

# Synthesis and Characterization of Poly( $\epsilon$ -caprolactone)–Graphite Oxide Composites

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**ABSTRACT:** The composites of poly( $\epsilon$ -caprolactone) (PCL) and graphite oxide (GO) were successfully synthesized by ring-opening polymerization of  $\epsilon$ -caprolactone with GO as the initiator. The composites with different GO content were synthesized and an exfoliated structure was found for all the composites from the wide angle X-ray diffraction study. An astounding

nucleating effect of GO on PCL crystallization was observed due to the good dispersion of GO in the composite. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1880–1884, 2007

**Key words:** poly( $\epsilon$ -caprolactone); graphite oxide; nucleating agent; ring-opening polymerization

## INTRODUCTION

Recently, polymer/inorganic nanocomposites have attracted much interest. The nanoscale inorganic particles or sheets dispersed into the polymer matrix can improve the physical properties of polymer.<sup>1</sup> Among various kinds of composites, polymer/graphite composites have gained increasing interest for their excellent mechanical, structural, physical, thermal, and electrical properties.<sup>2</sup> Graphite oxide (GO) has been used as an inexpensive substitute of carbon nanotube in nanocomposites.<sup>2,3</sup> Hydrophilic GO with lamellar structure was prepared by oxidation of natural graphite, and it has 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,<sup>4</sup> thus facilitating GO hydration and exfoliation in the aqueous media. Because of the water solubility of GO, for several kinds of the polymer/GO composites, water soluble polymers were used, and an intercalated structure was achieved in these polymer/GO composites.<sup>4,5</sup> For example, poly(aniline-*co*-*o*-anisidine)-intercalated GO composite<sup>6</sup> has higher electrical conductivity than pristine GO. Further, GO has been reported to improve the thermal stability of poly(vinyl alcohol).<sup>7</sup> Pan et al. have revealed that GO enhanced the mechanical properties of Nylon 6.<sup>8</sup>

Recently, aliphatic polyesters have attracted much research interests because of their biodegradability and biocompatibility.<sup>9,10</sup> Poly( $\epsilon$ -caprolactone) (PCL) is

one of the typical biodegradable aliphatic polyesters. It is fully biodegradable, biocompatible, and nontoxic to living organisms.<sup>11</sup> Also, PCL has good resistant ability to water, oil, solvent, and chlorine. The unique properties of PCL render it high potential in biomedical fields and it has been used in the development of controlled drug-delivery system as well as in surgical sutures and other resorbable fixation devices.<sup>11,12</sup> However, the PCL applications for such materials are limited because of its deficiencies in mechanical and barrier properties to water and gases.<sup>13</sup> One option is to incorporate an environmentally acceptable filler to improve the properties of such biodegradable polymers particularly for use as advanced materials.<sup>13</sup>

GO is originated from natural graphite and acts as an excellent host matrix for the interlayer accommodation of the long chain aliphatic hydrocarbons.<sup>14</sup> GO is expected to be a suitable filler to improve PCL mechanical and thermal properties, while maybe the PCL–GO composites have an electrical conductivity property, due to the nature of the graphite. Furthermore, the PCL and GO composites afford an exfoliated structure in which the individual graphite sheets are dispersed in the PCL polymer matrix and the surface treatment of graphite enhances the solubility of GO in solution.

In this work, we report first the synthesis of PCL–GO composites utilizing the GO as an initiator of the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone. The molecular weight of PCL should be controlled by hydroxyl content, that is, by the GO content. The structure of the composite is characterized by wide-angle X-ray diffraction (WAXD) and the thermal behavior of the composites is studied by different scanning calorimetry (DSC).

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## EXPERIMENTAL

### Materials

The graphite (Lot: M4P3193) and the potassium permanganate (Lot: M5E9617) were purchased from Nacalai Tesque (Kyoto, Japan) and were used as received. Sulfuric acid (>96%), nitric acid, hydrogen peroxide, and tin 2-ethylhexanoate were purchased from Kanto Chemical (Tokyo, Japan) and were also used as received. The  $\epsilon$ -caprolactone was purchased from Kanto Chemical (Tokyo, Japan) and distilled over  $\text{CaH}_2$  before use. PCL (molecular weight is about 20,000) was also purchased from Kanto Chemical (Tokyo, Japan) and used for comparison with synthesized samples.

### Preparation of graphite oxide

Graphite oxide (GO) samples were prepared by modifying the method proposed by Hummers.<sup>15</sup> Graphite powder (5 g) was put into a 500-mL flask containing 68% nitric acid (33 mL) and sulfuric acid (>96%, 200 mL), stirred for 30 min on an ice-bath, and then potassium permanganate 30 g was added into the solution. The solution temperature was raised gradually to about 40°C, maintained for 30 min at this temperature, and then the excess potassium permanganate was removed by the 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 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.<sup>16</sup>

### Synthesis of graphite hydroxide and PCL composite

The polymerization of  $\epsilon$ -caprolactone was carried out via the ROP with the OH groups on the surface of GO as initiators of ROP, similar to the method that had been reported in our previous work.<sup>17</sup> The ROP is catalyzed by tin 2-ethylhexanoate (0.5 g). In the typical experiment, the desired amount of GO (0.05 g, 0.15 g, 0.6 g) was suspended in  $\epsilon$ -caprolactone (10 g) by sonicating for 30 min, then the suspension including GO, tin 2-ethylhexanoate, and  $\epsilon$ -caprolactone was transferred to a three-necked flask, which was previously dried in vacuum oven at 140°C. The flask was then capped and heated at about 120°C for 20 h under vigorous stirring to afford black solid product. The obtained solid was separated by an ultra centrifugation at 110,000 rpm for 20 min and precipitated in chloroform/ethanol for three times to afford a gray solid.

### Preparation of PCL/GO blends

The desired amount of GO and PCL ( $M_n = 20,000$ ) was mixed under stirring in 15 mL chloroform for 2 h at room temperature, and then the mixture was maintained at the room temperature to afford the cast film.

### Characterization

The Fourier transform infrared (FTIR) spectrum was observed at room temperature on a PerkinElmer Spectra 2000 single-beam IR spectrometer with a resolution of 4  $\text{cm}^{-1}$ . The specimens were dispersed into KBr by mortar and were compressed to form disks. The UV/vis spectra of the product were recorded on a JASCO V-550 UV/vis spectrophotometer at room temperature.

<sup>1</sup>H NMR spectra were measured at room temperature and 600 MHz in  $\text{CDCl}_3$  solution on a Bruker Avance 600 MHz spectrometer with 30° pulse, 3.7-s pulse repetition time, 32 K data points, and 256 FID accumulations.

The WAXD patterns of the sample films were recorded in a  $\theta$  angle range of 2–50° at scanning speed of 1°/min on a Rigaku RU-200 X-ray diffractometer at 40 KV and 200 mA at room temperature. Nickel-filtered Cu K $\alpha$  X-ray radiation ( $\lambda = 0.15418$  nm) was used as source. The degree of crystallinity was estimated according to the method of Vonk.<sup>18</sup>

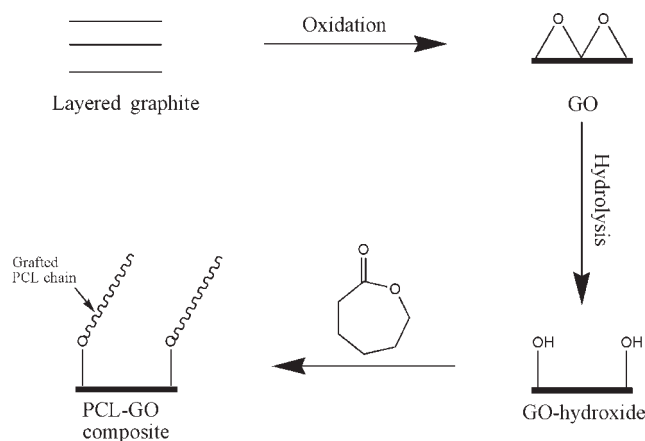
The spherulite growth rates were measured by polarized optical microscopy (POM) with an Olympus BX90 polarized microscope equipped with a Mettler FP82HT hot stage. The film samples were first heated from room temperature to 100°C and melted for 2 min. Subsequently, the samples were quenched to crystallization temperature 44°C.

Nonisothermal crystallization was studied with Pyris Diamond DSC (PerkinElmer, Tokyo, Japan) under nitrogen atmosphere. For the melt nonisothermal crystallization, the specimen (5–8 mg) was heated to 100°C in the DSC cell at a heating rate 10°C/min and held at this temperature for 3 min, and this was followed by cooling at 10°C/min to 0°C.

Thermogravimetric analysis (TGA) was carried out on Seiko (Tokyo, Japan) TG/DTA 220U with the Exstar 6000 Station. The samples were scanned from 25 to 550°C with the heating rate of 5°C/min in the protection of nitrogen flow.

## RESULTS AND DISCUSSION

As shown in Scheme 1, the  $\epsilon$ -caprolactone was polymerized in bulk with various amounts of layered GO. The polymerization was activated at about 120°C by tin 2-ethylhexanoate as an initiator and it should proceed via an insertion-coordination mecha-



**Scheme 1** Route for synthesis of exfoliated PCL-GO composites.

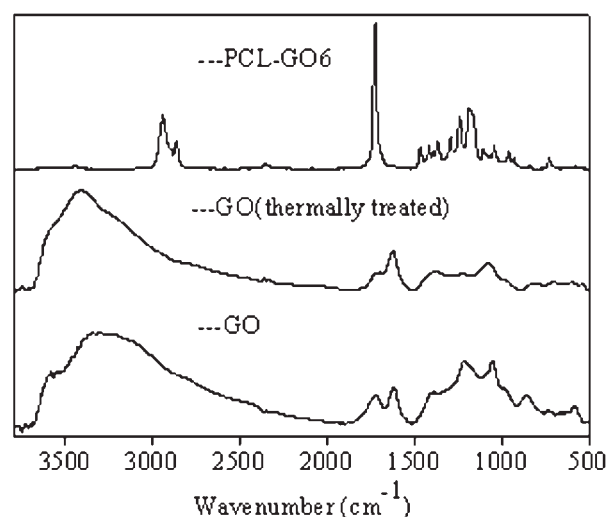
nism,<sup>19</sup> that is, the polymerization proceeds through the insertion of the monomer into the “graphite-OH” bond of the initiator via the selective acyl-oxygen cleavage of the lactone ring. The details of the sample composition were shown in Table I.

Figure 1 shows the FTIR spectra of GO, thermal by treated GO and PCL-GO6 composites. A broad band ranged from 3000 to 3700  $\text{cm}^{-1}$  is found for the oxidized graphite samples GO and thermally treated GO, indicating the presence of hydroxyl groups in GO. The FTIR band of the epoxy groups at about 800  $\text{cm}^{-1}$  disappeared in the spectra of thermally treated GO, due to the ring-opening of the epoxy groups of GO, during the thermal treatment.<sup>20</sup> The FTIR spectrum of the PCL-GO composites is agree well with the spectrum of PCL. The peaks of GO was masked by the peaks of PCL due to the relatively less content of GO.

Figure 2 are shown the UV/vis spectra of PCL-GO composites, PCL, and GO. The spectra of the composite PCL-GO and PCL were observed in the THF solutions and that of GO in water. GO shows very broad absorption with continuously decreasing intensity ranged to 800 nm. PCL shows characteristic peaks in the wavelength region shorter than 250 nm, while no evident absorption in the high wave length region. In the absorption spectrum from 285 to 800 nm, the PCL-GO composites show absorption curves with features characteristics for both PCL and GO, indicating that the PCL chain is attached to the surface of GO.

**TABLE I**  
Composition and the  $M_{narm}$  Values of PCL-GO Composites by  $^1\text{H}$  NMR

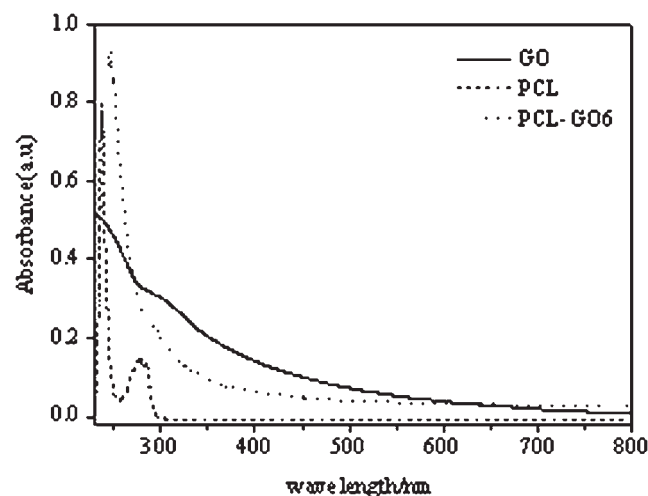
Samples	GO content (wt %)	$M_{narm}$ (g /mol)
PCL-GO0.5	0.5	11,400
PCL-GO1.5	1.5	9,120
PCL-GO6	6	6,600



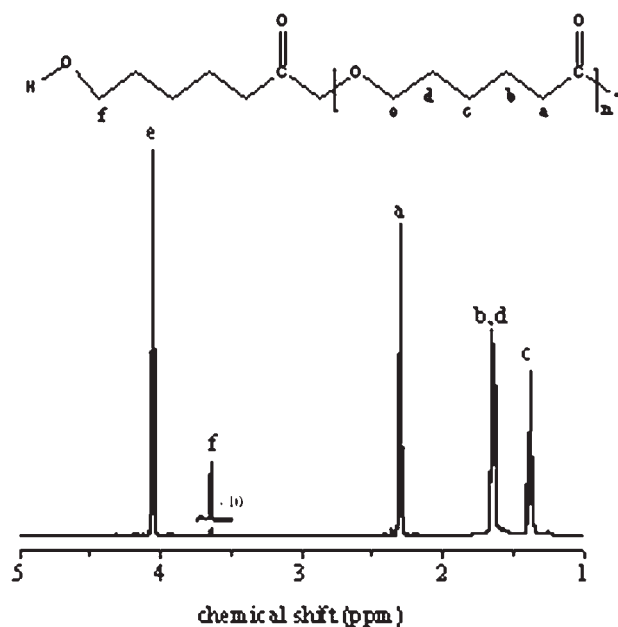
**Figure 1** IR spectra in KBr of the samples GO, thermally treated GO and PCL-GO composites.

Figure 3 shows the 600 MHz  $^1\text{H}$  NMR spectrum of the PCL-GO6 sample. The spectrum shows the typical resonances for PCL, indicating the production of PCL. The peaks at 4.1 and 3.7 ppm correspond to the methylene group of (*t*, 2H,  $-\text{CH}_2-\text{OOC}-$ ) and  $-\text{CH}_2-\text{OH}$  (*t*, 2H, chain end), respectively.<sup>11</sup> So, from the  $^1\text{H}$  NMR resonances, it is very convenient to calculate the number average molecular weight of every PCL arm chain ( $M_{narm}$ ) on the surface of GO. The  $M_{narm}$  values are shown in Table I. From the table, it is obvious that with the increase of the GO content, the  $M_{narm}$  value decreases. That is due to the increased ratio of initiator to monomer.

The solid-state structure of the composite was analyzed by the wide angle X-ray diffraction pattern, as shown in Figure 4. The GO shows diffraction peak at about  $2\theta = 10.66^\circ$  with the *d*-spacing 8.33 Å, corre-



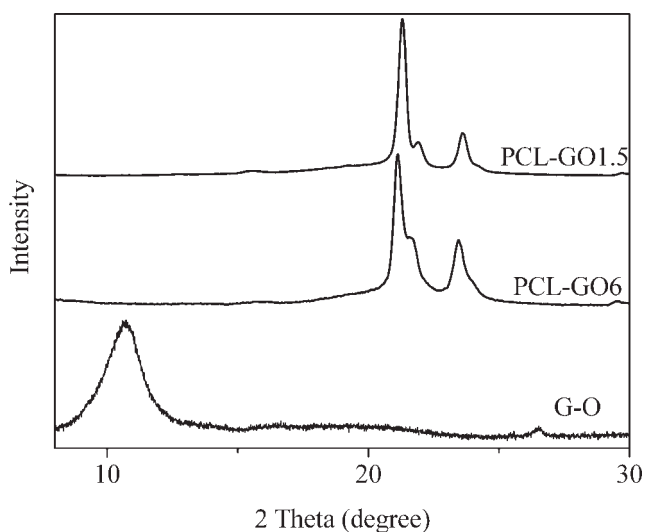
**Figure 2** The UV/vis spectra of GO in aqueous solution, PCL and PCL-GO6 composites in THF solution.



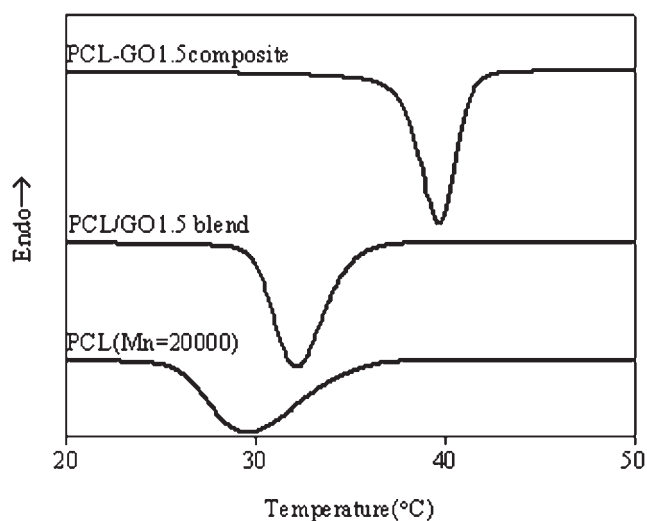
**Figure 3** 600 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  solution of PCL-GO6 composite.

sponding to the layered structure of GO. The WAXD patterns of composites that contain the highest and the lowest GO content were shown. The composites show a typical WAXD pattern of PCL, while the peak corresponding to the layered structure of GO was not observed. So, an exfoliated structure was obtained for the PCL-GO composites. The GO platelets are randomly dispersed in the PCL matrix.

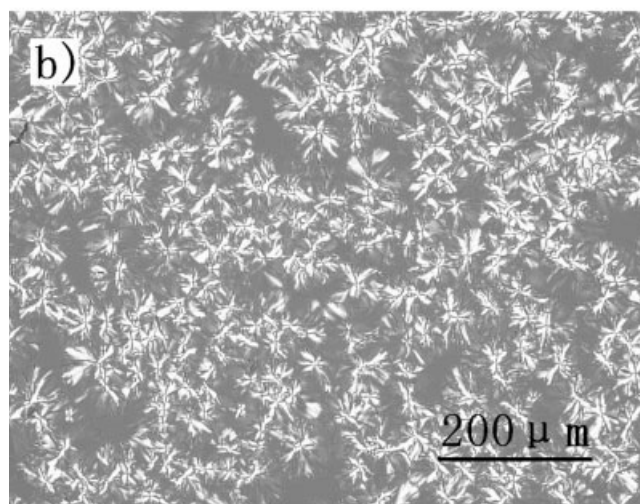
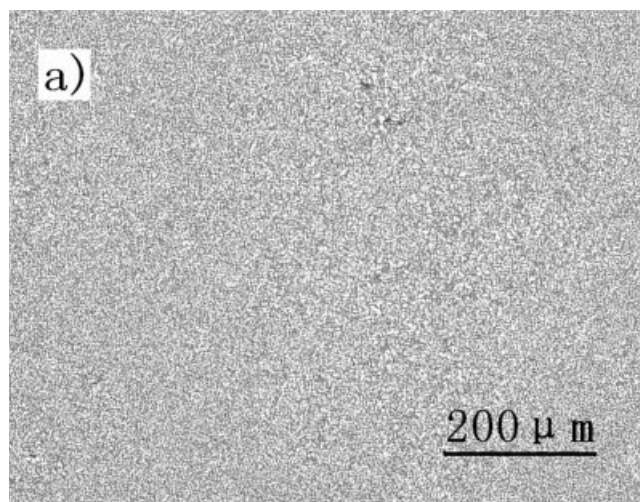
Figure 5 shows the melt crystallization behavior of PCL ( $M_n = 20,000$ ), PCL-GO1.5 composite, and PCL/GO1.5 blend. The crystallization peak temperature of pure PCL is observed at  $29.2^\circ\text{C}$ . The crystalli-



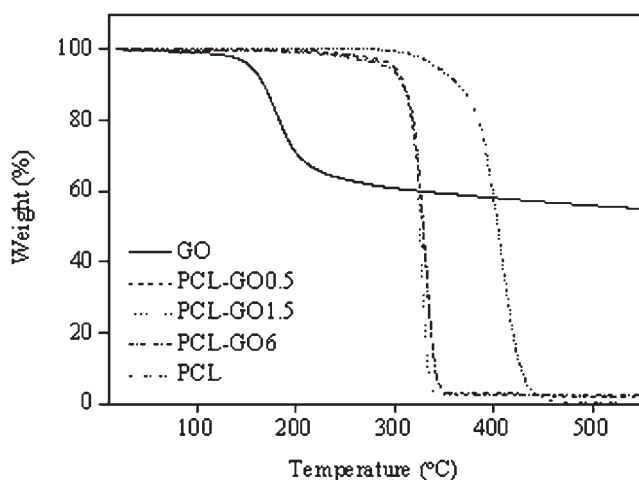
**Figure 4** The WAXD patterns of PCL-GO1.5 composite, PCL-GO6 composite and GO.



**Figure 5** DSC patterns of PCL, PCL-GO1.5 composite and PCL/GO1.5 blend.



**Figure 6** Polarized optical micrographs of PCL-GO6 (a) and pure PCL (b) at  $44^\circ\text{C}$ .



**Figure 7** The thermal degradation behavior of the composites (PCL-GO0.5, PCL-GO1.5, PCL-GO6), GO, and PCL.

zation peak temperature of PCL in the PCL/GO1.5 blend is 32°C, while that in the PCL-GO1.5 composite is about 39.7°C. So, the GO incorporated into the PCL matrix has great nucleating effect on the crystallization of PCL. Furthermore the nucleating effect found in the PCL-GO1.5 composite is much higher than that in the PCL/GO1.5 blend. An astounding nucleating effect was resulted from the exfoliated structure of GO in the PCL matrix and this effect is over that found in our previous work on the PCL cyclodextrin inclusion complex.<sup>21,22</sup> The nucleating effect of the exfoliated GO platelet on the crystallization of PCL is confirmed also by POM.

Figure 6 shows that the POM photos of pure PCL and PCL-GO6 samples crystallized at  $T_c = 44^\circ\text{C}$ . The spherulites of pure PCL are larger in size and smaller in numbers than those of the PCL-GO6 composite. These results prove that PCL-GO6 increases the nucleation density. This might be explained by a heterogeneous nucleation initiated with the introduction GO into PCL.<sup>23</sup> Grafted PCL chain is bonded to the surface of GO layer and greatly increase the interaction between PCL chain and GO layer. These GO layers, to which the PCL chains grafted, may act as the true nucleating agent to initiate nucleation. Heterogeneous nucleation decreases the surface energy barrier and increases the nucleation density for PCL crystallization.

Figure 7 shows the thermal degradation behavior of the composites, GO, and PCL, which was studied by TGA. Degradation temperatures of GO and PCL are compared with those of composites in this figure. The degradable temperature of GO is about 120°C and the characteristic degradable temperature of PCL is about 300°C. All the composites samples (PCL-GO0.5, PCL-GO1.5, and PCL-GO6) show the similar degradable properties and the degradable temperature shift to about 230°C, which is probably

due to the lowered thermal stability of PCL with the incorporation of GO.

## CONCLUSIONS

The PCL-GO composites were successfully synthesized through the ROP of  $\epsilon$ -caprolactone with GO as the initiator, and confirmed by UV study. Because of the introduction of PCL chain onto the surface of the GO, the PCL-GO composites can form clear solution in chloroform, greatly increasing the solubility of GO in organic solvent. Also, the incorporation of GO into PCL decreases the thermal stability of the PCL from the TG study. From the WAXD study, the disappearance of GO-layered peak indicates that for the PCL-GO composites GO was exfoliated in the PCL matrix. Just because that the PCL bonded to the surface of GO forming the exfoliated structure, the GO sheet shows an excellent nucleating effect on the crystallization of PCL, as found by DSC and POM observation. The nucleating effect of GO in the PCL-GO composites is much better than that of GO in the PCL/GO1.5 blend due to the better interaction of PCL with GO in the PCL-GO composites.

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