are presented in Fig. 2. The graphs show the stretching of hydroxyl group at 3413 cm^{-1}, the C=O carbonyl stretching at 1726 cm^{-1}, and the C–O-H stretching at 1228 cm^{-1} [14]. The high intensity of the main peaks in XGO confirms the presence of a large amount of oxygen functional groups after the oxidation process. The peak at 1627 cm^{-1} is related to the vibrations of adsorbed water molecules [13].

The morphology of the sample was studied using SEM and TEM. As shown in Fig. 3, graphite particles are in the platelet-like crystalline form of carbon. After acid oxidation and ultrasonication, XGO sheets become smaller and transparent. The sheet is so thin that electron beam can be passed through sample [13].

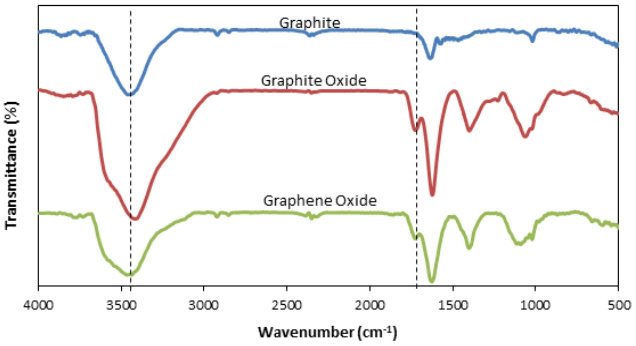

Fig. 2. FTIR spectra of graphite, GO, and XGO.

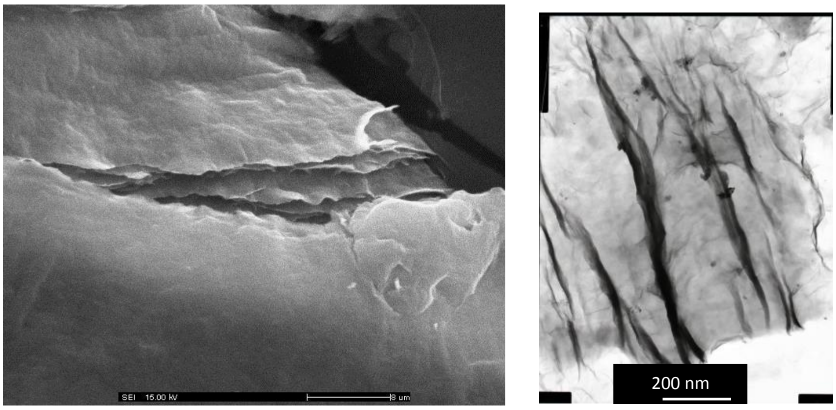

Fig. 3. SEM and TEM images of XGO.

3.2 Mechanical and thermal properties of PLA/XGO nanocomposites

The effects of XGO content on tensile properties of PLA matrix were presented in Fig. 4. The results show that the tensile modulus and tensile strength of polymer nanocomposites increases with increasing filler content. Mechanical properties of biopolymer were greatly improved by the addition of a small amount of XGO (0.5 wt%). They were attributed to the high interfacial adhesion between the hydrophilic filler and the hydrophobic polymer matrix [11]. Experimentally, it was found that the filler content is key parameter that substantially influence the mechanical properties of the nanocomposite samples. The surface treated nanosheets played an important role in tensile behavior of the composites because of its well dispersion and strong interfacial interaction between the nanosheets and PLA matrix.

TGA is an effective approach for evaluating the thermal stability of polymeric materials. The thermal degradation of neat PLA and biocomposites was investigated in terms of onset degradation temperature (T_{onset}), peak degradation temperature (T_{peak}) and weight percentage of the residue (w_{tR}) at 600 °C by thermal testing in pure nitrogen environment. The thermal stability of PLA/XGO composites increased with increasing filler content (Fig. 5). The observation also showed that polymer matrix and filler formed little char at high temperature, which is consistent to previous research [11]. This can be interpreted as the composites exhibited higher thermal stability compared with neat PLA because of the high thermal stability of filler [16].

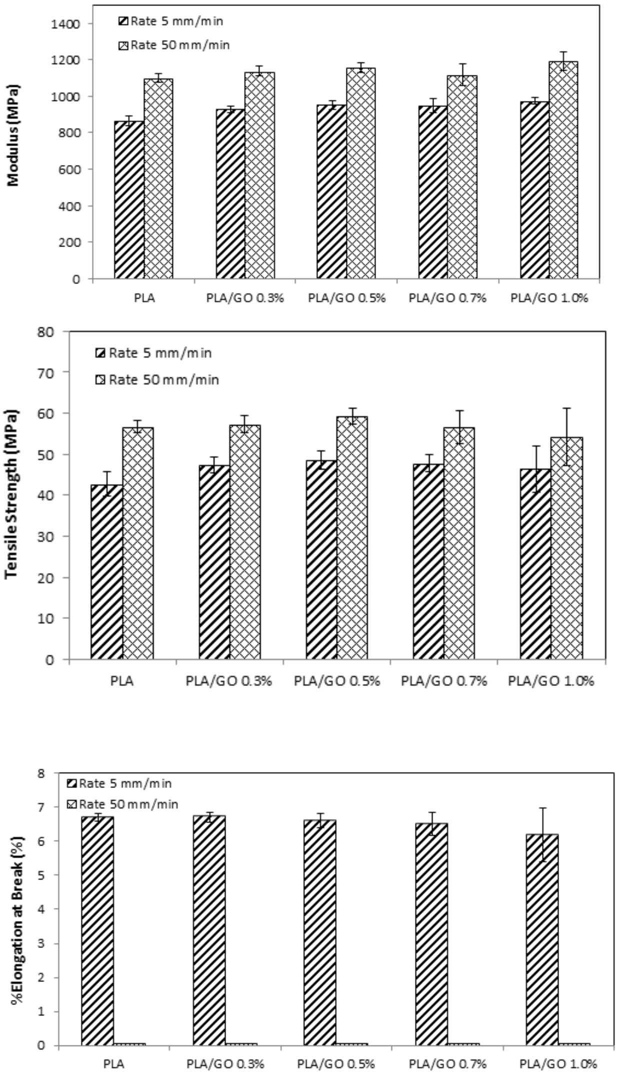

Fig. 4. Mechanical properties of neat PLA and PLA/XGO nanocomposites.

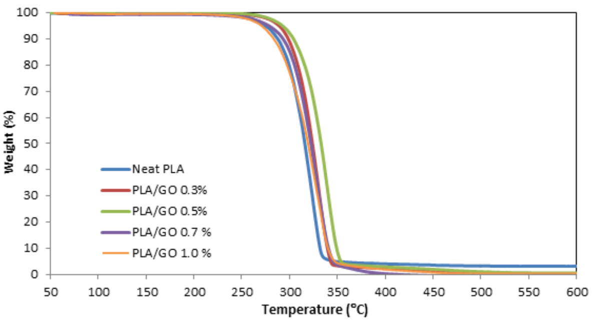

Fig. 5. Thermal properties of neat PLA and PLA/XGO nanocomposites.

4. Conclusions

The potential use of XGO composites is discussed in this paper. Effects of filler content on the mechanical and thermal properties of PLA matrix were studied. The enhanced adhesion between the filler and polymer matrix resulted in a PLA/XGO biocomposite with the excellent portfolio of mechanical and thermal properties, much better than those of the neat PLA counterpart. The mechanical properties in terms of the tensile modulus and tensile strength of these composites increased substantially compared to the biopolymer. The thermal stability of PLA/XGO composites increased with increasing filler content. These studies were aimed at adding value to the fillers. The PLA/XGO green composites can be considered for packing materials.

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Conflict of interest

The authors declare that there is no conflict of interest.

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