

Synergy Effect of Hybrid Fillers on the Positive Temperature Coefficient Behavior of Polypropylene/Ultra-High Molecular Weight Polyethylene Composites

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ABSTRACT: Hybrid nanocomposites of polypropylene/ultra-high molecular weight polyethylene (PP/UHMWPE, 70/30) with various amounts of carbon black (CB) and carboxylated multiwalled carbon nanotubes (c-MWNTs) were prepared by the solution mixing and melt blending techniques. The effects of the mixture of CB and c-MWNTs on the positive-temperature-coefficient (PTC) behavior and the negative-temperature-coefficient (NTC) behavior, as well as the room temperature resistivity, were studied. The transmission electron microscopy (TEM) images showed that the CB particles were aggregated at the interface, between PP and UHMWPE. This selective localization of the CB particles at the interface along with the formation of continuous conducting media leads to the

formation of additional conducting networks, resulting in a percolation threshold at a low CB content. A synergy effect of the hybrid conducting fillers of CB and c-MWNTs on the PTC behavior of the hybrid blends was also observed. The room temperature resistivity was reduced significantly by the incorporation of the c-MWNTs into the PP/UHMWPE/CB composite. The intensity and repeatability of the PTC effect in the nanocomposites were improved and the NTC effect weakened by incorporating a small amount (0.5 wt %) of c-MWNTs. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 116–124, 2010

Key words: nanocomposites; fillers; morphology; positive temperature coefficient; TEM

INTRODUCTION

Electrically conductive polymeric composites filled with conductive particles display a broad spectrum of properties and applications. Among them, carbon black (CB)-filled polymer composites show various electrical conductivities ranging from insulating to semiconducting or even conducting. One of the most attractive features of conductive polymer composites is their positive temperature coefficient (PTC) behavior, which leads to a sharp increase in their resistivity near the melting temperature of the polymer. After the maximum resistivity (R_{\max}) is attained, the PTC

behavior is sometimes followed by negative temperature coefficient (NTC) behavior, namely, a decrease in the resistivity. These polymeric PTC composite materials have a wide range of industrial applications and can be used as self-regulating heaters, current limiters, overcurrent protectors, microswitches, sensors, etc., with the advantages of excellent formability, moldability, light weight, and flexibility. The desired PTC performance includes low room-temperature resistivity (R_{RT}), high PTC intensity without NTC behavior, good reproducibility, and a high PTC transition temperature, together with a low conductive filler loading. This can be achieved by employing an immiscible polymer blend system instead of a single polymer system or by selecting a suitable type and combination of conducting fillers.

Polymeric PTC composites are generally composed of semicrystalline polymers and conductive particles such as CB and carbon fiber (CF). Noticeable PTC effects were previously reported for CB or carbon fiber reinforced composites with different polymers: polyethylene (PE),^{1,2} poly(vinylidene

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fluoride) (PVDF),³ ultra-high molecular weight polyethylene (UHMWPE),⁴ polyurethane (PU)⁵ and ethylene/ethylacrylate copolymer.⁶ The double PTC effects of CB-filled polymer blends of polypropylene (PP) and UHMWPE were reported by Feng and Chan.⁷ The percolation threshold at which a sharp decrease in the resistivity is observed, is related to the filler type. If CB is used as a conductive filler, a considerable amount is needed to achieve the percolation threshold, which is likely to hamper the preparation of CB/polymer composites containing more than 30 wt % CB by simple mixing techniques.⁸ However, when fiber is used as the filler, a relatively small amount of it is required. Fillers with high aspect ratios may also increase the tendency for continuous network structures to form in the polymer matrices.

In general, CB-filled semicrystalline polymer composites are difficult to use as thermistors in over-temperature and overcurrent protection, because of their NTC behavior and poor reproducibility. To overcome these disadvantages, researchers have suggested various methods of eliminating the NTC effect.^{2,7} One of these methods involves the incorporation of different types of fillers into the polymeric composites. Apart from the many unique thermal and optical properties of CNTs, they also display ultra-high electrical conductivity and mechanical strength.^{9,10} Hence, the incorporation of multiwalled carbon nanotubes (MWNTs) into the CB-filled polymers in this study was expected not only to reduce the required CB loading, but also to improve the electrical properties of the composites as well as to weaken their NTC behavior.^{11–13} In this research, a PTC composite material was fabricated by the melt mixing of conducting fillers consisting of c-MWNTs and CB particles, and polymeric materials composed of PP and UHMWPE, to investigate the influence of the hybrid conducting fillers on the PTC/NTC behavior of the blends.

EXPERIMENTAL

Materials

Polypropylene (PP) (J-170, Honam Petrochemical, Korea) and ultrahigh molecular weight polyethylene (UHMWPE) (XM-220, Mitsui Petrochemical Industries, Japan) were used for the preparation of the composites. MWNTs (diameter 10–15 nm, length 10–20 μm) produced by the catalytic vapor decomposition technique with a purity of >95% were purchased from Iljin Nanotech, South Korea. CB (V-XC72, Cabot Co), whose particle size is 18 nm and surface area is 257 m^2/g , was used.

Sample preparation

The MWNTs were oxidized using concentrated nitric acid according to the procedure reported elsewhere¹¹ to obtain carboxylated multiwalled carbon nanotubes (c-MWNTs). Different weight percentages of c-MWNTs were dispersed in xylene using an ultrasonicator for 30 min. PP was dissolved in xylene at 130°C for 30 min using a mechanical stirrer and mixed with the c-MWNTs solution for 30 min at 130°C to make the precursor master batch. The master batch of PP/c-MWNTs was obtained by precipitation induced by pouring the solution into methanol under vigorous agitation. After filtration, the master batch was dried in a vacuum oven at 70°C for 42 h.

The PP/C/CB/c-MWNTs hybrid nanocomposites were prepared by melt mixing using a Haake mixer (Rheocord 9000, German). PP was melt-mixed with the prepared master batch at 180°C for 10 min. Then, CB was added to the PP/c-MWNTs and mixed for 5 min. UHMWPE was added to the PP/CB/c-MWNTs composite and further mixed for 10 min. The composites were compression-molded at 180°C under a constant pressure for 5 min to obtain a sample sheet with a thickness of 1.5 mm for the PTC measurements. The weight ratio of PP to UHMWPE was kept at 70 : 30.

MEASUREMENTS

The volume resistivity of the fabricated hybrid nanocomposites was measured as a function of temperature using a computerized measurement system with a programmable oven. The temperature was increased at a heating rate of 2°C/min. A silver paste was coated on both sides of the specimen to ensure that the sample surface was in complete contact with the multimeter electrodes (Keithley 2000). To check the repeatability of the PTC behavior, the electrical resistivity of the same specimen was measured for three heating/cooling cycles.

The thermal behavior of the sample was measured by a differential scanning calorimeter (DSC) (TA 2910). About 6–8 mg of the sample was heated from ambient temperature (25°C) to 200°C at a heating rate of 5°C/min under a nitrogen atmosphere. The morphology of the fractured surface of the composites was investigated using scanning electron microscopy (SEM) (Hitachi S-4700, Japan). All of the samples were gold sputtered before their observation. Transmission electron microscopy (TEM) (JEOL JEM 2010F) observation was carried out at 100 kV. The TEM specimens were microtomed to ultra thin sections with a thickness of 70 nm. The laser Raman spectroscopy analysis was carried out by means of a Raman spectroscopy system (Nanofinder 30) with a

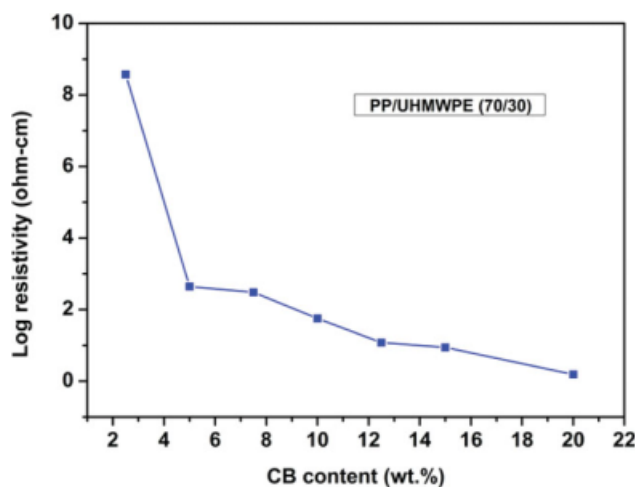


Figure 1 The room temperature resistivity as a function of the carbon black content for the PP/UHMWPE (70/30) composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

microscope equipped with 40 \times objectives and a charge coupled device (CCD) detector. The X-ray diffraction (XRD) patterns were recorded at a scanning speed of 4 $^\circ$ /min using a Diffractometer (Rigaku D/max 2500, Japan) at 40 kV and 30 mA using Cu-K $_{\alpha}$ monochromatic radiation.

RESULTS AND DISCUSSION

Figure 1 shows the log of the room temperature resistivity of the CB-filled PP/UHMWPE (70/30) composites as a function of the CB content. A sharp drop in the resistivity was observed at a CB content of 5 wt %, which is attributed to the percolation phenomenon. When the CB content was less than 2.5 wt %, the composites remained an insulating material, because the CB particles do not form the continuous tunnels required to transfer electrons. As the CB concentration approaches the percolation threshold, the CB particles come close enough to each other to transfer electrons. For the PTC studies, a minimum CB content of 5 wt % was used to maintain a sufficiently low room temperature resistivity. Figure 2 shows the log of the resistivity as a function of temperature for the CB-filled PP/UHMWPE (70/30) composites with different CB contents. The electrical resistivity of the composite increased steadily as the temperature was raised and rose more sharply near the melting temperature (T_m) as the polymer expanded, exhibiting a strong PTC effect. Although the CB particles seem to be homogeneously dispersed in the PP matrix during melt mixing, they are pushed out of the crystalline region in the form of impurities during cooling. Thus, at temperatures below the melting point of the PP crystals, the CB particles are dispersed only in the amorphous

region. As the crystallite melts during the heating of the composite, the CB particles disperse into the polymer melt and, thus, the interparticle distance is increased to such an extent that the electron tunneling between the conductive particles is hampered, resulting in a dramatic increase in the resistivity. For the system with a lower CB content, the NTC effect was noticeable, while it was not so obvious for the system with a high CB loading. Another interesting point was that the temperature at which the NTC effect appeared decreased with increasing CB content, because of the resultant higher thermal conductivity of the composite. Two sharp resistivity jumps were observed for the PP/UHMWPE composite with the lower CB content. The first resistivity jump occurred at about 150 $^\circ$ C, which is slightly higher than the melting point of UHMWPE. When the temperature was further increased, the composite did not show any NTC effect, but rather a strong second PTC peak at around 180 $^\circ$ C, which corresponds to PP. This phenomenon is referred to as the "double-PTC effect," in which the first and second resistivity jumps are defined as the first and second PTC effects, respectively.^{14,15} Figure 3 shows the PTC intensity, which is defined as $\log(R_{\max}/R_{RT})$, of the PP/UHMWPE (70/30) composite as a function of the CB content. A steep reduction in the PTC intensity was observed as the CB content was increased from 5 to 12 wt % and the rate of reduction became slower at CB contents above 15 wt %. This result clearly indicates that the PTC intensity strongly depends on the CB content.

Evidently, the highest PTC intensity appears at 12 wt % of CB content. From Figure 3, it can be concluded that: (i) when CB loading was higher than the upper limit of the percolation region, the CB

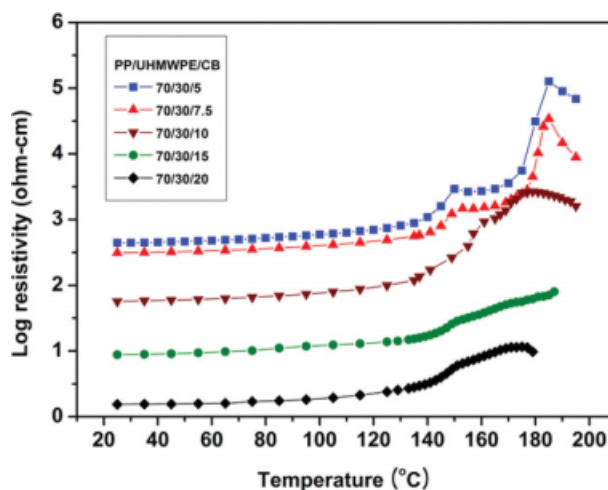


Figure 2 The resistivity as a function of temperature for the PP/UHMWPE (70/30) composites with various CB contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

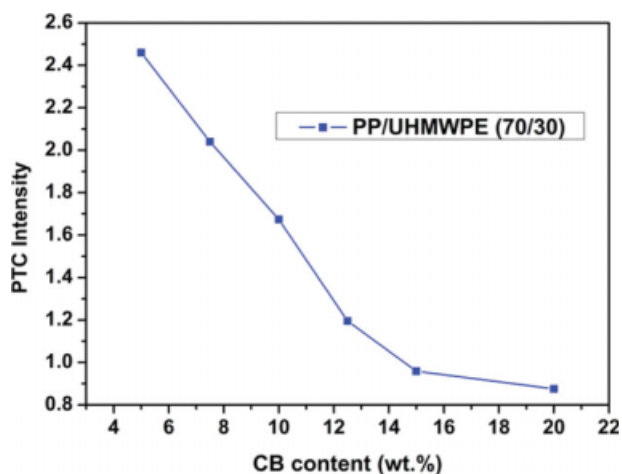


Figure 3 Plot of PTC intensity as a function of carbon black concentration of PP/UHMWPE (70/30) composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content dependence of PTC intensity behaved in a similar way to that of resistivity (i.e., the more CB was incorporated, the lower PTC intensity and electrical resistivity, because more and more continuous electric paths throughout matrix had already formed); and (ii) PTC effect became irregular when CB content approached the critical fraction so that the corresponding PTC intensity varied disorderly with CB content, which differs from the conventional expectation that PTC intensity increases with decreasing conductive filler loading [like item (i)] and exhibits maximum near the percolation threshold. The metastable nature of the conductive networks established around critical filler loading in the composites should be responsible for the abnormal phenomenon.

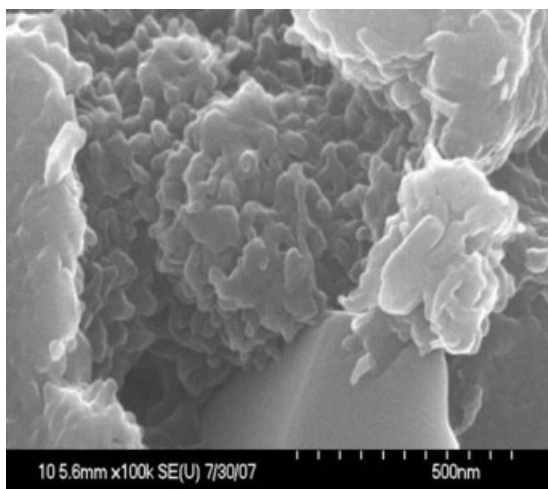


Figure 4 SEM micrograph of PP/UHMWPE composite containing 5 wt % CB.

Therefore, CB fraction of a reproducible PTC type composite with acceptable PTC effect should exceed the described percolation region. In the case of higher CB content, however, composite's PTC intensity could not be unconditionally raised for purposes of preventing the composite from overheating, while maintaining a relatively low room temperature resistivity so as to ensure sufficient electrothermal output. To solve the problem, polymer blends instead of monopolymer should be used as matrix resin, in which CB might be selectively distributed in one of the blending components and achieve sufficient conductivity at relatively low fraction on the blends basis.

The morphologies of the PP/UHMWPE/CB blends are presented in Figures 4 and 5. The SEM image of the PP/UHMWPE/5 wt % CB composite is shown in Figure 4. It clearly shows the two-phase structure of the composite. The UHMWPE region has less CB particles than the PP region. It is

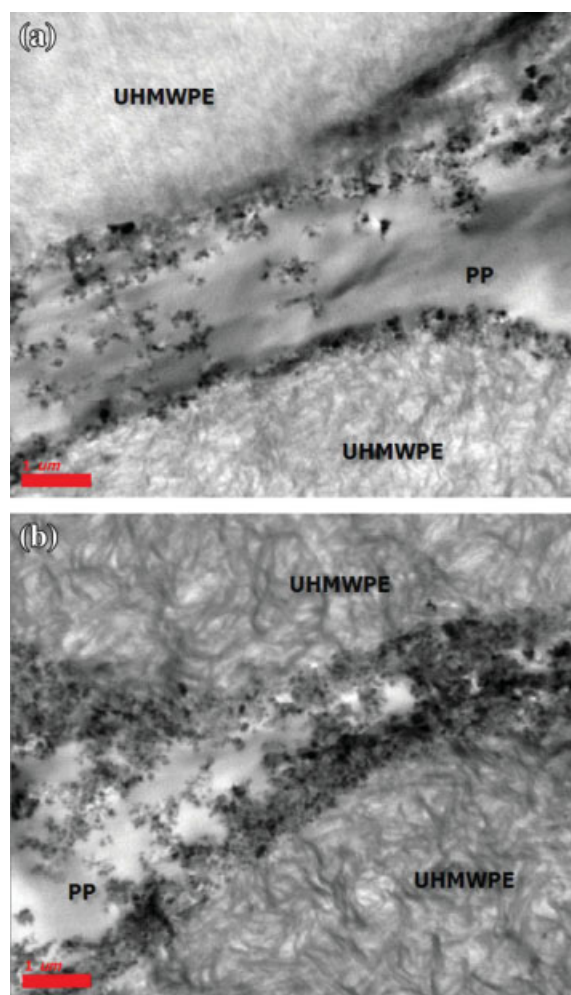


Figure 5 TEM images of the PP/UHMWPE/CB composites containing (a) 5 wt % and (b) 10 wt % CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

considered that the CB particles cannot easily enter into the UHMWPE resin because its viscosity is much higher than that of the PP resin. It is generally agreed that the CB particles are dispersed in the amorphous regions of a semicrystalline PP. This unequal distribution of CB particles in the PP and UHMWPE regions was explained by the thermodynamic model proposed by Sumita et al.,¹⁶ For the CB-filled PP/UHMWPE composites, the presence of a greater number of CB particles in the continuous phase PP region improves the conductivity with low loadings of CB, as compared to the one phase resin system. The aggregation of CB at the interface between the two resins also allows alternative conducting paths to be formed and improves the conductivity of the composite. The TEM images of the PP/UHMWPE composites containing 5 and 10 wt % of CB are shown in Figure 5(a,b), respectively. These images clearly show the distribution of CB at the interface between PP and UHMWPE, as well as in the continuous phase of the PP resin. Although many of the CB particles were distributed in the PP phase, they seemed to have a stronger affinity for the UHMWPE phase.⁸ As reported in previous studies,^{17,18} the CB particles have a stronger affinity for the UHMWPE phase ($\gamma_{PE} \sim 36$ dyne/cm) than for the PP phase ($\gamma_{PP} \sim 5 \sim 30$ dyne/cm). However, the CB particles cannot enter into the highly viscous UHMWPE resin and, thus, they become aggregated at the outer skin of UHMWPE.^{14,19} When there is no more room for additional CB particles at the interfaces between the UHMWPE particles and PP, they are forced to enter into the PP matrix.^{15,20} Comparing Figure 5(a) with (b), it can be seen that the CB conductive channels in the composite containing 5 wt % CB were considerably thinner and less than those in the composite containing 10 wt % CB. When the temperature is increased, the thermal expansion of the UHMWPE increases the inter particle distance between the conducting particles, resulting in a significant increase in the resistivity of the composite. The decrease in the number of conductive pathways increased the resistivity, so that a larger PTC effect could be observed in the composite with a low CB loading [Fig. 5 (a)]. In this case, the conductivity was partially the result of electron tunneling through the small gap distances separating the CB particles, as evidenced by the high resistivity values at room temperature. However, in the case of the composites with a higher CB loading, due to the larger dimensions of the CB channels [Fig. 5(b)], the expansion of the polymer melt would only decrease the dimensions of the conductive pathways, but not break them up. Therefore, the PTC effect was much smaller as compared to that of the composites with a lower CB loading. Furthermore, a high filler loading might keep the CB particles or their aggregates

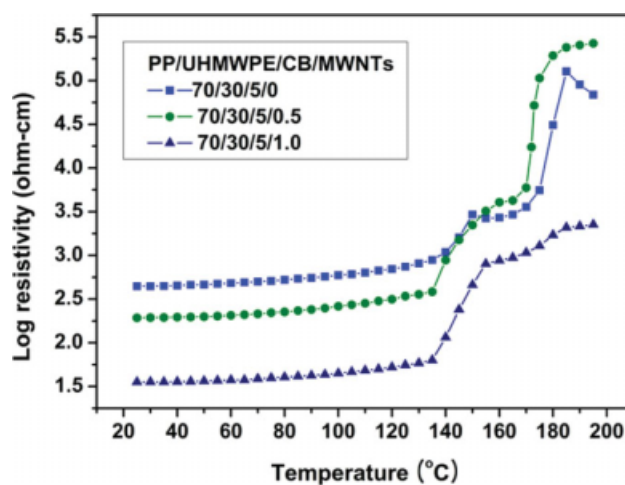


Figure 6 The PTC behaviors of the PP/UHMWPE/CB (70/30/5) composites with various MWNTs contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in direct contact with one another, even at temperatures above the T_m of the matrix, resulting in ohmic conduction instead of electron tunneling.²¹ Basing on the analyses of this section it can be concluded that the PTC intensity of CB filled polymer blends is determined by the concentration of CB in the filler rich phase and the structural continuity as well as melting behavior of this phase.

To increase the PTC intensity and weaken the NTC effect, c-MWNTs were introduced into the PP/UHMWPE/CB composite. Figure 6 shows the PTC behaviors of the PP/UHMWPE/CB/c-MWNT composites with various loadings of c-MWNTs. With the addition of a small amount of c-MWNTs, the PTC intensity and room temperature resistivity were much enhanced. Increasing the content of c-MWNTs lowers the room temperature resistivity, but not always the PTC intensity. The highest value of the PTC intensity was observed at a loading of c-MWNTs of 0.5 wt %. The incorporation of c-MWNTs into the PP/UHMWPE/CB composite provides the network structure with conductive pathways through the CB particles and/or CB aggregates and thereby bridges the conducting CB channels. Introducing c-MWNTs weakens the NTC effect of the composite, as shown in the figure. This may be due to the fact that their addition results in the formation of a network structure, due to their large aspect ratio, and this network structure can restrict the movement of the polymer chains in the melt and inhibit the agglomeration of the conducting fillers. Therefore, the NTC effect was thought to be eliminated and, consequently, the blends with c-MWNTs have a better PTC effect and a higher PTC temperature. This synergy effect is favorable for the PTC performance. Figure 7(a,b) show the TEM images of the PP/

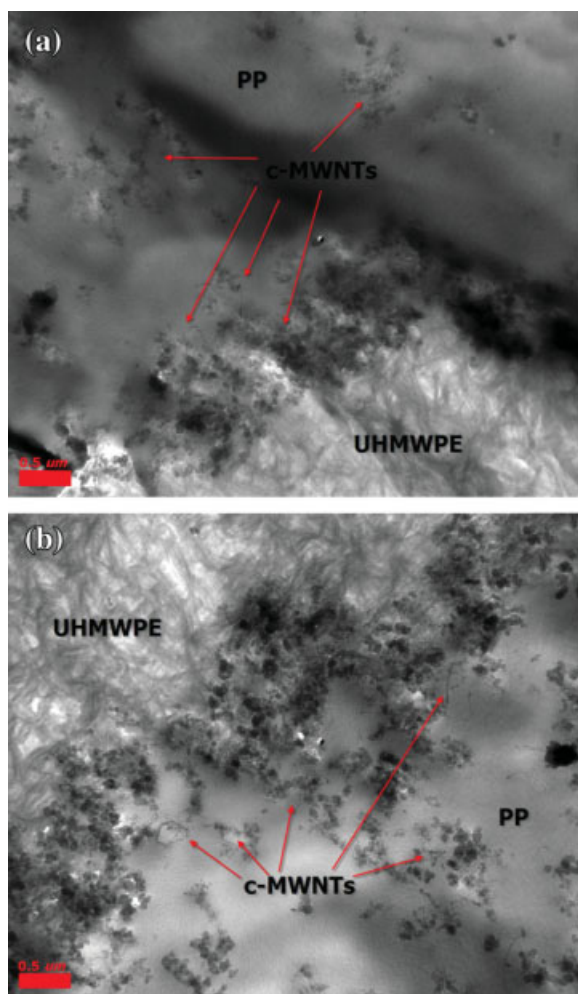


Figure 7 TEM images of the PP/UHMWPE/CB/c-MWNT composites containing (a) 5 wt % and (b) 10 wt % CB with 1 wt % c-MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UHMWPE/CB/c-MWNT composites containing 5 wt % CB and 10 wt % CB with 1 wt % c-MWNTs, respectively. From the figures, good dispersion of the c-MWNTs and the formation of network structures between the CB particles and c-MWNTs were clearly observed.

For the investigation of CB (dispersed) phases, Raman spectroscopy has been widely used,²² due to its high sensitivity to the hybridization state of carbon, with a frequency shift of the $\nu(\text{C}=\text{C})$ stretching modes in the range of about 300 cm^{-1} being observed, between the sp^2 bonds of graphite (1590 cm^{-1}) and the sp^3 structure of diamond (1320 cm^{-1}). Figure 8(a,b) show the laser Raman spectra in the range of $250\text{--}2000\text{ cm}^{-1}$ for the PP/UHMWPE (70/30) composites with various amounts of CB and c-MWNTs respectively. The Raman spectra [Fig. 8(a)] of all of the CB filled composites exhibit the “D-band” at about 1325 cm^{-1} , which originates from the

disordered state of carbon, and which makes an increasingly stronger contribution as the disordered state of the structure increases. They also show the “G-band” at about 1594 cm^{-1} , due to the tangential vibration of the carbon atoms, and the peak intensities and shape (widths) of the G and D bands increases as increase in the amounts of CB. The intensities of the G and D bands in the Raman spectra also increase with increasing amount of the c-MWNTs and the D band becomes sharper [Fig. 8(b)]. This result suggests that the level of disorder in the CB particles was altered by the introduction of the c-MWNTs.

Generally, thermoplastic composites exhibit poor repeatability of their resistivity-temperature curves during different heating/cooling cycles. According to previous reports, the repeatability of the electrical resistivity can be slightly improved by crosslinking induced by either peroxides or irradiation,²³ or by using mixtures of two kinds of CB with polyolefine,⁷

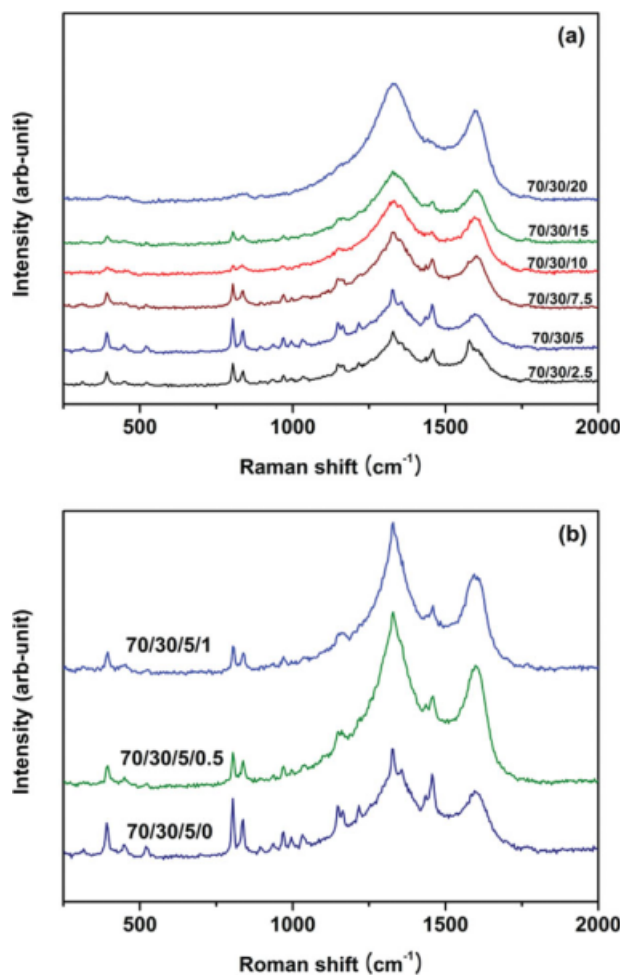


Figure 8 Laser-Raman spectra of PP/UHMWPE (70/30) composites with (a) different amounts of CB and (b) 5 wt % CB with c-MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

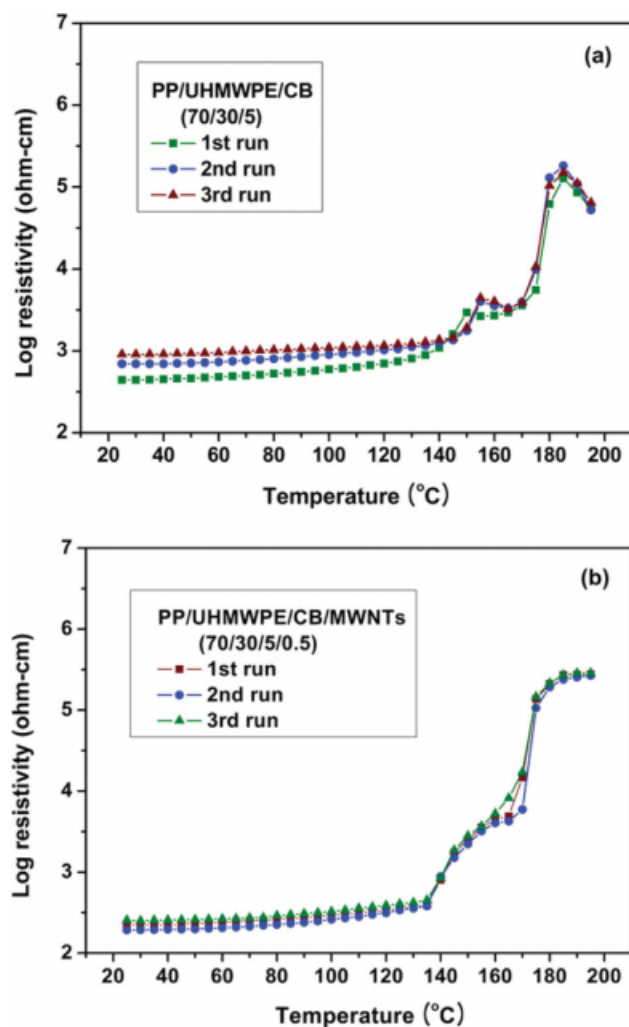


Figure 9 The plot of the resistivity versus temperature for the PP/UHMWPE/CB (70/30/5) composites during three heating cycles; (a) without c-MWNTs and (b) with 0.5 wt % c-MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

or by using immiscible blends.^{14,20} This is obviously due to the fact that the expansion/contraction processes accompanying the heating/cooling cycles cause the movement of the fillers, and this behavior is irreversible. However, in the case of the blends with UHMWPE^{2,5,7} good repeatability of the electrical resistivity was observed, since UHMWPE minimizes the migration of the CB, because of its high viscosity, even in the temperature range beyond its T_m . Figure 9(a,b) show the curves of the temperature dependence of the resistivity for the PP/UHMWPE blend containing 5 wt % of CB without and with c-MWNTs, respectively, during three heating cycles. The first run is different from the subsequent ones, while the latter two runs have good repeatability, as shown in Figure 9(a). Thus, minute changes of the CB distribution cause vast changes in the resistivity.

The thermoelectric behavior of the blend changes significantly between the first and subsequent heating/cooling cycles. These results confirmed the inference that the second PTC effect was due to the further intermixing between CB and the polymer particles at higher temperatures.³ It is clearly observed from Figure 9(b) that for the c-MWNTs filled composites, there were little or no changes in the shape of the resistivity versus temperature curves in the different heating/cooling cycles. A slight variation in the room temperature resistivity and first intense PTC peak with increasing number of heating/cooling cycles was noticed. The room temperature resistivity first decreases and then slightly increases with increasing number of heating cycles. The slight decrease in the initial resistivity may have been caused by the enhanced contact surface area which developed during the repeated heating cycles. The repeatability and PTC intensity of the nanocomposite materials incorporating the c-MWNTs were significantly improved by the network structure formed by the latter, which might have played the same role as the crosslinked polymer in the hybrid composites. This phenomenon was further confirmed by the DSC analysis.

The influence of the CB and c-MWNT contents on the melt behavior of the PP/UHMWPE blends was studied by DSC analysis. The DSC thermograms of the PP/UHMWPE composite containing 5 wt % of CB without and with 0.5 wt % c-MWNTs during three heating cycles are shown in Figure 10(a,b), respectively. The DSC thermograms clearly show two melting (T_m) peaks, which indicates that the blend is immiscible in nature and consists of two phases. After the first thermal cycle (from room temperature to 200°C at a heating rate of 5°C/min and subsequent cooling to room temperature), the endothermic peak of PP shifted to a lower temperature in the second and third heating cycles, since the crystal size becomes smaller during the fast cooling process.² In the second run, the DSC curves show similar profiles, indicating the good reproducibility of the thermal behavior of the composites. This is because the pseudotransition behavior is destroyed during the first heating cycle. A similar type of observation was made for LMWPE/UHMWPE.² After the incorporation of the c-MWNTs into PP/UHMWPE/CB, the DSC curves show similar melting profiles for all heating cycles. This result clearly indicates the good reproducibility of the melting curves of the nanocomposites incorporating the c-MWNTs as compared to those without the c-MWNTs. This result is consistent with the repeatability of the PTC behavior of the nanocomposites during different heating and cooling cycles. The crystallinity of UHMWPE in the hybrid composite was increased markedly from 11.75 to 15.01% by the

addition of the c-MWNTs, whereas that of PP remained almost the same (22.43 and 22.52%).²⁴ As can be seen from the DSC curves [Figs. 10(a,b)], the area under the UHMWPE melting peak increases after the incorporation of the c-MWNTs.

Figure 11 shows the XRD profiles of the nanocomposites. In the figure, line (a) indicates the XRD profiles of the PP/UHMWPE composite and lines (b) and (c) indicate those of the PP/UHMWPE composites containing 5 wt % of CB without and with 0.5 wt % of c-MWNTs, respectively. The XRD patterns of all of the systems showed six peaks in the 2θ range of 13–26°. The x-ray profile of the nanocomposite showed a higher intensity peak at a 2θ value of around 21°. These results indicate that the crystalline behavior of PP/UHMWPE was increased by the addition of the c-MWNTs.

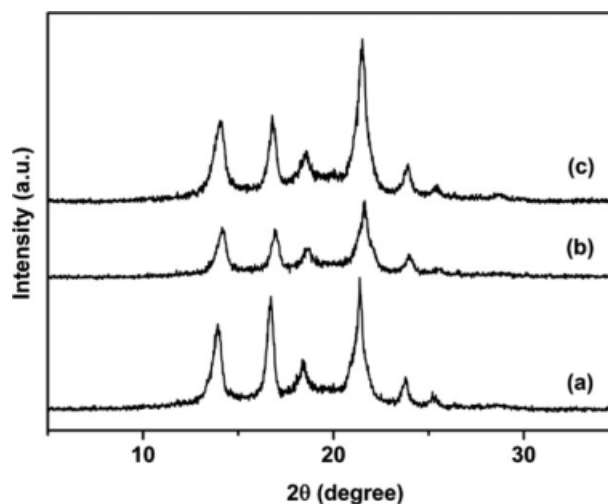


Figure 11 X-ray profiles for (a) PP/UHMWPE (70/30), (b) PP/UHMWPE/CB (70/30/5) and (c) PP/UHMWPE/CB/c-MWNT (70/30/5/0.5) nanocomposites.

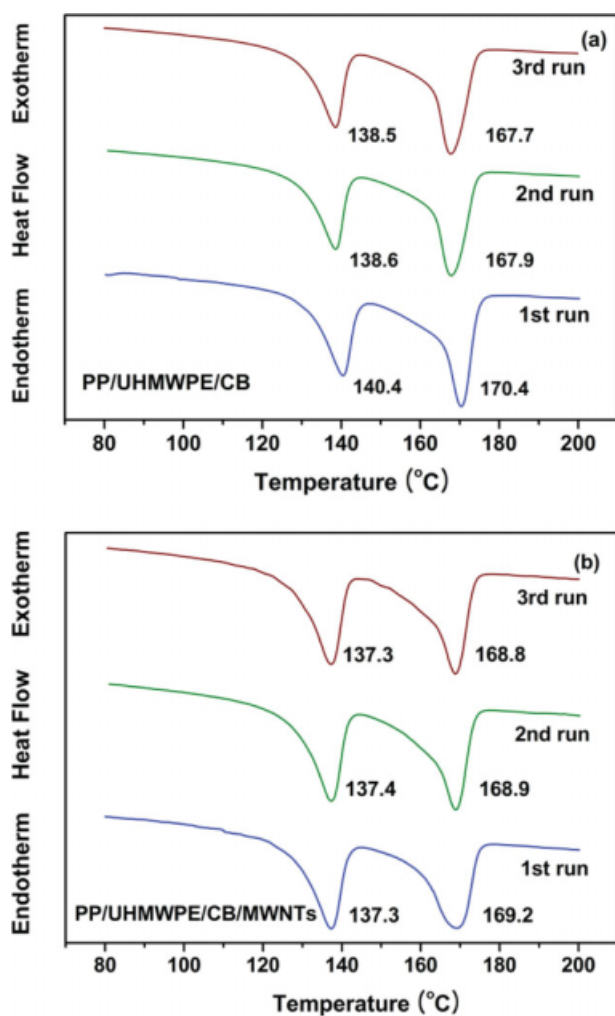


Figure 10 DSC thermograms during three heating cycles of the PP/UHMWPE/CB (70/30/5) composites; (a) without c-MWNTs and (b) with 0.5 wt % of c-MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

PP/UHMWPE/CB/MWNTs PTC nanocomposite materials were fabricated by solution mixing followed by melt blending. For these PTC composites, percolation threshold values were observed at a low content of CB. This is due to the segregation of CB in the interfacial regions of the UHMWPE and the PP. The TEM images confirm that the CB particles are mainly distributed at the interface between PP and UHMWPE and in the PP region. The composites with a low CB content exhibit a double-PTC phenomenon. The first PTC is due to the T_m of the UHMWPE, while the second is related to the T_m of the PP.

The composites incorporating c-MWNTs exhibit low room temperature resistivity. The CB and c-MWNTs play different roles in the formation of conductive pathways within the PP/UHMWPE/CB/c-MWNTs nanocomposites. It is well known that MWNTs provide charge transport over large distances, whereas CB enables charge transport over small distances. The incorporation of c-MWNTs into the PP/UHMWPE/CB composites provides long conductive paths that serve to bridge the disconnected CB particles and aggregates or short conductive paths. The formation of these bridges involving both the CB and MWNTs is referred to as a synergy effect, which enhances the continuity of the conductive pathways, thereby reducing the percolation threshold.

The improved PTC intensity and repeatability in the composites containing CB and c-MWNTs result from the synergistic effect due to the network structures of the c-MWNTs. The addition of c-MWNTs to the PP/UHMWPE/CB composites increases their viscosity, because it is not as easy for the conductive filler in the PP/UHMWPE/CB/c-MWNT composites

to aggregate or agglomerate as that in the PP/UHMWPE/CB composites at elevated temperature, and the NTC intensity is reduced to a relatively low level.

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