

Effect of Different Carbon Fillers on the Properties of PP Composites: Comparison of Carbon Black with Multiwalled Carbon Nanotubes

Zhen Zhou, Shifeng Wang, Yong Zhang, Yinxi Zhang

Research Institute of Polymer Materials, Shanghai Jiaotong University, Shanghai 200240, China

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ABSTRACT: Polypropylene (PP)/carbon composites were prepared via melt blending PP with carbon fillers, including multiwalled carbon nanotubes (MWNTs) and carbon black (CB). Field-emission scanning electron microscopy was used to research the morphology and dispersion of fillers in the PP matrix. The electrical properties, mechanical properties, and crystallization behaviors of PP/carbon composites were also

investigated. The results show that the influence of MWNTs on the properties of PP composites is different with CB, which can be ascribed to the structure and aspect ratio difference between MWNTs and CB. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4823–4830, 2006

Key words: composites; dispersions; melt; blends

INTRODUCTION

Conductive polymer composites (CPC) formed by the combination of conventional polymer with conductive fillers, such as metal powder,^{1,2} carbon black,^{3–5} and carbon fiber,^{6,7} have been widely used in many fields. The critical content of conductive filler required to form continuous conducting paths and impart electrical conductivity to the polymer matrix is called percolation threshold. Carbon black (CB) is the most widely used conductive filler because of its abundant source, low density, predominant electrical property, and low cost. But the CB content at percolation threshold of many CPC is high, such as ~ 10.88 vol % CB content for HDPE/CB,⁸ ~ 20 wt % CB content for poly(vinyl chloride)/CB,⁹ and ~ 20 wt % CB content for polyurethane/CB.¹⁰ High CB concentration will increase the melt viscosity and decrease the impact resistance, thus sacrifice the mechanical properties of the composites.^{11,12}

It is well known that carbon nanotubes (CNTs) have very high aspect ratios, predominant electrical and mechanical properties with an elastic modulus of ~ 1 TPa and fracture strain of 5–10%.^{13–17} There are two types of CNTs: single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs). Now MWNTs are being widely used to reinforce polymers because they can improve not only electrical properties, but also thermal conductivity and mechanical properties.¹⁸

CB is a finely divided solid composed of primary particles of spherical shape with diameters between a few tens and a few hundreds of nanometers that are fused together into aggregates.¹⁹ However, MWNTs are a collection of several concentric graphene cylinders. The typical diameters of MWNTs are in the 10–50 nm range, and the length of MWNTs is of the order of micrometers. So the effect of MWNTs on the properties of polypropylene (PP) should be different from the effect of CB on the properties of PP because of the structure difference between MWNTs and CB. In this article, PP/carbon composites were prepared via melt blending PP with conductive fillers, including MWNTs and CB. Field-emission scanning electron microscopy (FESEM) was used to research the morphology and dispersion of conductive fillers in the PP matrix. The electrical properties, mechanical properties, and crystallization behaviors of conductive PP composites were also investigated.

EXPERIMENTAL

Materials

PP (F401) was produced by Panjin Petrochemical Co. (China), with a melt flow index of 2.3 g/10 min. MWNTs were obtained from Tsinghua Nafine Nano-Powder Commercialization Engineering Centre (China), with average diameter of ~ 15 nm and of 98% purity. MWNTs were washed with concentrated hydrochloric acid for 2 h to remove the catalysts and their carrier, and then were purified with concentrated HNO₃ for 12 h to remove the amorphous carbon particles. Electrically conductive CB (V-XC72) was pro-

Correspondence to: Y. Zhang (yong_zhang@sjtu.edu.cn).

vided by Cabot Co. (USA), with average diameters between 20 and 30 nm and of 99.9% purity.

Sample preparation

Prior to blending, all materials were dried at 80°C and 9×10^3 Pa for 8 h. The PP composites were prepared by melt mixing of the dry blended components in a Haake RC90 rheometer (Haake Co., Germany) at 190°C and 60 rpm for 10 min. All blend ratios described are related to percentage by weight. The loadings of conductive fillers are 0.25, 0.5, 1, 2, 3, 5, 7.5, 10, and 12.5 wt %. The resultant blends were subsequently compression molded at 190°C to form sheets of 1 or 4 mm thickness.

Transmission electron microscopy

The microstructure of MWNTs and CB was observed by a JEOL JEM100-CX transmission electron microscope (TEM; JEOL, Japan). Prior to observation, a small quantity of MWNTs or CB was dispersed in toluene under ultrasonic vibration. The well-dispersed MWNTs/toluene or CB/toluene solution was dropped onto a Cu grid and evaporated for a few minutes.

Field-emission scanning electron microscopy analysis

The PP/CB and PP/MWNTs composites were fractured in liquid nitrogen and the freeze-fractured surfaces were observed under a JSM-7401F field-emission scanning electron microscope (JEOL). All samples were gold sputtered prior to observation.

Measurements of volume resistivity

For samples with electrical resistivity higher than $10^8 \Omega$ cm, the volume resistivity measurements were carried out using 1 mm sheet with a ZC36 high resistance meter (Shanghai Electrical Meter Factory, China) according to ASTM D 257. For moderately conductive samples with resistivity lower than $10^8 \Omega$ cm, 4 mm sheets were cut into specimens of 90 mm in length and 10 mm in width. And the volume resistivity was measured according to ASTM D 4496 with a set of low resistance measurement apparatus, consisting of current electrodes, potential electrodes, a power supply, a digital ampere meter, and a voltage meter.

Measurements of mechanical properties

Tensile tests were conducted using an Instron 4465 universal electromechanical tester (Instron Co., USA) (standard DIN 53504). All tests were conducted at

room temperature with test specimens dried before test.

DSC analysis

The crystallization behavior of the PP/carbon composites was analyzed using a PerkinElmer Pyris 1 differential scanning calorimeter (PerkinElmer, USA) under a nitrogen atmosphere. Samples of about 4 mg were taken from the molded sheet. Nonisothermal crystallization studies were performed as follows: the samples were heated to 200°C at a heating rate of 10°C/min, maintained at 200°C for 5 min to eliminate any previous thermal history, and then cooled to 50°C at a cooling rate of 10°C/min.

RESULTS AND DISCUSSION

The morphology of MWNTs and CB

Figure 1 shows the transmission electron micrographs of typical MWNTs and CB. As can be seen in the micrographs, the V-XC72 CB is a high structure CB, and many primary CB particles form primary aggregates with considerable branching and chaining. Compared with CB, MWNTs have higher aspect ratio. The length of the MWNTs is difficult to determine because of the aggregates, but is of the order of micrometers. The average diameter of the MWNTs is ~ 15 nm.

Dispersion of MWNTs or CB in the PP matrix

Figure 2 shows the field-emission scanning electron micrographs of the PP/CB composites with 0.5, 5, and 10 wt % CB content. The white parts in field-emission scanning electron micrographs represent the CB particles in the fractured surface. As can be seen in field-emission scanning electron micrographs, CB particles do not disperse uniformly in the PP matrix and tend to form agglomerates in partial areas at a low CB content of 0.5 wt %, and the distance between CB particles is large. The average diameters of CB agglomerates increase from ~ 100 to ~ 170 nm with the increasing of the CB content from 0.5 to 5 wt %. When the CB content reaches 10 wt %, the average diameter of CB agglomerates reaches ~ 360 nm. Compared with MWNTs dispersion in the PP matrix, one interesting observation can be made from the micrograph. CB particles disperse more uniformly in the PP matrix with the increasing CB content. At high CB content of 5 or 10 wt %, the distances between CB particles decrease and the CB particles are more likely to come into contact with each other.

The field-emission scanning electron micrographs of 0.5, 5, and 10 wt % PP/MWNTs composites are shown in Figure 3. It is clear from the micrographs that the dispersion of MWNTs in the PP matrix is not very

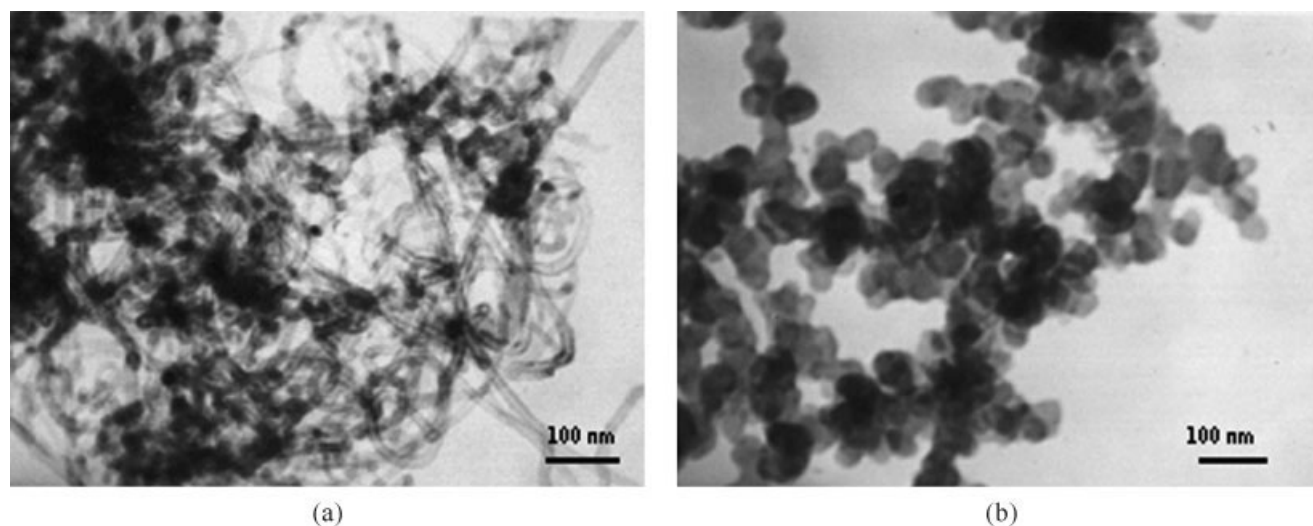


Figure 1 TEM micrographs of (a) MWNTs and (b) CB.

perfect even at the low content of 0.5 wt %. In some areas the concentration of MWNTs is high, but none of MWNTs can be found in some other areas. At high MWNTs content of 5 or 10 wt %, it can be found that approximately micrometer diameter clusters of MWNTs appear in partial areas and some MWNTs are entangled together. This can be ascribed to the strong intermolecular van der Waal's interactions among the nanotubes and interfacial interactions between MWNTs and PP matrix. As can be seen in Figures 3(c and e), the tendency of conglomeration of MWNTs is improved with the increasing MWNTs content. Compared with the 0.5 wt % PP/MWNTs composites, more MWNTs are entangled with each other and the diameter of MWNT clusters is larger. When the MWNTs content reaches 10 wt %, continuous conductive MWNTs network can be clearly seen, as shown in Figure 3(e).

Electrical properties of the PP/MWNTs and PP/CB composites

Figure 4 shows the volume resistivity as a function of weight fraction of MWNTs or CB in PP matrix. Either PP/MWNTs composites or PP/CB composites exhibit typical characteristics of percolation. The volume resistivity of the PP used in this study is about $10^{17} \Omega \text{ cm}$. At low filler loadings, slight change in volume resistivity can be observed and the composites are still insulating. Volume resistivity increases slowly with the increasing fillers content. In the vicinity of the percolation threshold, the volume resistivity decreases dramatically, by several orders of magnitude, and a transition from insulating to conductive materials occurs. A significant drop in volume resistivity is achieved for a percolation threshold of about 8.0 wt % for PP/MWNTs composites and a percolation threshold of about 9.5 wt % for

PP/CB composites. This indicates the formation of continuous conducting paths or network in the PP matrix. After the percolation is achieved, the volume resistivity of the PP composites does not greatly change with the increasing filler content.

As reported in the literature,⁴ for elongated particles, volume resistivity of composites decreases monotonically with the increase in the aspect ratio and with the decrease in the average particle orientation. Compared with CB, MWNTs have higher aspect ratio and branch structure, which easily leads to formation of continuous conducting paths or network in polymer matrix. So the percolation threshold of PP/MWNTs composites is lower than that of PP/CB composites. But the effect of MWNTs on conductivity of PP is not very predominant. Though high shear force and mixing energy are produced during melt mixing, MWNTs agglomerates can still withstand high shear force and remain entangled because of the strong intermolecular van der Waal's interactions among the nanotubes. And the poor interfacial interactions between MWNTs and PP matrix result in the poor dispersion of MWNTs in PP matrix.

Mechanical properties of PP/MWNTs and PP/CB composites

The effects of carbon filler content on tensile properties of PP composites are shown in Figure 5. At low content, tensile strength of PP composites increases with the increasing MWNTs or CB content. When MWNTs content reaches 0.5 wt %, the tensile strength of PP/MWNTs composite is the highest. With further increase of MWNTs, the tensile strength of PP/MWNTs composites decreases. The effect of CB on tensile strength of PP/CB composites is the same as that of MWNTs. However, the CB content at which PP/CB

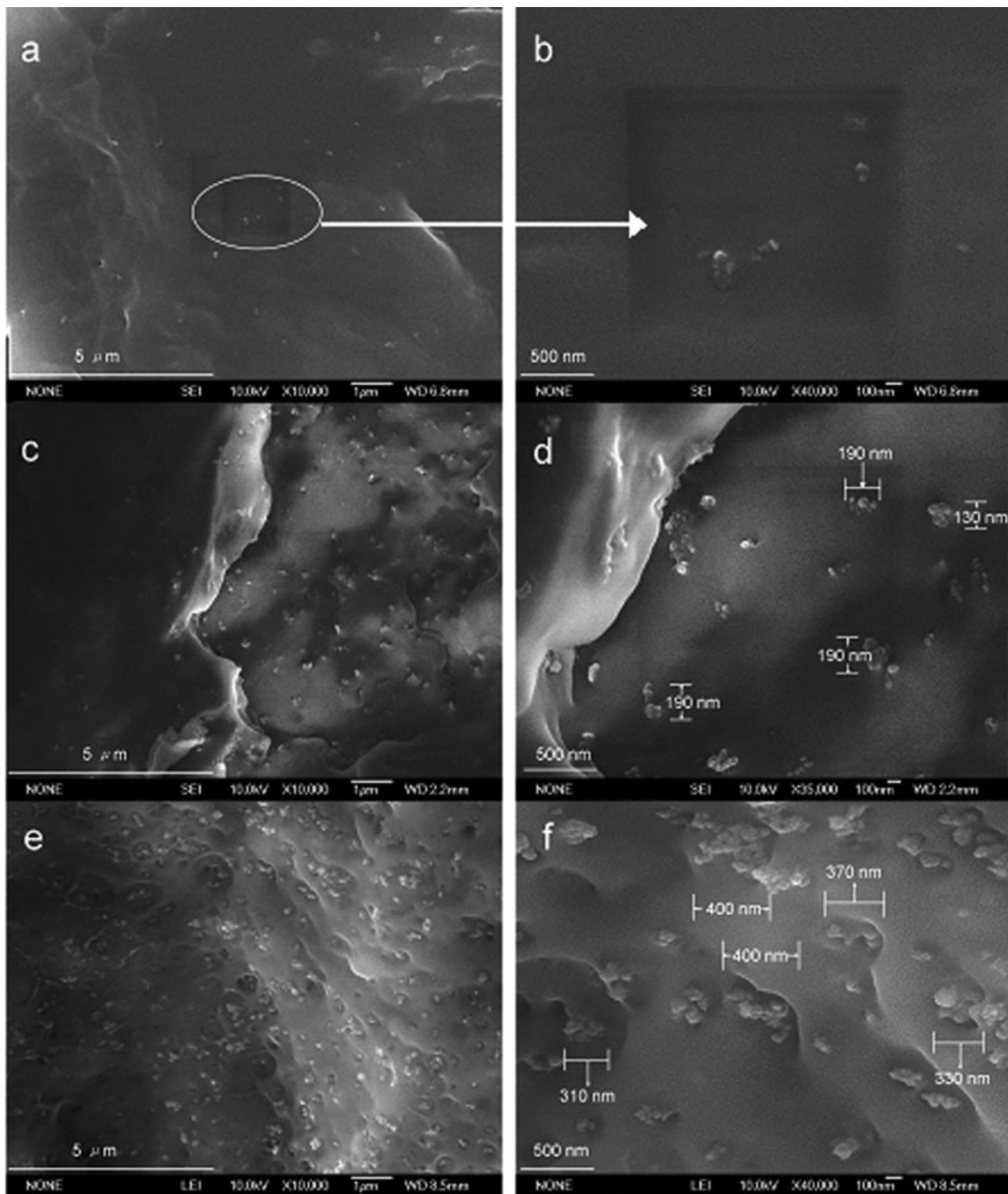


Figure 2 Field-emission scanning electron micrographs of the freeze-fractured surface of the PP/CB composite with a CB content of (a and b) 0.5 wt %, (c and d) 5 wt %, (e and f) 10 wt %.

composites attain the highest tensile strength is around 5.0 wt %. At low MWNTs or CB content, partial tensile strain can be transferred to MWNTs or CB embedded in PP matrix under tensile stress, which leads to the increase in tensile strength. With further addition of

MWNTs or CB, more agglomerates of MWNTs or CB form in PP matrix and many defects are introduced into polymer matrix because of the difficulty of homogeneously dispersing MWNTs or CB by melt mixing. These defects lead to a decrease in tensile strength. But

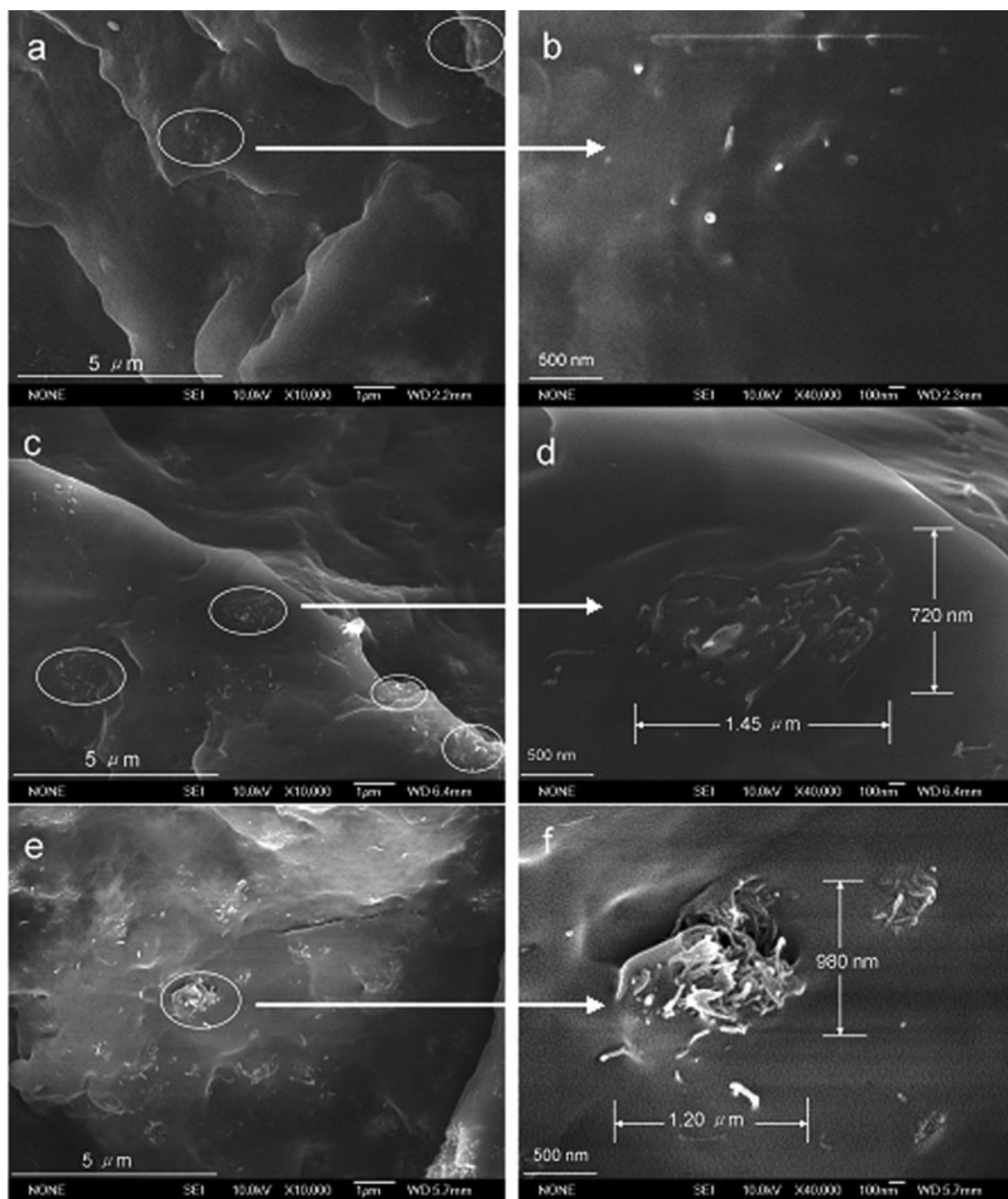


Figure 3 Field-emission scanning electron micrographs of the freeze-fractured surface of the PP/MWNTs composite with a MWNTs content of (a and b) 0.5 wt %, (c and d) 5 wt %, (e and f) 10 wt %.

it is clear that there is slight change in tensile strength as a function of filler loading. The elongation at break of PP composites decreases with the increasing filler content. Even at 0.25 wt % content, the elongation at break of PP/MWNTs and PP/CB composites

decreases from about 150% (the elongation at break of pure PP) to about 6%. The toughness of this PP is greatly reduced with the addition of MWNTs or CB. The embrittlement of other polymers with the addition of CNTs has also been reported.²⁰ This may be because

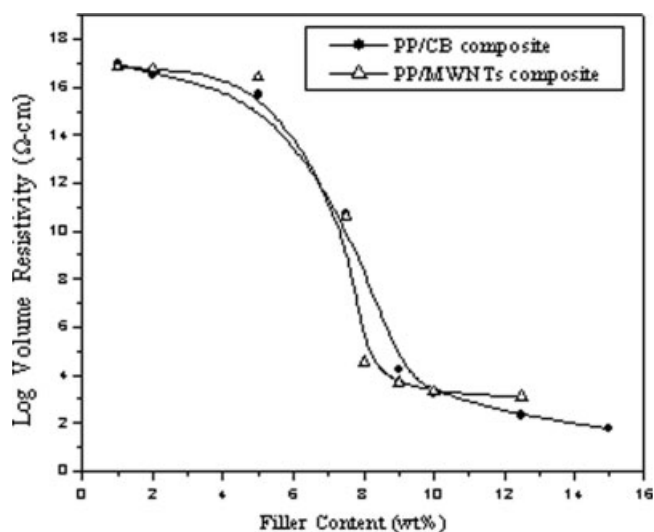


Figure 4 Effect of filler type and content on volume resistivity of PP/carbon composites.

either MWNTs or CB has poor interfacial interactions with PP matrix, and so defects would be introduced into polymer matrix with the addition of MWNTs or CB, which leads to a negative effect on bulk mechanical properties.

The effects of carbon filler content on impact strength of PP composites are shown in Figure 6. At low content, impact strength of PP composites increases with the increase in MWNTs or CB content. When MWNTs content reaches 3.0 wt % or CB content reaches 7.5 wt %, the impact strength of PP composites reaches the highest, and the impact strength of PP/MWNTs with 3 wt % MWNTs content is higher than that of PP/CB with 7.5 wt % CB content. With further

increasing of carbon fillers, the impact strength of PP/MWNTs or PP/CB composites decreases. When rigid MWNTs or CB particles are introduced into PP matrix, the resistance of PP composites to crack initiation and propagation are greatly improved according to prevention research.²¹ A large amount of energy can be absorbed by the PP matrix, which leads to the increase in impact strength of PP composites. With further addition of MWNTs or CB, agglomerates of MWNTs or CB form in PP matrix and many defects are introduced into polymer matrix because of the difficulty of homogeneously dispersing MWNTs or CB in polymer matrix. All these result in the decrease in the impact strength of PP composites.

Crystallization behaviors of the PP/MWNTs and PP/CB composites

From the DSC crystallization exotherms recorded as the samples were crystallized from the molten state at a given cooling rate, some useful parameters can be obtained to describe the nonisothermal crystallization.^{22,23} These parameters are defined below and illustrated in Figure 7.

T_p is the peak temperature of crystallization exotherm. $T_{onset} - T_p$ is the inverse measure of the overall rate of crystallization where T_{onset} is the temperature at the intercept of the tangents at the baseline and the high-temperature side of the exotherm. The smaller the $(T_{onset} - T_p)$, the greater the rate of crystallization is. S_i is the slope of initial portion of the exotherm, which is a measure of the rate of nucleation. The greater the initial slope, the faster the nucleation rate is. ΔW is the width at half-height of the exotherm peak determined after normalization of the peak to a constant mass of the samples, which is a measure of the

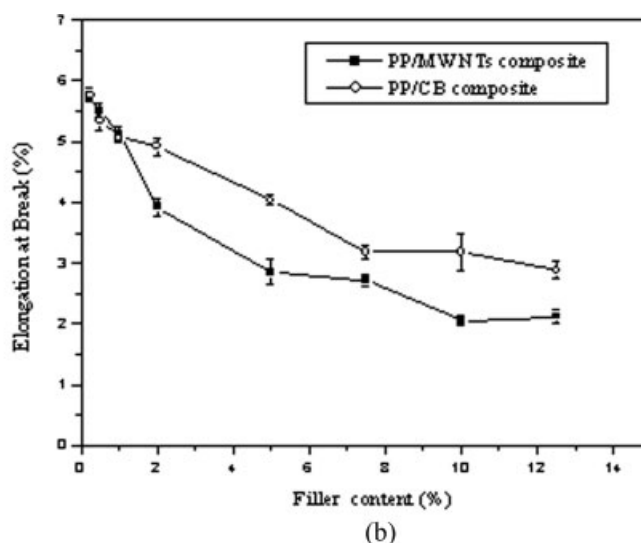
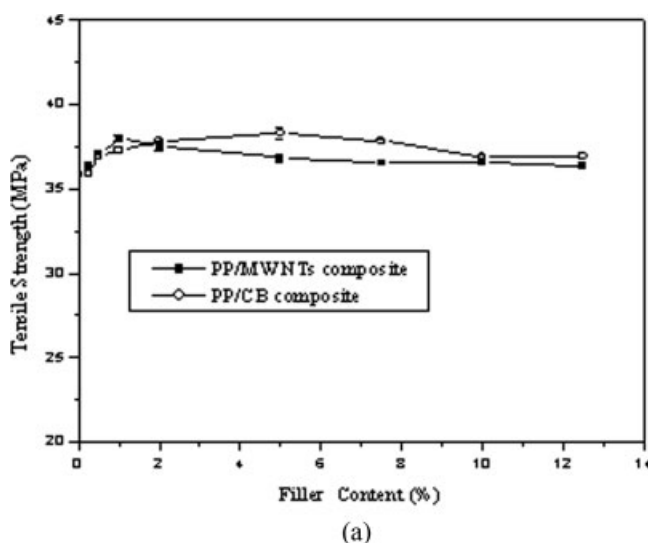


Figure 5 The effects of filler type and content on (a) tensile strength of PP/carbon composites and (b) elongation at break of PP/carbon composites.

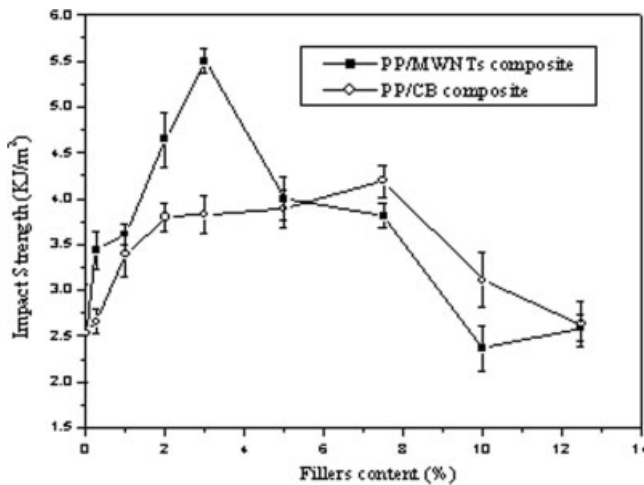


Figure 6 The effects of filler type and content on impact strength of PP/carbon composites.

crystallite size distribution. The narrower the crystallite size distribution, the smaller the ΔW will be.

A summary of the nonisothermal crystallization parameters of PP and PP composites determined from the normalized DSC thermograms is given in Table I. All the T_p values of PP in the PP/MWNTs composites are higher than that of neat PP (118.2 °C), and T_p increases with increasing MWNTs content. At low MWNTs content (0.5 wt %), T_p increases obviously from 118.2 to 124.9°C. However, there is slower increase of T_p when the MWNTs content is over 1.0 wt %. As can be seen in Table I, the effect of CB on the T_p values of PP in the PP/CB composites is same as that of MWNTs. All the $T_{\text{onset}} - T_p$ values of PP in the PP/MWNTs composites are smaller than that of neat PP, indicating that the addition of MWNTs into PP increased the overall rate of crystallization of PP. The $T_{\text{onset}} - T_p$ values of PP in the PP/MWNTs composites

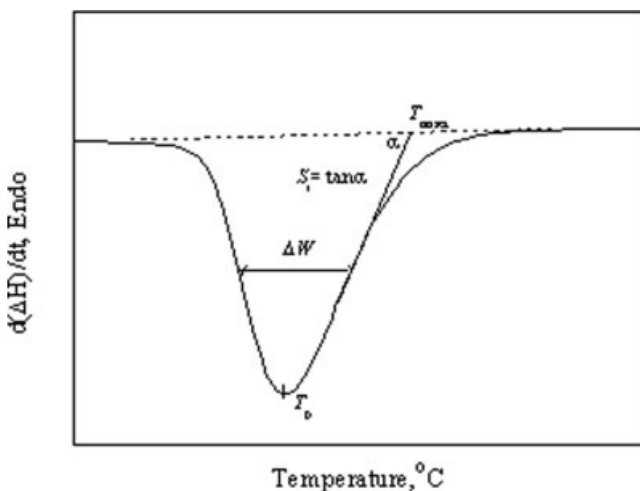


Figure 7 Schematic representation of the nonisothermal crystallization parameters determined from DSC crystallization exotherm.

TABLE I
Various Parameters of PP and the PP/CB Composites Determined from the Nonisothermal Crystallization Exotherm at a Cooling Rate of 5°C/min

Composition	T_p (°C)	T_{onset} (°C)	$T_{\text{onset}} - T_p$ (°C)	S_i	ΔW
PP	118.2	123.8	5.6	0.22	5.1
PP/MWNTs					
100/0.5	124.9	128.0	3.1	0.97	2.1
100/1.0	126.5	129.7	3.2	0.89	1.8
100/2.0	127.8	131.3	3.5	0.69	3.4
100/3.0	128.3	132.0	3.7	0.61	3.5
100/5.0	129.8	133.7	3.9	0.53	4.0
PP/CB					
100/0.5	123.9	127.4	3.5	0.76	3.8
100/1.0	127.6	130.8	3.2	0.95	3.7
100/2.0	128.8	132.1	3.3	0.96	3.3
100/3.0	128.6	131.9	3.3	1.01	3.5
100/5.0	129.9	133.2	3.3	0.92	3.3

increase with increasing MWNTs content. The addition of CB into PP also increased the overall rate of crystallization of PP. But the $T_{\text{onset}} - T_p$ values of PP in the PP/CB composites decrease with increasing CB content. After CB content reaches 2.0 wt %, the $T_{\text{onset}} - T_p$ values of PP remain invariable.

The parameters of the rate of nucleation (S_i) and the crystallite size distribution (ΔW) are also listed in Table I. S_i of all PP/MWNTs composites is greater than that of neat PP, implying the PP/CB composites have higher rate of nucleation. At a low MWNTs content of 0.5 wt %, S_i value of PP reached 0.97. With the increase of MWNTs content, S_i of the PP/MWNTs decreased. S_i of all PP/CB composites is also greater than that of neat PP. But S_i of the PP/CB increased with increasing CB content. When CB content reaches 3.0 wt %, the S_i of PP attained the greatest value. ΔW of all PP/MWNTs composites is smaller than that of neat PP, implying that the PP/MWNTs composites have more uniform crystallite size distribution. With the increase of MWNTs content, ΔW of the PP/MWNTs composites increased. The effect of CB on the ΔW of the PP/CB composites is different from that of MWNTs. At low CB content, ΔW of the PP/CB composites increased with increasing CB content. But when the CB content reached 2.0 wt %, ΔW of the PP/CB composites vary slightly.

Analysis of the data in Table I shows that MWNTs and CB particles can act as effective nucleating agents, increasing the peak temperature and the overall rate of the crystallization of PP. The rate of nucleation and narrow crystallite size distribution of PP increased with the addition of MWNTs or CB. But the effect of MWNTs on the crystallization behaviors of PP/MWNTs composites is different from that of CB. At low MWNTs content (0.5 wt %), PP/MWNTs composites get the greatest rate of crystallization, fastest nucleation rate, and narrower crystallite size distribution. But higher MWNTs content has negative effect

on the crystallization of PP. The rate of crystallization and rate of nucleation of PP decreased, and crystallite size distribution of PP broadened with the addition of MWNTs. However at low CB content, the nucleating effect of CB is small. The nucleating effect of CB is prominent at CB content between 2.0 and 5.0 wt %. Higher CB content has little enhancement effect on the crystallization of PP.

The difference in the effect on the crystallization of PP between MWNTs and CB may be explained by the structure and aspect ratio difference between MWNTs and CB. MWNTs have very high aspect ratio, and so they can easily form enough nucleation centers, leading to crystal growth in PP matrix even at very low content (0.5 wt %). But MWNTs are easy to aggregate because of the strong intermolecular van der Waal's interactions among the nanotubes, which leads to negative effect on crystal growth. Compared with MWNTs, CB has low aspect ratio. At low CB content, nucleation centers are not enough in PP matrix. The more the addition of CB particles, the more the formation of nucleation is; so the nucleating effect of CB improves with the increasing CB content. Higher CB content has little enhancement effect on the crystallization of PP. This is consistent with the study of Saroop and Mathur,²³ which concluded that the diffusion of crystallizing macromolecules was restricted in the crystallization front by increasing the concentration of rejected CB particles.

CONCLUSIONS

PP/carbon composites were prepared via melt blending PP with two types of carbon fillers: MWNTs and CB. Field-emission scanning electron micrographs show that MWNTs have poorer dispersion in the PP matrix compared with CB. Both individual MWNTs and agglomerations of MWNTs can be observed even at the low content of 0.5 wt %. The tendency of conglomeration of MWNTs is improved with the increasing MWNTs content. Volume resistivity measurements show that a significant drop in volume resistivity is achieved for a percolation threshold of about 8.0 wt % of PP/MWNTs composites and a percolation threshold of about 9.5 wt % of PP/CB composites, indicating that MWNTs are easier to form continuous conducting paths or network in the PP matrix than CB. At low content, the tensile strength of PP/MWNTs composites is higher than the tensile strength of PP/CB composites at the same content. The toughness of PP is

greatly reduced with the addition of MWNTs or CB. DSC analysis shows that PP/MWNTs composites get the greatest rate of crystallization at 0.5 wt % MWNTs content, fastest nucleation rate, and narrower crystallite size distribution. But higher MWNTs content has negative effect on the crystallization of PP. However at low CB content, the nucleating effect of CB is small. The nucleating effect of CB is prominent at CB content between 2.0 and 5.0 wt %. All experimental results show the strong intermolecular van der Waal's interactions between the nanotubes and poor interfacial interactions between MWNTs and polymer hinder the application of MWNTs in polymer composites, though MWNTs have predominant properties.

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