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Dynamic mechanical and morphological properties of polycarbonate/multi-walled carbon nanotube composites

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Abstract

Dynamic mechanical and morphological properties of the polycarbonate (PC)/multi-walled carbon nanotube (MWNT) composites were studied by dynamic mechanical thermal analysis (DMTA) and X-ray diffractometry, respectively. For the without annealed PC/MWNT composites containing the higher content of the MWNT (≥ 7.0 wt%), double tan δ peaks were observed, which could be explained by the phase separation morphology model. For the annealed PC/MWNT composites, a broad single tan δ peak was observed. From the X-ray diffraction of the annealed PC/MWNT composites, it was observed that more regular structure of the PC was obtained, which was consistent with the result of the thermal analysis of the annealed PC/MWNT composites. From the dynamic mechanical properties, thermal analysis, and X-ray diffraction of the annealed PC/MWNT composites, it is suggested that PC/MWNT composites show a broad single tan δ peak and partially crystalline structure of the PC in the PC/MWNT composites by annealing.

Keywords: Multi-walled carbon nanotube; Composite; Dynamic mechanical properties

1. Introduction

Since, the discovery of the carbon nanotube (CNT) by Iijima [1], the CNT has been intensively studied for the application of the polymer/CNT composites because of its superior properties [2–12]. For example, the CNT has Young's modulus up to 1 TPa [13]. Also, the CNT has very large aspect ratio, as high as 100–1000. Therefore, it has been suggested that the CNT is an ideal candidate for the polymer-filler composites.

In the polymer-filler composites, the glass transition temperature (T_g) of the polymer composites could be changed. The change of the T_g of the polymer composites is influenced by several factors such as filler size, filler loading content and aspect ratio of the filler [14–17]. For the poly(vinyl acetate) (PVAc)/tetraethoxysilane (TEOS) [14] and epoxy/multifunctional polyhedral oligomeric silsesquioxane composites [15], the glass transition region was broadened.

In contrast to the above results, some of the polymer composites showed double T_g behavior. Tsagaropoulos and Eisenberg [16] reported the double T_g behavior for the PVAc/silica, polystyrene (PS)/silica, poly(methyl methacrylate) (PMMA)/silica, poly(dimethylsiloxane) (PDMS)/silica, styrene–butadiene–rubber (SBR)/silica, and poly(4-vinylpyridine) (P4VP)/silica composites. Also, Verghese et al. [17] reported the double T_g behavior for the polycarbonate (PC)/carbon fiber (CF) composite. According to the Tsagaropoulos and Eisenberg [16], it has been proposed that the higher T_g was related to the polymer chain whose motion was restricted by the filler and the lower T_g was related to the T_g of the polymer matrix.

In this study, the T_g behavior and morphological properties of the PC/multi-walled carbon nanotube (MWNT) composites are reported using the dynamic mechanical thermal analysis and X-ray diffractometry, respectively. In particular, the effects of the MWNT content and thermal annealing on the properties of the PC/MWNT composites are investigated.

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2. Experimental

2.1. Materials

A MWNT was supplied by the Hyperion Catalysis International, Cambridge, MA, USA as a form of the PC/MWNT masterbatch. Hyperion masterbatch contains the 15 wt% MWNT. The MWNT was vapor grown and typically consists of 8–15 graphitic layer wrapped around a hollow 5 nm core [8]. Typical diameter of MWNT ranged from 10 to 15 nm, while length is between 1 and 10 μm [8]. The Hyperion masterbatch was diluted with PC supplied by LG Chem. with the commercial designation of PC 201 15. The characteristics of the PC and Hyperion masterbatch are summarized in Table 1.

2.2. Composite preparations

PC/MWNT composites were prepared by Prism twin screw extruder. The PC/MWNT composites, ranged from 1.5 to 15 wt% MWNT content, were prepared by diluting the Hyperion masterbatch with the PC. The temperatures of the extruder were set at 240 and 270 °C in feeding and barrel zone, respectively. Samples were compression molded using hot press at 260 °C for 5 min. For the preparation of the thermally annealed samples, the samples were annealed at 190 °C for 8 h. Before sample preparation, all the samples were dried under vacuum (<1 mmHg) at 100 °C for 24 h.

2.3. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out on advanced rheometric expansion system (ARES) in oscillatory torsional mode at 0.1% strain and 1 Hz frequency. The temperature was scanned between 50 and 230 °C at a rate of 5 °C/min.

2.4. Differential scanning calorimetry (DSC)

The thermal properties of samples were measured using Perkin–Elmer differential scanning calorimeter, model DSC-7. The temperature was scanned between 50 and 250 °C at a heating rate of 20 °C/min.

Table 1
Characteristics of PC and MWNT masterbatch used in this study

Sample	$\bar{M}_n$	$\bar{M}_w$	MWD	T_g (°C)[a]
PC[b]	11,000	30,000	2.7	156.6
MWNT masterbatch[c]	–	–	–	146.0

[a] Measured in our laboratory by DMTA.

[b] Supplied by LG chem. Co (PC 201 15).

[c] Supplied by Hyperion Catalysis International, Cambridge, MA, USA (PC/MWNT = 85/15 wt%).

2.5. X-ray diffraction

X-ray diffraction analysis was performed by Mac Science, MXP-HF. The accelerating voltage was 40 kV and the current was 100 mA. The scanning range was 1.8–40° with a scanning rate of 1°/min.

3. Results and discussion

3.1. Dynamic mechanical properties

Fig. 1 shows the storage modulus (G') of the PC and PC/MWNT composites with MWNT content. From Fig. 1, the storage modulus below the T_g (glassy region) of the PC and PC/MWNT composites maintains plateau and shows no significant difference among the samples. Above the T_g (rubbery plateau region), the storage modulus of the PC and PC/MWNT composites decreases with increasing the temperature. For the rubbery plateau region, the storage modulus of the composites is significantly increased with increasing the MWNT content. For example, the storage modulus of the PC and PC/MWNT (85.0/15.0) is 1.5×10^6 and 1.2×10^7 Pa, respectively, at 180 °C.

Fig. 2 shows the shifted tan δ vs temperature for the PC and PC/MWNT composites (each samples are vertically shifted for clarity). For the PC, the tan δ curve shows single peak (156.6 °C) corresponding to the T_g of the PC. For the above T_g of the PC, the values of tan δ curves of the PC/MWNT composites decrease with increasing the MWNT content. For the PC/MWNT (93.0/7.0) composite, double tan δ behavior is observed. The lower tan δ peak corresponds to the T_g of the PC and the higher tan δ peak corresponds to the polymer chain whose chain mobility is

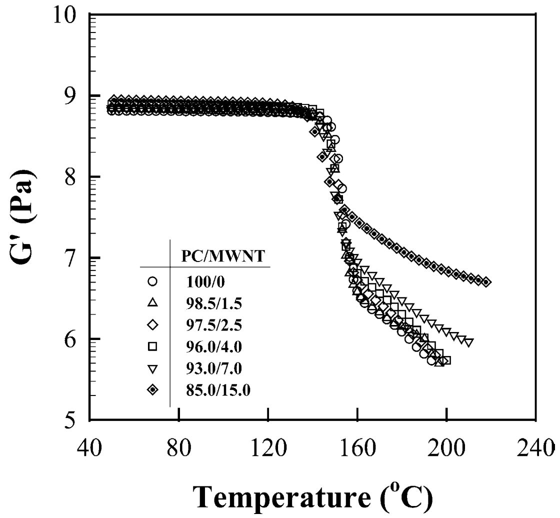

Fig. 1. Storage modulus (G') of the PC and PC/MWNT composites with MWNT content: (○) PC; (△) PC/MWNT (98.5/1.5); (◇) PC/MWNT (97.5/2.5); (□) PC/MWNT (96.0/4.0); (▽) PC/MWNT (93.0/7.0); (◈) PC/MWNT (85.0/15.0).

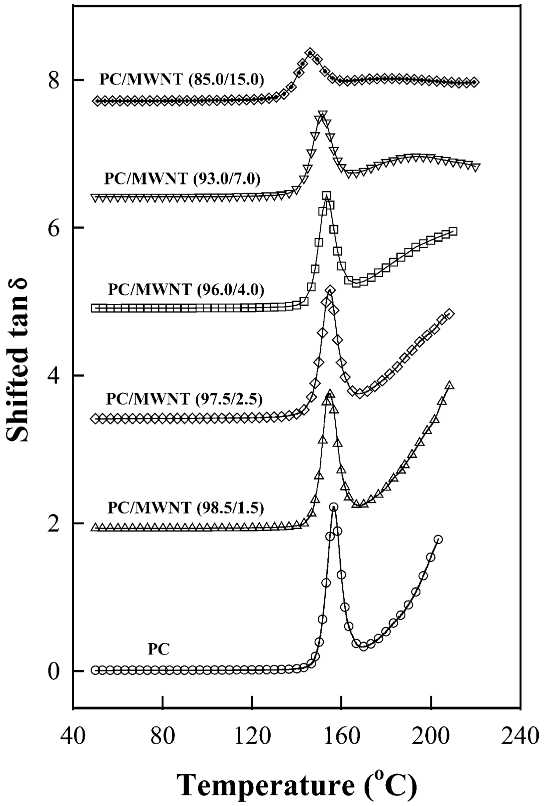

Fig. 2. Shifted tan δ vs temperature for the PC and PC/MWNT composites: (○) PC; (△) PC/MWNT (98.5/1.5); (◇) PC/MWNT (97.5/2.5); (□) PC/MWNT (96.0/4.0); (▽) PC/MWNT (93.0/7.0); (◈) PC/MWNT (85.0/15.0).

restricted by the MWNT. For the PC/MWNT (85.0/15.0) composite, the higher tan δ peak becomes broader, which may be considered that the mobility of the polymer chain becomes more restricted by the MWNT. Similar results were reported by Tsagaropoulos and Eisenberg [16] for the PVAc/silica, PS/silica, PMMA/silica, PDMS/silica, SBR/silica, and P4VP/silica composites. Also, Verghese et al. [17] reported double tan δ behavior for the PC/CF composites. To investigate the unusual 'double tan δ peaks of the polymer composites', Tsagaropoulos and Eisenberg [16] and Eisenberg et al. [18] suggested the phase separation morphology model. According to the phase separation morphology model, the lower tan δ peak of the polymer composites corresponded to the T_g of the polymer matrix, and the higher tan δ peak of the polymer composites corresponded to the T_g of the confined polymer chain by the filler.

Table 2 shows the area of the lower tan δ peak for the PC/MWNT (100/0), (98.5/1.5), (97.5/2.5), (96.0/4.0), (93.0/7.0), and (85.0/15.0) composites. From the Table 2, it is observed that the area of the lower tan δ peak decreases with increasing the MWNT content in the PC/MWNT composites. The area of the tan δ peak decreases from 21.6 to 11.5 for the PC and PC/MWNT (85.0/15.0), respectively, which suggests that the fraction of the PC confined by MWNT increases with increasing the MWNT content.

Table 2
Area of the lower tan δ peak for the PC and PC/MWNT composites

PC/MWNT (wt%)	Area (tan δ)
100/0	21.6
98.5/1.5	21.0
97.5/2.5	20.7
96.0/4.0	17.6
93.0/7.0	16.5
85.0/15.0	11.5

Fig. 3 shows the shifted tan δ vs temperature for the PC and PC/MWNT composites after annealing the samples at 190 °C for 8 h (each samples are vertically shifted for clarity). From Fig. 3, single tan δ peak is observed for the annealed PC/MWNT (98.5/1.5), (97.5/2.5), (96.0/4.0), (93.0/7.0), and (85.0/15.0) composites. From Fig. 3, the single tan δ peak of the annealed PC/MWNT composites is less intense and broader compared to the samples of the without annealed PC/MWNT composites.

Fig. 4 shows the shifted tan δ vs temperature for the annealed and without annealed samples of the PC/MWNT (97.5/2.5) and (96.0/4.0) composites. For the annealed samples of the PC/MWNT (97.5/2.5) and (96.0/4.0), the tan δ peak corresponding to the glass transition is broader compared to the without annealed samples. When the PC/

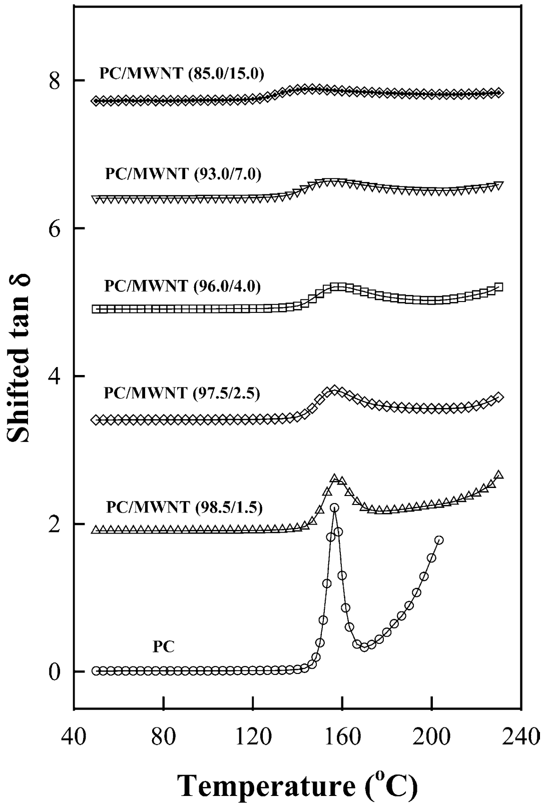

Fig. 3. Shifted tan δ vs temperature for the PC and PC/MWNT composites after annealing the samples at 190 °C for 8 h: (○) PC; (△) PC/MWNT (98.5/1.5); (◇) PC/MWNT (97.5/2.5); (□) PC/MWNT (96.0/4.0); (▽) PC/MWNT (93.0/7.0); (◈) PC/MWNT (85.0/15.0).

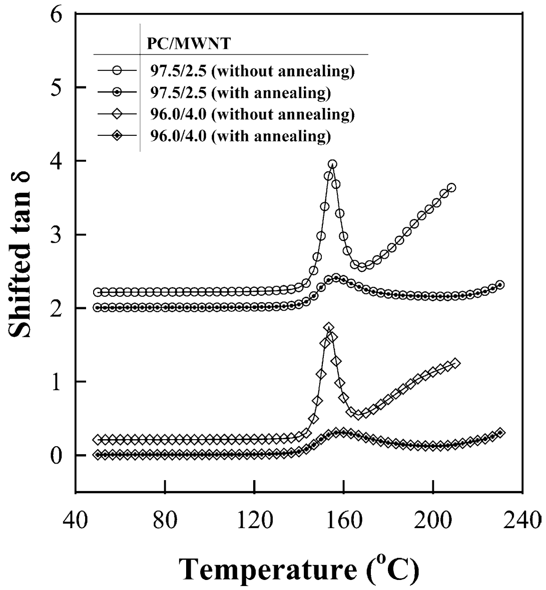

Fig. 4. Shifted tan δ vs temperature for the annealed and without annealed samples of the PC/MWNT (97.5/2.5) and (96.0/4.0) composites: (○) PC/MWNT (97.5/2.5) (without annealing); (⊙) PC/MWNT (97.5/2.5) (with annealing); (◇) PC/MWNT (96.0/4.0) (without annealing); (◈) PC/MWNT (96.0/4.0) (with annealing).

MWNT composites are annealed, it is thought that a segmental chain motion of the PC/MWNT composites is retarded because of the confinement of the PC by annealing the composites. Therefore, a broad glass transition region is observed for the annealed PC/MWNT composites.

Fig. 5 shows the shifted tan δ vs temperature for the annealed and without annealed samples of the PC/MWNT (93.0/7.0) and (85.0/15.0) composites. For the annealed samples of the PC/MWNT (93.0/7.0) and (85.0/15.0), broad single peak is observed. When the PC/MWNT (93.0/7.0) and (85.0/15.0) samples are annealed, it is thought that a segmental chain motion of the PC/MWNT composites is retarded and two tan δ peaks combine into the broad single tan δ peak. A broad single tan δ peak of the annealed PC/MWNT samples suggests that annealing of the PC/MWNT composites induces a structural change of the PC/MWNT composites such as the formation of crystalline structure of the PC in the presence of the MWNT. It has been reported that the crystallization of PC was observed in the presence of the MWNT with annealing condition [19].

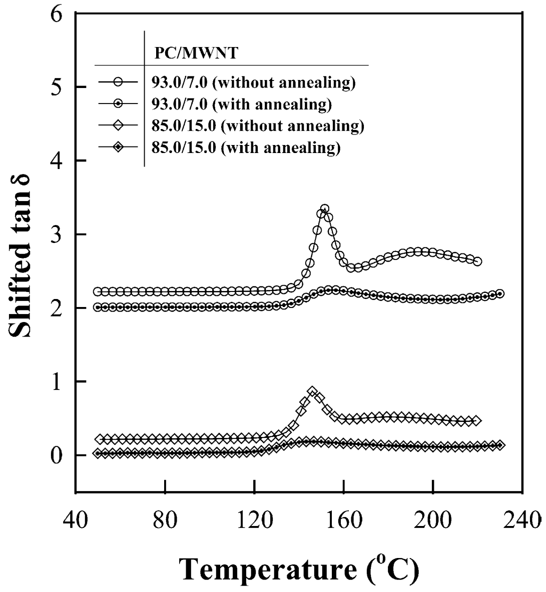

Fig. 5. Shifted tan δ vs temperature for the annealed and without annealed samples of the PC/MWNT (93.0/7.0) and (85.0/15.0) composites: (○) PC/MWNT (93.0/7.0) (without annealing); (⊙) PC/MWNT (93.0/7.0) (with annealing); (◇) PC/MWNT (85.0/15.0) (without annealing); (◈) PC/MWNT (85.0/15.0) (without annealing).

In summary, dynamic mechanical properties of the PC/MWNT composites analyzed by the DMTA showed the following behavior. For the without annealed PC/MWNT composites containing the low content of the MWNT ($\leq$4.0 wt%), single tan δ peak which corresponds to the T_g of the PC is observed. For the without annealed PC/MWNT composites containing the high content of the MWNT ($\geq$7.0 wt%), double tan δ peaks are observed, which can be explained by the phase separation morphology model [16]. From this model, it is suggested that the lower tan δ peak of the PC/MWNT composites corresponds to the T_g of the PC matrix, and the higher tan δ peak of the PC/MWNT composites corresponds to the confined PC chain by the MWNT. For the annealed PC/MWNT composites, a broad single tan δ peak is observed, which suggests that the structural change such as crystallization of the PC in the PC/MWNT composites are induced by annealing the PC/MWNT composites.

3.2. Morphological properties

Fig. 6 shows the DSC thermograms of the PC, without annealed sample of the PC/MWNT (85.0/15.0), and annealed sample of the PC/MWNT (85.0/15.0) at 190 °C

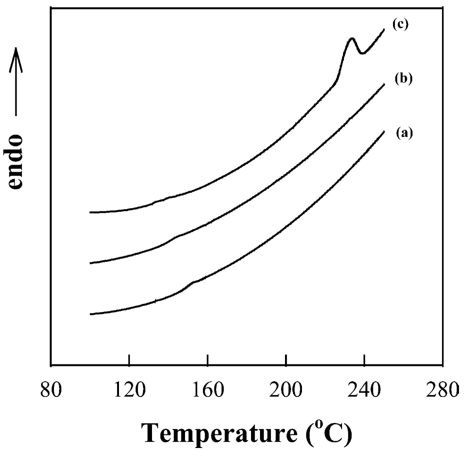

Fig. 6. DSC thermograms of the PC, without annealed sample of the PC/MWNT (85.0/15.0), and annealed sample of the PC/MWNT (85.0/15.0) at 190 °C for 8 h: (a) PC; (b) PC/MWNT (85.0/15.0) (without annealing); (c) PC/MWNT (85.0/15.0) (with annealing).

for 8 h. From Fig. 6(c), the crystal melting peak of the PC in the PC/MWNT (85.0/15.0) is observed after annealing the PC/MWNT (85.0/15.0) sample.

Fig. 7 shows the X-ray diffraction pattern of the PC and without annealed PC/MWNT composites. For the PC, the X-ray diffraction pattern shows a broad peak corresponding to the amorphous PC. For the PC/MWNT (93.0/7.0) and (85.0/15.0) composites, a new peak is shown at $2\theta=26.2°$. This new peak represents the interlayer spacing among the graphitic layer of the MWNT [20].

Fig. 8 shows the X-ray diffraction pattern of the PC/MWNT composites after annealing the samples at 190 °C for 8 h. For the annealed samples of the PC/MWNT composites, a sharp peak is observed compared to the without annealed samples of the PC/MWNT composites. This result indicates that the structure of the amorphous PC of the PC/MWNT composites changes to more regular structure by annealing in the presence of the MWNT, which is consistent with the results of the thermal analysis of the PC/MWNT composites. Similar results were reported by Takahashi et al. [19] that PC crystallization was observed in the presence of the carbon nanotube (CNT). From the above results of the dynamic mechanical properties, thermal analysis by DSC, and morphological properties by X-ray diffraction pattern, it is suggested that PC/MWNT composites show a broad single tan δ peak and partially crystalline structure of the PC in the PC/MWNT composites by annealing.

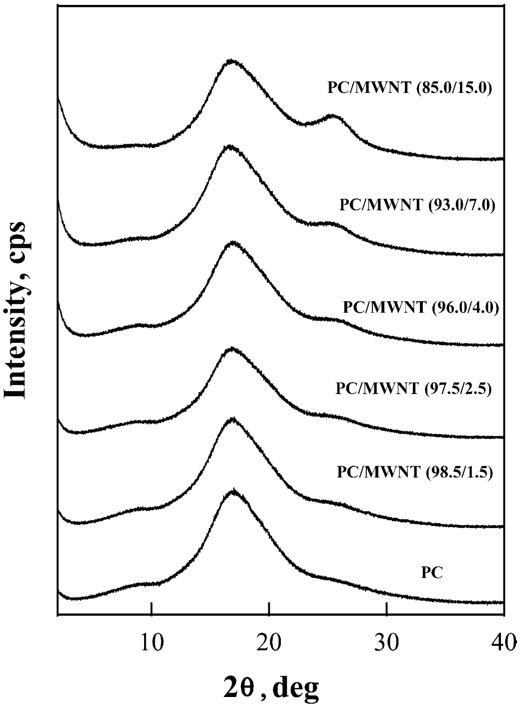

Fig. 7. X-ray diffraction pattern of the PC and without annealed PC/MWNT composites.

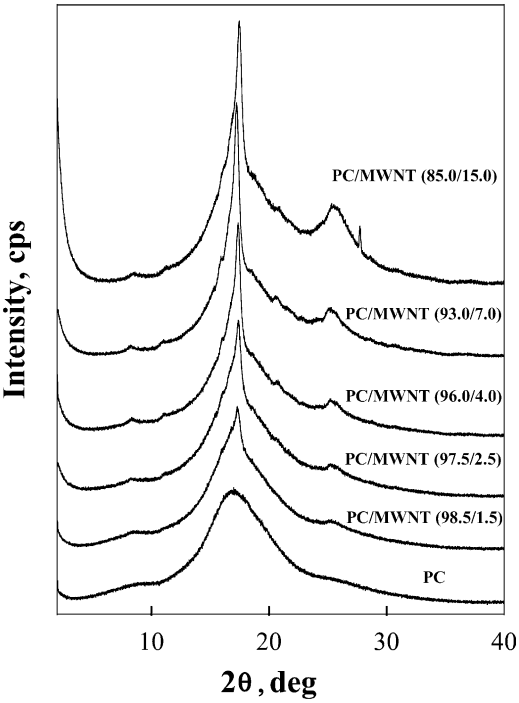

Fig. 8. X-ray diffraction pattern of the PC and PC/MWNT composites after annealing the samples at 190 °C for 8 h.

4. Conclusions

In this study, the dynamic mechanical and morphological properties of the PC/MWNT composites were studied by dynamic mechanical thermal analysis (DMTA) and X-ray diffractometry, respectively.

From the results of the dynamic mechanical properties of the without annealed PC/MWNT composites containing the low content of the MWNT (≤ 4.0 wt%), single tan δ peak corresponding to the T_g of the PC was observed. For the without annealed PC/MWNT composites containing the high content of the MWNT (≥ 7.0 wt%), double tan δ peaks were observed, which could be explained by the phase separation morphology model. For the annealed PC/MWNT composites, a broad single tan δ peak was observed, which suggested that partially crystalline structure of the PC/MWNT was obtained by thermal annealing.

In the study of the DSC analysis of the PC/MWNT composites, the crystal melting peak of the PC/MWNT (85.0/15.0) composite was observed after annealing the sample. From the X-ray diffraction pattern of the annealed PC/MWNT composites, it was observed that more regular structure of the PC was obtained, which was consistent with results of the thermal analysis of the PC/MWNT composites.

From the above results of the dynamic mechanical properties, DSC and X-ray diffraction of the PC/MWNT composites, it can be concluded that the PC/MWNT composites show a broad single tan δ peak and partially crystalline structure of the PC in the PC/MWNT composite by annealing the sample.

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