

Crystallization Behavior of Poly(ϵ -caprolactone)/Graphite Oxide Composites

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Received 3 April 2007; accepted 9 June 2007

DOI 10.1002/app.26976

Published online 7 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of poly(ϵ -caprolactone) (PCL)/graphite oxide (GO) composites were synthesized through the ring-opening polymerization of ϵ -caprolactone with GO as an initiator. The crystallization behavior of the PCL–GO composites and the effects of the PCL–GO composites as nucleation agents on the crystallization behavior of PCL were also studied. The introduction of GO as PCL–GO composites shortened the crystallization half-time for both the

isothermal crystallization and nonisothermal crystallization of PCL, and this clearly indicated that GO in the PCL–GO composites had a great nucleating effect on the crystallization of pure PCL. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4225–4232, 2007

Key words: biodegradable; crystallization; nucleation; polyesters; spherulites

INTRODUCTION

Recently, polymer nanocomposites based on organophilic layered materials have aroused much interest because these composites have unexpected properties, such as large increases in the thermal stability and mechanical strength.¹ Several articles have been published on the synthesis and properties of composites of biodegradable polymers and layered organic materials.^{2–4} Among those organic and biodegradable composites, polymer composites with graphite oxide (GO) have been reported many times and have gained much attention because of their novel properties, such as excellent thermal properties⁵ and electrical conductivity properties.³

GO is a layered material produced by the oxidation of graphite.⁶ It has a large number of polar groups, such as hydroxyl, epoxide, ether, and carboxylate groups, on the surface of the graphite layers, and they make GO hydrophilic,⁷ thus facilitating GO hydration and exfoliation in aqueous media. Because of the water solubility of GO, for many polymer–GO composites, water-soluble polymers are used, and an intercalated structure has been achieved in polymer–GO composites.⁸ For example, poly(aniline-*co*-*o*-anisidine)-intercalated GO composites³ have higher electrical conductivity than pristine GO. Furthermore, GO has been reported to improve the thermal stability of

poly(vinyl alcohol).⁵ Pan et al.⁹ revealed that GO enhanced the mechanical properties of nylon 6.

Following these successful investigations, we expect to use biodegradable polymers such as poly(ϵ -caprolactone) (PCL), starch, and polylactide, which are of interest for disposable packaging applications for environmental reasons. Actually, biodegradable polymers reinforced by GO have been reported. Among the few biodegradable polymers, as one of the commercially available biodegradable polymers, PCL has attracted a lot of attention.¹⁰ PCL is a typical biodegradable aliphatic polyester. It is fully biodegradable, biocompatible, and nontoxic to living organisms.¹¹ Also, PCL has good resistance to water, oil, solvents, and halogens. The unique properties of PCL give it high potential in biomedical fields, and it has been used in the development of controlled drug delivery systems and in surgical sutures and other resorbable fixation devices.^{11,12} However, the applications for the polymer is limited because of its deficiencies in thermal stability, mechanical properties, and barrier properties to water and gases.^{2,10}

GO originates from natural graphite and acts as an excellent host matrix for the interlayer accommodation of long-chain aliphatic hydrocarbons,¹³ and it is expected to be a suitable filler to improve the mechanical and thermal properties of PCL. Furthermore, PCL and its GO composites (PCL–GO) can afford an exfoliated structure, in which the individual graphite sheets are dispersed in the PCL polymer matrix. The synthesis of PCL–GO composites with GO hydroxyl groups as initiators via the ring-opening polymerization (ROP) of ϵ -caprolactone and their characterization

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TABLE I
Composition and Gel Permeation Chromatography Data for the PCL–GO Composites

Sample	GO (g)	ϵ -Caprolactone (g)	GO (wt %)	M_n (g/mol)	M_w/M_n	M_n arm
PCL–GO0.5	0.05	10	0.5	25,800	1.56	11,400
PCL–GO1.5	0.15	10	1.5	22,200	1.46	9,120
PCL–GO6	0.6	10	6	16,900	1.42	6,600

M_n , number-average molecular weight; M_w , weight-average molecular weight.

have been reported in our previous work.¹⁴ In this article, we primarily investigate the crystallization kinetics of PCL–GO composites and their effect as nucleating agents on the crystallization of pure PCL.

EXPERIMENTAL

Materials

The graphite (lot M4P3193) and potassium permanganate (lot M5E9617) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan), and used as received. Sulfuric acid (>96%), nitric acid, hydrogen peroxide, and tin 2-ethylhexanoate were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and used as received. ϵ -Caprolactone was purchased from Kanto Chemical and distilled over CaH_2 before use. PCL (molecular weight $\approx 20,000$) was also purchased from Kanto Chemical and used for comparison with synthesized samples.

Preparation of GO

The GO samples were prepared with a modification of the method proposed by Brodie.¹⁵ Graphite powder (5 g) was put into a 500-mL flask containing 68% nitric acid (33 mL) and sulfuric acid (>96%, 200 mL) and stirred for 30 min in an ice bath, and then potassium permanganate (30 g) was added to the solution. The solution temperature was raised gradually to about 40°C and maintained for 30 min at this temperature, and then the excess potassium permanganate was removed by a treatment with hydrogen peroxide and washed many times with boiled distilled water; at last, the product (GO) was obtained by centrifugation at 11,000 rpm for 20 min and dried in a vacuum at 50°C for 3 days. To hydrolyze the epoxy groups, the parent GO was thermally treated in a vacuum oven at 100°C for 3 h.¹⁶

Synthesis of the PCL–GO composites

The polymerization of ϵ -caprolactone was carried out via ROP with the OH groups on the surface of GO as initiators of the ROP according to a method reported in our previous work.¹⁷ The ROP was catalyzed by tin 2-ethylhexanoate (0.5 g). In a typical experiment, the desired amount of GO (0.05 g, 0.15 g, 0.6 g) was suspended in ϵ -caprolactone (10 g) by sonication for 30

min. Then, the suspension including GO, tin 2-ethylhexanoate, and ϵ -caprolactone was transferred to a three-necked flask (previously dried in a vacuum oven at 140°C), and the flask was capped and heated at about 120°C for 20 h under vigorous stirring to afford a black, solid product. The obtained solid was separated by an ultracentrifugation at 110,000 rpm for 20 min and precipitated in chloroform/ethanol three times to afford a gray solid. The details of the sample composition are shown in Table I.

Blend sample preparation

To investigate the effects of PCL–GO composites as nucleation agents on the crystallization of PCL, a blend sample of PCL–GO1.5 (1.5 wt % GO) was prepared, with chloroform as a common solvent. Conventional blends of PCL with 2, 5, 10, and 20 wt % PCL–GO6 composites were prepared via solution casting with chloroform as a common solvent.

Characterization

Differential scanning calorimetry (DSC) analysis

The nonisothermal and isothermal crystallization were investigated on a Pyris Diamond differential scanning calorimeter (PerkinElmer, Tokyo, Japan) with nitrogen as the purge gas. Samples with a weight of 5–7 mg were packed in the aluminum sample pans. For the isothermal crystallization, after melting at 100°C for 3 min, the samples were quenched to the desired crystallization temperature at a cooling rate of 100°C/min and were kept at the crystallization temperature for 60 min. The melt nonisothermal crystallization temperature was measured through crystallization from the melt on the Pyris Diamond differential scanning calorimeter; the sample was directly heated to 100°C in the DSC cell and held for 2 min, and this was followed by cooling at a rate of 10°C/min until the completion of the melt crystallization. The peak temperature of the DSC melt crystallization curve was recorded as the melt nonisothermal crystallization temperature. On the basis of the DSC curve, the effectiveness of the nucleating agents was evaluated, and the crystallization kinetics of PCL were analyzed for a series of PCL–GO composites and PCL/PCL–GO6 blends.

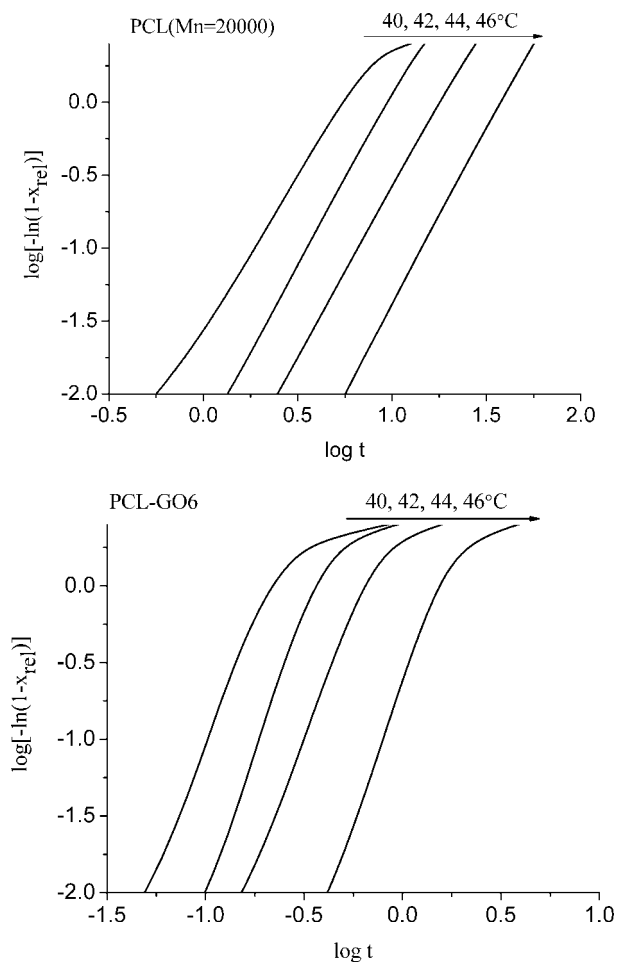


Figure 1 Isothermal kinetic curves for PCL-GO6 and PCL.

Measurements of the spherulitic growth rate by polarized optical microscopy (POM)

The growth of spherulite crystals was followed with a BX50 polarized light microscope (Olympus, Tokyo, Japan) equipped with a Mettler FP82HT hot stage (Mettler Württ, Germany). Samples weighing 2 mg were placed in the hot-stage sample holder between a microscope glass slide and a cover slip. The samples were heated to 100°C and held at this temperature for 3 min, and then they were cooled to the desired crystallization temperature at a cooling rate of 20°C/min.

RESULTS AND DISCUSSION

Isothermal crystallization

The isothermal crystallization of polymers can be described by an Avrami equation. The relative degree of crystallinity (X_{rel}) at time t is given by¹⁸

$$X_{rel} = \frac{X_c(t)}{X_c(\infty)} = \int_0^t \frac{dH(t)}{dt} dt / \int_0^\infty \frac{dH(t)}{dt} dt \quad (1)$$

where $X_c(t)$ and $X_c(\infty)$ are the degrees of crystallinity at time t and at the end of crystallization, respectively,

and $dH(t)/dt$ is the rate of heat flow in the process of isothermal crystallization at time t . Time t was measured from the moment when the sample was cooled to the appropriate crystallization temperature. The value of X_{rel} can be obtained with the following expression:^{18,19}

$$1 - X_{rel} = \exp(-Kt^n) \quad (2)$$

where n is the Avrami exponent, which is determined by the mode of crystal nucleation and crystal growth geometry in the actual circumstances, and K is the parameter of the isothermal crystallization rate. Taking a double logarithm of eq. (2) gives

$$\log[-\ln(1 - X_{rel})] = n \log t + \log K \quad (3)$$

The plot of $\log[-\ln(1 - X_{rel})]$ versus $\log t$ gives a linear line, whose slope and intercept on the ordinate are n and $\log K$, respectively. In the experiments of isothermal crystallization at time t , $dH(t)/dt$ was recorded and then integrated against time t to give the values of $X_c(t)$ and $X_c(\infty)$. When X_{rel} is 0.5 in eq. (3), the crystallization half-time ($t_{1/2}$), which is the time taken for 50% of the total volume crystallization, is

$$t_{1/2} = \left(\frac{\ln 2}{K} \right)^{1/n} \quad (4)$$

Plots of $\log[-\ln(1 - X_{rel})]$ versus $\log t$ are shown in Figure 1. Each curve shows an initial linear portion in an early stage of crystallization.^{20,21} Also, for the two samples given, all the curves of the isothermal kinetics are almost parallel to one another. This indicates that the crystallization mechanism for the samples, at different crystallization temperatures, is the same. The values of n and K were determined from the initial linear portion in Figure 1 and are listed in Table II. Avrami exponent n of pure PCL and the PCL-GO6 composite is between 2 and 3. According to the Avrami equation, in the ideal state of nucleated crystallization for three-dimensional crystallization growth, the n value should be exactly 3.¹⁸ In the actual process of crystal growth, however, the practical cir-

TABLE II
Values of Avrami Parameters n , K , and $t_{1/2}$ for the Isothermal Crystallization of PCL in Its Pure State and the PCL-GO6 Composite

Sample	Crystallization temperature (°C)	n	K (min ⁻ⁿ)	$t_{1/2}$ (min)
Pure PCL	40	2.11	0.02742	4.62
	42	2.29	0.00552	8.25
	44	2.27	0.00135	15.63
	46	2.4	0.00049	20.5
PCL-GO6	40	2.86	70.27324	0.2
	42	3.22	24.79134	0.33
	44	3.08	3.52371	0.59
	46	3.19	0.21257	1.45

cumstance cannot satisfy the ideal state that the Avrami equation is supposed to have, causing the deviation of the n value from 3. For both pure PCL and the PCL-GO6 composite, the depression of the n value is probably attributable to the existence of thermal crystallization during the crystallization process.

For the pure PCL and PCL-GO6 composite samples, the value of K increases as the crystallization temperature decreases, whereas the $t_{1/2}$ value increases as the temperature increases. These results indicate that with an increasing crystallization temperature, the crystallization rate decreases. This can be explained by the fact that the melt crystallization exhibits the temperature dependence that is characteristic of nucleation-controlled crystallization associated with the proximity of the melting temperature. In addition, at, for example, 44°C, the $t_{1/2}$ value of the PCL-GO6 composite is much lower than the value of pure PCL; obviously, this means that GO in the PCL-

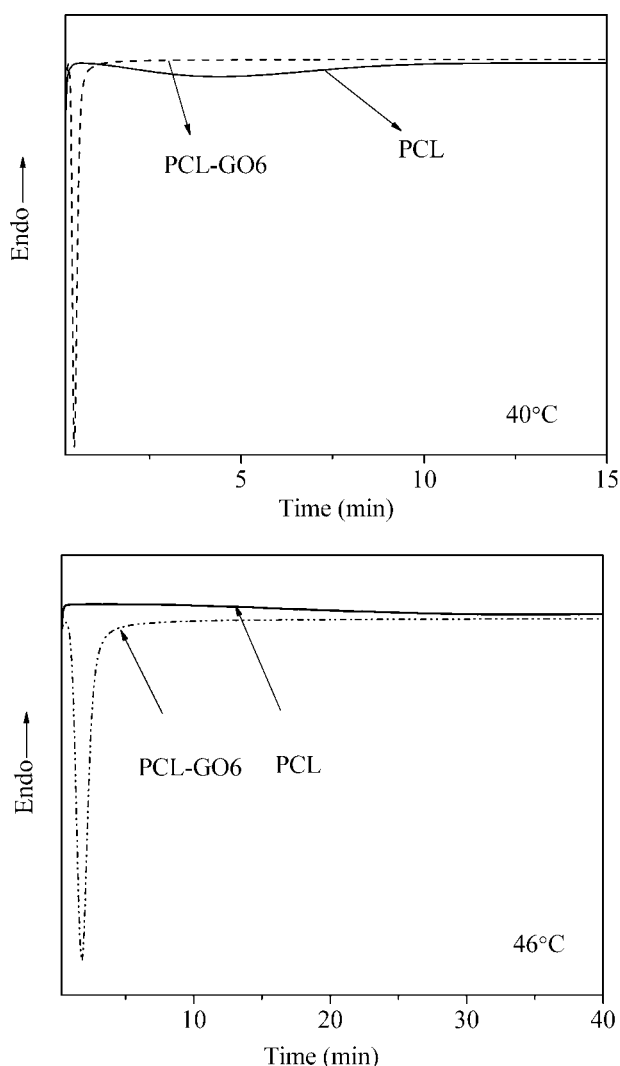


Figure 2 DSC isothermal crystallization curves of PCL-GO6 and PCL at 40 and 46°C.

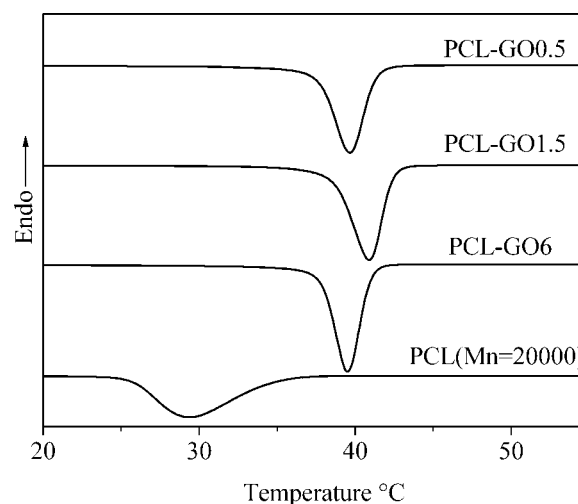


Figure 3 DSC cooling curves of PCL-GO0.5, PCL-GO1.5, PCL-GO6, and PCL. The cooling rate was 10°C/min.

GO composite has a great effect as a nucleating agent on the crystallization of pure PCL and makes the crystallization process very fast.

Figure 2 shows the DSC isothermal crystallization curves of PCL-GO6 and PCL at 40 and 46°C, respectively. Clearly, the isothermal crystallization rate of the PCL-GO6 composite is much higher than that of pure PCL (number-average molecular weight = 20,000) at each crystallization temperature. It confirms that GO in the PCL-GO composite effectively enhances the crystallization of PCL.

Nonisothermal crystallization kinetics

Figure 3 shows the DSC cooling curves of PCL-GO0.5, PCL-GO1.5, PCL-GO6, and PCL with a cooling rate of 10°C/min. The crystallization temperatures of PCL-GO0.5, PCL-GO1.5, and PCL-GO6 are much higher than those of pure PCL, and this indicates that the exfoliated GO sheet has an excellent nucleating effect on the crystallization of PCL. Among the three composite samples, the crystallization temperature of PCL-GO1.5 is higher than that of the other samples. This is due to the fact that at first, with increasing GO content, GO acts as a nucleating agent and improves further, increasing the crystallization of PCL; then, with the content of GO further increasing, the solid particle of GO limits the segment mobility of polymer PCL during the crystallization process.

Figure 4 shows the DSC nonisothermal crystallization behavior of the PCL/PCL-GO6 blends with 2, 5, 10, or 20% PCL-GO6 composites. The peak crystallization temperature of the blend sample PCL/PCL-GO6 20% is higher than those of the other blend samples. With increasing content of the PCL-GO6 composite, the peak crystallization temperature also increases. This indicates that the PCL-GO composite actually

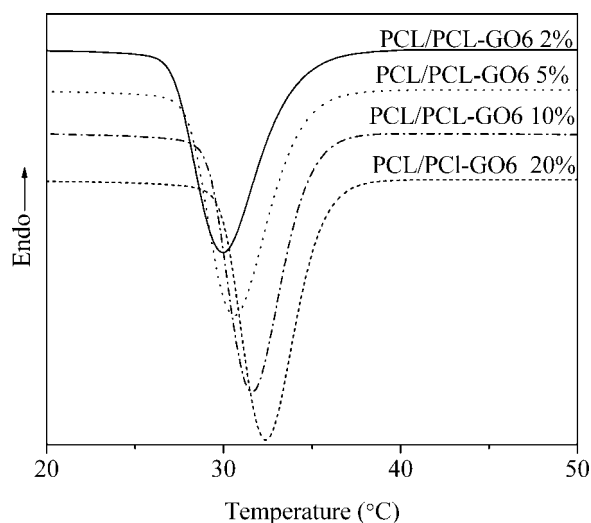


Figure 4 Nonisothermal crystallization behavior of PCL/PCL-GO6 blends with different PCL-GO6 contents: 2, 5, 10, and 20%. The cooling rate was 10°C/min.

acts as an excellent nucleating agent for the crystallization of PCL.

Figure 5 shows the DSC nonisothermal crystallization behavior of the PCL-GO1.5 composite, PCL-GO1.5 blend, PCL/PCL-GO6 20% blend, and pure PCL. The peak crystallization temperatures of the PCL-GO1.5 composite, PCL-GO1.5 blend, and PCL/PCL-GO6 20% blend are all higher than the crystallization temperature of pure PCL. Furthermore, for these samples, the crystallization temperature is in the order of PCL-GO1.5 composite > PCL/PCL-GO6 20% > PCL-GO1.5 blend. The nucleating effect of GO in the PCL-GO composite is better than that in the PCL/

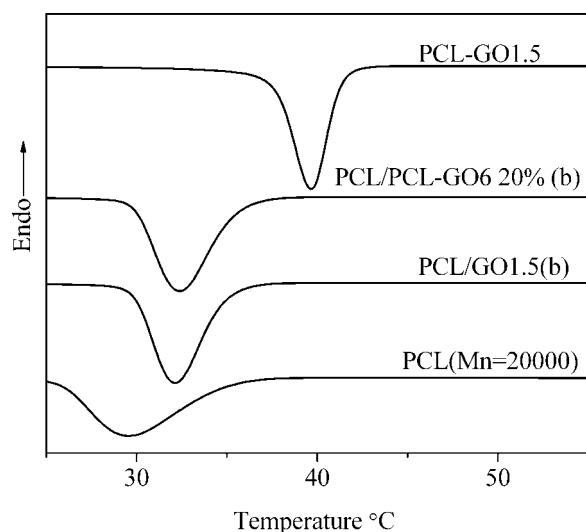


Figure 5 Nonisothermal crystallization behavior of the PCL-GO1.5 composite, PCL-GO1.5 blend, PCL/PCL-GO6 20% blend, and pure PCL. The cooling rate was 10°C/min.

PCL-GO6 20% and PCL-GO1.5 blends. This result is due to the fact that the grafted PCL chain is bonded to the surface of the GO layer and the interaction between the PCL chain and the GO layer has greatly increased. Hence, during the crystallization process, PCL on the surface of GO is easy to nucleate and then to crystallize. However, in blends, the interaction between the polymer chain and GO is very weak, and the nucleation effect of GO in the blends is not as obvious as that in the PCL-GO composite.

The nonisothermal DSC cooling measurements were performed to characterize the crystallization behavior of the PCL-GO composite, and the results were compared with those of pure PCL. The samples were subjected to the thermal treatments described in the Experimental section, and the crystallization exothermic curves were recorded. The measured heat flow curves against the temperature at different cooling

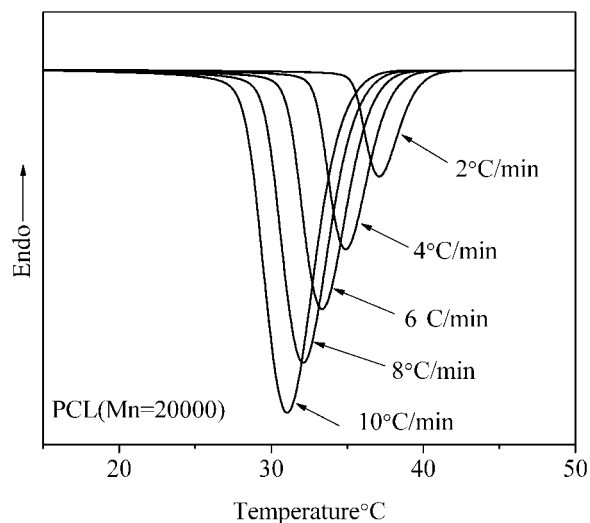
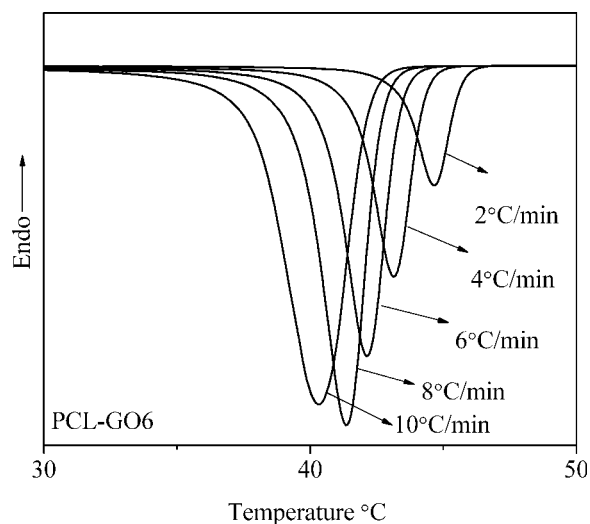


Figure 6 Nonisothermal crystallization exothermic curves of PCL-GO6 and pure PCL.

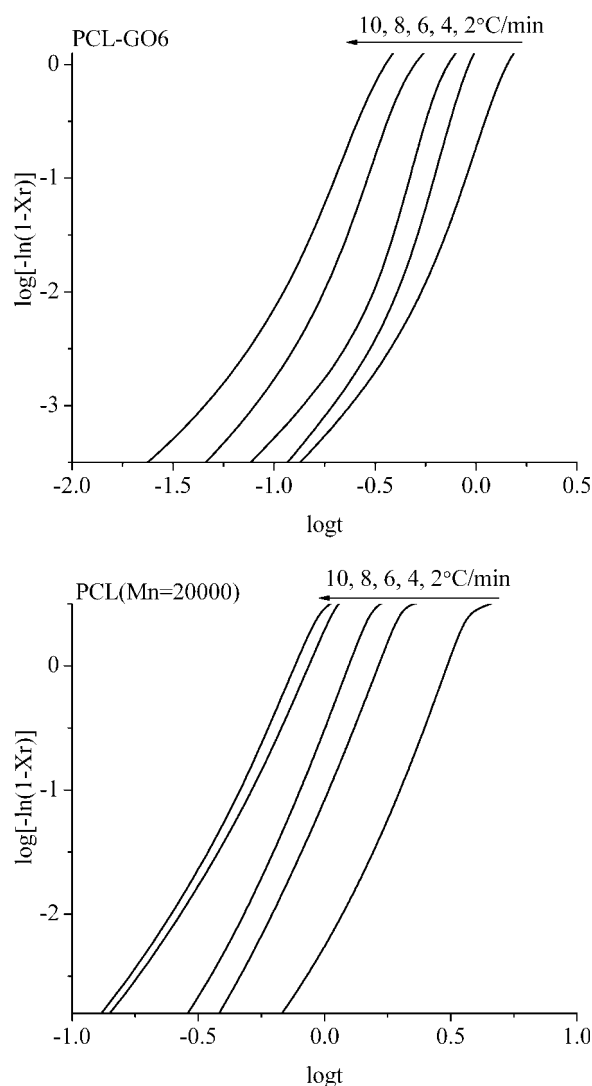


Figure 7 Plots of $\log[-\ln(1 - X_r)]$ versus $\log t$ for the PCL-GO6 composite and pure PCL.

rates (from 10 to 2 °C/min) are shown in Figure 6. All samples showed similar crystallization exothermic curves and similar changes in the curves with the cooling rates; this indicated that they crystallized by a similar mechanism. The peak temperature of the melt nonisothermal temperature shifts to a lower temperature region as the cooling rate increases. The relative degree of crystallinity (X_r), as a function of the crystallization temperature, is defined as follows:¹⁸

$$X_r = \frac{\int_{T_0}^T \left(\frac{dH_c}{dT}\right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH_c}{dT}\right) dT} \quad (5)$$

where T_0 and T_∞ represent the temperatures at the onset and end of crystallization, respectively. dH_c/dT is the rate of heat flow in the process of isothermal crystallization at time t . During the melt nonisothermal crystallization process, the relation between crys-

tallization time t and corresponding temperature T is given by¹⁸

$$t = \frac{T_0 - T}{\phi} \quad (6)$$

where ϕ is the cooling rate. According to eq. (6), the temperature-dependent relative crystallinity can be transformed into the time-dependent relative crystallinity. Several theoretical methods have been proposed to predict and analyze nonisothermal crystallization kinetics.^{22,23} In this work, we employed the Avrami equation for the analysis of the crystallization kinetics for the PCL-GO composite series and PCL.^{18,24} On the basis of the assumption that the nonisothermal crystallization is the result of infinite isothermal processes, the primary nonisothermal stage could be described by the Avrami equation as follows:

$$1 - X_{rel} = \exp(-Kt^n) \quad (7)$$

where exponent n is a mechanism constant depending on the type of nucleation and the growth process and K is a composite rate constant involving both nucleation and growth rate parameters. Considering the nonisothermal character of the process investigated, Jeziorny²⁵ pointed out that the value of K should be adequately corrected. The factor to be considered is cooling rate ϕ . The final form of the parameter, characterizing the kinetics of melt nonisothermal crystallization, is given as follows:

$$\log K_c = \frac{\log K}{\phi} \quad (8)$$

With eq. (7), the values of $\log[-\ln(1 - X_r)]$ have been plotted against $\log t$ for all PCL-GO composite samples, as shown in Figure 7. A good linear relationship can be found between $\log[-\ln(1 - X_r)]$ and $\log t$ over a wide range of crystallinity, implying that the Avrami equation is suitable for the kinetic study. The values of $\log K$ and n are taken from the intercept and slope, respectively, of the linear fitting of $\log[-\ln(1 - X_r)]$ versus $\log t$ plots. From the slope and intercept of the

TABLE III
Values of Avrami Parameters n , K_c , and $t_{1/2}$ for the Melt Nonisothermal Crystallization of PCL in Its Pure State and the PCL-GO6 Composite

Sample	ϕ (°C/min)	n	K_c (min ⁻ⁿ)	$t_{1/2}$ (min)
Pure PCL	2	4.26	0.0815	1.65
	4	4.49	0.559	1.04
	6	4.48	0.829	0.96
	8	4.06	1.071	0.89
	10	3.86	1.089	0.88
PCL-GO6	2	4.57	0.426	1.11
	4	5.25	1.077	0.91
	6	5.16	1.314	0.88
	8	4.32	1.471	0.84
	10	3.72	1.456	0.81

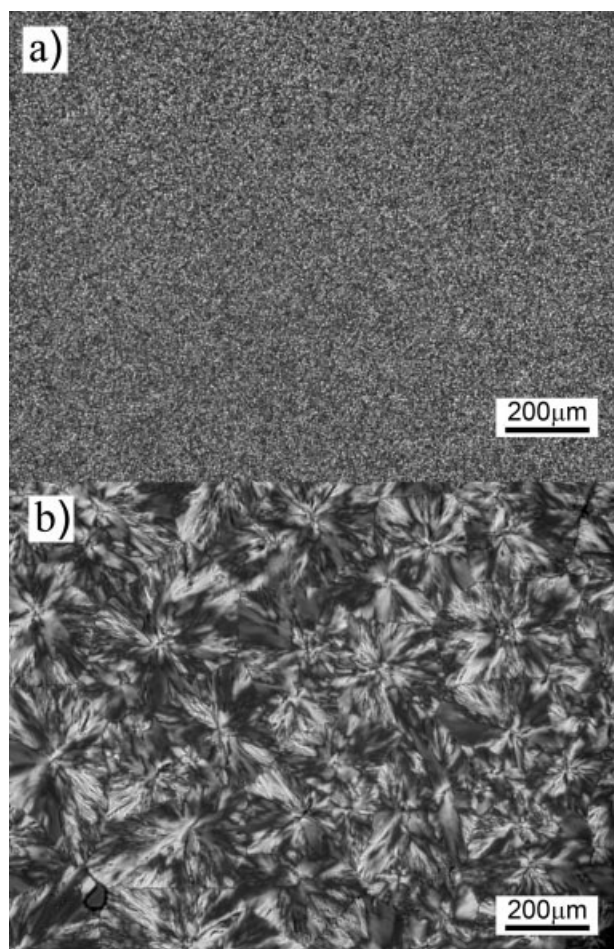


Figure 8 Polarized optical micrographs of (a) PCL-GO6 and (b) pure PCL crystallized at 46°C.

linear part of the lines shown in Figure 7, Avrami index n and rate constant K_c , for both pure PCL and PCL-GO6 composite samples, can be determined.

$t_{1/2}$, defined as the time at which the extent of crystallization is 50% completed, was obtained with an equation similar to eq. (4). The resultant K and n values are summarized in Table III:

$$t_{1/2} = \left(\frac{\ln 2}{K_c} \right)^{1/n} \quad (9)$$

The values of n for melt nonisothermal crystallization are higher than those for isothermal crystallization (as stated previously) for both PCL-GO6 and PCL samples. As is known, the Avrami equation assumes that, during the crystallization process, the nucleation rate remains constant, although the nucleation rate during crystallization is actually temperature-dependent. When a sample undergoes isothermal crystallization, the nucleation rate remains constant, although when a sample undergoes melt nonisothermal crystallization, it is no longer constant. Therefore, higher values of n for the melt nonisothermal crystallization are attribut-

able to much more complicated processes occurring during the melt nonisothermal crystallization. In addition, the value of the half-time in the melt nonisothermal crystallization process of the PCL-GO6 composite is lower than the value of pure PCL, and this confirms that the PCL-GO composite has a great effect as a nucleating agent on the crystallization of pure PCL.

Polarized optical microphotographs

In Figure 8 are shown polarized optical microphotographs for PCL-GO6 and pure PCL samples crystallized at a crystallization temperature of 46°C. The spherulites of pure PCL are larger in size and smaller in number than those of the PCL-GO6 composite. These results prove that PCL-GO6 increases the nucleation density. This might be explained by heterogeneous nucleation initiated with the introduction of GO into PCL.²⁶ A grafted PCL chain is bonded to the surface of the GO layer, and it greatly increases the interaction between the PCL chains and the GO layers. These GO layers bonded to the PCL chain may act effectively as true nucleating agents to initiate nucleation. Heterogeneous nucleation decreases the surface energy barrier and increases the nucleation density for PCL crystallization. It is therefore natural that the crystallization rate of PCL increases with the introduction of the PCL-GO composite into pure PCL.

CONCLUSIONS

In this work, we have primarily investigated the crystallization kinetics of PCL-GO composites and their effects as nucleating agents on the crystallization of pure PCL. A series of PCL-GO composites were prepared through ROP of ϵ -caprolactone initiated by GO. PCL-GO composite and pure PCL blend samples were also prepared. The effect of GO as a nucleating agent on the crystallization of PCL was studied with DSC. GO in the PCL-GO composite had an excellent nucleating effect on the PCL crystallization, whereas the nucleating effect of GO in the PCL-GO blend and PCL/PCL-GO blend was weaker than that of the PCL-GO composite because of the weaker interaction between GO and the PCL chain. According to the POM observations, the nucleation density increased with the introduction of GO into PCL. GO comes from natural graphite, and it has been proved that GO improves the thermal properties and mechanical properties of polymers; thus, GO can be considered a promising nucleating agent.

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