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ULTRAHIGH MOLECULAR MASS POLYETHYLENE/ CARBON NANOTUBE COMPOSITES
Crystallization and melting properties

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Abstract

Ultrahigh molecular mass polyethylene (UHMMPE) is filled with carbon nano-tubes (CNTs) by solution in the presence of maleic anhydride grafted styrene-(ethylene-co-butylene)-styrene copolymer (MA–SEBS) as a compatibilizer. The UHMMPE/CNT composites crystallized from melt were prepared at a cooling rate of 20°C min^{-1}. The melting and crystallization behaviors of UHMMPE/CNT composites were investigated by differential scanning calorimetry. The results showed that onset melting temperature (T_m) and degree of crystallinity (X_c) of UHMMPE/CNT composites crystallized from solution are higher than those from melt due to the larger crystalline lamellar thickness. The onset crystallization temperature (T_c) of UHMMPE/CNT composites tends to shift to higher temperature region with increasing CNT content in the composites. T_m and T_c of UHMMPE phase in UHMMPE/CNT composites decrease with the addition of MA–SEBS. Moreover, the crystallization rate of UHMMPE phase in UHMMPE/CNT composite is increased due to the introduction of CNTs. MA–SEBS acts as compatilizer, enhances the dispersion of CNTs in the UHMMPE matrix. Thereby, the crystallization rate of UHMMPE phase in UHMMPE/CNT composite is further increased with the addition of MA–SEBS.

Keywords: carbon nano-tubes, composite, crystallinity, maleic anhydride grafted styrene-(ethylene-co-butylene)-styrene copolymer, ultrahigh molecular mass polyethylene

Introduction

Ultrahigh molecular mass polyethylene (UHMMPE) is an engineering plastic which has a wide spectrum of applications due to its high strength, excellent toughness, high resistance to chemicals and physical abrasion, and low friction coefficient. However, the long-term performance of UHMMPE is poor due to their weak creep and fatigue strength, which is originated from the visco-elasticity of UHMMPE [1]. Recently, carbon nano-tubes (CNTs) are used to reinforce polymer matrix due to their high aspect ratio, strength, elastic modulus, flexibility and unique conductivity along with other properties [2-4]. However, the properties of polymer/CNT composites are not excellent as scientists expected due to the poor dispersion of CNTs in polymer matrix

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[5, 6]. How to modify the surface characteristics of CNT and improve the properties of polymer/CNT composites have attracted considerable attention [7, 8]. Recently, the authors [9, 10] found that CNTs can reinforce the polypropylene-matrix composites, and maleic anhydride grafted styrene-(ethylene-co-butylene)-styrene copolymer (designated as MA–SEBS) is an efficient compatibilizer to polyolefine-matrix composites [11]. For polymer-matrix composites, there are some relationships between their thermal behaviours and morphological structure [12–14], thereby, it is important to investigate the thermal properties of composites. In the present work, UHMMPE is filled with CNTs in the presence of MA–SEBS as a compatibilizer in order to enhance the dispersion of CNTs in the UHMMPE matrix, and we focus to investigate the crystallization and melting behaviors of UHMMPE/CNT composites.

Experimental

UHMMPE powder used in this work was supplied by the Second Factory of Auxiliary Agents in Beijing, China. Its molecular mass is $2.7\cdot10^6$ g mol^{-1}. The CNTs used were obtained from Central Normal University in China. The diameter of CNTs is 30–40 nm. The MA–SEBS (Kraton F1901X) containing 1.84% of maleic anhydride was supplied by Shell Chemical Company.

The UHMMPE/MA–SEBS/CNT composites with different content were prepared by solution blended, followed by evaporating xylene. DSC measurements were conducted using a Perkin-Elmer DSC-7 instrument. The melting behaviour of UHMMPE/CNT composites crystallized in solution was determined at a heating rate of 20°C min^{-1}, and the melts were crystallized at a cooling rate of 20°C min^{-1}. Then, the UHMMPE/CNT composites crystallized from melt were heated at a heating rate of 20°C min^{-1} in order to study their melting properties. The testing sample was thin sheet, and its mass was about 8 mg. The whole analysis was carried out in dry nitrogen atmosphere.

Results and discussion

Effect of crystallizing condition on the T_m and crystallinity of UHMMPE/CNT composites

Figure 1 shows melting curves of UHMMPE/CNT composites crystallized in different states. The symbols of samples are listed in Table 1.

The melting points and enthalpy values of fusion (ΔH_m) of UHMMPE/CNT composites crystallized from solution are determined from melting curves. The degree of crystallinity (X_c) of the UHMMPE/CNT composite was calculated using the formula below:

$$X_\mathrm{c}=100\frac{\Delta H_\mathrm{m}}{\Delta H_{100}} \quad (1)$$

where ΔH_m is the enthalpy of fusion corrected for per gram of UHMMPE in the composite, and ΔH_{100} is the enthalpy of fusion for a 100% crystalline UHMMPE taken as 289.3 J g^{-1} according to the literature [15]. The results are listed in Table 1.

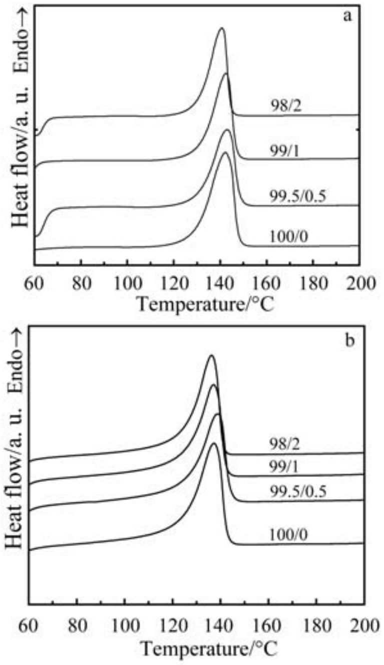

Fig. 1 Melting curves of UHMMPE/CNT composites; a – crystallized from solution; b – crystallized from melt

From Table 1, it is found that X_c of UHMMPE phase in UHMMPE/CNT composite increases slightly with the addition of CNT. As the content of CNT is higher than 1%, X_c of UHMMPE phase in composite obviously decreases. Moreover, the onset melting point (T_m) of UHMMPE phase in the composites increases with the addition of CNTs, and subsequently decreases when the content of CNT is higher than 2%. It can be explained from the aggregating state of UHMMPE chains. In general, the crystalline lamellar thickness l_c, was estimated with Thomson–Gibbs equation [16]:

$$T_m = T_m^0\left(1-\frac{2\sigma_e}{l_c \Delta H_{100}}\right) \tag{2}$$

where $T_m^0 = 418.7$ K is the melting point for a hypothetical crystal of infinite size for which surface energy effects may be disregarded [17]. The fold surface energy σ_e, that relates to the surface energy of the crystal end faces at which the chains fold [17], was taken as $93 \cdot 10^{-7}$ J cm^{-2}. The enthalpy of fusion of the crystal ΔH_{100} was taken to be 289.3 J $g^{-1} \approx 289.3$ J cm^{-3} [15]. The calculated values of l_c are also listed in Table 1.

Table 1 T_m, X_c and calculated l_c values of UHMMPE/CNT composites crystallized in different states

UHMMPE/CNT	T_m/ °C	ΔH_m/ J g^{-1}	X_c/ %	l_c/ nm	T_{mp}/ °C	T_c/ °C	ΔT/ °C
100/0							
crystallized from solution	129.6	214.6	74.2	16.7	–	–	–
crystallized from melt	124.1	140.1	48.4	12.5	–	–	–
99.5/0.5							
crystallized from solution	131.3	216.3	74.8	18.7	138.7	110.2	28.5
crystallized from melt	126.0	141.2	48.8	13.7	–	–	–
99/1							
crystallized from solution	131.5	198.9	68.7	19.0	136.9	111.4	25.5
crystallized in melt	125.3	135.0	46.7	13.2	–	–	–
98/2							
crystallized from solution	130.1	196.5	67.9	18.0	136.6	111.6	25.0
crystallized from melt	125.0	134.5	46.5	12.5	–	–	–

In general, larger lamellar thickness corresponds to higher melting temperature, chain regularity and crystallinity, and vice versa. From this table, we can notice that l_c increases to 19.0 from 16.7 nm after the UHMMPE is blended with CNT. However, further increasing in the content of CNT, CNTs restrict the motion, fold and crystallization of molecular chains, and hence T_m and X_c of UHMMPE in the composite decrease significantly.

Effect of MA–SEBS on the T_m and crystallinity of UHMMPE/CNT composites

Figure 2 shows melting curves of UHMMPE/MA–SEBS/CNT composites crystallized in different states. The symbols and resulting data of samples are listed in Table 2.

Table 2 shows T_m and X_c of UHMMPE/CNT composites crystallized from melt. The phenomena are similar with the above. Comparing the UHMMPE/CNT composites crystallized in different states, we can see that T_m and X_c of UHMMPE/CNT composites crystallized from solution are higher than those from melt due to the larger crystalline lamellar thickness.

From Table 2, it can be seen that T_m and X_c of UHMMPE phase in UHMMPE/CNT composites decrease with the addition of MA–SEBS, obviously. It indicates that MA–SEBS acts as compatibilizer to improve the interaction between UHMMPE and CNT. This observation is in accordance with the crystallinity and melting behaviors of compatibilized composites [14].

Crystallization rate of UHMMPE/CNT composites

Figure 3 shows the crystallization curves of UHMMPE/CNT and UHMMPE/ MA–SEBS/ CNT composites. The onset crystallization temperatures (T_c) of all sam-

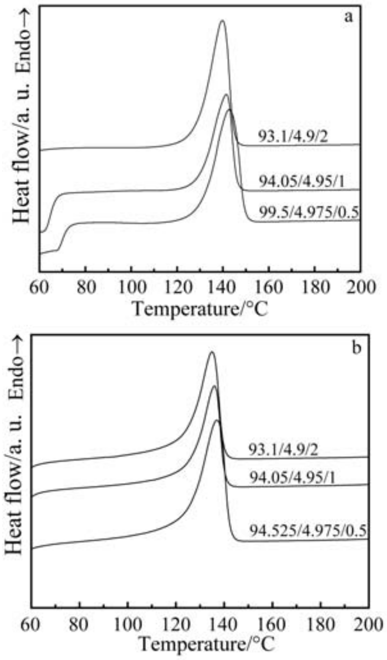

Fig. 2 Melting curves of UHMMPE/MA–SEBS/CNT composites; a – crystallized from solution; b – crystallized from melt

Table 2 T_m and X_c of UHMMPE/MA–SEBS/CNT composites crystallized in different states

UHMMPE/MA–SEBS/CNT	T_m/ °C	ΔH_m/ J g^{-1}	X_c/ %	T_{mp}/ °C	T_c/ °C	ΔT/ °C
94.525/4.975/0.5						
crystallized from solution	131.0	200.4	69.3	136.8	110.8	26.0
crystallized from melt	124.4	135.9	47.0	–	–	–
94.05/4.95/1						
crystallized from soltuion	130.1	192.8	66.7	135.8	110.9	24.8
crystallized from melt	125.1	139.4	44.7	–	–	–
93.1/4.9/2						
crystallized from solution	128.6	189.4	65.5	134.8	110.2	24.6
crystallized from melt	124.2	119.4	41.5	–	–	–

ples are listed in Tables 1 and 2. Apparently, T_c of UHMMPE/CNT composites tends to shift to higher temperature region with increasing CNT content in composites. With the addition of MA–SEBS, T_c of UHMMPE/MA–SEBS/CNT composite is lower than that of UHMMPE/CNT composite.

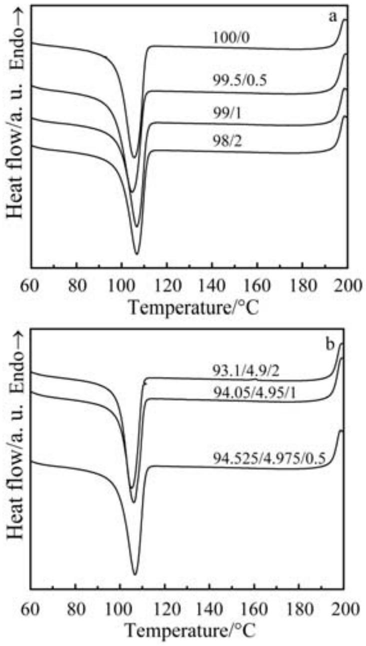

Fig. 3 Crystallization curves of a – UHMMPE/CNT and b – UHMMPE/MA–SEBS/CNT composites

It is generally known that the degree of supercooling, ΔT, can be used to characterize the crystallization behaviour of polymer melts. It is defined by the difference between the peak melting temperature (T_{mp}) and onset crystallization temperature (T_c). A decrease in ΔT generally indicates that the crystallization rate of polymer is increased. The ΔT values of the specimens investigated are given in Tables 1 and 2.

From these tables, it is evident that the crystallization rate of UHMMPE phase in UHMMPE/CNT composite is increased due to the introduction of CNTs. Moreover, it is interested that the crystallization rate is further increased with the addition of MA–SEBS. It can be explained that CNTs act as nucleation sites for UHMMPE spherulites, and hence increase the crystallization rate of UHMMPE. When the MA–SEBS is added into UHMMPE/CNT composite, MA–SEBS acts as a compatibilizer, improves the dispersion of CNT in the UHMMPE matrix. The well-dispersed CNTs further increase the crystallization rate of UHMMPE.

Conclusions

Based on the results obtained we can draw some conclusions. T_m and X_c of UHMMPE/CNT composites crystallized from solution are higher than those from melt due to the larger crystalline lamellar thickness. T_c of UHMMPE/CNT composites tends to shift to higher temperature region with increasing CNT content in the composites. T_m and T_c of UHMMPE phase in UHMMPE/CNT composites decrease with the addition of MA–SEBS. The crystallization rate of UHMMPE phase in

UHMMPE/CNT composite is increased due to the introduction of CNTs. MA–SEBS acts as compatilizer, enhances the dispersion of CNTs in the UHMMPE matrix. Thereby, the crystallization rate is further increased with the addition of MA–SEBS.

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