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Effect of Functionalization and Alignment of Graphene Nanoplatelets on the Thermal Conductivity of Polylactide Based Nanocomposites

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ABSTRACT

To increase the thermal conductivity of polylactide (PLA) for engineering applications, graphene nanoplatelets (GNP) reinforced PLA nanocomposites were fabricated. The compatibility between nanofillers and polymer was improved by non-covalently modifying GNP with tannic acid (TA). Solution blending and compression molding processes were employed to fabricate PLA nanocomposites. It was hypothesized that the two-dimensional GNP morphology in conjunction with the hot press process promoted particle alignment and thus nanocomposites anisotropy. Measurements revealed that the in-plane thermal conductivity (0.61 W/mK) at 4 wt% TA-functionalized GNP was 1.5 times of that in the throughplane direction (0.41 W/mK), constituting a 300% improvement compared to pure PLA (0.21 W/mK). The developed fabrication process thus indicates a high potential for the manufacture of polymer nanocomposite structures requiring high thermal conductivity for thermal management applications.

KEYWORDS: Polylactide, Graphene Nanoplatelets, Thermal Conductivity, Anisotropy

1 INTRODUCTION

Polylactid acid (PLA), a type of biocompatible thermoplastic polymer also known as polylactide, is frequently considered a sustainable alternative to petroleum-based plastics. However, PLA has certain shortcomings for engineering applications, such as comparatively low properties in terms of strength, thermal and electrical conductivity, and thermal stability. In recent years, a number of studies have focused on enhancing the mechanical and electrical properties, and thermal stability of PLA through nanofiller modification (Spinelli et al., 2019).

Increasing attention has also been paid to enhancing the thermal conductivity of filler-reinforced PLA composites. In fact, improvements in thermal conductivity may enable many potential applications of PLA in the field of electronics and electrical devices. The thermal conductivity of neat PLA is only about 0.1 W/mK (Botlhoko et al., 2018) at room temperature, which cannot meet the requirements of many modern electrical systems. It has been demonstrated in the technical literature that the high thermal conductivity of inorganic fillers can efficiently improve the thermal conductivity of PLA, such as by incorporating carbon nanofibers (Nakamura and Iji, 2011), carbon nanotubes (Lebedev et al., 2017) and expanded graphite (Horny et al., 2016).

Teng et al. (2011) described an effective covalent-modification method to functionalize vapor-grown carbon nanofiber (VGCF) with polylactide (PLA). At 10wt% functionalized carbon nanofibers the thermal conductivity of the prepared PLA/PLA-VGCF nanocomposite increased to 1.24 W/mK over that of pure PLA (0.19 W/mK). Mortazavi et al. (2013) used expanded graphite (EG) as the reinforcing nanofiller. The thermal conductivity of PLA/EG composites at 6.75 wt% filler loading was enhanced by almost 100% as compared to that of the neat PLA.

To the best of the present authors' knowledge, only limited research has been reported in the technical literature about utilizing graphene nanoplatelets (GNP) as the reinforcement to increase the thermal conductivity of PLA (Fina et al. 2018, Lin et al., 2018, Mosanenzadeh et al., 2016). Mosanenzadeh et al. developed PLA composites by embedding highly thermally conductive hybrid filler systems, hexagonal boron nitride (hBN) and GNP, into the PLA matrix. The effective thermal conductivity of the sample was found to be more than 12 times that of neat PLA, reaching 2.77 W/mK with hybrid fillers consisting of equal portions of GNP and hBN.

GNP, which are composed of a few layered graphene sheets, are widely regarded an attractive reinforcing nanofiller for polymer composites because of excellent intrinsic mechanical and electrical properties as well as high thermal conductivity (Selvam et al., 2017, Sun et al., 2017). The most important factors contributing to achieving desired properties in GNP/polymer composites are a homogeneous dispersion of GNP and strong interfacial adhesion between nanofillers and polymer matrix. However, due to the inherent strong π - π stacking interaction and Van der Waals forces between GNP (Shazali et al., 2018a, He et al., 2018), GNP tends to aggregate to minimize surface free energy (Shazali et al., 2018b), leading to poor interfacial interactions between the fillers and polymer during nanocomposite fabrication.

For GNP, in order to increase the compatibility and dispersibility, two common strategies have been proposed for surface functionalization, i.e., (i) non-covalent coupling through physical stabilization, and (ii) covalent functionalization through chemical functionalization (Sarsam et al., 2016, Keramati et al., 2016, Shazali et al., 2018c). The covalent functionalization method would deteriorate the properties related to the transport of electrons, phonons or/and other quantum effects in GNP (Mu et al., 2014), and as a result, the intrinsic thermal conductivity of GNP would be reduced. To avoid this problem, a non-covalent preparation method was utilized in the present work. Non-covalent functionalization of GNP is based on Van der Waals force or π - π staking interactions by wrapping the graphene surface with, e.g., surfactants, polymer or small molecules (Li et al., 2015, Choi et al., 2010).

In the present study, an effective method was developed to improve the thermal conductivity of PLAbased nanocomposites through non-covalent functionalization of GNP with tannic acid (TA). Subsequently, TA functionalized GNP (f-GNP) reinforced PLA nanocomposites were successfully fabricated using solution-mixing followed by a compression molding process. The chemical structures of pristine GNP and TA-functionalized GNP were quantitatively analyzed and characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD). Differential scanning calorimetry (DSC) was carried out to investigate the non-isothermal crystallization behavior of PLA nanocomposites. Furthermore, the effect of f-GNP incorporation on the thermal conductivity of PLA was investigated and compared with measurements from PLA nanocomposites with untreated GNP and neat PLA.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Graphene nanoplatelets (trade name xGnP®, grade M15) was obtained from XG Sciences Inc., (Lansing, MI, USA) with average thickness of 6-8 nm, surface area of 120-150 m²/g, density of 2.2 g/cm³, maximum length 15 μ m, and thermal conductivities of 3000 W/mK and 6 W/mK in the direction parallel and perpendicular to the platelet surface, respectively (Web-1). A commercially available poly (lactic acid) (trade name 4043D) was purchased from Filabot Co., Ltd. (Barre, VT, USA). The PLA pellets were transparent and have a glass transition temperature of 55-60°C, a density of 1.25 g/cm³, a melting temperature range of 145-160°C, and a decomposition temperature of approximately 250°C. Reagent grade chloroform, TA and other chemicals, purchased from Fisher Scientific (Ottawa, ON, Canada) were used as received without further purification.

2.2 Sample Preparation

Preparation of f-GNP:

A certain amount of unmodified GNP was dispersed into chloroform, then TA with a GNP/TA mass ratio of 5:1 was added into the GNP/chloroform mixture under vigorous magnetic stirring for 30 minutes

at room temperature (20°C). Subsequently, the mixture was treated in an ultrasound bath (Q500, Qsonica, Newtown, CT, USA) employing a pulse-pause technique (40 seconds on, 20 seconds off) at a power of 50 W for 60 minutes. During sonication, the mixture was put into an ice-bath to maintain the mixture temperature below 10°C, preventing quick evaporation of chloroform. After that, the mixture was further subjected to magnetic stirring for 4 to 5 hours at room temperature in the fume hood. The obtained suspension then underwent vacuum filtration using a polyvinylidene fluoride or polyvinylidene difluoride membrane filter (type DuraporeTM hydrophilic, 0.22 µm pore size, MilliporeSigma, Burlington, MA, USA). Subsequently, dark residue was washed by a deionized water/isopropanol mixture (volume ratio 3:1) three times until uncombined TA was removed completely, and then dried at 80°C in the oven to obtain f-GNP.

Preparation of PLA/GNP nanocomposites

Prior to any processing, as-received PLA pellets, pristine and functionalized GNP were dried in an oven at 80°C in order to the minimize moisture content and prevent hydrolytic degradation. PLA nanocomposites with GNP and f-GNP loading of 0, 0.5, 1.0, 2.0, and 4.0 wt% were prepared via solution mixing followed by hot compression molding using chloroform as a mutual solvent. The detailed preparation procedures were as follows. The transparent PLA/chloroform solution was prepared by addition of 20 g of PLA into 300 mL of chloroform while agitating vigorously in a laboratory three-neck, round-bottom flask under magnetic stirring at ambient temperature for 6 h until completely dissolved. Simultaneously, desired amounts of GNP (or f-GNP) were dispersed into chloroform (concentration of 1 mg/mL). The mixture was subjected to a high intensity ultrasonic processing (Q500), at 80% amplitude and power of 50-60 W employing aforementioned pulse-pause technique for 3 hours to obtain a uniform suspension prior to mixing with the PLA solution. During the sonication process, the beaker was placed in the ice bath in order to avoid temperature rise and solvent evaporation. Continuous refilling of the bath ice was required to maintain sonication efficiency and prevent overheating.

In the next step, a GNP suspension was mixed with the PLA solution. To ensure a homogeneous dispersion of GNP in the PLA solution, the PLA-GNP-chloroform mixture was mechanical stirred at 950 rpm for 60 minutes using an impeller agitator from Calframo Ltd. (Georgian Bluffs, ON, Canada). Then, further sonication for an additional 60 minutes in the ice-bath was implemented before the solution was poured into a custom-made steel mold. The walls of mold were previously coated with a mold-release agent (Frekote 700 NC, Henkel Corporation, Düsseldorf, Germany) to ease sample removal.

The prepared mixtures were left in the fume hood under an ambient condition for approximately 12 hours to evaporate the bulk solvent. The resulting neat PLA and PLA/GNP nanocomposite cast films were subsequently dried further at 120°C in an oven for 12 hours to remove any remaining solvent.

All prepared nanocomposites were compression molded into sheets with circular shape (thickness 4 mm and diameter of 100 mm). A four-column manual hydraulic press was used (model 4386 12 ton, Carver, Wabash, IN, USA) at 145°C under 15 MPa pressure for 3 minutes. Preheating of 5 minutes occurred prior to pressing, and samples were cooled slowly to room temperature in air under pressure. During the pressing process, aluminum plates were used to avoid contaminating the press platens.

In the present paper, the different PLA nanocomposites are identified as "PLA/x-f-GNP" and "PLA/x-GNP" for simplicity, where x indicates the weight percentages of f-GNP and GNP relative to PLA in the sample. Samples containing 0.5, 1.0, 2.0, and 4.0 wt % GNP were thus denoted correspondingly as PLA/0.5-GNP, PLA/1-GNP, PLA/2-GNP, PLA/4-GNP, and PLA/0.5-f-GNP, PLA/1-f-GNP, PLA/2-f-GN), PLA/4-f-GNP in all figures and tables. Neat PLA samples were fabricated using similar procedures for the sake of comparison. Upon completion of fabrication, all sample sheets were cut to the desired sizes and stored in sealed plastic bags for the future testing.

2.3 Characterization Methods

Functionalization reactions on GNP were assessed using FT-IR. 32 scans were recorded from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ using an IFS-48 FT-IR spectrometer (Bruker, Ettlingen, Germany). Before FT-IR measurements, f-GNP and GNP were pressed into pellets with potassium bromide powder.

Using DSC analysis the thermal characteristics, such as glass transition temperature (T_g), cold crystallization temperature (T_{cc}), exothermic enthalpy of cold crystallization (ΔH_{cc}), endothermic enthalpy of melting (ΔH_m) and melting temperature (T_m) of PLA and PLA/GNP (or f-GNP) samples were determined using a DSC-Q 1000 instrument (TA Instruments, New Castle, DE, USA) under nitrogen flow (60 mL/min). Samples with mass of 5-7 mg were contained in standard Tzero aluminum pans during testing, while the same empty encapsulated aluminum pan and lid was used as the reference. The thermograms were recorded following a heating-cooling-heating procedure as follow. The samples were heated first from 30°C to 180°C at a rate of 10°C/min and then kept isotherm for 5 minutes to erase the anterior thermal history. The samples were then cooled down to 30°C scanned at a cooling rate of 20°C/min, and then held for 3 minutes. Finally, in the second heating scan, samples were heated again to 180°C at a heating rate of 2°C/min. Only the second heating scans were considered for data analyses.

The crystalline structure and dispersion characteristics of GNP and f-GNP in PLA nanocomposites were assessed using XRD analysis (Ultima IV, Rigaku, Tokyo, Japan). Samples were thin sheets of approximately 2 mm thickness. The diffraction patterns were collected at a 2θ range of 10-60° at a scan rate of 5°/min and a scan step size of 0.05°. The instrument was operated at 40 kV and 44 mA using Cu-K α irradiation (wavelength $\lambda = 1.542$ Å). GNP and f-GNP were in powder form while PLA and PLA/GNP nanocomposites samples were cut from compression molded specimens.

The thermal conductivity of PLA-based nanocomposites was measured using a Hot Disk TPS-2500S instrument (Thermtest Inc., Fredericton, NB, Canada) in conjunction with a Kapton sensor (type 5501, Thermtest Inc.) in the standard method (anisotropic).

3 EXPERIMENTAL RESULTS

3.1 FT-IR characterization of GNP and f-GNP

FRIR analysis was performed to characterize the chemical structure of f-GNP and GNP particles. The TA molecule can form noncovalent bonds with GNP by π - π stacking and Van der Waals force. Based on the FT-IR spectra of GNP and f-GNP, shown in Figure 1, a broad peak around 3423 cm⁻¹ corresponds to the stretching vibrations of -OH, with a small peak at about 1629 cm⁻¹ and 1085 cm⁻¹ resulting from the C=C and C-O, respectively. Moreover, a peak at 1712 cm⁻¹ and 1573 cm⁻¹ occurred only for f-GNP because of absorption related to TA of on the surface of GNP (Zhao et al., 2018).

3.2 XRD analysis

XRD analysis was used to characterize the microstructure of pristine GNP and f-GNP. The diffraction patterns of GNP and f-GNP, shown in Figure 2, all demonstrate an intense 2θ peak at 26.4°, assigned to the (002) diffraction plane of the graphite nanoplatelets (He et al., 2019). The peak intensity for f-GNP decreases sharply, indicating that f-GNP are a much less crystalline than pristine GNP.

3.3 DSC results

DSC was employed to assess the thermal transitions of all PLA/GNP samples. As mentioned above, thermal histories of samples were erased through an initial heating cycle, and the effect of nanofillers on the crystallization kinetics of PLA was evaluated using the second heating cycle. The estimated values of T_g and melting properties (melting temperatures T_{m1} , T_{m2}) of all PLA nanocomposites and pure PLA are summarized in Table 1. The degree of crystallinity (χ) was determined using Eq.(1).

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times (1 - \varphi_f)} \tag{1}$$

where $\Delta H_{\rm m}$ is the melting enthalpy of samples, $\Delta H_{\rm cc}$ is the cold crystallization enthalpy, $\Delta H_{\rm m}^0$ is the theoretical melting enthalpy of 100% crystalline PLA matrix (93.0 J/g, Chieng et al., 2014), and $\varphi_{\rm fis}$ is the weight percentage of GNP (f-GNP) in PLA nanocomposites.



Figure 1: FT-IR spectra of GNP and f-GNP

Figure 2: XRD patterns of f-GNP and GNP

Sample	$T_{\rm g}$ (°C)	$T_{\rm m1}$ (°C)	$T_{\rm m2}$ (°C)	Crystallinity (%)
PLA	57.2	150.7	155.8	2.88
PLA/0.5-f-GNP	57.4	148.6	155.8	3.53
PLA/0.5-GNP	57.3	148.6	155.9	3.26
PLA/1-f-GNP	57.8	148.6	155.8	4.50
PLA/1-GNP	57.7	149.6	156.1	3.89
PLA/2-f-GNP	57.6	151	156.6	8.33
PLA/2-GNP	57.5	151	156.2	7.36
PLA/4-f-GNP	57.7	151.3	156.6	9.11
PLA/4-GNP	57.7	150.6	156.5	8.97

Table 1: DSC data of neat PLA and its nanocomposites

In the second heating process, several typical thermal events were observed, including glass transition, cold crystallization and melting behavior, as shown in Figure 3. For clarity, only the neat PLA and its nanocomposites with GNP (f-GNP) loading of 2.0 and 4.0 wt.% are showed in Figure 3. Compared to neat PLA, no significant changes in T_g were observed for the various nanocomposites as a function of nanofiller content and type.

Likewise, the two melting temperature (T_{m1} and T_{m2}) also did not seem to be influenced by the incorporation of the different kinds of fillers compared with neat PLA, with values between 148°C and 152°C. These results indicate that the PLA/GNP nanocomposites have a similar lamellar thickness with PLA/f-GNP, because T_m has a tight relation with the lamellar thickness (Najafi et al., 2012). It is interesting to note that PLA and PLA nanocomposites exhibited a double melting behavior. This double-peak melting phenomenon indicates either melt recrystallization of α -crystals (Lashgari et al., 2016) or polymorphism (Pan et al., 2008) in the system.

As presented in Table 1, the degree of crystallinity (χ) of pure PLA is about 2.88% while χ for the PLA nanocomposites increased significantly. This improvement was likely induced by a nucleating effect by nanofiller particles, as demonstrated in other works by Haggenmueller et al. (2007). The χ value is slightly higher for PLA/f-GNP samples compared to PLA/GNP at the same filler content, which can likely be attributed to a better dispersion of f-GNP in the polymer matrix, leading to more heterogeneous nucleation sites (Lin et al., 2018). Crystallinity increased with nanofiller content, to a maximum of 9.11% at 4.0 wt% f-GNP in PLA, i.e., approximately a 300% enhancement.

3.4 XRD results

XRD analysis was performed to evaluate the state of filler exfoliation in the nanocomposites. For clarity, X-ray diffractograms for neat PLA and its GNP and f-GNP nanocomposites are shown in Figure 4

only filler loadings of 2.0 wt.% and 4.0 wt %. For pure PLA, a weak scattered intensity distribution from 11.5° to 20.6° with broad maximum peak around at 2θ of approximate 16.7° was observed, which confirms the pure polymer was predominantly in amorphous structure (Sullivan et al., 2016). With the incorporation of GNP and f-GNP the diffraction peak intensity at 16.7° becomes much stronger compared to neat PLA, indicating the enhanced crystallinity of PLA in presence of GNP and f-GNP, which gives strong indication of a nucleating effect of graphene particles, which is consistent with research (Girdthep et al., 2017). Referring to Figure 4, characteristic 2θ peaks at 15.0°, 16.7°, 19.0° and 22.5° for all nanocomposites can be ascribed to stable semicrystalline α -phase crystals of PLA (Kashi et al., 2018, Reghat et al., 2017), corresponding to (010) (Pluta and Galeski 2002), (200)/(110) (Hoogsteen et al., 1990), (203) (Pluta and Galeski 2002) and (015) (Pan et al., 2008) planes, respectively, compared with the broad maximum peak of PLA. Based on the XRD results, i.e. only α -phase crystals of PLA are present in the nanocomposites, the double melting endotherms observed in Figure 3 are a result of melt recrystallization and not polymorphism (Sullivan et al., 2016).

As shown in Figure 4, all diffractograms for PLA nanocomposites exhibit a 2θ peak at about 26.5°, indicating that there is no peak shift for GNP or f-GNP in the nanocomposites. According to Bragg's Law, the GNP and f-GNP sheets still keep their close-stacked structure even after ultrasonication and mechanical stirring, which may be due to the strong bonds between GNP layers that keep them tightly interlinked with one another (Hussain et al., 2006).

3.5 Thermal conductivity results

Figure 5a shows the in-plane thermal conductivity of PLA nanocomposites as a function of GNP and f-GNP loading. As depicted in the figure, thermal conductivity of both PLA/GNP and PLA/f-GNP nanocomposites increased with nanofiller loading. Overall, at the same nanoparticles content, the thermal conductivity of PLA/f-GNP was larger than that of PLA/GNP nanocomposites. Referring to Figure 5b, the value for the thermal conductivity in the through-plane direction remained nearly unchanged (at about 0.2 W/mK) for low GNP and f-GNP loading (less than 1.0 % wt). Values then increased gradually with reinforcement content, reaching 0.41 W/mK and 0.38 W/mK for PLA/f-GNP and PLA/GNP nanocomposites at 4.0 wt% filler loading, respectively. For both GNP and f-GNP, the thermal conductivity in the in-plane direction was significantly greater than in the through-thickness direction at same filler loading. The strongly anisotropic thermal conductivity characteristic suggests nanofiller alignment in the in-plane direction.



Figure 3: DSC curves for pure PLA and its GNP and f-GNP nanocomposites



Figure 4: X-ray diffractograms for pure PLA and its GNP and f-GNP nanocomposites



Figure 5: a) In-plane and b) through-plane thermal conductivity of PLA-based nanocomposites

At 4.0 wt% nanofiller content the in-plane thermal conductivity reached 0.61 W/mK for PLA/f-GNP naocomposites, which is a 17% improvement compared to its PLA/GNP counterpart (0.52 W/mK) and an about threefold improvement compared to neat PLA (0.21 W/mK). After the non-covalent modification the interfacial adhesion between f-GNP and PLA is enhanced and the surface chemistries between them is matched (Shenogina et al., 2009), promoting good dispersion of f-GNP in PLA compared to unmodified GNP. Also, enhanced interfacial bonding and good dispersibility may have reduced phonon scattering (Gulotty et al., 2013) at the interface f-GNP and PLA, improving electron or phonon transport (Kazi et al., 2015) and thus thermal conductivity of the PLA/f-GNP nanocomposites.

4 CONCLUSIONS

In the present study, GNP was noncovalent functionalized with tannic acid in order to increase the thermal conductivity of GNP-based PLA nanocomposites. The chemical structure of unmodified GNP and modified GNP (f-GNP) was characterized by FT-IR and XRD analyses. PLA nanocomposites were prepared by solution-mixing followed by hot-pressing. Thermal properties and microstructure of PLA nanocomposites were examined using DSC and XRD analysis. Because of the improved dispersion of f-GNPs in the PLA matrix and enhanced interfacial compatibility between f-GNP and PLA, the thermal conductivity of PLA/f-GNP was found to be larger than that of PLA/GNP nanocomposites. The observed significant improvements in thermal conductivity may enable PLA nanocomposites to be employed in a variety of applications requiring thermal management, such as in solar absorbers and electronic devices.

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