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Preliminary study of polylactic acid/graphene oxide nanocomposites prepared by melt

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ABSTRACT

Poly(lactic acid) (PLA) is one of the most promising biodegradable polymers as it is produced from renewable resources. Amazingly, due to the depletion of petroleum resources, PLA is now viewed as a valuable biosourced polymer alternative in long-term applications such as automotive and electronics. Unfortunately, some disadvantages such as relatively poor mechanical properties and slow degradation rate have limited its wider application. Therefore, these drawbacks could be overcome by addition of nano-sized particles and hence, to improve the properties of PLA. Graphene oxide (GO) has the shape of exfoliated sheet stably dispersed in water due to the plenty of hydrophilic functional groups. The functional groups help the adsorption of polar molecules and hydrophilic polymers on GO. In this study, the melt blending of PLA and GO is expected to form the brittle nanocomposites. An additive, polyethylene glycol (PEG) is added as plasticizer during processing as an alternative to avoid the problem. As a biodegradable plasticizer, PEG is added to increase the mobility of the GO within the PLA. In way to enhance the dispersion of GO in PLA matrix, supercritical CO₂ method is the best way can be implemented in processing because it is non-toxic, non-flammable and chemically inert. The ternary system composed of the polymer, supercritical fluid (SCF) and nanoparticle gives ample choice for scientific investigations. The dispersion of nanoparticle in matrix caused by the rapid gas expansion. The surface and morphology of nanocomposite can be examined using XRD, SEM, TEM and FESEM. Furthermore, the FTIR is used to characterize the functional group. The thermal properties are investigated using DSC, TGA and DMA. Lastly, the biodegradation studies will be conducted as accelerated weather testing, microbiological experiment and barrier properties. This preliminary review highlights a few main researches in PLA-based nanocomposites that will support the method can be used in further studies.

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INTRODUCTION

Since the basic monomer (lactic acid) are produced from renewable resources (carbohydrates) by fermentation, PLA complies with the rising worldwide concept of sustainable development and is classified as an environmentally friendly material. GO is highly hydrophilic and readily exfoliated in water compared to graphene, yielding stable dispersion consisting mostly of single layered sheets. GO are expected to provide advantages such as ease of dispersion in polymer matrixes due to their oxygenated surface functionalities, leading to stable dispersibility in aqueous or organic solutions by electronic repulsion (Sun, X., *et al.*, 2008; Paredes, J.I., *et al.*, 2008) and possible chemical interactions of oxygenated surface functionalities in GO nanosheets fabricated with polymer matrix.

1. Polymer nanocomposites:

Polymer composites have been classified into three categories namely, conventional composite, intercalated nanocomposite and exfoliated nanocomposite depending on the type of dispersion. First, conventional composites, the filler loading is on the higher side (30-60 vol. %) as compared to the nanocomposites (1-5 wt. %). In intercalated nanocomposites, the arrangement is regular insertion of the polymer in between the silicate layers at the molecular level while in exfoliated nanocomposites, individual layers of the silicate layers are randomly dispersed into the polymer phase.

It was reported that the improvement in mechanical and electrical properties of graphene based polymer nanocomposites are much better in comparison to that of clay or other carbon filler-based polymer nanocomposites (Stankovich, S. *et al.*, 2006; Quan, H., Zhang, B., Yuen, R.K.K., and Li, R.K.Y., 2009; Eda, G.

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and Chhowalla, M., 2009; Liang, J., *et al.*, 2009; Kim, H., Macosko, C.W., 2009). Table 1.1 shows the comparison between graphene and other conventional nanofiller (Kuilla, T., *et al.*, 2010). Although CNTs show comparable mechanical properties compared to graphene, still graphene is better nanofiller than CNT in certain aspects, such as thermal and electrical conductivity.

Table 1.1: Properties of graphene, CNT, nano sized steel and polymers (Kuilla, T., *et al.*, 2010).

Materials	Tensile strength	Thermal conductivity (W/mk) at room temperature	Electrical conductivity (S/m)
Graphene	130± 10 GPa	$(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$	7200
CNT	60 – 150 GPa	5 – 6	3000 – 4000
Nano sized steel	1769 Mpa	0.46 – 0.52	1.35×10^6
Plastic (HDPE)	18 – 20 MPa	0.13 – 0.142	Insulator
Rubber (natural rubber)	20 – 30	0.04	Insulator
Fiber (Kevlar)	3620 MPa		Insulator

Kuilla *et al.*, prepared graphene oxide sheet-incorporated epoxy composites and the level of thermal expansion was examined using a thermo-mechanical analyzer (Kuilla, T., Srivasta, S.K., Bhowmick, A.K., 2009). A very poor thermal conductivity was showed by epoxy resins but the inclusion of graphene sheets resulted in significant improvements. The addition of 1 wt.% GO to the epoxy resins had a similar effect on improving the thermal conductivity to that of filling with 1 wt.% of SWNT (single wall carbon nanotube). The addition of 5 wt.% GO-filled epoxy resin showed a thermal conductivity of ~1 W/mK, which is 4 times higher than that of the neat epoxy resin.

Yoon *et al.*, reported improvements in the thermomechanical and surface chemical properties of nanocomposite nanofibers of poly(D, L-lactic-co-glycolic acid), PLGA were achieved by adding 2-dimensional nanoscale fillers of graphene oxide (GO) nanosheets to PLGA nanofibers (Yoon, O.J., *et al.*, 2011). The significant enhancement of storage and loss moduli of the PLGA/GO (2 wt.%) nanocomposite nanofibers caused by enhanced chemical bonding between the oxygenated functional groups of the highly dispersible GO nanosheets and the hydroxyl groups of the polymer chains in the PLGA matrix, resulting in strong interfacial interactions between the nanofiller and polymer matrix.

2. Preparation Methods of Polymer Nanocomposites:

The method of *in situ* polymerization, solution blending and melt mixing are the most synthesis strategies of the polymer matrix composites.

In *in situ* polymerization, the first fabrication step starts with the dispersion of graphene oxide or reduced graphene oxide (rGO) in monomer followed by the polymerization of the monomers. A research has been performed on producing epoxy based nanocomposites using *in situ* polymerization where sheets are first dispersed into resin followed by curing by adding hardener (Rafiee, M.A., *et al.*, 2010).

Solution intercalation is the most suitable technique to fabricate polymer-based composites provided the polymer is readily soluble in common aqueous and organic solvents, such as water, acetone, N,N'-dimethyl amide (DMF), chloroform, dichloro methane (DCM) and toluene. The polar polymers such as polymethyl methacrylate (PMMA), N,N-dimethylaminopropyl (PAA), polyacrylonitrile (PAN) and polyesters have been successfully mixed with GO in solution blending where the GO surface was usually functionalized by isocyanates, alkylamine, alkylchlorosilanes, etc. to improve its dispersability in organic solvents (Singh, V., *et al.*, 2011).

This study focusing on melt blending method. Solvent-free is main criteria why melt blending is choose. Besides, its wide application can be found in industry where the processing technique normally used extruder or melt mixer. Lincoln and Claude (Lincoln, V.F., Claude, Z., 1983) proposed the incorporation of intercalated graphite into an organic using conventional processing techniques such as extrusion, lay-up, injection molding and pressing in 1980s. Since that time, many researches have been conducted on exfoliated graphite reinforced polymers using graphite particles of various dimensions and a wide range of polymers.

Kim and Jeong (Kim, I.H., Jeong, Y.G., 2010) prepared polylactide/exfoliated graphite (PLA/EG) nanocomposites by melt-compounding and investigated their morphology, structures, thermal stability, mechanical, and electrical properties. For PLA/EG nanocomposites, The analyzed nanocomposites revealed that graphite nanoplatelets of PLA/EG nanocomposites were dispersed homogeneously in the PLA matrix without forming the crystalline aggregates, unlike PLA/NG composites. Thermal degradation temperatures of PLA/EG nanocomposites increased propotional with the increment of EG content up to 3wt%, whereas those of polylactic acid/natural graphite (PLA/NG) composites remained constant regardless of the NG content. The improvement by 10 K for thermal degradation temperature of PLA/EG nanocomposite with only 0.5 wt % EG was showed over PLA homopolymer.

3. Supercritical fluid method (SCFs):

Supercritical carbon dioxide (CO₂) is well established for use as a processing solvent in polymer applications

such as polymer modification, polymer composites, polymer blending and microcellular foaming. Moreover, SCFs can improve product quality as compared to conventional organic solvents.

Kong *et al.* reported a method of annealing GO in supercritical fluids (SCFs), which is environmentally more friendly conversion (Kong, C.Y., *et al.*, 2012). Besides of the low densities (thus low viscosity/high diffusivity) and diminished surface tension, the SCFs also found to enable lower-temperature crystallization of amorphous nanomaterials in a fluid-assisted calcinations process.

Pu *et al.* used a supercritical CO₂ processing technique for intercalating and exfoliating layered graphite (Pu, N.W., *et al.*, 2009). The result from atomic force microscopy (AFM) shows that the typical graphene sheet contains about 10 atomic layers. This technique offers a low-cost, simple approach to large-scale production of pure graphene sheets without the need for complicated processing steps or chemical treatment.

Polymer blends also have been applied in a non-reactive way by batch mixing and extrusion with supercritical CO₂ as a plasticizing agent (Elkivoch, M.D., Lee, L.J., Tomasko, D.L., 1999; Lee, M., Park, C.B., Tzoganakis, C., 1998; Lee, M., Tzoganakis, C., Park, C.B., 2000). The functional supercritical CO₂ in blends leads to decreased shear thinning and a finer dispersion of the minor component. For example, Fig. 1.1 clearly shows transmission electron microscopy (TEM) of the effect of supercritical CO₂ on the dispersion of the minor phase, PMMA, in a polymethyl methacrylate/polystyrene (PMMA/PS) blend (Elkivoch, M.D., Lee, L.J., Tomasko, D.L., 2000). The effect of CO₂ on a dispersed phase can also be seen through earlier completion of phase inversion compared to blending without CO₂. CO₂ effectively utilized for reduction of the droplet size of the disperse phase.

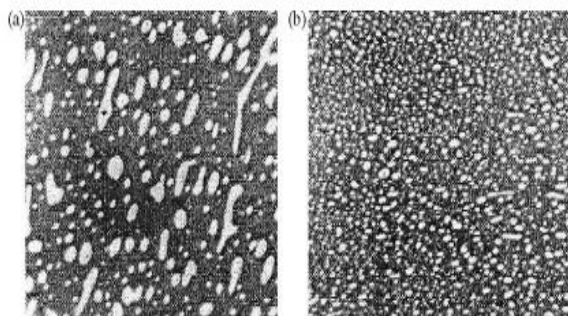


Fig. 1.1: TEM micrographs of PMMA/PS (25/75) blend: (a) without CO₂; (b) with supercritical CO₂ (Elkivoch, M.D., Lee, L.J., Tomasko, D.L., 2000).

4. Plasticizer in Nanocomposites:

Poly(lactic) acid is characterized by excellent optical properties and high tensile strength but unfortunately, it is rigid and brittle at room temperature limiting its use and melt-processability for food packaging. Plasticizers with rather high molecular weight and low mobility are necessary because the low molecular plasticizers have the problem of migrating, owing to their high mobility within the PLA matrix.

Hassouna *et al.* studied of plasticizing PLA with PEG to improve the ductility of PLA while maintaining the plasticizer content at maximum 20 wt%. They used a reactive blending of anhydride-grafted PLA (MAG-PLA) copolymer with PEG, with chains terminated with hydroxyl groups (Hassouna, F., *et al.*, 2011).

Sheth *et al.* melt-blended PLA and PEG using a counter-rotating twin-screw extruder at 120 – 180 °C. They reported that the blend concentration caused the PEG form miscible to partially miscible blends with PLA. The plasticized PLA samples have high elongation with a concomitant reduction in modulus values for below 50% PEG. However, the blend crystallinity increases, resulting in an increased modulus and a considerable decrease in the elongation at break for above 50% PEG content (Sheth, M., *et al.*, 1997).

MATERIAL AND METHOD

1. Raw Materials:

The raw materials will be used are polylactic acid (PLA) with the melting point is 180 °C. The filler, graphene oxide (GO) and plasticizer, poly(ethylene) glycol (PEG).

2. Preparation of Nanocomposite:

(1) Preparation of PLA/GO/PEG nanocomposites:

Prior to the mixing step, GO powder and PLA are dried overnight in a vacuum at 100 °C to remove any residual moisture. This drying purposed to prevent excessive hydrolysis (molecular weight drop) which can compromise the physical properties of the polymer. The all materials were pre-mixed using dry mixer.

PLA/GO/PEG composites are prepared by melt blending using twin-screw extruder. The percentage of

materials PLA/GO/PEG are sample 1(100:0:0), 2(94.5:0.5:5.0), 3(94.0:1.0:5.0), 4(93.0:2.0:5.0) and 5(92.0:3.0:5.0). These experiments will be carried out to study the effect of GO loading on properties of nanocomposites. The loading of PEG is fixed at 5% loading.

The pre-mixed nanoparticles and polymer are fed into twin screw extruder operating at 190 °C. The screw speed is set to 20 rpm. The PEG will be added continuously. When the addition and melting of the nanoparticles/polymer mixture ended and the torque stabilized, the rotor speed was increased to 60 rpm. During the mixing process, the temperature was set to 200 °C and the mixing duration was kept at 4 min. At the end of mixing, the extrudate is flushed.

(2) Processing Using Injection Molding:

The extrudate then formed to pellet using injection molding. The pellet is used for mechanical properties testing. The PEG will be added in certain amount to act as plasticizer.

(3) Supercritical CO₂ process:

Supercritical CO₂ methods applied to enhance the dispersion of GO in PLA as comparison to pellet from injection molding. Polymer nanocomposite extrudates will be cut into small pieces and will be placed in an autoclave. The gas injection is fed. The nanocomposites were soaked with CO₂ with vary conditions, the pressure will be vary at 6.9, 9.7, 12.4, 15.2 and 17.9 MPa and the temperature ranges from 40 to 90 °C. The critical temperature and pressure of CO₂ are 31.1 °C and 7.4 MPa, respectively. The rapid depressurization then applied.

3. Characterization:

The structure of composites is characterized by X-ray diffraction (XRD). The crystalline region of materials can be studied. The morphology aspect of the final composites is examined by transmission electron microscopy (TEM). TEM is used to investigate the dispersion and distribution state of GO nanoparticles in PLA. TEM can be used to observe the cross-sections by slicing and thinning the sample, and observe the surface morphology by controlling the thickness of the sample within 100 nm. TEM also can be used to characterize nanocomposite and crystalline structure. The surface morphology of nanocomposites will be studied using scanning electron microscopy (SEM).

Field Emission Scanning Electron Microscopy (FESEM) is widely used to observe the surface and cross-sections, and measure the thickness of different samples. FESEM not only observe the surface, but also the transverse, tilt and cross-sections, as well as analyze the elemental composition by the energy dispersive X-ray analysis. Chemical structure of PLA and GO nanocomposites are evaluated by fourier transform infrared (FTIR) spectroscopy in transmission from 400 to 4000 cm⁻¹. The variation of functional groups of materials and nanocomposites can be studied.

4. Testing:

(1) Thermal Properties:

The thermal properties of nanomaterials after extrusion are investigated by several testings. The glass transition (T_g), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), and melting temperature (T_m) will be examined using Dynamic Scanning Calorimetry (DSC) equipment. Thermogravimetric Analysis (TGA) is carried out on 10 mg samples. The thermal degradation temperatures taken into account were the temperature at 5% of weight loss (T_{5%}) and the temperature of maximum weight loss rate (T_{max}). The influence of the plasticizer on viscoelastic properties of PLA and GO loading will be analyzed by means of a dynamic mechanical analyzer (DMA).

(2) Mechanical Properties:

Tensile strength and tensile modulus are evaluated at room temperature following ASTM D638 method using an Instron tensile testing machine. The flexure test method measures behavior of materials subjected to simple beam loading using Instron testing machine. Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a force is applied.

5. Biodegradation Behavior:

(1) Accelerated weather testing:

Weather testing of polymers is the controlled polymer degradation and polymer coating degradation under lab or natural conditions. Accelerated Weathering testing is a laboratory simulation of the damaging forces of weather for the purposes of predicting the relative durability of materials exposed to outdoor environments. Glass transition temperatures of the un-aged and aged samples were measured with a Mettler Toledo DSC 822e differential scanning calorimeter. The DSC program used was -40 °C (initial temperature), a ramp of 20 °C/min to 60 °C (final temperature), under nitrogen flow. T_g was taken as the midpoint of the inflection in the DSC curve. The tensile strength and biodegradable behaviour also will be studied.

(2) Microbiological Experiment:

In microbiological experiment, weight loss as a function of the exposure time to soil burial of control and nanocomposite specimens will be analyzed. Despite these potential problems, weight loss data will be examined to qualitatively analyze the effect of microbial attack on the PLA nanocomposites. Samples are cut into rectangular shape (2 x 3 cm²) and then will be dried until constant weight in an oven to remove the moisture before testing (m_0). Specimens were put into cups made of an aluminium mesh to permit the access of microorganisms and moisture and the easy retrieval of the degraded samples. The specimens into the holders are buried at 8 cm depth from the soil surface in order to ensure aerobic conditions of degradation. The relative humidity was kept around 40% by adding water periodically and the temperature was 20 ± 2 °C.

Soil moisture fluctuation was followed gravimetrically by using the oven drying method (ASTM D2216). Water sorption during soil burial was determined gravimetrically. Samples are removed from the soil at specific intervals (t), carefully cleansed with distilled water, superficially dried with a tissue paper and weighed (m_h). Water uptake (%WS) was quantified by the following equation:

$$\%WS = \frac{m_h - m_t}{m_0} \times 100$$

where m_0 and m_t are the initial and the residual mass at time = t, respectively, and m_h is the humid mass of the specimens after wiping with a tissue paper. The reported values are the average of two measurements. After water sorption determination, samples are dried under vacuum and at room temperature to constant weight. The specimens were weighed on an analytical balance in order to determine the average weight loss (%WL):

$$\%WL = \frac{m_t - m_0}{m_0} \times 100$$

(3) Barrier Properties:

The apparatus and methodology described in the ASTM E96 will be used to measure the Water Vapor Permeability (WVP) of the film (ASTM, 1995). Film specimens are conditioned for 48 h in a chamber at 25 °C and 52% relative humidity (Mg(NO₃)₂ saturated solution) before being analyzed. Films are sealed on cups containing distilled water. Test cups will be placed in a desiccator cabinet maintained at temperature and relative humidity (LiCl saturated solution) controlled. To determine film thickness and plasticizer effect on WVP, tests will be done at 30 °C. To study temperature influence on WVP, samples will be analyzed in a temperatures range between 5 and 40 °C. A fan is used to maintain uniform conditions at all test locations over the specimen. Periodical weightings monitored the weight changes. Weight loss is plotted over time and when steady state (straight line) was reached 6 h more are registered. The WVP was calculated from the slope (G) of a linear regression of weight loss versus time.

$$WVP = \frac{G \cdot x}{A \cdot p}$$

where x is the film thickness; A is the area of exposed film and p is the differential water vapor partial pressure across the film. This method uses Fick's first law and Henry's law to calculate film WVP and assume that film solubility and diffusivity are constant. WVP measured values are corrected for air gap distance between water level and the film position according to procedures outlined in Gennadios *et al* (Gennadios, A., Weller, C.L., Gooding, C.H., 1994).

RESULT AND DISCUSSIONS

The further study will be carried out later as this paper only discussed on the preliminary research and a little touch reviews based on the polylactic acid and graphene oxide. The dispersion of GO in PLA by performing the supercritical fluid CO₂ method will be enhanced, hence improved the mechanical properties of nanocomposites.

Conclusion:

PLA has low toxicity, has made it an ideal material for food packaging and film wrap and other consumer products. PLA is characterized by excellent optical properties and high tensile strength. PEG is one of recognized material that can decrease the brittleness during processing. Supercritical CO₂ is a valuable tool in polymer processing. Hence, the replacement of conventional organic solvents with environmentally less harmful fluids, CO₂, is a major motivation for its use. The wide range of applications suggests a bright future for CO₂ assisted polymer processing, but it also indicates the need for deeper understanding of specific interactions in polymer-CO₂ systems, for the accumulation and modeling of a variety of experimental rheology and phase equilibrium data, and for the simulation studies to supplement experimental work.

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