Thermal and Mechanical Properties of a Poly(ε-caprolactone)/Graphite Oxide Composite

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ABSTRACT: The effect of graphite oxide (GO) as the enforcing filler on the properties of poly(ε-caprolactone) (PCL) was investigated in this study. Through the introduction of GO, the Young's modulus of PCL was increased from 340 to 1000 MPa, and the tensile strength of PCL was increased from 15 to 26 MPa. Furthermore, the interlayer distance of GO (0.6 nm) was found to expand to 1.1 nm in the PCL/GO composite, which indicated the intercalation of the PCL chain into the GO layers. Because of this intercalation structure of the PCL/GO composite, GO showed a higher reinforcing effect than graphite on the mechanical properties of PCL. The intercalation should have enabled much effective load transfer in the PCL/GO composites. Moreover, GO showed a nucleating effect toward the crystallization of PCL, as the nonisothermal crystallization peak temperature shifted from 25°C for pure PCL to about 34°C for the PCL/GO composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1395–1400, 2008

Key words: biodegradable; blends; composites; fillers; polyesters

INTRODUCTION

Nowadays, the total amount of plastic products in the world is about 100 million tons per year, and the needs for plastics are increasing year by year.[1] The success of polymeric materials lies in their processability, mechanical strength, low cost, resistance to chemical and biological attack, and so on. These properties have led to useful applications of polymers but have also created a disposal problem. Concern is rising that plastic waste will accumulate in the environment and lead to long-term environmental and waste-management problems.[1] Biodegradable plastics offer a promising alternative toward solving these problems. Biodegradable polymers that are produced from renewable raw materials have advantages over traditional polymers.[2] They do not give any net increase in carbon dioxide production.[1] Biodegradable polymers offer new possibilities for industrial use of agricultural products in developed countries.[3]

Recently, aliphatic polyesters have attracted much research interest due to their biodegradability and biocompatibility.[4–6] Poly(ε-caprolactone) (PCL) is one such typical aliphatic polyester.[7] It is fully biodegradable, biocompatible, and nontoxic to living organisms.[7] Also, PCL has good resistances to water, oil, solvent, and chlorine. The unique properties of PCL give it high potential in biomedical fields, and it has been used in the development of controlled drug-delivery system and in surgical sutures and other resorbable fixation devices.[7,8] For example, PCL is a ductile polymer, with a rather low Young's modulus, which impedes its use for engineering applications. The addition of fillers may provide a good way to improve the mechanical properties of PCL.

Inorganic particles are widely used as reinforcement materials for polymers.[9–11] Among inorganic materials, graphite oxide (GO) has recently attracted much research attention as a composite with polymers. GO is layer-structured compound and can be obtained by the oxidation of natural graphite.[12,13] GO is a typical two-dimensional solid in the bulk form, with strong covalent bonding within the layers. Weak interlayer interaction is observed due to the existence of hydrogen-bonding interaction between intercalated water molecules.[14–16] Some functional groups, such as hydroxyl and carbonyl groups, embedded in the carbon sheets in the GO lamellae make GO hydrophilic. It has been reported that some polar organic molecules and polymers, including alcohols,[17] poly(ethylene oxide),[18,19] poly(vinyl alcohol),[20,21] poly(vinyl acetate),[22] even poly(furfuryl alcohol),[20] and others,[21] can easily be inserted into the GO lamellae to form intercalated composites. It has been suggested that, in these composites, there were strong intermolecular forces

between GO and the polymers, such as hydrogen bonding and Coulomb forces. Also, an incorporation of GO into the polymers greatly improved the thermal stability and electrical and mechanical properties of the polymers.[17–21,23,24]

It has been reported that PCL has been blended with polyphenols, lignin, and other compounds, and the resulted blends had better mechanical properties than pristine PCL.[22,25–29] Because of the inorganic nature of GO, GO was expected to be a good filler for PCL. In this study, we investigated the use of GO as a filler to enforce PCL, and we also investigated the poly(ε-caprolactone)/graphite (PCL/G) blend. The effects of graphite and GO on the crystallization and mechanical properties of PCL were thoroughly studied. Two blend methods were used in this study, with or without ultrasound, and the effects of ultrasound on the structure and properties of the PCL/GO composites were also thoroughly investigated. PCL/GO composites were expected to show much better mechanical properties than PCL/G composites due to the presence of functional groups on GO and the better interaction between the PCL chain and GO.

EXPERIMENTAL

Materials

The PCL sample (number-average molecular weight = 1.74×10^5, weight-average molecular weight/ number-average molecular weight = 1.57; Celgreen PH7) was purchased from Daicel Chemical Industries, Ltd. (Tokyo, Japan). Before use, PCL was purified by precipitation into ethanol from a chloroform solution.

GO was synthesized from graphite powder by oxidation with $KMnO_4$ in concentrated H_2SO_4 according to a method reported by Hummers and Offeman.[13] Graphite powder (5 g) was put into a 1000-mL flask containing 60% nitric acid (18.4 mL) and 98% H_2SO_4 (100 mL) and stirred for 30 min in an ice bath. Then, $KMnO_4$ (30 g) was added gradually with stirring and cooling so that the temperature of the mixture was not allowed to reach 20°C. After 30 min, the solution temperature was raised gradually to 38°C and maintained for a further 30 min. After this reaction, to remove the excess $KMnO_4$ and stop the reaction, 30% H_2O_2 was added until the color of mixture changed from purplish black to bright yellow, and then, we added a large amount of distilled water (800 mL). The mixture was repeatedly washed with large amounts of distilled water and filtered. Next, the product was dried in air on the hot stage at 50°C and then *in vacuo* at 50°C for 3 days. Before use as a filler, GO was dried *in vacuo* at 100°C for 48 h to be thermally decomposed and to increase its functional groups, such as phenol and/ or aromatic diol.

Sample preparation

PCL/GO composite

At first, GO was dispersed in dimethylformamide (DMF) by ultrasonic treatment for 24 h at 50°C. The concentration of GO in this solution was 0.1 g/100 mL. PCL was dissolved in DMF at 90°C (1.0 g/20 mL). An adequate amount of DMF solution, including dispersed GO, was added to the PCL solution (20 mL) under stirring at 90°C. After DMF was removed by vaporation, the product was dried *in vacuo* at 90°C for 3 days and at 25°C for 1 week.

PCL/GO composite treated with ultrasound (PCL/GO-s)

The mixture of PCL and GO solutions were treated with an ultrasonicator during mixing. PCL/GO-s was prepared by a similar method of the mixing of PCL and GO solutions, but the mixture of these solutions was treated with ultrasound for 24 h before DMF was vaporized. After ultrasonic treatment, the solution was vaporized under stirring at 90°C and dried *in vacuo* at 90°C for 3 days and at 25°C for 1 week. Here, the numerical value of the sample code indicates the weight percentage content of the filler (e.g., PCL/GO10 is the PCL/GO composite with 10 wt % GO).

PCL/G composite

The graphite powder used for the synthesis of GO was dispersed in DMF by stirring, and the concentration was adjusted to be 0.1 g of powder/100 mL. PCL was dissolved in DMF at 90°C (1.0 g/20 mL). An adequate amount of DMF solution, including dispersed graphite, was added to the PCL solution (20 mL) under stirring at 90°C. After a conventional casting technique from DMF solution onto a Teflon Petri dish as a substrate under stirring at 90°C, the product was dried *in vacuo* at 90°C for 3 days and at 25°C for 1 additional week.

Preparation of melt crystallization films

The samples of melt-crystallized films were used for the measurements of Fourier transform infrared spectroscopy, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and tensile tests. The solvent-cast films were inserted between the polytetrafluoroethylene sheets with an aluminum spacer (0.3 mm in thickness) and were compression molded at 100°C for 5 min under a pressure of 5 MPa

with a Mini Test Press-10 (Toyo Seiki Seisaku-Sho, Ltd., Tokyo, Japan). The molten samples were then cooled to 30°C and kept for 1 week in air.

Analytical procedure

The WAXD measurements were made on a RU-200 (Rigaku Co., Tokyo, Japan) operated at 40 kV and 200 mA. Nickel-filtered Cu Kα X-ray radiation (λ = 0.15418 nm) was used as the X-ray source. The WAXD patterns were recorded in the 2θ range 2–35° at a scanning speed of 1.0°/min at ambient temperature.

The DSC thermograms of the sample (5–8 mg) presealed into an aluminum pan were recorded on a PerkinElmer Pyris Diamond DSC (Yokohama, Japan). An indium standard was used for the calibration, and nitrogen was used as the purge gas. DSC was used to detect the thermal transitions and to monitor the rate of heat flow during the nonisothermal crystallization of the sample from the molten state. The weight of the sample used in the DSC measurements was kept in the range 5–8 mg. In the temperature program for the nonisothermal crystallization, the sample was at first heated to above the melting temperature (T_m) of the polymer (100°C), annealed for 5 min at this temperature, then cooled to 0°C at 10°C/min (cooling scan), kept at 0°C for 3 min, and finally reheated to above 100°C at 10°C/min (heating scan). The crystallization temperature (T_c) and corresponding crystallization enthalpy (ΔH_c) values were taken as the peak and the area of the crystallization exotherm in the cooling scan, respectively. The values of T_m and melting enthalpy (ΔH_m) were taken as the position of the peak and the area of the melting endotherm in the heating scan, respectively.

The tensile tests were performed at 23 ± 1°C and at 23 ± 2% relative humidity with a Shimadzu EZ tester (Kyoto, Japan). The tensile properties were measured with a constant deformation rate of 50 mm/min for dumbbell-shaped specimens with a width of 4.76 mm, a length of 22.25 mm, and a thickness of 0.3 mm. For each sample, more than five specimens were tested.

RESULTS AND DISCUSSION

X-ray analysis of the composite films

Figure 1(A) shows the X-ray diffraction patterns of the composite films of PCL with 10 wt % filler. The WAXD pattern of PCL/G10 showed two characteristic peaks at 2θ = 23.9 and 26.5°, corresponding to the diffraction peaks of graphite, which indicated that the structure of graphite in the PCL matrix remained unchanged. Compared with the WAXD pattern of PCL, all PCL composites showed almost the same WAXD patterns, except for the diffraction
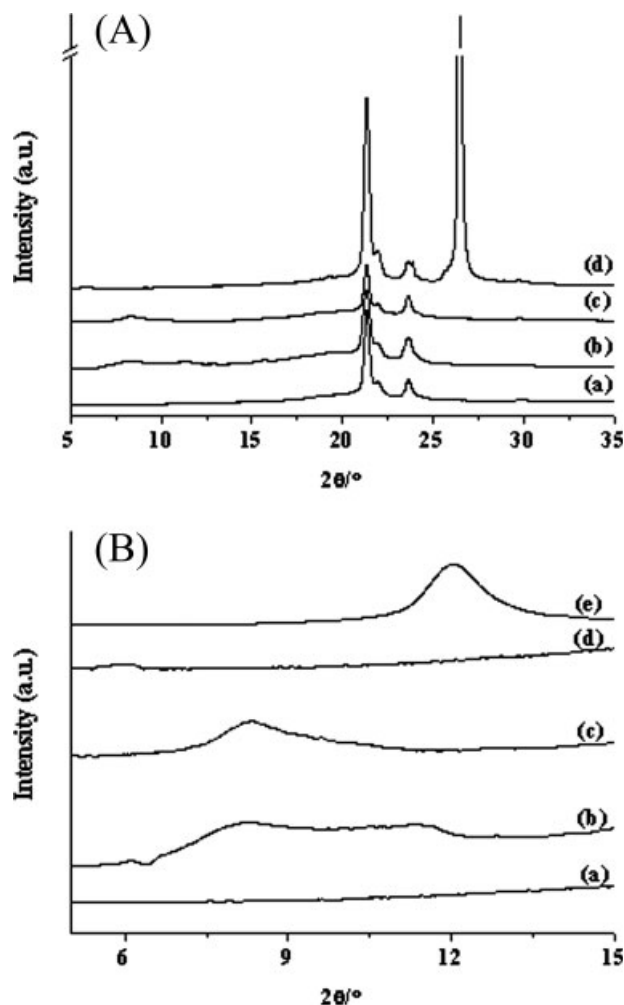

Figure 1 (A) WAXD patterns of pristine PCL and the PCL composites [(a) pristine PCL, (b) PCL/GO10, (c) PCL/GO-s10, and (d) PCL/G10] and (B) extended figures of wide-angle X-ray diffraction patterns [(a) pristine PCL, (b) PCL/GO10, (c) PCL/GO-s10, (d) PCL/G10, and (e) GO (×0.1)].

peaks of graphite. So, the crystalline structure of the PCL component was not changed by the addition of graphite.

Figure 1(B) shows the enlarged view (2θ = 5–15°) of the WAXD patterns of PCL, the PCL composites, and GO. The strong peak at 2θ = 11.9° corresponded to the (001) diffraction peak of GO, which is a typical layered material [see Fig. 1 (B), curve b]. This 2θ value corresponded to an interlayer distance of about 0.6 nm. The WAXD patterns of PCL and PCL/G10 showed no peak in the range between 5 and 15°, whereas those of PCL/GO10 and PCL/GO-s10 showed noticeable peaks. Compared with the diffraction pattern of the GO film before the addition of PCL, the diffraction peaks of PCL/GO10 and PCL/GO-s10 were shifted to a lower angle. Notably, the GO peak of PCL/GO-s10 was clearly shifted to a lower angle, 2θ = 8.6°. The 2θ value of PCL/GO-s10
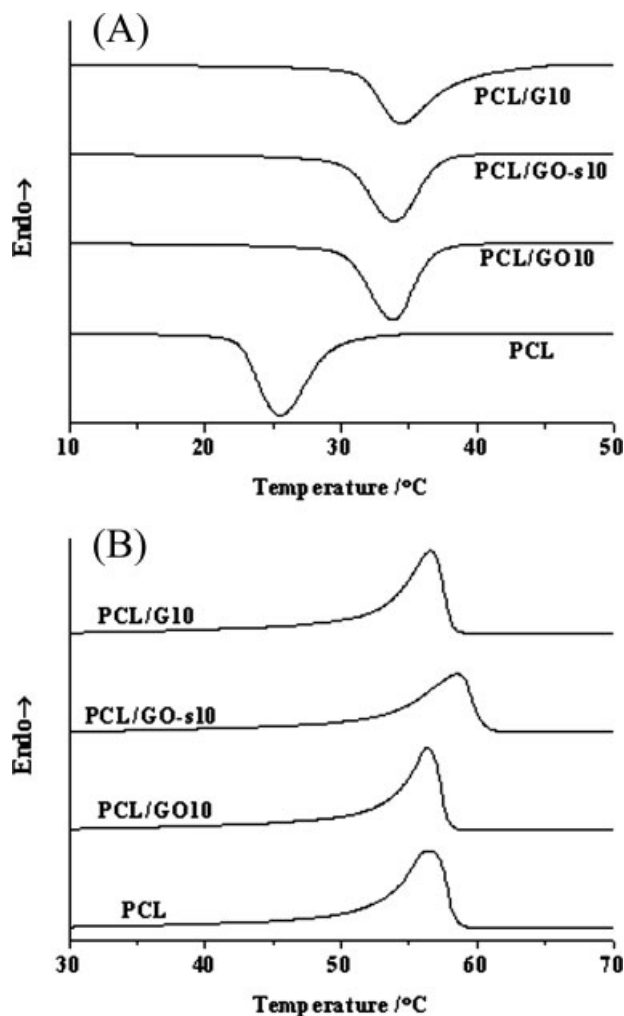
Figure 2 DSC (A) cooling and (B) heating curves of the PCL composites.

TABLE I
Thermal Properties of PCL and the PCL Composites

Sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PCL	25.5	−53.0	56.3	57.4
PCL/GO1	33.2	−56.0	56.4	60.8
PCL/GO5	33.8	−55.2	56.1	59.8
PCL/GO10	33.8	−53.1	56.4	57.8
PCL/GO-s1	31.3	−56.0	56.5	60.3
PCL/GO-s5	33.6	−53.8	57.8	59.3
PCL/GO-s10	33.9	−50.4	58.5	56.0
PCL/G1	33.8	−55.9	56.3	60.9
PCL/G5	33.9	−55.3	56.6	60.4
PCL/G10	34.4	−55.6	56.5	60.3

corresponded to an interlayer distance of about 1.1 nm. We suggest that the increase in this interlayer distance value was caused by the intercalation of PCL to the interlayer of GO because the DMF solution was not detected in the PCL/GO-s10 by the DSC heating measurement in the temperature range up to 200°C. A similar intercalation structure was also found in the PCL/clay composites studied by Gorrasi et al.[30]

Nonisothermal crystallization and melting behavior

Figure 2 shows the DSC cooling and heating curves of PCL and the PCL composites. In Table I are summarized the values of the temperature and enthalpy of crystallization and melting. Figure 3 shows the DSC heating curves of the PCL/GO-s composites. The values of ΔH_c and ΔH_m were normalized by the weight content of PCL in the composite.

The T_c values of all of the PCL composites increased about 8°C compared with that of pure

PCL. This was due to the nucleating effect of GO and graphite on the PCL crystallization, although the volume content of each filler was not related to T_c. However, compared with the DSC cooling curves of the PCL composites, the crystallization of PCL in PCL/G10 was faster than those in PCL/GO10 and the PCL/GO-s10, as the DSC peak temperature for the former was higher than those of the latter, which indicated that graphite had a better nucleating effect on the crystallization of PCL than GO. The degree of crystallinity of PCL in PCL/GO, PCL/GO-s, and PCL/G decreased continuously with increasing volume fraction of the fillers, whereas the T_c did not change much. Notably, ΔH_c of the PCL/GO-s10 composite decreased about 6 J/g compared with that of the PCL/GO-s1 composite, although there was no change in ΔH_c and ΔH_m of the PCL/G composites induced by the change of the volume fraction of graphite.

All PCL/G and PCL/GO composites showed the same melting point as neat PCL. On the other hand, the melting points of the PCL/GO-s composite
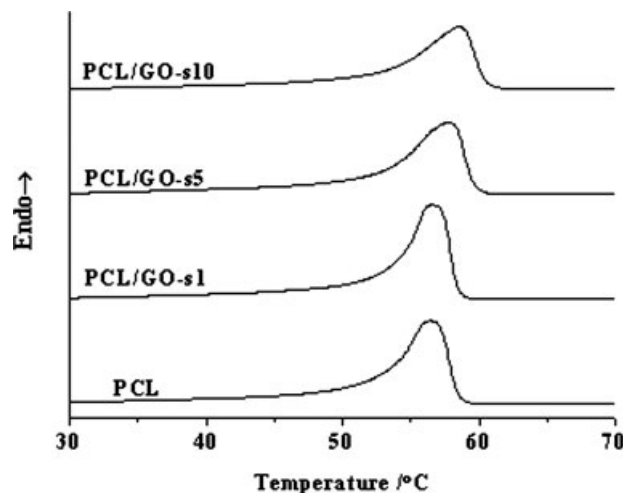

Figure 3 DSC heating curves of the PCL/GO-s composites.

TABLE II
Mechanical Properties of PCL and the PCL/GO, PCL/GO-s, and PCL/G Composites

Sample	Tensile yield stress (N/mm^2)	Elongation at break (%)	Young's modulus (N/mm^2)
PCL	15.6 ± 0.2	853.8 ± 144	340.2 ± 18
PCL/GO1	16.9 ± 0.4	735.3 ± 116	411.4 ± 30
PCL/GO5	20.3 ± 0.3	218.7 ± 169	712.4 ± 44
PCL/GO10	19.6 ± 0.6	97.4 ± 74	708.6 ± 46
PCL/GO-s1	17.8 ± 0.1	792.2 ± 17	467.3 ± 16
PCL/GO-s5	21.3 ± 0.7	87.8± 79	707.5 ± 7
PCL/GO-s10	26.5 ± 0.5	12.5 ± 6	1037 ± 102
PCL/G1	16.4 ± 0.4	728.0 ± 94	389.5 ± 23
PCL/G5	17.0 ± 0.3	659.7 ± 16	480.9 ± 21
PCL/G10	18.3 ± 0.3	632.5 ± 29	577.8 ± 46

increased with increasing volume fraction of GO (see Fig. 3).

The decrease in ΔH_c and ΔH_m and the increase in the T_m observed for the PCL composites could be probably attributed to the fact that the PCL/GO-s5 and the PCL/GO-s10 formed an intercalated structure of the composites. After intercalation of the PCL chain into the layer of GO in the composites, the mobility of the PCL chain was restricted by the GO layer so that it was hard for it to crystallize between the GO layers, which resulted in a decrease in the crystallinity.

Tensile tests of the blend films

The tensile properties—yield stress, Young's modulus, and elongation at break—were measured and are listed in Table II and Figures 4 and 5. In the case of the PCL composites with low filler content, that is, 1 wt % of GO or graphite, the elongation at break was slightly decreased, but the yield stress and the Young's modulus were slightly increased compared with those of pristine PCL.

On the other hand, a decrease in the elongation at break and an increase in the yield stress and the Young's modulus were observed with increasing volume of graphite and GO in all of the PCL/G, PCL/GO, and PCL/GO-s composites, although, due to the load transfer between the polymer and the inorganic particles, GO, the yield stress and Young's modulus increased with increasing volume fraction of the fillers. Interestingly, the values of the mechanical properties of the PCL/GO and PCL/GO-s composites were different from the increasing filler content compared with those of the PCL/G composites. Elongation at break exhibited a pronounced decrease from 850% (neat PCL) to less than 100% (PCL/GO10) and to less than 20% (PCL-GOs10), although it was not so decreased for the PCL/G10 composite, about less than 650%. Yield stress increased from about 15 to 20 N/mm^2 (PCL/GO10) and to more than 26 N/mm^2 (PCL/GO-s10). Additionally, Young's modulus significantly increased from 350 N/mm^2 to more than 700 N/mm^2 (PCL/GO10) and to more than 1000 N/mm^2 (PCL/GO-s10).
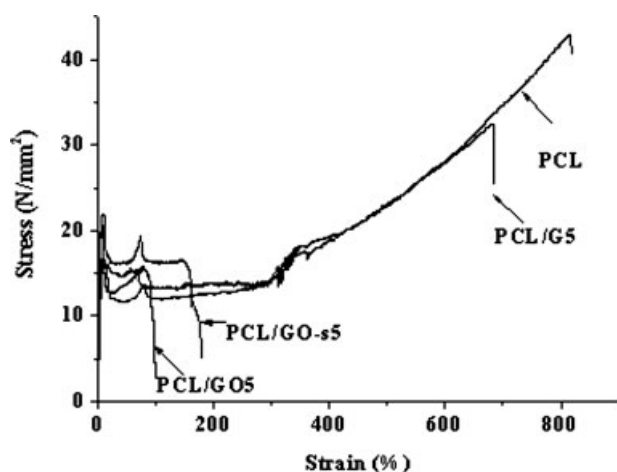

Figure 4 Stress–strain curves of the PCL composites with 5 wt % filler added.
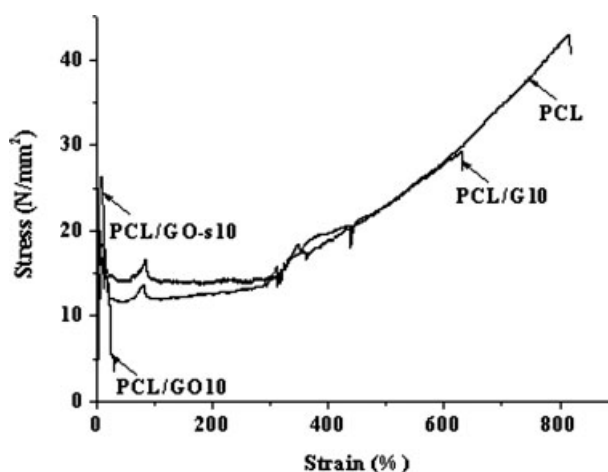

Figure 5 Stress–strain curves of the PCL composites with 10 wt % filler added.

The mechanical properties were unchanged in the PCL/GO5 and PCL/GO10 composites except for the elongation at break, whereas the yield stress and Young's modulus of the PCL/GO-s10 became larger than those of the PCL/GO-s5. These differences were attributed to the fact that the intercalation of GO was improved by ultrasonic treatment, which was proven by our previous WAXD study (Fig. 1). A significant decrease in the elongation at break, improvements in the yield stress, and the Young's modulus suggested the formation of an intercalation structure for the PCL/GO and PCL/GO-s composites.

CONCLUSIONS

Composites of PCL and GO were prepared through a solvent-casting method. In this study, we compared the structure and thermal and mechanical properties of PCL and PCL/GO, PCL/GO-s, and PCL/G composites and investigated the effects of GO and graphite as fillers and of ultrasonic treatment in the mixing of PCL with GO on the properties of PCL.

From the WAXD patterns, the interlayer distances of GO were found to expand from about 0.6 to 1.1 nm in the PCL/GO and PCL/GO-s composites, which indicated an intercalation of PCL into the GO layers in the PCL/GO composites. From the thermal analysis, it was found that the PCL/GO-s composites showed increase in nonisothermal crystallization peak temperature with increasing filler volume, which indicated that GO had a good nucleating effect on the crystallization of PCL. The PCL/GO and PCL/GO-s composites showed a dramatic increase in both yield stress and Young's modulus, whereas the elongation at break significantly decreased compared to those of PCL and the PCL/G composites. The relatively high yield stress and Young's modulus in the PCL/GO composite compared to those of the PCL/G composite were probably due to the relatively better interaction between PCL and GO than between PCL and graphite due to the intercalation of the PCL and GO layers, which achieved a better load transfer in the PCL/GO-s composites. Graphite is abundant in the nature, so GO could be a good and cheap filler for PCL.

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