

Effects of Functionalized Graphenes on the Isothermal Crystallization of Poly(L-lactide) Nanocomposites^{*}

Li-fen Zhao^{**}, Qi Li, Ru-liang Zhang, Xiu-juan Tian and Lei Liu

School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Abstract The effects of graphene oxide (GO) with polar groups and functionalized GO (fGO) with nonpolar groups on the isothermal crystallization of poly(L-lactide) (PLLA) were compared. Functionalized GO was obtained by grafting octadecylamine and characterized by FTIR, WAXD and TGA. Isothermal crystallization kinetics of PLLA/GO and PLLA/fGO nanocomposites were investigated by combining DSC data and Avrami equation. The results showed that fGO could improve PLLA crystallization rate more obviously than GO. By analyzing the morphology obtained from POM, SEM and TEM, it was found fGO with large layer space dispersed better in PLLA and supplied more nucleation sites than GO. Therefore, for the multilayer graphene, increasing the layer spaces is important to improve its dispersion in polymers, which will cause the crystal kinetics changing of polymers.

Keywords: Crystallization; Graphene oxide; Poly(L-lactide).

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INTRODUCTION

With the improving awareness of environmental protection, more and more attentions have been paid to biodegradable polymers in the last decades. In varieties of biodegradable polymers, poly(L-lactide) (PLLA) is very important because of its superior properties of biodegradability, biocompatibility and processing property^[1]. However, some properties of PLLA, such as its brittleness, low crystallization rate and heat deflection temperature, need to be improved to satisfy high performance applications^[2, 3].

Incorporation of nanoparticles is an efficient method for improving the properties of PLLA. Many nanofillers including nano-hydroxyapatite (HA)^[4, 5], montmorillonite (MMT)^[6, 7], carbon nanotube (CNT)^[8], etc. have been used to modify PLLA. In recent years, graphene as a novel nanomaterial has drawn significant interests because of its remarkable mechanical, electrical, and thermal properties^[9–11]. Therefore, many works about the structures and properties of PLLA/graphene nanocomposites were reported^[12–16]. For instance, Kim and Jelong prepared PLLA/exfoliated graphite nanocomposites and improved the mechanical, electrical, and thermal properties of PLLA with a low exfoliated graphite loading^[15].

However, because the intense π - π stacking interaction between graphene platelets and weak interactions with polymers, graphene is easy to agglomerate. In order to overcome the agglomeration of graphene and improve the miscibility with polymer materials, many works have focused on preparation of functional

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^{**} Corresponding author: Li-fen Zhao (赵丽芬), E-mail: lfzhao2009@126.com

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graphene. In the published works, the functional graphene can be classified into two kinds. In the modification of polar polymers, polar groups, such as hydroxyl, epoxy and carboxylic acid groups and isocyanate were often incorporated into graphene. Graphene oxide (GO) with abundant polar oxygen-containing functional groups is a typical kind of functional graphene that was most often used in polar polymers, such as the present discussing polymer of PLLA^[17]. In the modification of nonpolar polymers, alkylamine or silane were often used as compatilizer by grafting onto graphene to improve the miscibility^[18, 19]. For example, alkylamine-functionalized graphene were used to modify polyolefin-based nanocomposites^[20]. An obvious question appears, is this kind of functional graphene with nonpolar groups suitable for modification of polar polymer? If we use this kind of functional graphene, such as, modified by alkylamine which includes methylene chain to prepare composites of PLLA/graphene, what are the changes of structures and properties? However, based on the principle of similarity-intermiscibility, little work were designed on preparing alkylamine functionalized graphene to modify PLLA.

PLLA is a semicrystalline polyester and its crystalline structure has great effects on the properties. Therefore, large amount of works about its crystallization behaviors have been published^[21–23]. For PLLA/graphene or PLLA/GO nanocomposites, there are also some works concerning the crystallization behavior^[24–27]. By virtue of different methods, many investigations found the graphene or graphene oxide could serve as nucleating agents and accelerate the crystallization kinetics of PLLA. Therefore, the aim of this work is to clarify the effects of graphene with nonpolar groups on the crystallization behavior of PLLA. For comparing, the effect of polar graphene oxide was also studied. Thus, GO and functional GO with alkylamine were first prepared and characterized by FTIR, XRD and TGA. Then, the isothermal crystallization kinetics was studied by combining DSC data and Avrami equation. By virtue of POM, SEM and TEM, the reasons of the difference of crystallization kinetics were discussed. The results obtained are expected to help us to design nanocomposites with new ideas.

EXPERIMENTAL

Materials

PLLA with $M_w = 250000$ was provided by Nature-works and purified by dissolution and precipitation. First, the PLLA was dissolved in tetrahydrofuran (THF), then precipitated from methanol, and dried thoroughly under vacuum before investigation. Natural graphite with a particle size of 400 meshes was purchased from the Qingdao Zhongtian Company. Octadecylamine was obtained commercially from Aladdin-Reagent Company.

Preparation of GO and Octadecylamine-functionalized Graphene (fGO)

GO was synthesized according to the modified Hummers' method^[28, 29] from natural graphite in our own laboratory and the AFM images were shown in our previous reports^[17]. GO were first dispersed in DMF *via* ultrasonication for 3 h. Then octadecylamine was added slowly and followed by grafting reaction which was refluxed for 24 h at 100 °C. The precipitate was purified by repeating dispersion in ethanol and filtration through a 0.2 μm PTFE membrane. The filtered product was dried in a vacuum oven at 60 °C for 24 h, then the octadecylamine-functionalized graphene oxide was obtained and denoted as fGO.

Preparation of PLLA Nanocomposites

The PLLA nanocomposites were prepared by solution mixing. A given weight of GO or fGO was dispersed in THF by ultrasonication (Scientz-IIID) for 90 min at room temperature. A certain amount of PLLA was also dissolved in THF. Then PLLA solution and GO or fGO suspension were mixed together at certain ratios and magnetically stirred until they formed a homogenous mixture. Then the solvent was evaporated at 40 °C for 2 h and the mixture was further dried in vacuum at 40 °C for one week to drive off residual solvent. The PLLA nanocomposites with the weight composition of PLLA/0.2%GO (PLLA/0.2GO), PLLA/0.5%GO (PLLA/0.5GO), PLLA/1%GO (PLLA/1GO), PLLA/0.2%fGO (PLLA/0.2fGO), PLLA/0.5%fGO (PLLA/0.5fGO) and PLLA/1%fGO (PLLA/1fGO) were prepared.

Characterization of GO and fGO

The FTIR spectra were collected over the wave number range 400–4000 cm^{-1} using a FTIR spectrometer (Nicolet 380). The WAXD patterns were recorded on a Rigaku D/Max2500PC diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation (wavelength $\lambda = 0.154$ nm, 40 kV, and 110 mA) in the 2θ range from 4° to 30° with scanning steps of 0.02° .

Characterization of Nanocomposites

Differential scanning calorimetry

A Mettler-Toledo differential scanning calorimeter (DSC) (TGA/DSC1/1600LF) under nitrogen at a flow rate of 20 mL/min was used to characterize the crystallization behavior and T_g data. Because the crystallization rate of PLLA during isothermal melt crystallization is very low, isothermal cold crystallization procedures were studied. The samples were first melted at 190°C for 3 min and then quenched to 25°C . After holding at 25°C for 1 min, the samples were then heated to the isothermal crystallization temperature for cold crystallization.

Polarized optical microscopy

A POM (Nikon Optiphot-2) equipped with a charge-coupled device (CCD) digital camera was used to observe the crystallization morphology. The samples were prepared by casting the nanocomposite solutions with a concentration of 0.01 g/mL on a covered glass slide (20 mm $\times$ 20 mm). After the solvent was volatilized, the samples were melted on a hot stage at 190°C for 3 min and then transferred onto another hot stage at 120°C for isothermal crystallization. After a certain time, the POM images were taken at room temperature.

Scanning electron microscopy

Scanning electron microscopy (SEM) investigation was performed using a Nova Nano SEM 450 scanning electron microscope (FEI Co., Ltd.) with an acceleration voltage of 5 kV. The sample was cryogenically broken in liquid nitrogen and was coated with gold in vacuum before observation.

Transmission electron microscopy

The morphology of GO and fGO in PLLA was studied by transmission electron microscopy (TEM) using a JEOL JEM-2100F microscope with an acceleration voltage of 200 kV. PLLA/0.5GO and PLLA/0.5fGO was dispersed in THF by ultrasonication. Then the dispersions were dripped onto copper grids for observation.

Wide angle X-ray diffraction

To study the crystallization structure of nanocomposites, the WAXD patterns were recorded on the same diffractometer as used in testing GO and fGO. The samples were prepared by melting at 190°C and then transferred quickly to ice water. After 1 h, the samples were transferred into an oven at 120°C for 72 h to finish an isothermal cold crystallization. Finally, the crystallization structure was studied by WAXD as the same steps as characterization of GO and fGO.

Thermogravimetric analysis

Thermo gravimetric analysis (TGA) measurements were done on a Mettler-Toledo simultaneous thermogravimetric analyzer (TGA/DSC1/1600LF). Sample weights about 10 mg were used for all analyses. Analyses were carried out from 100°C to 800°C , using a heating rate of 5 K/min to avoid the errors brought by rapid expansion of GO at a fast heating rate. All TGA analyses were carried out under a nitrogen atmosphere with a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Characterization of GO and fGO

FTIR was used to testify the chemical structure of pristine GO and alkylamine grafted GO (fGO) (as shown in Fig. 1). There are four major characteristic peaks including a broad peak at 3440 cm^{-1} (O—H stretching vibration), and peaks at 1720 cm^{-1} (C=O stretching), 1624 cm^{-1} (C=C stretching vibration) and 1070 cm^{-1} (C—O—C stretching in epoxy group) in GO spectrum. After being functionalized by octadecylamine, the

characteristic peaks of carbonyl (1720 cm^{-1}), hydroxyl (3440 cm^{-1} and 1624 cm^{-1}) and epoxide groups (1070 cm^{-1}) disappeared, indicating GO was reduced. The appearance of 1530 cm^{-1} (N—H bending vibration) and 1214 cm^{-1} (C—N stretching vibration) bands implied that amine was grafted to GO. The two intense peaks at 2920 cm^{-1} (C—H asymmetric stretching) and 2852 cm^{-1} (C—H symmetric stretching) confirmed that the long chain alkylamine was grafted to GO successfully.

WAXD was further used to testify the structure of GO and fGO. It can be found from Fig. 2, there is only one characteristic peak at 11.2° of GO corresponding to the inter layer spacing of 0.79 nm . The increase of d value compared to pristine graphene (0.34 nm)^[17] indicated the graphene was oxidized completely. After functionalization by alkylamine, there appeared two new peaks at 4.82° and 20.76° , corresponding to the inter layer spacings of 1.82 nm and 0.43 nm , respectively. The first peak with large d value indicates the interaction and covalent linkage of alkylamine onto GO. The peak at 20.76° indicates the reduction effects of GO during the functional reaction with alkylamine. However, because of the existence of alkylamine, the inter layer spacing is still larger than that of pristine graphene. The results of WAXD are in agreement with previous results obtained by FTIR. Both of them indicated the alkylamine was grafted to GO successfully, as well as the reduction of GO.

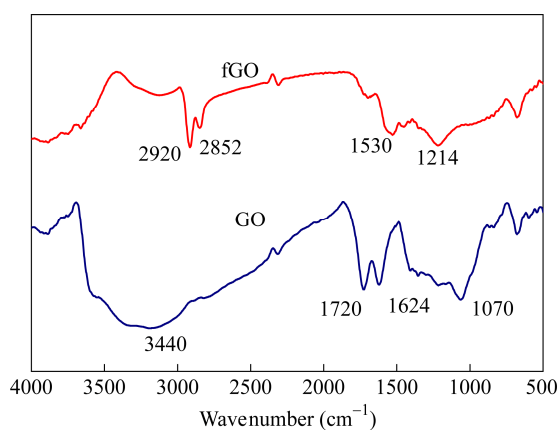


Fig. 1 FTIR spectra of GO and octadecylamine-functionalized GO in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$

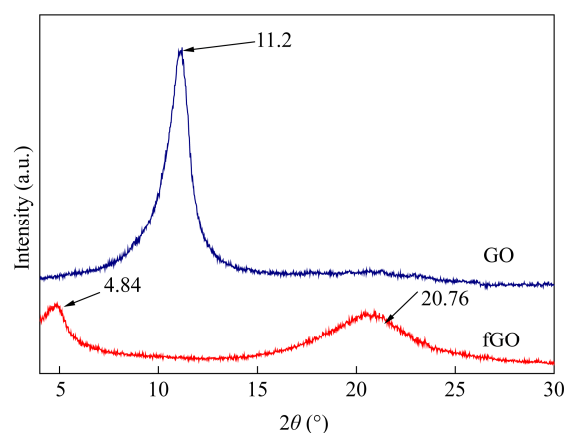


Fig. 2 The WAXD patterns of GO and octadecylamine-functionalized GO

To further determine the quantity of alkylamine in the fGO samples, thermogravimetric analysis measurements were done as shown in Fig. 3. For GO sample, TGA showed about 30% weight loss in the temperature range of 160°C to 210°C which can be attributed to degradation of oxygen groups of GO. While most of the weight loss (about 40%) for fGO is in the temperature range of 200°C to 500°C and the weight loss is related with the degradation of alkylamine. The total weight loss of GO at 700°C is 49.9% and that of fGO is 37.2%. This 12.7% difference in weight loss can be determined as the quantity of alkylamine, which was grafted onto the GO sheets^[30].

Isothermal Crystallization of PLLA and PLLA Nanocomposites

To investigate the effects of GO and fGO on the crystallization behaviors of PLLA, the isothermal crystallization kinetics of neat PLLA, PLLA/0.5GO and PLLA/0.5fGO samples in the temperature range of 120°C to 130°C was first studied by DSC. Considering that the melt crystallization rate of PLLA is very slow, the isothermal cold crystallization process was adopted in this work. Figure 4 shows the relative crystallinity (X_t) versus crystallization time for neat PLLA, and PLLA/GO composites. It can be found that for the same sample, the crystallization rate decreased with increasing isothermal crystallization temperature in the studying temperature ranges. The reason can be attributed to the decreasing of nucleation rate with increasing crystallization temperature.

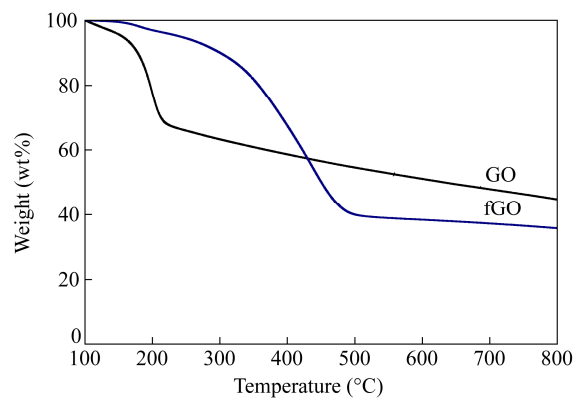


Fig. 3 TGA curves of GO and fGO

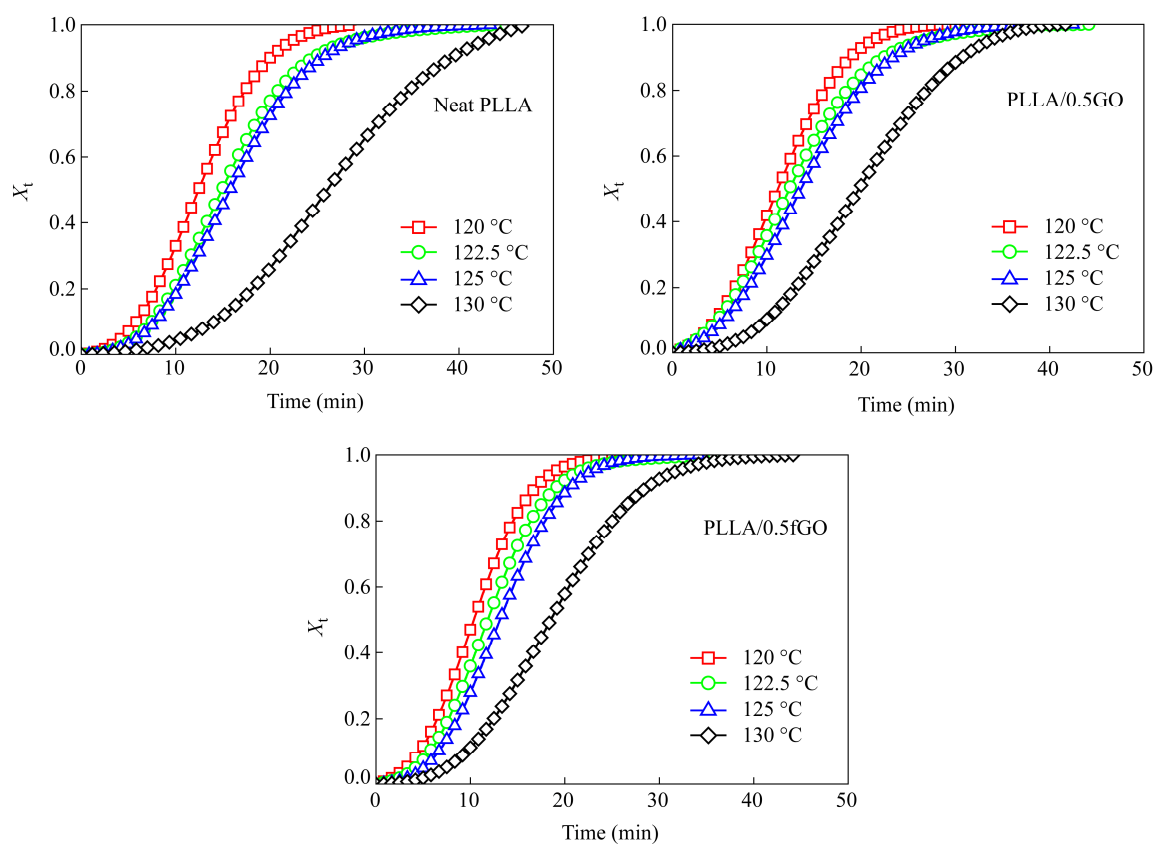


Fig. 4 Plots of relative degree of crystallinity versus crystallization time at different temperatures for PLLA, PLLA/0.5GO and PLLA/0.5fGO

But for the different samples of PLLA/GO composites, the difference of crystallization kinetics needs to be analyzed by Avrami equation^[31, 32] (as shown in Eq. 1).

$$1 - X_t = \exp(-kt^n) \quad (1)$$

In Eq. (1), X_t represents the relative crystallinity, k is crystallization rate constant and n is the Avrami index which depends on the spatial dimensions of crystal growth and nature of nucleation. Figure 5 is the Avrami plots of neat PLLA and PLLA/GO composites. The parameters k , n and $t_{0.5}$ calculated from Eqs. (1) and (2) are listed in Table 1.

$$t_{0.5} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (2)$$

The values of n of all the samples are all between 2.0 to 2.8 and they have very small difference, which indicates that the incorporation of GO and fGO does not change the crystallization mechanism of PLLA.

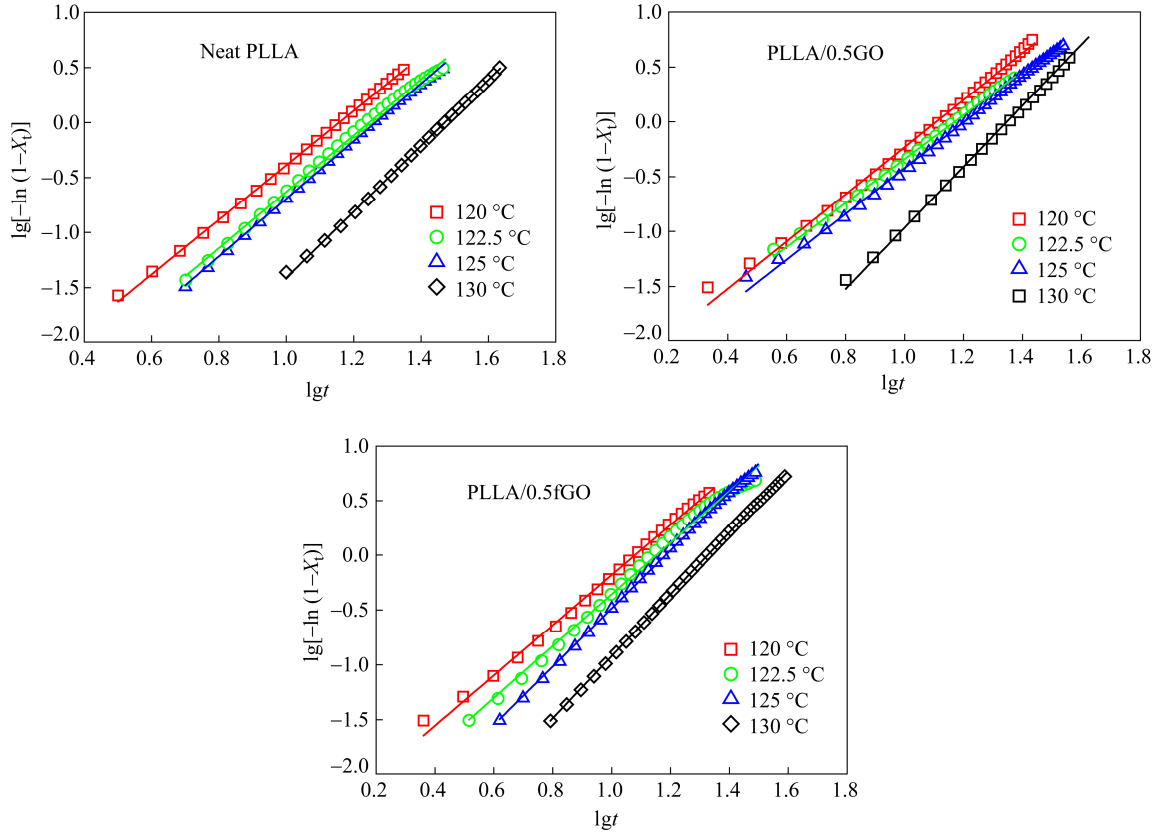


Fig. 5 Avrami plots of neat PLLA, PLLA/0.5GO and PLLA/0.5fGO

Table 1. Isothermal crystallization kinetics parameters of neat PLLA, PLLA/0.5GO and PLLA/0.5fGO obtained by Avrami fit

Samples	T_c (°C)	n	K (min ⁻ⁿ)	$t_{0.5}$ (min)
Neat PLLA	120	2.4	1.7×10^{-3}	12.2
	122.5	2.6	6.2×10^{-4}	15.1
	125	2.6	5.5×10^{-4}	16.3
	130	2.6	1.6×10^{-4}	26.6
PLLA/0.5GO	120	2.2	4.2×10^{-3}	10.8
	122.5	2.0	4.6×10^{-3}	12.3
	125	2.1	3.1×10^{-3}	13.3
	130	2.6	3.2×10^{-4}	19.5
PLLA/0.5fGO	120	2.29	3.4×10^{-3}	10.2
	122.5	2.50	1.5×10^{-3}	11.8
	125	2.64	7.6×10^{-4}	13.2
	130	2.76	2.2×10^{-4}	18.4

However, according to the value of $t_{0.5}$, the crystallization rate varied obviously with addition GO and fGO. For neat PLLA, $t_{0.5}$ is 26.6 min while that of PLLA/0.5GO and PLLA/0.5fGO is 19.5 min and 18.4 min respectively. It was reported by Kim *et al.*^[12], that GO had heterogeneous nucleation effects on the crystallization behaviors of PLLA. As a consequence, it is believed the reason about the increasing of crystallization rate could be ascribed to heterogeneous nucleation effects of nanofiller. An interesting thing is that the difference of crystallization rate for PLLA/0.5GO and PLLA/0.5fGO samples. From Table 1, it can be found that PLLA/0.5fGO sample shows a faster crystallization rate than PLLA/0.5GO at every isothermal crystallization temperature, which suggests the different effects of GO and fGO on the crystallization behavior of PLLA.

Therefore, the morphology of composites after crystallization was further investigated to analyze these effects. POM images of the samples after isothermal crystallization at 120 °C for 24 h are shown in Fig. 6. It can be observed that although all the samples forms spherulites with Maltese-cross, the spherulite diameters of composites are obviously smaller than those of neat PLLA. For example, the diameter of neat PLLA spherulites is about 40 μm , while that of PLLA/0.2GO and PLLA/0.2fGO is about 30 μm and 20 μm respectively. With increasing the weight ratio of GO and fGO to 0.5%, as shown in Figs. 6(a₂) and 6(b₂), the spherulites became smaller. The decreasing of spherulites size suggests that GO and fGO has nucleation effect on PLLA crystallization. Additionally, the spherulites in PLLA/fGO are smaller than those in PLLA/GO with the same composition which indicates fGO can supply more nucleation sites than GO. The POM images of PLLA/GO and PLLA/fGO after crystallization at 120 °C for 1 h were further gathered to investigate the different nucleation effects, as shown in Fig. 7. In the same composition, it can be found that PLLA/fGO forms lager number of nucleation sites than that of PLLA/GO.

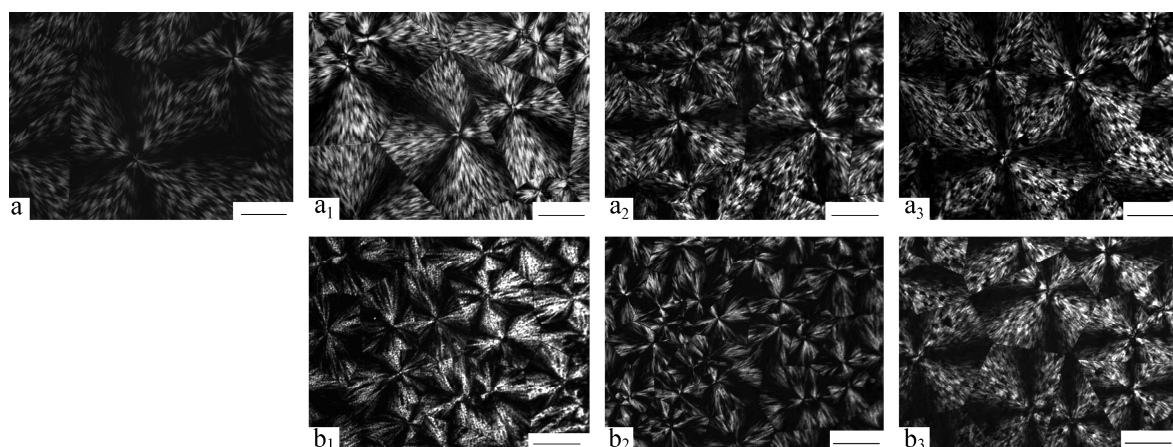


Fig. 6 Polarized optical micrographs of neat PLLA, PLLA/GO and PLLA/fGO with different compositions after isothermal crystallization at 120 °C for 24 h: (a) neat PLLA, (a₁) PLLA/0.2GO, (a₂) PLLA/0.5GO, (a₃) PLLA/1GO, (b₁) PLLA/0.2fGO, (b₂) PLLA/0.5fGO and (b₃) PLLA/1fGO (The scale bars are 10 μm .)

However, when the ratio of GO and fGO increased to 1% (Figs. 6a₃ and 6b₃), the spherulites of composites is not smaller than that of composites with 0.5% GO and 0.5%fGO. Additionally, the number of spherulites per area in PLLA/1GO and PLLA/1fGO is smaller than that in samples with less GO and fGO. As seen in Figs. 7(a₃) and 7(b₃), some spherulite centers became black as arrow labeled. It suggests when the composition of GO and fGO is too high, both of them will aggregate and the aggregated GO or fGO will serves as nucleation sites. The image of PLLA/1fGO obtained by optical micrograph with parallel light (see Fig. S1) showed more clearly that large pieces of fGO gathered in the spherulite centers and supported less nucleation sites. Therefore, the diameters and numbers of spherulites did not change linearly as shown in Fig. 6 and Fig. 7. However, in any case, fGO can supply more nucleation sites than GO.

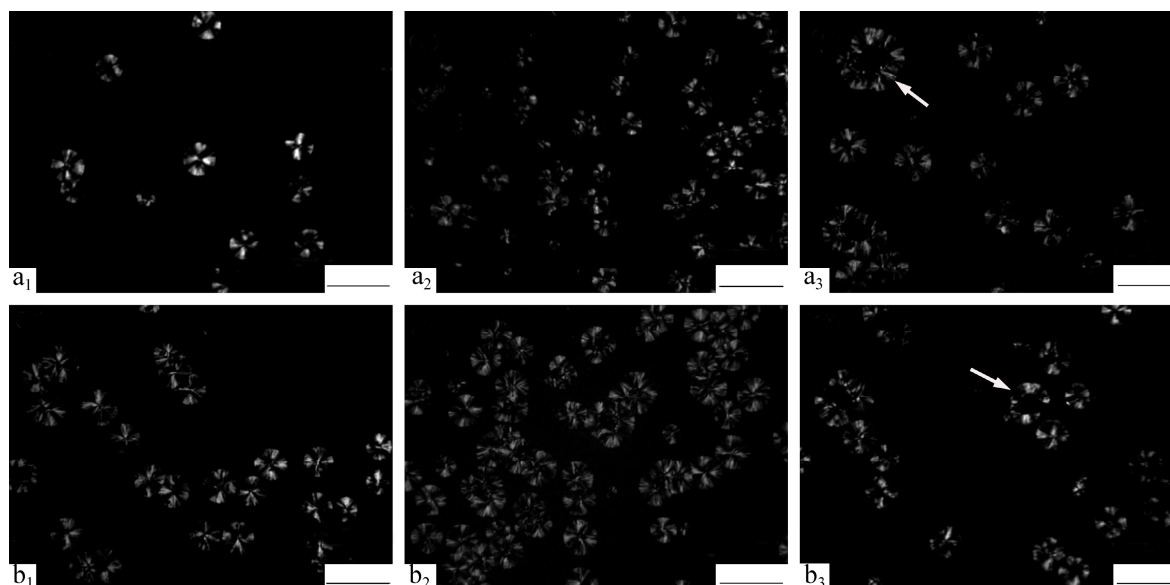


Fig. 7 Polarized optical micrographs of neat PLLA, PLLA/GO and PLLA/fGO with different compositions after isothermal crystallization at 120 °C for 1 h: (a₁) PLLA/0.2GO, (a₂) PLLA/0.5GO, (a₃) PLLA/1GO, (b₁) PLLA/0.2fGO, (b₂) PLLA/0.5fGO and (b₃) PLLA/1fGO (The scale bars are 10 μ m.)

According to the previous FTIR result, there are only long chain alkyalamine on the surface of fGO, which is not good to the dispersion of GO in PLLA. While the carbonyl group, hydroxyl and epoxide groups on the surface of GO will improve the interaction of GO and PLLA. Then, why could fGO afford so many nucleation sites? SEM was used to observe the fracture surface morphologies of PLLA/0.5GO and PLLA/0.5fGO (seen in Fig. 8). It can be observed aggregation of GO and fGO appears in both samples (Figs. 8a and 8c). However, the number of layers of GO in PLLA/0.5GO is more than that of fGO in PLLA/0.5fGO. Additionally, the size of GO regions in PLLA/0.5GO reaches 13 μ m because of aggregation, while that of fGO is about 1.5 μ m. It suggests again that GO is easier to aggregate than fGO in the composites.

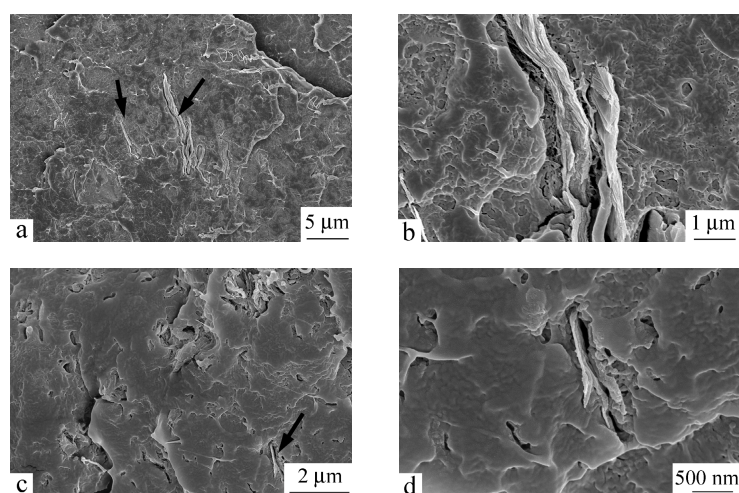


Fig. 8 SEM images of fracture surfaces of PLLA/0.5GO and PLLA/0.5fGO: (a) PLLA/0.5GO, (b) an enlargement of the arrow labeled region of (a), (c) PLLA/0.5fGO and (d) an enlargement of the arrowed labeled part of (c)

Figure 9 is the TEM images of PLLA/0.5GO and PLLA/0.5fGO cast ultrathin films. As seen, in both samples, the aggregations of GO and fGO are not very serious. By comparison of the morphology in big magnification (Figs. 9b and 9d), it still can be found that the wrinkling side in PLLA/0.5GO is thicker than that of PLLA/0.5fGO which implies again that fGO dispersed better than GO. Therefore, the dispersion of GO and fGO in PLLA is not in accordance with our inference which only based on the interactions of chemical groups. In spite of the great difference of polarity between long chain alkyalamine and PLLA, the large layer space can still guarantee the dispersion of fGO in PLLA. Thus, with the same weight composition of nanofiller in composites, the well dispersed fGO supplies more heterogeneous nucleation sites.

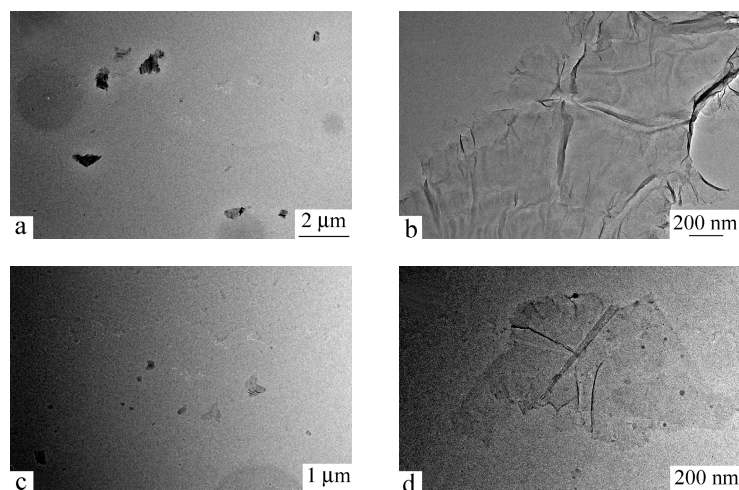


Fig. 9 TEM images of PLLA/0.5GO and PLLA/0.5fGO cast films: (a) and (b) PLLA/0.5GO, (c) and (d) PLLA/0.5fGO

To further verify this kind of phenomenon, the isothermal crystallization curves at 125 °C of PLLA/GO and PLLA/fGO with different compositions were gathered by DSC (Fig. 10). The crystallization rate can be compared roughly according to the time of exothermic peak (t_p). It can be observed that PLLA/GO and PLLA/fGO have smaller t_p values than that of the neat PLLA sample. Besides that, the t_p values of PLLA/fGO with different compositions are all smaller than those of PLLA/GO. For example, the t_p value of PLLA/0.2fGO is 8.7 min, while that of PLLA/0.2GO is 11.9 min. Therefore, it can be concluded that PLLA/fGO has a faster crystallization rate than PLLA/GO under the same condition, which is in accordance with the previous

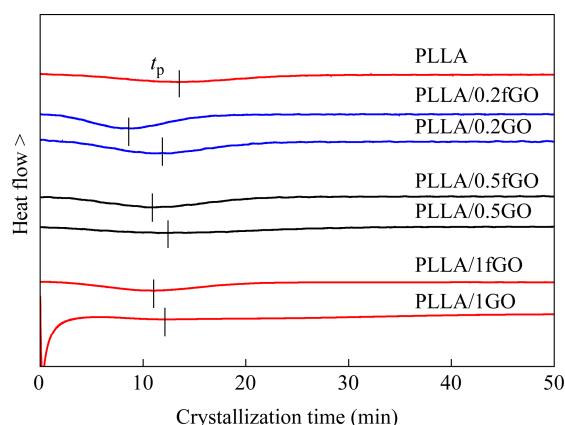


Fig. 10 Heat flow versus time for the isothermal crystallization of PLLA/GO and PLLA/fGO with different weight ratios at 125 °C

conclusions obtained from kinetics investigation about PLLA/0.5GO and PLLA/0.5fGO samples. An interesting thing that should be noted is that by comparing the t_p values of PLLA/GO and PLLA/fGO with different compositions, it can be observed that the t_p values increases with increasing the ratios of GO or fGO. It may be related with the effects of dispersion, nucleation and confined crystallization due to GO or fGO, which needs further investigation.

The crystal structure of PLLA, PLLA/GO and PLLA/fGO formed at 120 °C were further studied by WAXD (Fig. 11). It can be found that all the samples show two characteristic diffraction peaks at 16.7° and 19.0°, which correspond to (200)/(110) and (203) crystal planes, respectively^[27]. It indicates that both GO and fGO can not change the crystal structure of PLLA.

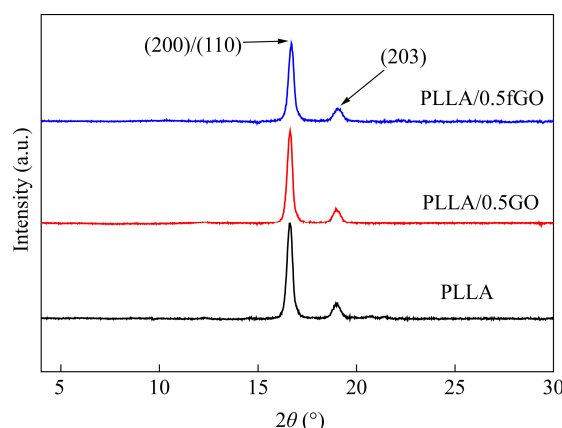


Fig. 11 WAXD patterns of neat PLLA, PLLA/0.5GO and PLLA/0.5fGO films after isothermal crystallization at 120 °C for 72 h

CONCLUSIONS

GO and fGO were prepared and their effects on the isothermal crystallization of PLLA were investigated. According to the FTIR, WAXD and TGA results, the alkylamine was grafted to GO and the GO was reduced. Therefore, GO with polar groups and fGO with nonpolar groups were obtained. Their effects on the isothermal crystallization kinetics of PLLA were compared by DSC. The results showed that fGO could improve PLLA crystallization rate more obviously than GO. By virtue of POM, SEM and TEM, the reason was determined as that fGO with larger layer space dispersed well in PLLA and supplied more nucleation sites than GO. Therefore, for the multilayer graphene, increasing the layer spaces is also important to improve its dispersion in polymer, as well as decreasing the difference of polarity.

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