

Crystallization behavior of poly(trimethylene terephthalate)/multi-walled carbon nanotube composites

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Poly(trimethylene terephthalate) (PTT) has in recent years, attracted much interest for its application in fibers and engineering thermoplastics, due to its outstanding properties such as good resilience and elastic recovery [1, 2]. As a typical semicrystalline polymer, the crystallization behavior of PTT is the primary property that affects its physical properties and processing conditions, and thus many articles have appeared describing this topic [3–10]. In previous works, we reported the crystallization kinetics of PTT including the secondary crystallization process, and the crystallization behavior of PTT at high undercoolings was also explored [6, 7]. A series of copolyesters based on PTT with modified thermal properties have been prepared and their composition dependence of thermal properties was also presented [8–10]. Moreover, recently increasing attention has been given to the fabrication and the property studies of polymer/carbon nanotubes (CNTs) composites due to the high aspect ratio, nanosize in diameter, very low density, excellent physical properties of CNTs, and the remarkably enhanced physical properties of the composites [11–15]. However, so far there is a little research on the crystallization behavior of such polymer nanocomposites, especially in the nucleation effect of CNTs on the polymer

matrix despite of its potential, academic, and technological values. In this communication, PTT composites with multi-walled carbon nanotubes (MWNTs), in which the nanotube consists of several layers of coaxial carbon tubes [16, 17], were prepared, and the influence of MWNT on crystallization of PTT matrix was discussed. To our knowledge, it is the first time that poly(trimethylene terephthalate)/multi-walled carbon nanotube composites were prepared and their crystallization behavior was presented.

PTT ($[\eta] = 0.0795 \text{ m}^3/\text{kg}$ at 298 K) used in this study is the same polymer which has been described in one of our previous articles [6]. MWNTs were purchased from Bill Nanotech Co., Ltd (Shenzhen, China). These MWNTs were produced via the chemical vapor deposition (CVD) method and have lengths up to a few microns and diameters between 70 and 100 nm. The purchased MWNTs were purified to remove amorphous carbon and iron impurities [18]. In a typical experiment, an MWNT sample was heated and refluxed in an aqueous HNO_3 solution (2.6 M) for 13 h. After filtering through a Teflon-PTFE membrane, the remaining solid was washed with deionized water until the pH was neutral. The purified MWNTs were then functionalized by tetrabutyl titanate to enhance the compatibility of MWNT with PTT. To fabricate PTT–MWNT composites, weighed PTT sample was dissolved in the solution of 1:1 (w/w) 1,1,2,2-tetrachloroethane/phenol at 353 K to form a clear solution. Appropriate amount of functionalized MWNT was weighed according to the required percentage, and was added to the solution. The mixture was refluxed with stir for 4 h to form a homogeneous suspension and then sonicated for 1 h. Finally, the mixture was cast into an aluminum mold in the form of a film. The mold with the suspension was vacuum dried in an oven at 373 K for 48 h. The resultant composite was denoted according to the weight percentage of MWNT in

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the nanocomposites. For example, PTT–MWNT100/0 and PTT–MWNT99.9/0.1 are referred to neat PTT and composite with 0.1 wt% MWNT respectively.

DSC measurements were carried out on a TA Q200 equipment, calibrated with indium and tin standards, under a nitrogen atmosphere. The specimens were heated to 553 K at a scanning rate of 10 K/min, and kept at this temperature for 5 min in order to remove the thermal history. The DSC cooling traces were recorded at the rates of 2, 5, 10, and 30 K/min, respectively. For an accurate determination of the non-isothermal kinetic characteristics, the apparatus was calibrated at various scanning rates. The thermal lag between sample and pan holder temperatures was estimated according to the procedure of Eder and Wlochowicz [19]. A BM-11 polarized light microscopy (PLM) (Jiangnan Optics and Electronics Co. Ltd., Nanjing, China) was used to observe the morphology of sample films (thickness of about 150 μm) at different crystallization temperatures, and the microstructures were recorded by a CCD camera.

Figure 1 shows the DSC traces obtained with a cooling rate of 10 K/min for neat PTT and its composites. Evidently, the composite exotherms are much sharper than that of neat PTT. According to the DSC data for both cooling and heating scans summarized in Table 1, the melting temperature (T_m) remains approximately constant, or increases slightly, as a result of the addition of the MWNT to PTT. But it is clear that the melting crystallization peak (T_{mc}) of PTT was remarkably enhanced by the addition of the MWNT. Generally, supercool temperature (ΔT , $\Delta T = T_m - T_{mc}$) can characterize the sample crystallization and nucleation effect [20]. Usually the lower ΔT predicts the higher nucleation and crystallization rates. The values for all the PTT/MWNT nanocomposites were 28.9–38.8 K smaller than that of neat PTT (46.4 K). The composite with 5.0 wt% MWNT exhibits the highest T_{mc} (471.5 K) and the lowest ΔT (28.9 K). As for PTT with 7.0 wt% MWNT, its nucleation effect and crystallization rate are slightly

lower than that of PTT–MWNT95.0/5.0. One plausible reason might be that the addition of excess amount of nucleating agent beyond a certain level does not necessarily increase the number of nucleation sites proportionately, but cause the molecular mobility reduction, for instance, because of viscosity growth with the overloading of MWNT in PTT matrix. These results imply that the crystallization of PTT may be accelerated with solution blending with 0.05–7.0 wt% MWNT, and MWNT takes the role of an effective nucleating agent.

Typical plots of the dynamic crystallization of neat PTT and PTT–MWNT99.95/0.05 are shown in Fig. 2. It is seen that the crystallization exotherm shifts to lower temperatures with increasing cooling rates for both PTT and PTT–MWNT99.95/0.05, respectively. Figure 3 showed the development of the relative crystallinity as a function of crystallization time t at different cooling rates. The overall non-isothermal crystallization kinetics was studied using the modified Avrami equation [21, 22]:

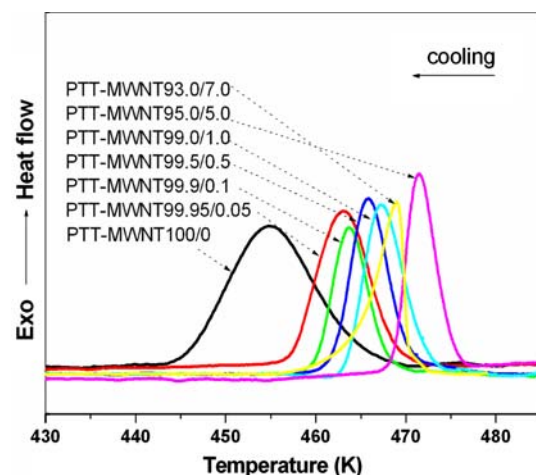


Fig. 1 DSC cooling scans of PTT–MWNT composites from melt

Table 1 DSC data for PTT/MWNT composites

Sample designation	MWNT content (wt%)	Heating		Cooling		ΔT (K)
		T_m (K)	ΔH_m (kJ/kg)	T_{mc} (K)	ΔH_{mc} (kJ/kg)	
PTT–MWNT100/0	0	501.3	52.6	454.9	–48.2	46.4
PTT–MWNT99.95/0.05	0.05	501.9	51.2	463.1	–47.9	38.8
PTT–MWNT99.9/0.1	0.1	501.7	55.7	463.8	–49.6	37.9
PTT–MWNT99.5/0.5	0.5	503.0	54.3	465.8	–44.3	37.2
PTT–MWNT99.0/1.0	1.0	501.8	49.5	467.3	–46.1	34.5
PTT–MWNT95.0/5.0	5.0	500.4	49.0	471.5	–43.0	28.9
PTT–MWNT93.0/7.0	7.0	502.1	53.2	469.1	–47.5	33.0

Note: ΔH_m and ΔH_{mc} are heat of fusion during heating runs and heat of crystallization during cooling runs, respectively. Scanning rate is 10 K/min.

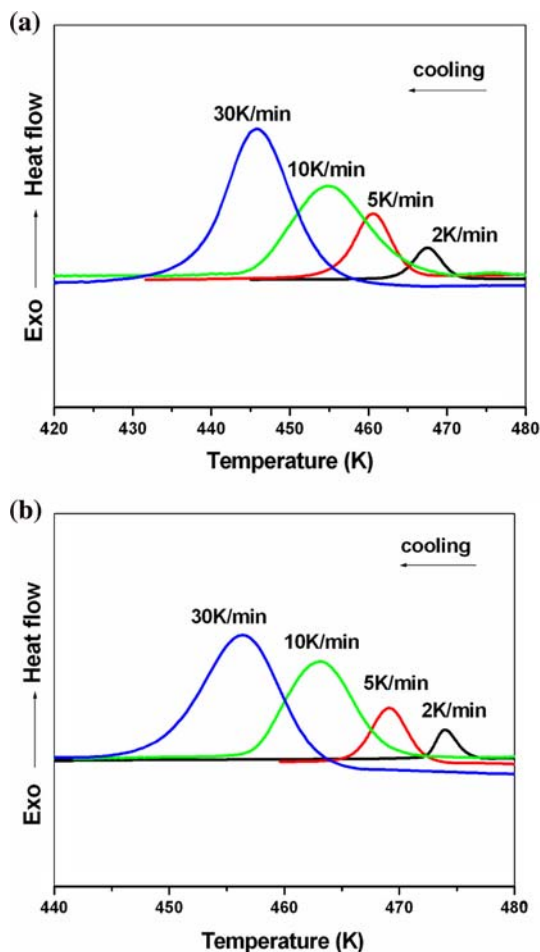


Fig. 2 DSC scans of (a) neat PTT and (b) PTT–MWNT99.95/0.05 non-isothermal crystallization at different cooling rates

$$\log[-\ln(1 - X_t)] = \phi \log Z_c - n \log t$$

where X_t is the relative degree of crystallinity at crystallization time t , and obtained from the area of the DSC exothermic peak at time t divided by the total area under the exothermic peak as shown in:

$$X_t = \left(\int_0^t (dH/dt)dt \right) / \left(\int_0^\infty (dH/dt)dt \right).$$

n is the Avrami exponent, which describes qualitatively the mechanisms of crystallization, ϕ is the constant cooling rate, and Z_c is growth rate constant of the non-isothermal crystallization. A summary of the non-isothermal crystallization kinetic data obtained from the modified Avrami equation is given in Table 2.

The growth rate constants, Z_c s, both for neat PTT and PTT–MWNT99.95/0.05 increase with increasing cooling rate, and this is reasonable since Z_c is a measure of the crystallization rate, which gets faster with supercooling. Furthermore, the value of Z_c of PTT–MWNT99.95/0.05 is

Table 2 Non-isothermal crystallization kinetic parameters for PTT and PTT–MWNT99.95/0.05 based on modified Avrami analysis

Sample	ϕ (K/min)	N	Z_c (min ⁻ⁿ)
PTT–MWNT100/0	2	3.3	0.024
	5	3.6	0.096
	10	3.2	0.167
	30	3.7	3.224
PTT–MWNT99.95/0.05	2	2.9	0.347
	5	2.7	0.657
	10	3.0	1.257
	30	2.6	11.452

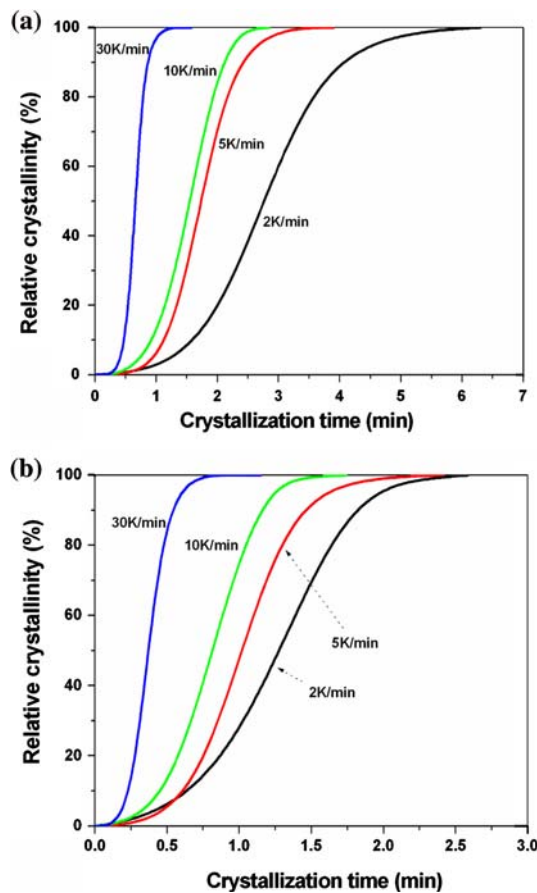
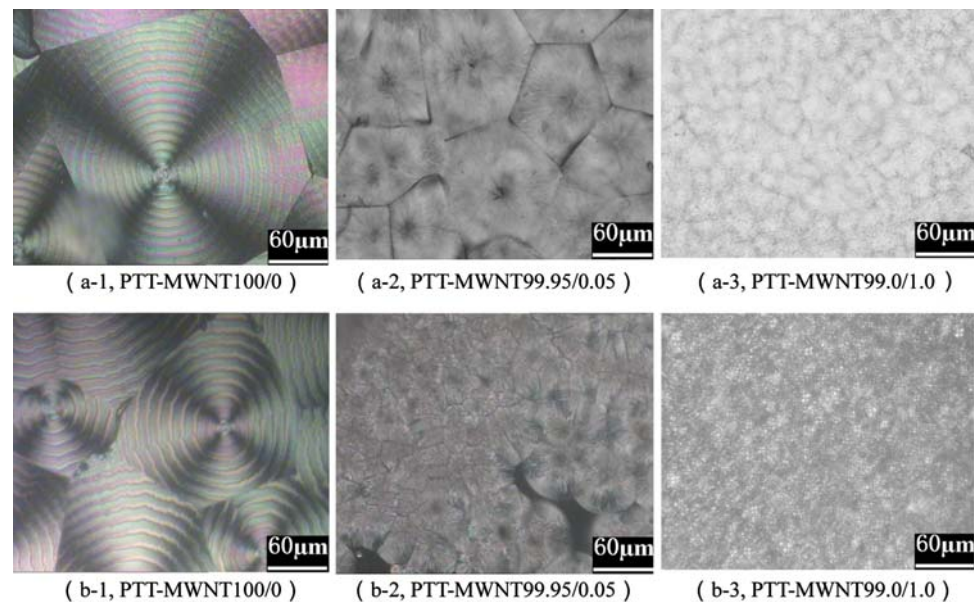


Fig. 3 Development of relative crystallinity for (a) neat PTT and (b) PTT–MWNT99.95/0.05 as a function of time in non-isothermal crystallization

always larger than that of neat PTT for a fixed cooling rate. This proves that the crystallization has been accelerated because of the presence of the nanoparticles. The value of Avrami exponent n for neat PET is 3.2–3.7, whereas with MWNT it becomes 2.6–3.0. Although the fractional values of n make the proposition of well-defined mechanism of crystallization somewhat difficult, it can be used to

Fig. 4 PLM images of PTT crystallized at 475 K (a) and 455 K (b)



qualitatively signify the mechanism of crystallization [20]. The value of about 3.2–3.7 of n for neat PTT indicates a three-dimensional spherulite growth, and is still indicative of heterogeneity in the process, because the theoretical value of n should be 4.0 for three-dimensional growth with homogeneous nucleation. This may be attributed to the presence of polymerization catalyst in the resultant PTT, which can act as heterogeneous nucleating agent in the crystallization process. Some authors have presented the similar point of view on PTT crystallization [23]. However, as we increase the heterogeneity of PTT matrix by deliberate addition of MWNT, the value of n comes down to 2.6–3.0 for PTT containing trace amount of MWNT. These dropped n values of PTT–MWNT99.95/0.05 should be consistent with the growth of heterogeneously nucleated spherulites with increasing foreign inclusions and this further elucidated the strong nucleation effect of MWNT for PTT crystallization.

Figure 4 shows the PLM micrographs of PTT and PTT–MWNT nanocomposites after melting at 553 K for 5 min and then quenching at 455 and 475 K to crystallization for 10 min. Large spherulites tended to form at higher crystallization temperatures with a low nucleation density for both PTT matrix and its nanocomposites. For the neat PTT matrix, the PLM image exhibits a typical Maltese-cross spherulite. By adding the MWNT into PTT, it can be clearly seen that the amount of spherulites of PTT/MWNT nanocomposite with only 0.05 wt% MWNT is much higher than that of neat PTT. PTT containing 1.0 wt% MWNT crystallized from a very large number of nuclei and produced extremely small spherulites, which were unresolvable at the magnifications used. Based on these observed PLM images, the nucleation density and nucleation rates of PTT–MWNT nanocomposites are higher than

that of PTT, which is consistent with the DSC data. This may be due to the small size and large specific surface area of MWNTs, and good dispersion of MWNTs in the PTT matrix.

In summary, the results in present work revealed that MWNT can effectively influence the crystallization development of PTT, and the addition of MWNT expedites the process of crystallization by providing more nucleation sites to the crystallizing phase, which results in the formation of smaller spherulites, giving better processability of the matrix. This might provide a generic method to nucleate semicrystalline polymers such as polyesters, polyamides, and polyolefins, etc. Detailed studies of crystallization behavior of PTT/MWNT composites, with an emphasis on the relationship between the interfacial interactions of MWNT with matrix and crystallization kinetics of the composites, are in progress and the experiments are currently under development.

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