

Morphology, Crystallization, and Mechanical Properties of Poly(ethylene terephthalate)/Multiwall Carbon Nanotube Nanocomposites Via *In Situ* Polymerization with Very Low Content of Multiwall Carbon Nanotubes

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ABSTRACT: So far, the reported content of multiwall carbon nanotubes (MWNTs) in polymer/MWNTs nanocomposites is usually above 0.1 wt %. In this article, we will report our work on the study of the morphology, crystallization, and mechanical properties of poly(ethylene terephthalate) (PET)/MWNTs nanocomposites prepared by *in situ* polymerization with very low content of MWNTs (from 0.01 to 0.2 wt %). Well-dispersed MWNTs with a big network throughout PET matrix were observed by SEM. The very small amount of MWNTs displayed a great nucleating effect on the PET crystallization. The crystallization temperature was improved for 6.4°C by using only 0.01 wt % MWNTs. The decreased chain

mobility of PET by adding MWNTs was evident by the formation of imperfect or smaller/thinner crystallites with low melting temperature. An increased storage modulus was also achieved for the nanohybrids with MWNT content less than 0.05 wt %. Our result indicates that using very low content MWNTs (less than 0.1 wt %) is a simple way to achieve good dispersion, yet with remarkable enhancement for polymer/MWNTs modification. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3695–3701, 2007

Key words: poly(ethylene terephthalate); carbon nanotubes; morphology; crystallization; low content

INTRODUCTION

Since their discovery in 1991,¹ carbon nanotubes (CNTs) have attracted much attention worldwide because of their unusual mechanical, thermal, and electrical properties. CNTs can be classified into two types: single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs). MWNTs comprise concentric SWNTs held together by weak van der Waals's forces.² Because of the mass production and price reduction, MWNTs are more affordable for applications in structural materials.

As expected for the high aspect ratio, introducing CNTs into a polymer matrix improves the mechanical properties and electrical conductivity of the original polymer matrix.^{3–7} However, CNTs are generally insoluble and severely bundled, their homogeneous dispersion in polymer matrices represents a significant challenge. It is now well known that CNTs can be solubilized through chemical modification or func-

tionalization. In many approaches, the chemical oxidation in aqueous media^{4–10} is utilized widely. Furthermore, some other approach should be paid attention, such as ultrasonication,¹¹ using surfactant,³ and mechanochemical reaction,¹² etc. There are three main approaches to prepare the polymer/MWNTs nanocomposites: (i) melt extrusion,^{13,14} (ii) *in situ* polymerization, and (iii) solution mixing.¹⁵

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester with various excellent properties and is widely used in many application such as fiber, films, packing, and engineering plastics in electronics. Thus, any enhancement of PET in crystallization, antistatic, mechanical, and other properties will lead to a great potential industrial application. Nogales et al.¹⁶ used an *in situ* polycondensation reaction process to achieve low percolation thresholds in SWNTs and thermoplastic poly(butylenes terephthalate) (PBT) composites and the percolation threshold is about 0.2 wt % of SWNTs. They interpreted that agglomeration might enhance the formation of the conducting network. Lee et al.¹⁷ had grafted MeO- and EtO- to the surface of MWNT via a Friedel–Crafts reaction to obtain the well-dispersed MWNT in PET. The crystallization temperature (T_c) of EtO-MWNTs/PET with the content of 0.4 wt % MWNTs was 26.6°C higher than that of neat PET. Hu et al.¹⁸ applied coagulation method to prepare PET/MWNTs nanocomposites and achieved the percola-

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tion threshold of 0.6 wt % (based on viscosity) for rheological property and 0.9 wt % for electrical conductivity. In their opinion, the difference of the percolation threshold between rheological property and electrical conductivity is mainly attributed to the fact that the denser of MWNTs network required for electrical conductivity is more than that for rheological property.

So far, the reported content of MWNTs formed the network in polymer matrix is usually above 0.1 wt %. Actually, an even more diluted concentration of MWNT is necessary for the disentanglement and better dispersion of MWNT in polymer. In this article, we will report our work on the study of the morphology, crystallization, and mechanical properties of PET/MWNTs nanocomposites prepared by *in situ* polymerization with very low content of MWNT (from 0.01 to 0.2 wt %). By reducing the content of MWNT, one expects a cheaper price and a better dispersion. The question is, can remarkably enhanced properties be achieved by using very low content of MWNT in polymer matrix? Our result indicates that using very low content MWNT (less than 0.1 wt %) is a simple way to achieve good dispersion yet with remarkable enhancement for polymer/MWNTs nanocomposites.

EXPERIMENT

Materials

Ethylene glycol (EG), Sb_2O_3 , and terephthalic acid (TPA) were purchased from market and were used as received. Triphenyl phosphite (TPP) (CR) was purchased from Kelong Chemical Reagent (Chengdu, China) and used as received.

The MWNTs (Chengdu Organic Chemistry, Chengdu, China), with the length of about 50 μm and diameter of 10–20 nm, were prepared by a thermal chemical vapor deposition method. The purity of the pristine MWNTs was above 95%, with many metallic catalysts and sheet-like amorphous carbon [Fig. 1(a)]. Before they were used, further purification was necessary. In a typical purification, a raw-MWNTs sample (4.0 g) was mixed with an aqueous HNO_3 solution (2.6M, 700 mL) and stirred at 70°C for 24 h. Finally, the solution was filtered through a cellulose nitrate filter (pore size = 0.2 μm) and dried at 60°C in a vacuum oven for 24 h. The as-prepared MWNTs were obtained. In the functional treatment, the as-prepared MWNTs were added in the concentrated H_2SO_4 (98%) and HNO_3 (65%) mixed solution (3 : 1 by volume) for 24 h at room temperature with stirring.

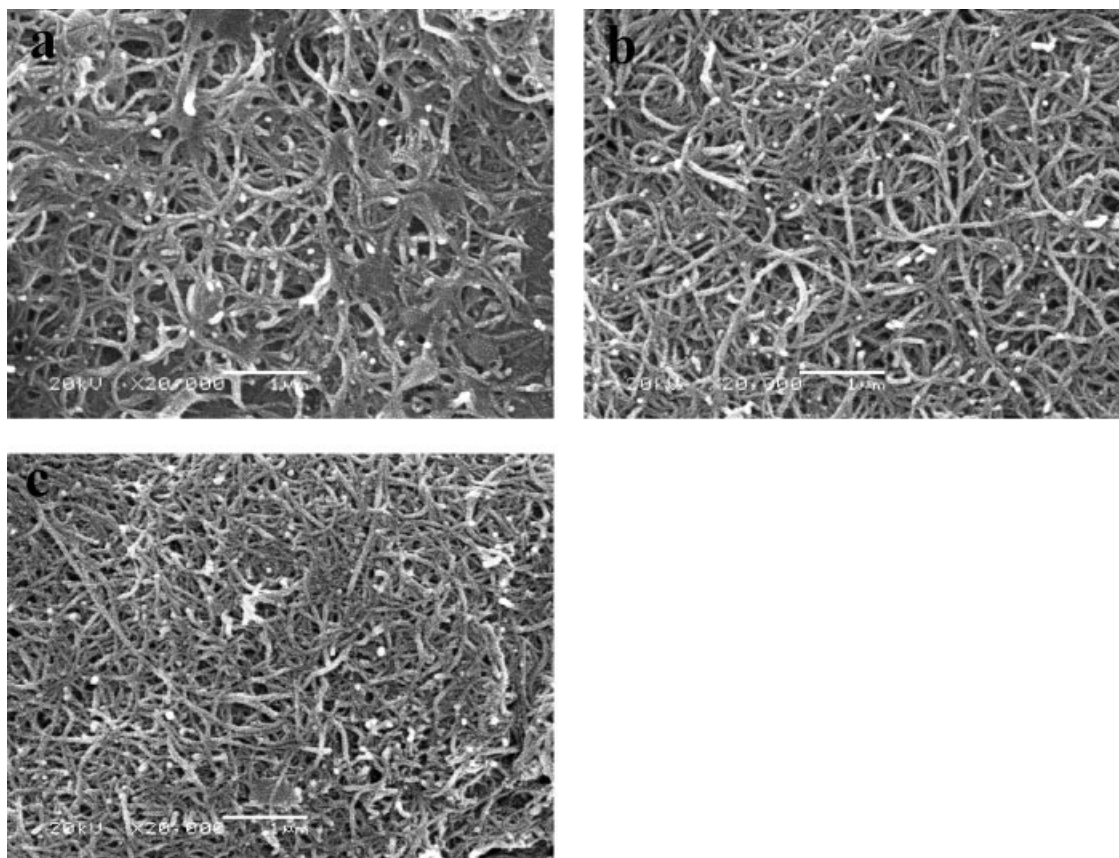


Figure 1 SEM images of (a) raw-MWNTs (20,000 \times); (b) as-prepared MWNTs (20,000 \times); (c) MWNTs-COOH (20,000 \times). Scale bar is 1 μm .

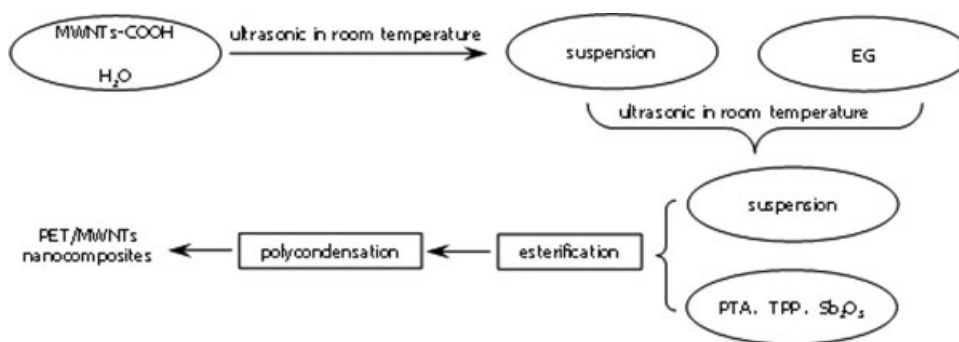


Figure 2 Schematic illustration of the preparation of PET/MWNTs nanocomposites.

Finally, the solution was also filtered, washed, and dried as mentioned earlier, thus MWNTs-COOH was obtained and used for the preparation of PET/MWNTs nanocomposites.

In situ synthesis of PET/MWNTs nanocomposites

An appropriate amount of MWNTs-COOH was first dispersed in H₂O with ultrasonic for 10 min, and then the aqueous solution was mixed with 50 mL EG with ultrasonic for another 10 min. The dark mixture, TPA, Sb₂O₃, and TPP were added into the autoclave. With stirring and heating, the composites were obtained through esterification and polycondensation (Fig. 2). The nanocomposite was extruded from the reactor by compressed nitrogen and cut into pellets. The contents of MWNT were 0.01 wt % (0.01/100), 0.05 wt % (0.05/100), 0.1 wt % (0.1/100), and 0.2 wt % (0.2/100) (MWNTs/PET), respectively. In all the cases, the samples had similar molecular weight ($[\eta] \sim 0.74\text{--}0.84$ dL/g ISO1228-1975(E)). The pellets were dried in an oven at 128°C for 6 h before injection-molding. The specimens for DMA experiment were obtained using a PS4035ASE injection-molding machine. The temperatures were chosen as 280/280/270/265°C from die to hopper.

Instrumentation

FTIR spectra of the MWNTs were recorded between 400 and 4000 cm⁻¹ on a Nicolet-560 FTIR spectrometer. The sample was coated on a KBr plate.

The melting behavior of prepared PET/MWNTs nanocomposites was studied by DSC with a Perkin-Elmer DSC Pyris-1. Every sample (about 4.5–5.5 mg) was subjected to heating from room temperature to 280°C as quick as possible, held at 280°C for 3 min to eliminate the thermal history, and cooled down to 20°C at scan rate of 10°C/min. Then the same sample was heated again to 280°C with the rate of 10°C/min.

The morphologies of the MWNTs and composites were examined under an acceleration voltage of 20 kV with a JEOL JSM-5900 LV for SEM experiment.

Dynamic mechanical analysis (DMA) measurements were carried out on a TA Company Q800, with the three-point bending clamp. The temperature was from 45 to 100°C with the rate of 3°C/min. The frequency was 1 Hz and the amplitude of the variations was fixed to 10 μm.

RESULTS AND DISCUSSION

Pretreatment of MWNTs

In many cases, the pretreatment of MWNTs is the key to achieve good dispersion in solutions or polymer matrices. In our work, the raw-MWNTs can only be suspended in H₂O or EG for a few hours after ultrasonic treatment, and then forming precipitate. After treated with 2.6M HNO₃ for 24 h, the metallic catalyst and amorphous carbon were eliminated [Fig. 1(b)], and the MWNTs can be well dispersed in EG and H₂O, remaining for about 24–48 h and 3–4 days, respectively. We thought the differences of remaining time between H₂O and EG could come from the hydrogen-bonding effect. After treated by HNO₃, the surface of MWNTs generated –COOH and –OH, so the interaction in the form of hydrogen-bonding between MWNTs and solvents would accelerate the dispersion of MWNTs and prevent the reaggregate during processing. The difference of the solvent's ability of forming hydrogen-bonding results in different settling time. The similar result was found by Kumar.¹⁹ In our work, the MWNTs treated by HNO₃ is called as-prepared MWNTs. The as-prepared MWNTs was further functionalized with concentrated H₂SO₄/HNO₃ (3 : 1) solvent for more –COOH groups on the outside surface of MWNTs to accomplish better solubility and dispersion. It is called MWNTs-COOH. With decreased diameter [Fig. 1(c)], FTIR result shows that the absorbance at 1714 cm⁻¹ is increased dramatically for MWNTs-COOH (Fig. 3), which indicates that the mixed solvent can lead to local damage on MWNTs (maybe interconnection among MWNTs) and generate more –COOH groups. This type of MWNTs could be dispersed very

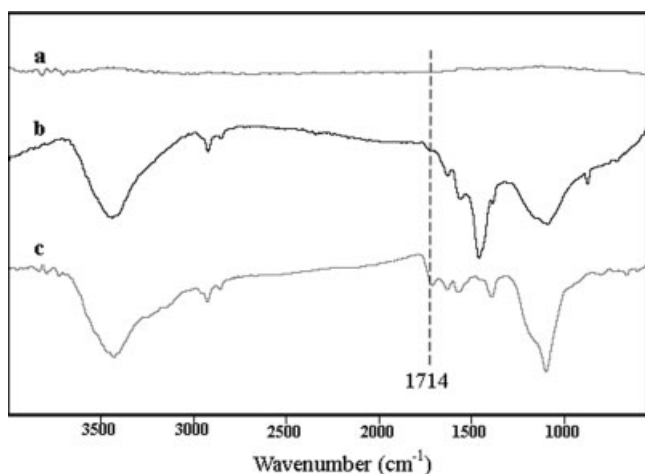


Figure 3 FTIR spectra of (a) raw-MWNTs; (b) as-prepared MWNTs; (c) MWNTs-COOH.

stably in H₂O and EG for several months (Fig. 4) and were used for the preparation of PET/MWNTs nanocomposites. As well known, the treatment will destroy MWNTs and decrease the mechanical and electrical properties, so the extent of functionalization should be balanced.

SEM morphology of PET/MWNTs nanocomposite

The nanocomposite samples for SEM were fractured at liquid nitrogen temperature. Because the MWNTs were embedded into the matrix and the content of MWNTs was very small, the fractured surfaces were etched in NaOH/ethanol (10 wt %) for 72 h at room temperature to remove the PET coating on the outside of MWNTs. As shown in Figure 5, compared to others, the sample with the MWNTs content of 0.01 wt % has the best MWNTs dispersion. And in the bigger region, the dispersion of MWNTs is homogeneous (from high magnification to low magnification). This result is quite different from many other reports in which the well dispersion of MWNTs was observed

only in a relatively small area. Interestingly, the well-dispersed MWNTs form a big network throughout the matrix with the lowest content. Other reports also obtained the similar results^{16,18,20,21} for electrical or rheological properties, but the content is much higher and there were always only the illustrations, and no direct evidence was obtained from SEM or TEM photos. The lumps under the MWNTs are PET matrix. After functionalized, the surface of MWNTs is grafted by many —COOH and —OH groups. So, the interaction may be a chemical bonding by esterification between monomer and MWNTs or electrostatic adsorption (or π - π conjugation) between the surface of MWNTs and the PET chain. The exact mechanism of interaction between the polymer and the MWNTs is unclear at this moment and needs further investigation. With increasing of MWNTs content, the lumps changes from isolated to continuous and the density of network is increased. In these cases, the high MWNTs are wrapped tightly by PET matrix and cannot be easily exposed. So, in one hand, the increase of the content of MWNT will hinder the dispersion of MWNTs, but on the other hand, can promote the formation of network and the interaction between the filler and the matrix. The optimum content of MWNTs will be our next research point.

DSC experiment

The effect of MWNTs on the crystallization and melting behavior of PET can be investigated by DSC cooling and heating experiments. And also, from the change of crystallization temperature (T_c) and melting temperature (T_m) of PET, one could deduce the dispersion of MWNTs in the matrix. For this reason, the DSC experiment was carried out on the prepared PET/MWNTs nanocomposites, and the result is shown in Figure 6. One observes an increased T_c from 194.2°C for neat PET to 200.6, 202.9, 203.3, and 203.8°C in the cooling process for the nanohybrids with 0.01, 0.05, 0.1, and 0.2 wt %, respectively,

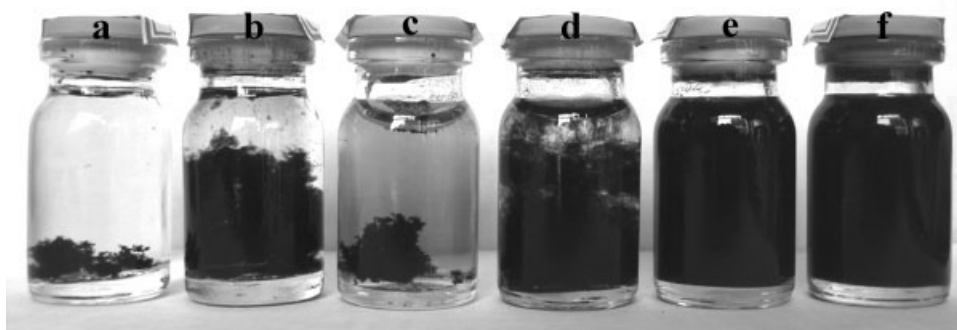


Figure 4 Digital photos of MWNTs treated with ultrasonic for 10 min in solvent after 15 days: (a) raw-MWNTs in H₂O; (b) raw-MWNTs in EG; (c) as-prepared MWNTs in H₂O; (d) as-prepared MWNTs in EG; (e) MWNTs-COOH in H₂O; (f) MWNTs-COOH in EG.

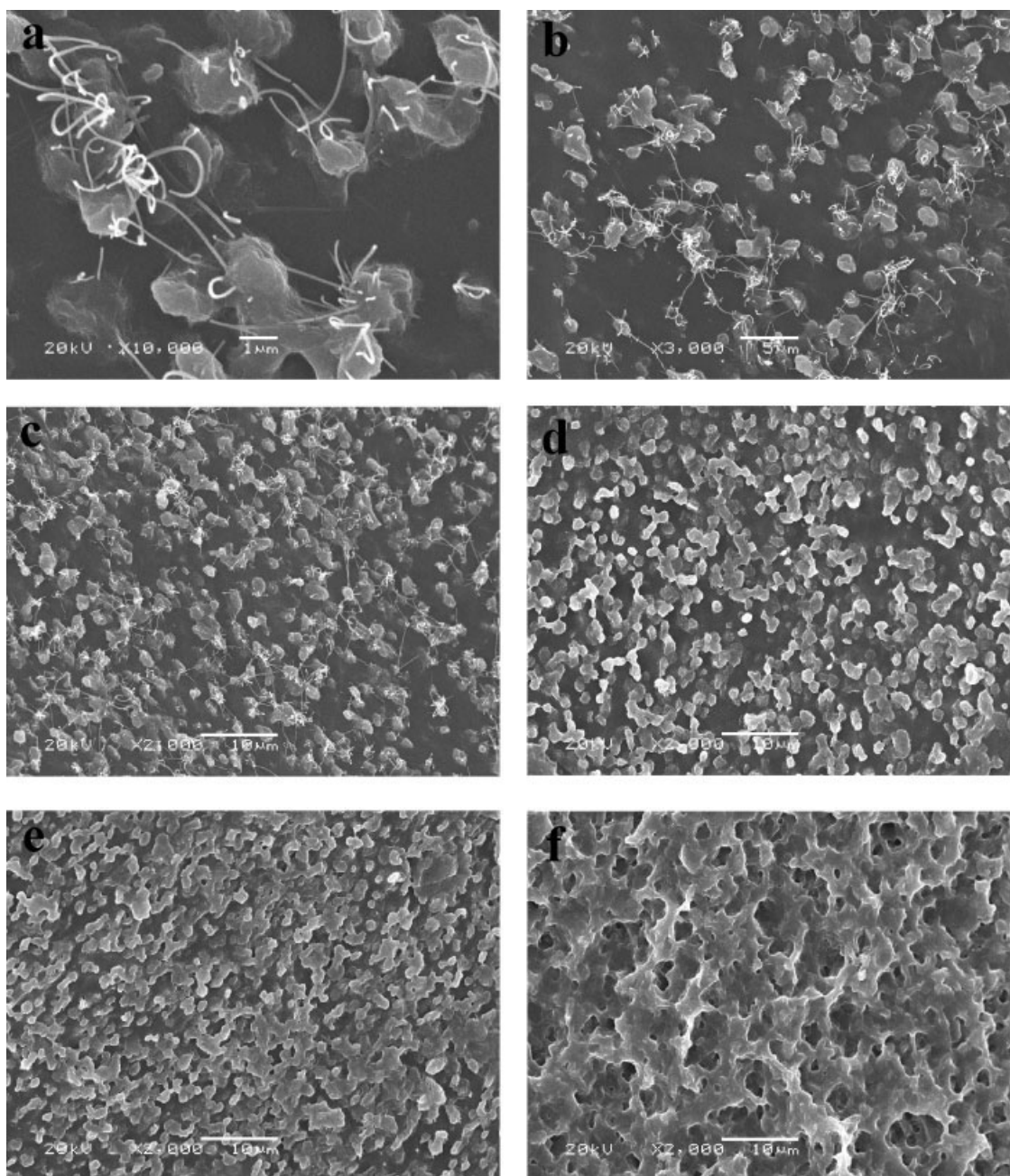


Figure 5 SEM images of fracture surface of PET/MWNTs samples with the content of (a), (b), and (c) 0.01; (d) 0.05; (e) 0.1; (f) 0.2 wt %. The samples were etched in NaOH/ethanol solution.

[Fig. 6(a)]. It is obvious that very small amount of MWNTs (only 0.01 wt %) can serve as a good nucleating reagent for PET and accelerate the rate of crystallization greatly. With the increasing of the MWNTs content, the nucleating efficiency is reduced remarkably, although the T_c keeps increased. Other many similar results can be found in literatures.^{17,22,23} In our opinion, the nucleating efficiency is closely related to the dispersion and the content of MWNTs. The dispersion may be the major factor. Well-dispersed single MWNTs could provide more nucleation sites than many aggregate MWNTs. During the heat-

ing scan, on the other hand, one observes two melting endotherms for each sample [Fig. 6(b)]. The lower one represents the melting of imperfect or smaller/thinner crystals, and the higher one represents more perfect bigger crystallites.^{24,25} It is interesting that the area of melting peak located at the low temperature is increased with the content of MWNTs increasing. At the same time, the area of melting peak located at the higher temperature peak is gradually decreased. The well-dispersed MWNTs could provide more nucleating sites for the crystallization of PET, resulting in an increase of the crystallization rate; however, the

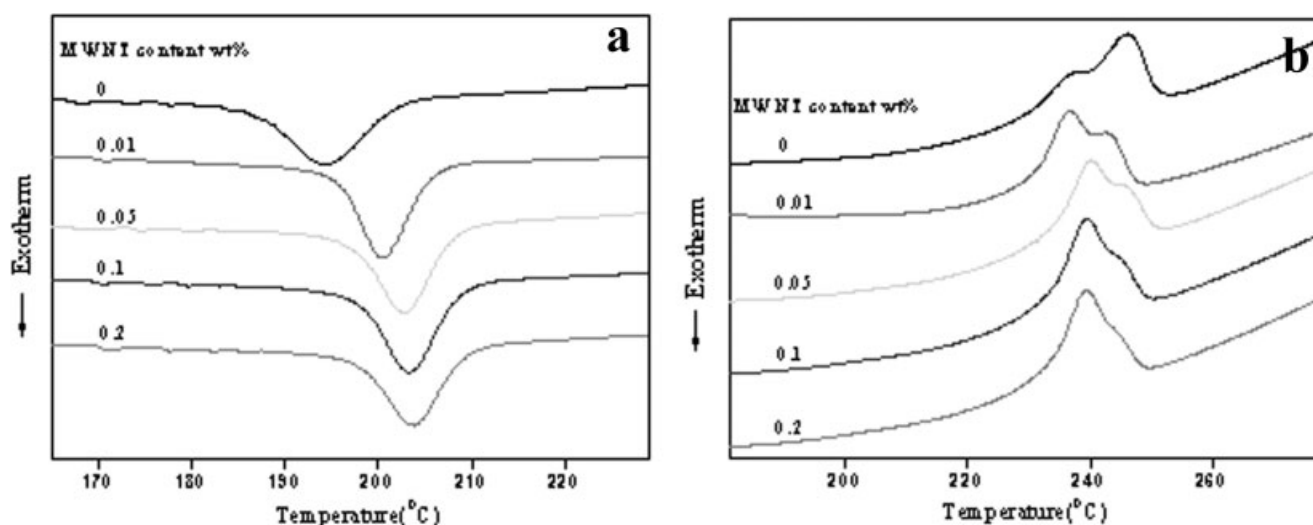


Figure 6 DSC graphs obtained with heating and cooling rate of 10°C/min: (a) the cooling scan after first heating; (b) the second heating scan.

mobility of PET chains will be also restricted, resulting in more imperfect or smaller/thinner crystallites. So, the peak of lower temperature is stronger than the higher one. With the content of MWNTs increased, the area of lower temperature is even larger while the higher one is nearly disappeared.

Dynamic mechanical properties

The mechanical enhancement of PET by using small amount of MWNTs was investigated via DMA measurements, and the result is shown in Figure 7. The storage modulus of PET is increased from 266 to 328 MPa as MWNTs content is increased to 0.05 wt %. This could be understood as because of the well-dispersed MWNTs and the formation of MWNTs

network throughout the matrix as the content of MWNTs is very low. When the content is above 0.1 wt %, the storage modulus is decreased dramatically, even lower than that of neat PET (290 MPa for nanohybrid with 0.1 wt % and 220 MPa for 0.2 wt %). This may be because of the poor dispersion of MWNTs at higher content, or changed mobility of PET chains thus imperfect or smaller/thinner crystallites as indicated by DSC experiment mentioned earlier. Our result is similar to that obtained by Kim,²⁶ who has observed the multiple melting peaks of PET and ascribed the increased mechanical property to the more perfect crystallites.

CONCLUSIONS

In conclusion, after two-step acid treatment of MWNTs and via *in situ* polymerization, a uniform dispersion of MWNTs with very low content throughout PET matrix can be achieved, as confirmed by SEM. The well-dispersed MWNTs form a big network in the matrix. With the increasing of MWNTs content, the MWNTs are wrapped more tightly with denser network, and no MWNTs are exposed through chemical etching. The good dispersed MWNTs show a great nucleating and restricted effect on the PET crystallization, resulting in an increased crystallization temperature and a formation of imperfect or smaller/thinner crystallites with low melting temperature. Using very low content MWNTs (less than 0.1 wt %) is a simple way to achieve good dispersion, yet with remarkable enhancement for the storage modulus of PET. Since the prepared PET/MWNTs nanocomposites have also shown much improved mechanical properties, a cheaper price when compared

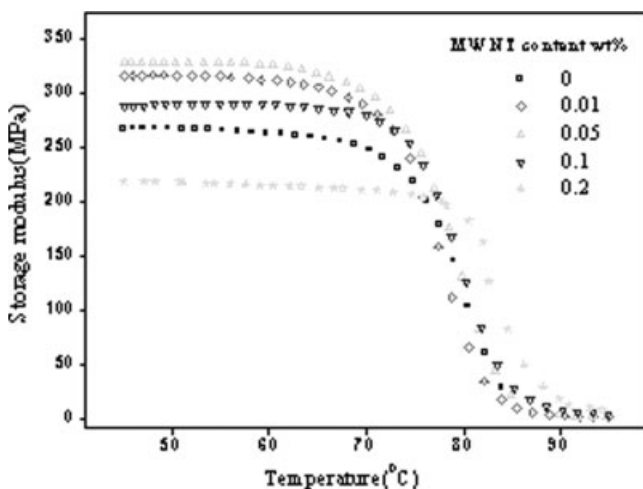


Figure 7 DMA curves of dynamic mechanical behavior of samples with different MWNTs content.

with polymer nanocomposites with high MWNT content, it can be expected that these materials may play important roles in future industrial application.

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