Promoting the dispersion of graphene and crystallization of poly (lactic acid) with a freezing-dried graphene/PEG masterbatch

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A B S T R A C T
For poly (lactic acid) (PLA) nanocomposites, improving the dispersion of nanofillers and promoting the crystallization rates of PLA matrix are crucial to the final properties. Here, we proposed a facile “freezing-dried masterbatch” strategy to fulfill the two goals simultaneously in the preparation of PLA/graphene composites. After graphene oxide (GO) sheets are dispersed in poly (ethylene glycol) (PEG) aqueous solution and hydrazine hydrate is added to transform GO sheets into graphene sheets, the resulting mixture was freezing-dried to get the masterbatch of PEG and graphene. By simply melt blending the masterbatch with pristine PLA, PLA composites with excellent mechanical properties and thermal stability are prepared. For example, with 0.25 wt % of graphene, the composite prepared using the freezing-dried masterbatch has a tensile stress of 61.6 MPa, a tensile modulus of 1256 MPa, and a toughness value of 4.86 MJ/m3. The values are respectively 50.9, 125.5, 200.0% higher than that of the control sample of PLA-PEG and 11.5, 25.5, 124.0% higher than that of PLA composite prepared by directly blending with 5 wt % PEG and 0.25 wt % graphene. Morphological observations and crystallization behavior investigations reveal that graphene shows well dispersion in PLA composites, and the crystallinity and crystallization rates of PLA are greatly improved, which may be the reason for the improved mechanical properties.

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1. Introduction

Poly (lactic acid) (PLA) is a plant-derived biodegradable polymer, which can be obtained from natural source such as corn starch and may be a sustainable alternative to petrochemical-derived polymers [1]. As a thermoplastic and aliphatic polyester, PLA has been used to produce beverage packages, biomedical supplies, food wares, vehicle interiors, films, and fiber [2,3]. Unfortunately, some significant disadvantages of PLA such as relatively poor mechanical properties, slow crystallization rate, and low thermal stability hinder its applications for more demanding requirements [4,5]. In order to overcome these problems, blending with nanoscale particles are one of the commonly used methods [6,7]. Due to the large aspect ratio and excellent strength, some nanoparticles such as carbon nanotubes, layered silicate, and graphene sheets, have been widely used as fillers of PLA to produce composites with good performance or unexpected properties [8–10].

Graphene has attracted much attention in recent years due to its outstanding electrical, thermal, and mechanical properties [11,12]. The extraordinary properties of graphene sheet combined with high aspect ratio make it ideal filler for polymer composites [13–15]. However, the lack of active groups on graphene sheets and strong van der Waals interactions generally induced the aggregation, leading to the poor dispersion of graphene in polymer matrices during the process of melt mixing or solution coagulation. In order to avoid the aggregation of graphene in PLA matrix, functionalizing graphene oxide (GO) sheets, which have improved compatibility with polymer hosts, stands out as a primary strategy to incorporate graphene sheets uniformly into PLA matrices [16–18]. Polymer grafted graphene fulfilled improved dispersion in epoxy resin and enhanced the mechanical properties of nanocomposites [19]. Poly (vinylidene fluoride)/GO nanocomposites are fabricated by one-step water-assisted mixing extrusion via injecting GO suspension into polymer melt [20]. Graphene also has been successfully modified by polymers, small molecules and biomolecules via non-covalent interactions to afford functional composites [21]. Fu et al. fabricated poly (vinyl alcohol)/graphene nanocomposite by using nanocellulose to assist the dispersion of graphene in water [22]. Zhang et al. utilized esterification between...
the carboxylic acid-functionalized GO and the end hydroxyl groups of polyethylene glycol (PEG) to improve the dispersion of GO in PLA, which takes advantage of the good compatibility between PEG and PLA [17]. Actually, PEG, which manifests the desirable compatibility with PLA even at the loading of 30 wt % and could improve the chain motion of PLA, has been the most investigated plasticizer for PLA [23]. Though the grafting methods indeed exhibit great benefits to disperse GO, complex synthetic procedures and a lot of organic solvent are generally involved in the synthesis process. To simplify the fabrication process and fulfill the dispersion of graphene in PLA, Lu et al. utilized the desirable compatibility of PEG with both GO and PLA, improving the dispersion of reduced GO in PLA through directly melt mixing [24]. Due to the strong stacking of GO when water is gradually evaporated, the GO in directly dried GO/PEG mixture is heterogeneous and difficult to re-disperse in PLA matrix. More importantly, the reduction level of GO in the composite is not likely to be high just after undergoing the melt processing temperature of 200 °C. In other words, this method cannot be used to prepare well dispersed and high-reduced GO-based PLA composites using GO as raw material.

Freeze-drying, which is an environmentally friendly process, is frequently used to prepare aerogels in the past years [25]. We have previously found that the melt mixing of PLA and the freeze-dried graphene could promote the dispersion of graphene sheets in PLA matrix [26]. On account of the aforementioned issues such as slow crystallization rate, complex procedures, and worse graphene dispersion of PLA composites, in this study, we proposed a facile “freezing-dried masterbatch” strategy to simultaneously fulfill the good dispersion of graphene sheets in PLA matrix and the improved crystallization ability of PLA. In our method, GO and PEG were dissolved in water to get homogeneous solution. After GO was reduced into graphene by adding hydrazine hydrate, freezing and lyophilization were used to fabricate the masterbatch of graphene and PEG, which was then melt mixed with PLA to prepare PLA composites. It is found that compared with PLA composites prepared by directly melt mixing with PLA, PEG and graphene sheets, the modulus, toughness, and the thermal stability, as well as the crystallization rates of PLA composites prepared using our freezing-dried masterbatch have impressive improvements. This simple and environmentally friendly strategy may simultaneously overcome two major problems to prepare high-performance PLA/graphene nanocomposites, i.e. the poor dispersion of graphene in matrix and the poor crystallization ability of PLA, to some extent, and therefore demonstrates great value in the practical applications.

2. Experimental section

2.1. Materials

The PLA (4032D) employed in this work was supplied by Nature Works Co. (MinnesotA). PEG (Mn = 6000 g/mol) and N2H4·H2O (98%) were supplied by Aladdin. GO was synthesized from graphite powder provided by Shengtai Graphite Company (China) based on the reported method.

2.2. Preparing the masterbatch of PEG and graphene

After PEG was dissolved in deionized water and stirred with a magnetic stirrer for 1 h at room temperature, GO aqueous solution was then gradually added into the PEG solution. The mixed solution was kept in ultrasonic bath for 5 min and stirred for 2 h. Subsequently, 1 mL N2H4·H2O was added into the mixed solution. After 24 h stirring, the solution was injected into large amount of liquid nitrogen to be frozen and then freezing-dried for 7 day to prepare the masterbatch of PEG and graphene. The masterbatch (the weight ratio of PEG:graphene = 5:0.01/0.05/0.25/0.50) with good dispersion of graphene in PEG was obtained. As comparison, graphene used for direct melt mixing was also prepared by the same procedure without the adding of PEG.

2.3. Preparation of PLA composites

The PLA composites are prepared by directly melt mixing of PLA and the masterbatch at 180 °C using Haake Polylab OS torque rheometer (ThermoFisher, Massachusetts). The roller speed was set as 60 rpm and the mixing time was 5 min. The resulting composite is remarked as PLA-PEG-f-X (f means freezing-drying; X stands for the graphene content, that is, 0.01, 0.05, 0.25, and 0.50 wt %; and the content of PEG in PLA composites is fixed at 5 wt %). All the specimens for tensile test were hot compression molded at 180 °C for 3 min. Standard specimens for flexural test were injection molded at barrel temperature of 180 °C. As comparison, control samples are prepared by directly melt mixing of PLA, PEG, and graphene, which is remarked as PLA-PEG (the graphene content is 0) and PLA-PEG-m-X (m means directly melt mixing; X stands for the graphene content).

2.4. Characterization

The tensile properties were tested by an SANS universal testing machine (Shenzhen, China) at a crosshead speed of 5 mm/min, and the flexural performances were tested at 2 mm/min at room temperature. For each sample, the average value reported was derived from at least five specimens. X-ray diffraction patterns (XRD) from 2θ = 5-40° were recorded by X’ pert PRO (PANalytical, Netherlands). The dispersion of graphene in the PLA composites was investigated with transmission electron microscopy (TEM, FEI, Oregon). The fracture surface morphologies of samples were observed by 5136 MM scanning electron microscopy (Tescan, Czech). Crystallization evolution was observed using a DM2500P polarizing microscope (POM, Leica, Germany). To imitate the crystallization behavior during the composites fabrication process, the melted samples were cooled to room temperature with 50 °C/min and the crystallization morphology evolution during cooling process was observed. Differential scanning calorimetry (DSC) measurement was performed on a DSC-1 calorimeter (Mettler Toledo, Switzerland) under a nitrogen flow of 50 mL min⁻¹. The cold crystallization of samples was investigated by recording the trace from 25 to 200 °C with a rate of 20 °C min⁻¹. For the isothermal crystallization, the samples were first held at 200 °C for 3 min to eliminate the thermal history, and then cooled with a rate of 30 °C min⁻¹ to 130 °C. Thermal gravimetric analysis (TGA) was undertaken by a Pyris-1 thermogravimetric analyzer (Perkin-Elmer, Massachusetts) from 80 to 500 °C at a heating rate of 20 °C/min with a nitrogen gas flow of 40 mL/min.

3. Results and discussion

3.1. Mechanical properties

The tensile stress-strain curves of PLA composites are shown in Fig. 1a and b. The tensile strength of PLA–PEG, which has a content of PEG with 5 wt %, is 40.5 MPa and the elongation-at-break is 8.1%. It is found that the tensile strength of PLA composites is gradually increased with improving graphene content. Notably, even with the same content of graphene, the PLA composites prepared with freezing-dried masterbatch mostly show higher tensile strength and elongation-at-break than PLA composites prepared by directly melt mixing method. For example, with only 0.25 wt % graphene, the tensile strength of PLA-PEG-f-0.25 is increased by 50.9% from
40.5 to 61.1 MPa. The elongation-at-break for PLA-PEG-f-0.25 is increased to 11.4%, exhibiting a yielding phenomenon in stress-strain curves and a typical ductile destruction. As shown in Fig. 1c, it is apparent that the tensile modulus of PLA composites is gradually increased with graphene content increasing from 0 to 0.25 wt %. The tensile modulus of PLA-PEG-f-0.25 is 1256 MPa, 125.5% higher than 557 MPa of PLA-PEG, and the tensile modulus of PLA-PEG-m-0.25 is 1001 MPa, 79.7% higher than PLA-PEG. Compared with the PLA composites prepared by direct melt mixing method, the PLA composites prepared by freezing-dried masterbatch strategy show better tensile modulus. However, with the graphene content increasing to 0.5 wt %, the modulus for both PLA composites are reduced, which may due to the stacking of graphene sheets.

Usually, strain energy density at break ($W_b$) is used to evaluate the toughness of materials under tensile fracture [27]. By the equation of $W_b = \int_0^{\varepsilon_b} s \, d\varepsilon$, $W_b$ could be obtained through integrating the area under the stress-strain curves. As shown in Fig. 1d, the toughness value of PLA-PEG is 1.62 MJ/m$^3$. With the direct melt mixing method to blend PLA with graphene and PEG, the toughness values of PLA-PEG-m-0.05 and PLA-PEG-m-0.25 are 1.74 and 2.17 MJ/m$^3$. Comparatively, with the freezing-drying method to
blend PLA with the masterbatch, the toughness values of PLA-PEG-f-0.05 and PLA-PEG-f-0.25 are 3.57 and 4.86 MJ/m$^3$, 105.2 and 124.0\% higher than that of PLA-PEG-m-0.05 and PLA-PEG-m-0.25.

The bending stress of PLA composites is shown in Fig. 2a. With the increasing of graphene content, the bending stress is firstly improved and then decreased. The bending stress of PLA-PEG-f-0.25 is 77.6 MPa, 46.4\% higher than 53 MPa of PLA-PEG and 6.0\% higher than 73.2 MPa of PLA-PEG-m-0.25. With the graphene content increasing to 0.50 wt\%, the values of PLA-PEG-f-0.50 and PLA-PEG-m-0.50 are respectively decreased to 70.0 and 69.5 MPa. With the graphene content increasing from 0 to 0.50 wt\%, the bending modulus is gradually improved (as shown in Fig. 2b). The bending modulus for PLA-PEG-f-0.50 and PLA-PEG-m-0.50 are 2813 and 2744 MPa, about 46.4 and 42.8\% higher than 1922 MPa of PLA-PEG composites, respectively. The enhanced mechanical properties of composites may be attributed to the better dispersion of graphene sheets with high strength, which leads to the strong interaction between graphene sheets and the matrix.

3.2. The dispersion of graphene in PLA composites

For polymeric composites, the dispersion of filler is vital to the final properties. The dispersion status of graphene sheets in composites containing 0.25 wt\% is evaluated by TEM observation. For PLA-PEG-m-0.25 which is prepared by direct melt mixing method, the flakelike aggregates of graphene sheets appear, indicating the poor dispersion in PLA matrix (Fig. 3a). As comparison, for PLA-PEG-f-0.25 prepared by a freezing-drying method, it is obvious
that graphene sheets are prone to be exfoliated into individual sheets and disperse homogeneously in the matrix (Fig. 3b). It can be concluded that, with the freezing-drying method to disperse graphene in PEG firstly, graphene sheets fulfill a better dispersion in PLA composites during the melt mixing of PLA and the freezing-dried masterbatch of PEG and graphene.

The fracture surfaces of PLA composites are observed by SEM. As shown in Fig. 4a, PLA-PEG exhibits a smooth fracture surface without prominent plastic deformation. Prepared by the direct melt mixing method, PLA-PEG-m-0.25 and PLA-PEG-m-0.50 exhibit relative rough fracture surface (Fig. 4b and c). Compared with PLA-PEG-m-0.25, the stacking of graphene sheets of PLA-PEG-m-0.50 is more serious. With the freezing-drying method to disperse the same graphene content in PLA composites, the fracture surface of PLA-PEG-f-0.25 and PLA-PEG-f-0.50 is more rough (Fig. 4d–f). Taking PLA-PEG-f-0.25 (Fig. 4d and e) as an example, crumpled, wrinkled, or even folded graphene sheets are found well distributed throughout the PLA matrix. Some graphene sheets are found stacking while the majority of graphene sheets are well embedded in the matrix, indicating a good affinity with PLA. The well dispersion of graphene in the PLA matrix and the unique properties of graphene may account for the good mechanical properties of PLA composites.

3.3. The crystallization status of prepared PLA composites

Since PLA is a semicrystalline polymer, the mechanical properties are influenced by the degree of the crystallinity to some extent [28,29]. The melt curves for PLA and PLA composites are shown in Fig. 5 and the crystallinity of PLA composites is calculated using DSC according to related literature [30,31]. With 5 wt % PEG adding into PLA matrix, the cold-crystallization temperature (Tc) is decreased from 92.2 to 85.0 °C. This phenomenon is attributed to the plasticizing effect of PEG. In the heating process, it could be seen that Tg and glass transition temperature (Tg) of PLA composites are increased with the graphene content and better dispersion of graphene, which would reduce the chain mobility of PLA. The crystallinity (Xc) of all samples is calculated using the following equation: Xc = (ΔHm − ΔHcc)/93.6 × 100%, where ΔHm is the melting enthalpy, ΔHcc is the cold crystallization enthalpy, and 93.6 is the melting enthalpy in J/g of 100% crystalline PLA [32]. As listed in Table S1, with 5 wt % PEG introduced into PLA matrix, the crystallinity of PLA-PEG is increased to 6.5%. Compared with PLA-PEG, the crystallinity of PLA-PEG-m-0.05 and PLA-PEG-0.05 is 15.2 and 21.1%, even with only 0.05 wt % graphene. For PLA-PEG-f-0.25, the crystallinity is 24.8%, which is higher than PLA-PEG-m-0.25. The higher crystallinity may be attributed to the better dispersion of graphene sheets.

XRD patterns of PLA-PEG, PLA-PEG-m-0.25, and PLA-PEG-f-0.25 are used to evaluate the crystallization status (see Fig. S1). A broad amorphous peak around 16° indicates an amorphous microstructure of PLA. Compared with PLA-PEG-m-0.25, the intensity of the diffraction peak of PLA-PEG-f-0.25 at 16.8° becomes stronger. The stronger peak is attributed to reflections of a crystal of PLA, which indicates the increased crystallization of PLA-PEG-f-0.25. POM is also used to observe the crystallization morphology of PLA composites. PLA-PEG, PLA-PEG-m-0.25, and PLA-PEG-f-0.25 are firstly heated at 200 °C for 5 min and then cooled to room temperature with 50 °C/min, imitating the crystallization behavior of the samples in the fabrication process. As shown in Fig. 6, compared with PLA-PEG, PLA composites with 0.25 wt % graphene show more crystalline domains and crystallite structure. Since the better dispersion of graphene for PLA-PEG-f-0.25, it has a better heterogeneous nucleating effect than PLA-PEG-m-0.25 (Fig. 6b and c).

The DSC, XRD, and POM results fully indicate that there is some crystalline structure for the prepared PLA composites. The significantly increased elongation-at-break, tensile strength, tensile and bending modulus of PLA-PEG-f-0.05 and PLA-PEG-f-0.25 may be attributed to good dispersion of graphene sheets, effective load transfer across graphene-PLA interface, and the increased crystallinity.

3.4. The isothermal crystallization behaviors of PLA composites

To further observe the crystallization behaviors of different samples, isothermal crystallization is conducted using the POM with hotstage. Here, the morphology evolutions of PLA composites isothermally crystallized at 130 °C are shown in Fig. 7. Only a few nuclei appear in PLA-PEG after 3 min. As comparison, PLA-PEG-m-0.01 and PLA-PEG-f-0.01 show more nuclei after same durations. The morphology differences for PLA-PEG, PLA-PEG-m-0.01 and PLA-PEG-f-0.01 are more obvious after 10 min. Even with only 0.01 wt % graphene, the heterogeneous nucleation ability for PLA

![Fig. 6. POM photographs of the morphology of PLA-PEG (a), PLA-PEG-m-0.25 (b), and PLA-PEG-f-0.25 (c).](Image 62x565 to 274x727)
crystallization is improved. With 0.25 wt % graphene adding into PLA composites, much more nuclei appear in PLA composites after 1 min. Compared with PLA-PEG-m-0.25, PLA-PEG-f-0.25 shows more crystallization after 5 min. This may be attributed to that better dispersed graphene in PLA-PEG-f-0.25 provides more nucleation sites to induce PLA crystallization.

The DSC thermograms of PLA composites (see Fig. S2) at various isothermal crystallization temperatures are adopted to investigate the crystallization rates. The crystallization time to reach the maximum of exothermic peak of isothermal crystallization curve is increased with increasing temperature. With 0.25 wt % graphene adding into PLA-PEG, the time to reach the maximum of exothermic peak for PLA-PEG-f-0.25 and PLA-PEG-m-0.25 is greatly decreased compared with PLA-PEG.

The relative degrees of crystallinity ($X_t$) changing with time at different temperatures are given in Fig. 8. Taking 130 °C as an isothermal crystallization example (Fig. 8a), the half time of crystallization ($t_{1/2}$) for PLA is 19.2 min. With the PLA sample containing 5.0 wt % of PEG, the $t_{1/2}$ for PLA-PEG is decreased to 8.2 min. For the composites prepared using our freezing-dried masterbatch, the $t_{1/2}$ of PLA-PEG-f-0.25 is further decreased to 3.4 min, which is lower than the value of 6.9 min for PLA-PEG-m-0.25. Similar phenomenon is also applied to other temperatures (Fig. 8b–e). It is well known that the formation rate of nuclei and the growth rate of crystals together determine the overall crystallization rate, and the nucleation rate is the dominant factor at high temperatures. The crystallization rates of PLA-PEG-f-0.25 are much higher than PLA-PEG-m-0.25 at higher isothermal crystallization temperatures like 130 °C (Fig. 8a). The results indicate that the freezing-dried masterbatch plays the role of nucleating agents and promotes the nucleation rate significantly.

The Avrami model is used to analyze the isothermal crystallization kinetics of our samples. Nonlinear sections are existed in Avrami plots (see Fig. S3) of PLA, PLA-PEG, PLA-PEG-m-0.25, and PLA-PEG-f-0.25, indicating a secondary crystallization which is caused by the impingement of spherulites in later stage of crystallization process [33]. The Avrami exponent $n$ values determined for these PLA composites are around 2.5–2.7 at experimental temperatures. The values are close to those in related literature [34]. It indicates the initial spherulitic growth, platelike growth over time, and a combination of the two mechanisms. Assuming that the crystallization process of PLA is activated thermally, the activation energy ($\Delta E$), which is closely related to transportation of segments to crystallization surface, could be described by the Arrhenius equation: 

$$\frac{1}{n} \ln K_a(T) = \ln A_0 - \Delta E/(RT_C),$$

where $A_0$ is a temperature independent pre-exponential factor, $K_a(T)$ is the
crystallization kinetic constant, \( \Delta E \) is the activation energy which is closely related to the segment transportation [35]. Fig. 9 shows a plot of \((1/n) \ln K_n(T)\) versus \(1/T\) for PLA, PLA-PEG, PLA-PEG-m-0.25, and PLA-PEG-f-0.25. By calculation, the \( \Delta E \) of PLA is 111.3 kJ/mol while the \( \Delta E \) of PLA-PEG is 76.5 kJ/mol. With 0.25 wt % graphene adding into PLA composites, the \( \Delta E \) of PLA-PEG-m-0.25 and PLA-PEG-f-0.25 is 121.3 and 180.6 kJ/mol. This confirms that graphene sheets of PLA-PEG-m-0.25 and PLA-PEG-f-0.25 in composites interrupt the transportation of adjacent PLA chain segments. However, they still show far higher crystallization rates than PLA and PLA-PEG, which indicates that the heterogeneous nucleation of graphene may be the dominant factor for the overall crystallization rate. Comparing with PLA-PEG-m-0.25, the sample PLA-PEG-f-0.25 has both higher \( \Delta E \) and crystallization rate. The increased segment transportation obstruction and improved nucleation effect further reveal that the graphene in PLA-PEG-f-0.25 has better dispersion than that in PLA-PEG-m-0.25.

3.5. The thermal stability of PLA composites

Fig. 10a shows the TGA curves of PLA and PLA composites. All the composites decompose in a one-step process. Compared with pristine PLA, it is apparent that the TGA curve of PLA-PEG moves to lower temperature with 5 wt % PEG adding into PLA matrix. Compared with PLA-PEG, the TGA curves shift to higher temperatures with the incorporation of graphene. The peak temperature of DTG curve (Fig. 10b) represents the maximum rate of weight losing. This temperature for PLA-PEG-f-0.25 is 382.4 °C, 11.2 °C higher than that of PLA-PEG and close to the decomposition temperature of pristine PLA. Similarly, the samples PLA-PEG-f-0.25 and PLA-PEG-f-0.01 show better thermal stability than PLA-PEG-m-0.25 and PLA-PEG-m-0.01, respectively. The improved thermal stability for composites prepared using freezing-drying masterbatch may be also attributed to the good isolation effect of graphene sheets due to better dispersion.

4. Conclusions

With the freezing-drying masterbatch strategy to disperse graphene sheets in PEG firstly, we prepared PLA composites with graphene sheets well dispersed. Since the excellent dispersion of graphene sheets, effective load transfer across graphene-PLA interface, and induced increased crystallinity, the PLA composites possess better tensile and bending properties as well as thermal stability. The good dispersion of graphene was crucial to the nucleation and crystallization of PLA. The graphene sheets act as fillers which decreases the motion rate of PLA chains while it accelerates the overall crystallization with a nucleating effect. Considering the resultant masterbatch can be easily introduced to fabricate PLA/graphene composites with traditional processing techniques, the environmentally friendly freezing-drying strategy has great potential in the practical applications.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2017.03.031.

References


Fig. 10. TGA curves (a) and DTG curves (b) for PLA and PLA composites.