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Double positive temperature coefficient effects of carbon black-filled polymer blends containing two semicrystalline polymers

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Abstract

Carbon black (CB)-filled polypropylene (PP)/ultra-high molecular weight polyethylene (UHMWPE) composites were prepared by the conventional melt-mixing method. The effects of the PP/UHMWPE weight ratio, CB content and CB particle size on the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effects, as well as the room temperature resistivity of the composites were elucidated in detail. When the PP/UHMWPE weight ratio is larger than 3/7, the PTC and NTC behaviors of 10 wt% CB-filled PP/UHMWPE composites are similar to those of a CB-filled neat PP composite. However, when the weight ratio equals or is smaller than 3/7, the composites exhibit a PTC effect that is similar to that of a CB-filled neat UHMWPE composite. The elimination of the NTC effect in CB-filled polymer blend composites can be achieved by using a very high viscosity polymer as one of its components. The results of an optical microscopic study indicate that the CB particles are selectively localized at the interface between the PP matrix and the UHMWPE particles and in the PP matrix of the composites. This selective localization of the CB particles is attributed to the fact that the viscosity of the UHMWPE particles is so high that the CB particles cannot go inside the UHMWPE particles. In addition, a novel physical phenomenon—double-PTC effect—is observed and quantitatively characterized. The balance between the PTC intensity and the resistivity at room temperature can be achieved by using a mixture of large and small CB particles.

Keywords: Double positive temperature coefficient; Carbon black-filled polymer blends; Semicrystalline polymers

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1. Introduction

It is well known that when the temperature is above the melting point of semicrystalline polymers, non-crosslinked carbon black (CB)-filled semicrystalline polymer composites exhibit a very sharp decrease in resistivity. This phenomenon is referred to as the negative temperature coefficient (NTC) effect [1–5]. In general, non-crosslinked CB-filled semicrystalline polymer composites cannot be used as thermistors in over-temperature and over-current protections due to their NTC effects and poor reproducibility in thermal cycling. In order to overcome these disadvantages, researchers have proposed and developed many methods to eliminate the NTC effect of CB-filled semicrystalline polymer composites [6–17]. Among these methods, the first approach used is to crosslink the semicrystalline polymer matrix by a crosslinking agent, such as a peroxide [6–8] or silane [9]. For instance, Narkis [6] successfully used a peroxide to crosslink CB-filled high-density polyethylene (HDPE) composites without sacrificing the positive temperature coefficient (PTC) intensity. In addition to the use of a crosslinking agent, Gamma and electron beam radiations have been used to crosslink CB-filled semicrystalline polymer composites [7,8,11–17]. It was also reported that a third filler could be used to stabilize the polymer matrix and eliminate the NTC effect of CB-filled semicrystalline polymer composites [10].

Even though crosslinked CB-filled HDPE composites have been used as thermistors and self-regulating heaters in the industry for many years, the mechanism for eliminating the NTC effect has not been fully understood. However, the absence of the NTC effect in the crosslinked CB-filled semicrystalline polymer composites is related to an increase in the viscosity of the polymer matrix, leading to a significant reduction in the mobility of the CB particles in the composites [8]. Based on this idea, it is possible to use a very high viscosity semicrystalline polymer matrix to eliminate the NTC effect. Recently, CB-filled ultra-high molecular weight polyethylene (UHMWPE) composites prepared by a sintering method have been studied extensively by Chan et al. [14]. The CB-filled UHMWPE

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Table 1
Materials used in this study

Material	Grade	Supplier
PP	Profax PD382 (MFR = 3 g/10 min)	Himont
UHMWPE	Hi-fax 1900	Montell
CB	V-XC72	Cabot
CB	N660	Columbian chemicals

composites did not show any NTC effect except a small decrease in resistivity at the temperature just above the melting point of the UHMWPE. This decrease was immediately followed by a steady increase in resistivity upon a further temperature increase. For the CB-filled UHMWPE composites, the elimination of the NTC effect is attributed to the extremely high viscosity of UHMWPE matrix [14]. However, the production rate of the sintering method is very low. Thus, the preparation of CB-filled UHMWPE composites by the conventional melt-mixing method is an attractive alternative.

In this work, CB-filled PP/UHMWPE composites were prepared by the conventional melt-mixing method and the effects of the PP/UHMWPE weight ratio, CB content and CB particle size on the PTC and NTC behaviors of the composites were investigated.

2. Experimental

The materials used in this investigation are listed in Table 1. CB-filled PP/UHMWPE composites were prepared by the conventional melt-mixing method. The compounding was conducted on a Haake mixer at 200°C and 30 rpm for 15 min. As the PP/UHMWPE weight ratio decreased, the torque of the mixer increased. The PP/UHMWPE weight ratio was reduced until the torque reached the allowable maximum for the mixer (300 Nm). The compounds were compression-molded into 2 mm thick sheets using a hot press at 200°C and 16 MPa.

The sample size for the measurements of the PTC and NTC effects was $15 \times 10 \times 2$ mm^3. The resistivity along the sample length as a function of temperature was measured using a computerized system, comprising a computer, a multimeter, and a programmable oven. The heating rate was 2°C/min. Prior to the electrical measurements, silver paint was coated on the samples as the electrode material reduce to contact resistance.

The melting behavior of the composites was determined using a differential scanning calorimeter (DSC) (TA 2910). The instrument was calibrated with indium as a standard and all measurements were conducted under nitrogen atmosphere. The weight of the samples for DSC measurements was 10–12 mg. The samples were heated to 200°C at a heating rate of 2°C/min.

The morphology of the composites was investigated by using an optical microscope (OM) operating at the transmission mode. Thin sections of the composites of 1 μm in thickness were prepared by a cryomicrotome (Leica) at −100°C.

3. Results and discussion

3.1. Effect of PP/UHMWPE weight ratio

It is well known that CB-filled neat UHMWPE

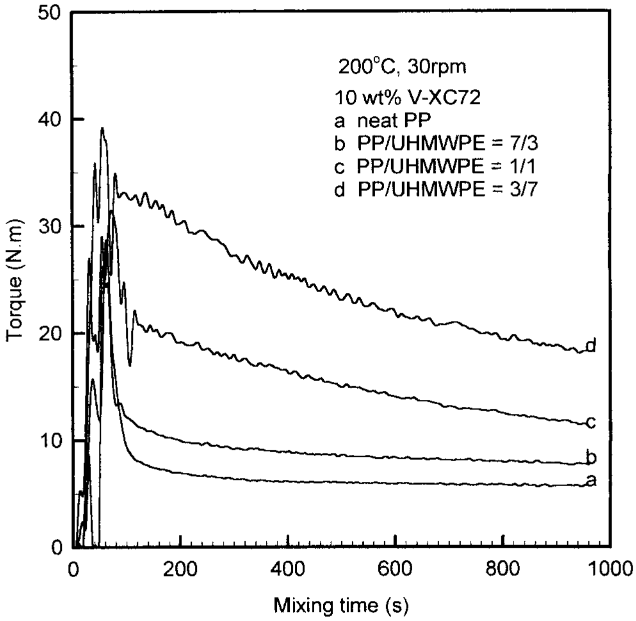

Fig. 1. Torque as a function of mixing time for 10 wt% CB(V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios.

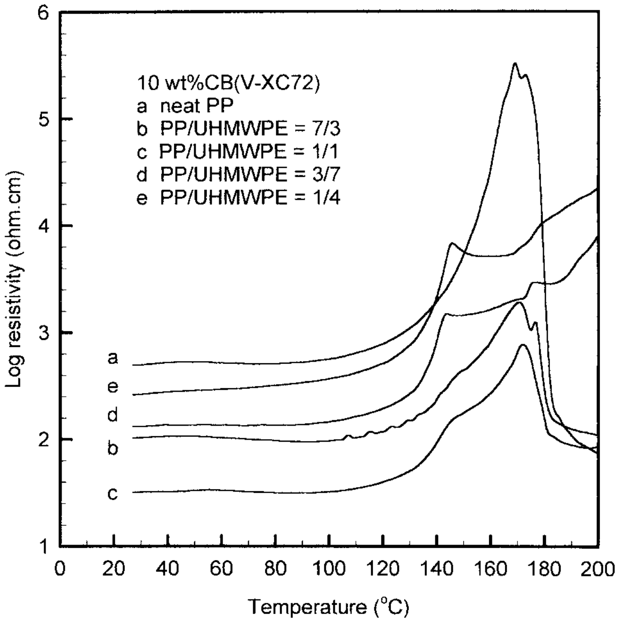

Fig. 2. Log resistivity as a function of temperature for 10 wt% CB(V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios.

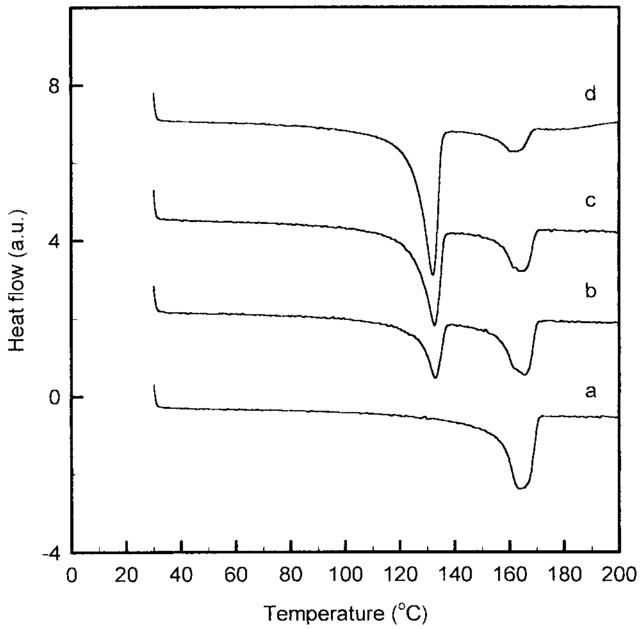

Fig. 3. DSC scans for 10 wt% CB(V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios. (a) PP; (b) PP/UHMWPE = 7/3; (c) PP/UHMWPE = 1; and (d) PP/UHMWPE = 3/7.

composites cannot be prepared by the conventional melt-mixing method due to their extremely high viscosity. In order to prepare CB-filled UHMWPE composites by the conventional mixing process, PP was used as the second component of the polymer matrix to reduce the viscosity of the compound. By gradually decreasing the PP content in the PP/UHMWPE blends, the maximum UHMWPE content could be determined without having the torque of the mixer higher than the allowable value. Fig. 1 shows the mixing torque of 10 wt% CB (V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios as a function of mixing time. It is very clear that as the PP/UHMWPE weight ratio decreases, the mixing torque of the composite increases significantly and longer time is needed to attain the steady state. In this study, the lowest PP/UHMWPE weight ratio that could be used is 1/4.

PP/UHMWPE composites with 10 wt% CB (V-XC72) and the PP/UHMWPE weight ratio ranging from 1/4 to 7/3 were prepared to determine the effect of the PP/UHMWPE weight ratio on the PTC and NTC behaviors of the composites. Fig. 2 is a plot of the log resistivity of the composites as a function of temperature. Clearly, the PP/UHMWPE weight ratio of the composites can significantly influence the PTC and NTC effects. As shown in Fig. 2, the CB-filled PP/UHMWPE composites with a large PP/UHMWPE weight ratio (greater than 3/7) show a major jump in the resistivity at about 170°C followed by a sharp NTC effect. The electrical properties of these composites are not too different from that of a CB-filled PP composite. However, when the PP/UHMWPE weight ratio equals or is lesser than 3/7, a major jump in the resistivity is observed at about 140°C followed by a small decrease in the resistivity and then a gradual increase is observed with further increase in temperature. When temperature increases to near the melting point of PP, a small sharp jump in resistivity is also observed. We refer to this phenomenon as the double-PTC effect, which will be discussed in more detail in a later section.

To reveal the PTC mechanism of the composites, a differential scanning calorimeter was used to study the melting behaviors of the 10 wt% CB (V-XC72)-filled composites with various PP/UHMWPE weight ratios. Fig. 3 shows the DSC scans of the composites obtained at a heating rate of 2°C/min. A comparison of Figs. 2 and 3 shows that the melting of the UHMWPE and PP crystallites and the sharp increases in the resistivity of the composites occur in a similar temperature range. Hence, the PTC effect observed at 140 and 170°C is attributed to the volume expansion as a result of the melting of UHMWPE and PP crystallites, respectively.

Fig. 4(a)–(f) displays the optical micrographs of the 10 wt% CB(V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios. As depicted in these micrographs, a two-phase structure is observed. The light areas are identified as the UHMWPE particles due to the fact that the viscosity of these UHMWPE particles is so high that CB particles cannot go inside the UHMWPE particles, while the dark areas forming a continuous phase are identified as a mixture of PP and CB. The interface between the PP matrix and the UHMWPE particles is much darker, indicating that a much higher concentration of CB is located at the interface. Such a CB distribution in the PP/UHMWPE composite can be explained by a thermodynamic model proposed by Sumita [19]. For the CB-filled PP/PE composites, CB particles should be preferentially localized in the PE phase. However, the CB particles can only be accumulated at the interface between the PP matrix and the UHMWPE particles due to the extremely high viscosity of UHMWPE. In order to confirm that CB is indeed segregated at the interface, a composite containing only 2 wt% of CB(V-XC72) was prepared. As shown in Fig. 5, the segregation of CB at the interface can clearly be seen at this low concentration of CB. When the interfacial regions between the PP matrix and UHMWPE particles are saturated with CB particles, the excess CB particles are forced to be dispersed in the PP matrix.

From Fig. 4(a)–(f), we can deduce that there are two types of conductive pathways formed in these composites c. The first type is the conductive paths in the PP matrix that are not in any way connected to the CB located at the interface between the PP matrix and the UHMWPE particles. We refer to this type of conductive paths as type M (matrix). The second type is the conductive paths in the PP matrix that are connected to the CB located at the interface between the PP matrix and the UHMWPE particles. We refer to this type of conductive paths as type I + M (interface + matrix).

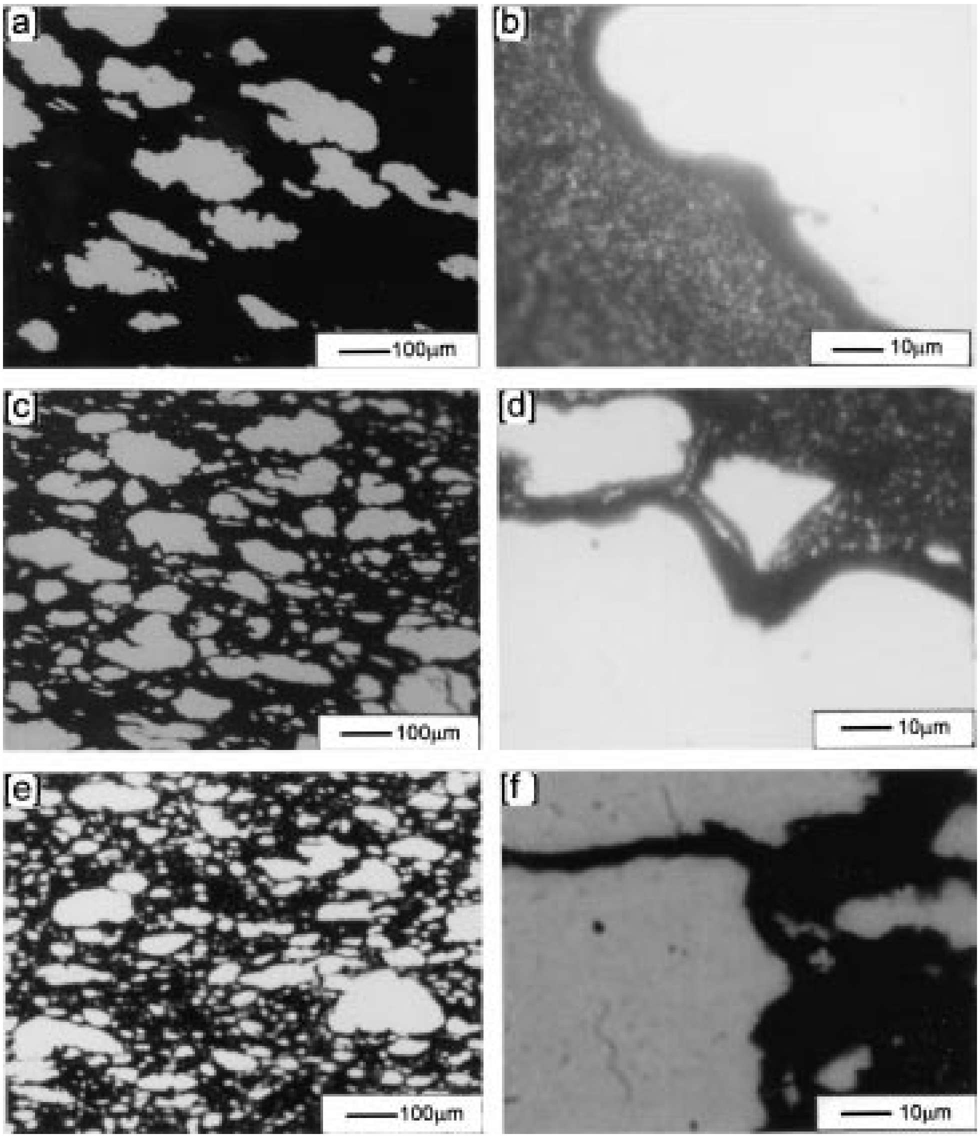

Fig. 4. Optical micrographs of 10 wt% CB(V-XC72)-filled PP/UHMWPE composites with various PP/UHMWPE weight ratios. (a) and (b) PP/UHMWPE = 7/3; (c) and (d) PP/UHMWPE = 1; and (e) and (f) PP/UHMWPE = 3/7.

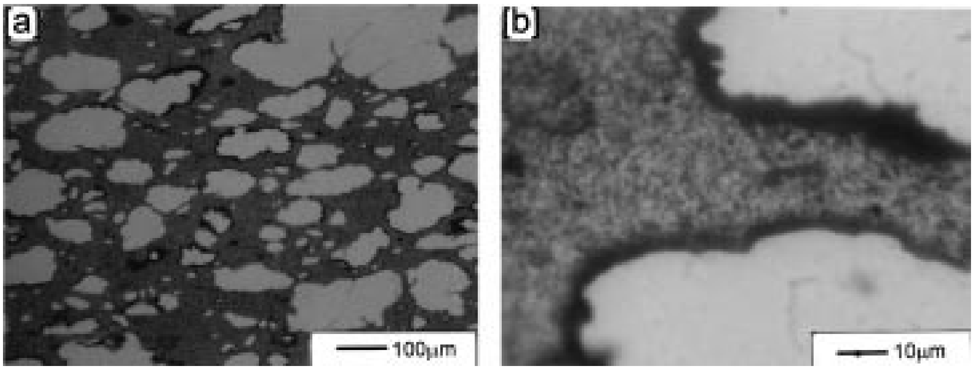

Fig. 5. Optical micrographs of 2 wt% CB(V-XC72)-filled PP/UHMWPE composite with a PP/UHMWPE weight ratio = 7/3.

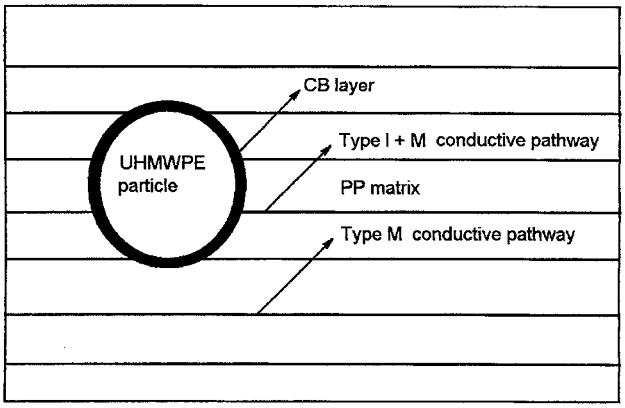

Fig. 6. Schematic diagram of the two types of conductive pathways in the CB-filled PP/UHMWPE composites.

Fig. 6 shows a schematic diagram of these two types of conductive pathways in the composite.

For the 10 wt% CB(V-XC72)-filled composites, when the composites have a high PP/UHMWPE weight ratio (greater than 3/7), the number of the UHMWPE particles is small. Hence, most of the CB is dispersed in the PP matrix instead of at the interface between the UHMWPE particles and the PP matrix. Thus, type M conductive pathways dominate the electrical resistivity of the composites due to the low UHMWPE content. As a result, when the temperature is at the T_m of UHMWPE, the large volume expansion of UHMWPE only breaks up type I + M conductive pathways and does not significantly affect type M conductive paths. Hence, the melting of the UHMWPE does not contribute significantly to the PTC effect of the composite. When the temperature attains the T_m of PP, the large volume expansion of PP as a result of the melting of PP crystallites breaks up most of type M conductive pathways as well as type I + M conductive pathways, resulting in a major jump in the resistivity of the composite. When the temperature is over the T_m of PP, the viscosity of the PP phase in the composites greatly decreases. Hence, flocculated structures are formed, leading to a very sharp NTC effect. The PTC behavior of these composites (curves b and c of Fig. 2) is similar to that of the CB-filled PP composite (curve a of Fig. 2). In addition, as the PP/UHMWPE weight ratio decreases, the room temperature resistivity of the composites also decreases. This can be explained by the fact the CB concentration of the PP matrix increases as the PP/UHMWPE weight decreases. Thus, the resistivity of type M paths decreases.

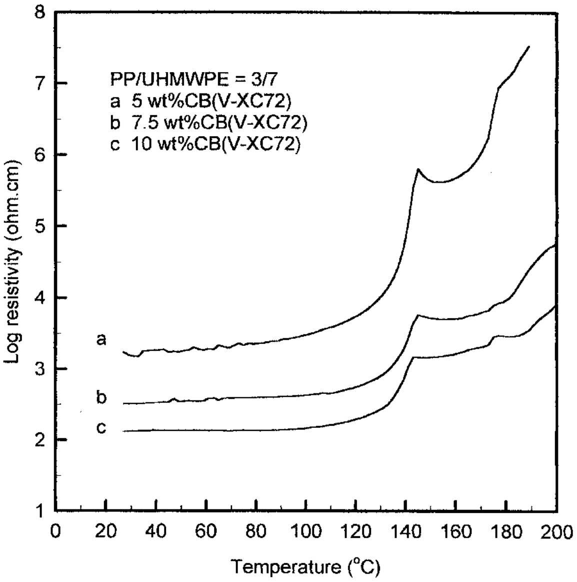

Fig. 7. Log resistivity as a function of temperature for CB-filled PP/UHMWPE(3/7) composites with various CB(V-XC72) contents.

However, in the case of the composites with a low PP/UHMWPE weight ratio (less than or equal to 3/7), the number of UHMWPE particles increases significantly, as shown in Fig. 4(e). In this case, the interfacial areas become much larger and much of the CB is localized at the interface between the UHMWPE particles and the PP matrix. Consequently, the CB concentration in the PP matrix is even lower than that of the composites having a larger PP/UHMWPE weight ratio, and type I + M conductive pathways become more important because the number of type I + M conductive paths increases significantly. This is consistent with the observation that the room temperature resistivity of the composites increases when the PP/UHMWPE weight ratio is less than 1. When the temperature increases to the T_m of UHMWPE, the large volume expansion of UHMWPE due to the melting of the UHMWPE crystallites breaks up most of the type I + M conductive pathways, resulting in a major jump in the resistivity. As the temperature further increases to the T_m of PP, a small jump in the resistivity occurs. This increase in the resistivity can be attributed to the volume expansion of the PP phase as a result of the melting of the PP crystallites. When the temperature is above the T_m of PP, no flocculated structures are believed to be formed due to the high viscosity of the composite. Hence, no NTC effect is observed. These findings are in total agreement with the results as shown in Fig. 2. Thus, for the 10 wt% CB(V-XC72)-filled PP/UHMWPE composites, morphology can significantly influence the PTC and NTC effects as well as the room temperature resistivity of the composites.

3.2. Effect of CB content

The effect of the CB content on the PTC behavior of CB-filled single semicrystalline polymer composites has been studied extensively [5–9,11–16]. Generally, low CB content composites show a higher room temperature resistivity and a higher PTC intensity while higher CB content composites exhibit a lower room temperature resistivity and a lower PTC intensity. Fig. 7 displays the log resistivity of CB-filled PP/UHMWPE (3/7) composites with various CB contents as a function of temperature. Obviously, the CB content can significantly influence the PTC behavior of the

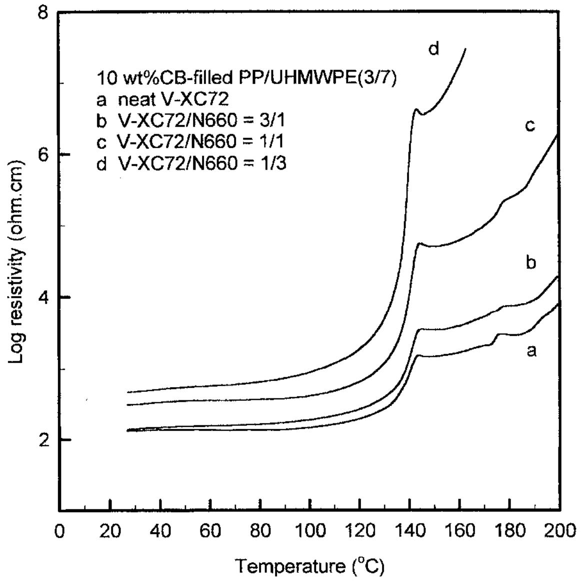

Fig. 8. Log resistivity of CB-filled PP/UHMWPE(3/7) composites containing 10 wt% CB with different (V-XC72/N660) weight ratios.

composites. As the temperature increases, the first sharp rise in resistivity occurs at about 140°C and the second sharp rise appears at about 170°C. This observation is different from that observed for CB-filled single semicrystalline polymer composites which only exhibit one sharp rise in the resistivity. We refer to this phenomenon as the double-PTC effect. In addition, we define the first and the second rises in resistivity as the first and second PTC effects, respectively. Based on the DSC results, the first and the second PTC effects are caused by the large volume expansions due to the melting of UHMWPE and PP crystallites, respectively. Thus, the first and second PTC intensities are controlled by type I + M and type M conductive pathways, respectively.

The intensity of both the first and second PTC effects depends strongly on the CB content. At low CB contents, for instance, 5 wt% CB, the PTC intensities are relatively large. Because the CB is distributed at the interface between the UHMWPE particles and the PP matrix before it is dispersed in the PP matrix. The CB concentration at the interface is much higher than that in the PP matrix. Hence, type I + M paths are more conductive than type M paths. Therefore, at the temperature below the melting point of PP, type I + M paths control the resistivity of the composite. At the melting point of the PE, type I + M paths break up, resulting in a large first PTC intensity. When the temperature increases to the melting point of PP, the second PTC effect is observed.

However, as the CB content increases, the CB concentration at the interface between the UHMWPE particles and PP matrix remains relatively constant, while the CB concentration in the PP matrix increases because the particle size of UHMWPE does not change during the melt-mixing process due to their extremely high viscosity. Therefore, the conductivity of type M paths increases and becomes more important in controlling the resistivity of the composite. In this case, when the temperature reaches the T_m of UHMWPE, the breaking up of type I + M conductive paths produces a PTC effect with a lower intensity, because the resistivity of type I + M paths increases much faster than that of type M paths when the UHMWPE melts. As the resistivity of type I + M paths is higher than that of type M paths, then type M conductive paths control the resistivity of the composite. Thus, the first PTC intensity produced by type I + M paths is much reduced as the CB content increases. Similarly, as the CB concentration in the PP matrix increases, the second PTC intensity produced by the M paths is reduced accordingly, as shown in Fig. 7. In addition, the room temperature resistivity of the composites decreases as the CB content increases, resulting from the increase in the CB concentration in the PP phase.

3.3. Effect of CB particle size

In our previous study, it has been found that the average particle size of N660 is larger than that of V-XC72, and 10 wt% N660-filled poly(viriylidene fluoride) (PVDF)/HDPE composites exhibit a higher PTC intensity and room temperature resistivity than those of 10 wt% V-XC72-filled PVDF/HDPE composites with the same PVDF/HDPE volume ratio [18]. The reason for this difference in the PTC intensity lies in the fact that the entanglement between the particles and polymer chains increases [18] and the number of conductive pathways is smaller. When the number of conductive paths is small, the resistivity of the composite is sensitive to even a small decrease in the number of the conductive paths. The degree of entanglement between a large-size CB and the polymer chains is much higher than that between a small-size CB and the polymer chains, thus the movement of the polymer chains caused by thermal expansion due to the melting of the crystallites may introduce a major deformation of the conductive network structure and break up a large number of the conductive paths. Therefore, composites with a larger particle-size CB show a higher PTC intensity, but their room temperature resistivity is usually higher. This is a major disadvantage for the use of large CB particles in many industrial applications. A balance between the PTC intensity and the room temperature resistivity is then attempted by using a mixture of large- and small-sized CB particles in the composites.

PP/UHMWPE (3/7) composites were produced by using a mixture of N660 and V-CX72 at various weight ratios. Fig. 8 shows the effect of the CB weight ratio (N660/V-CX72) on the PTC effect and the room temperature resistivity of the composites. As predicted, a balance between the PTC intensity and the room temperature resistivity can be achieved by varying the weight ratio of V-XC72 to N660. A lower weight ratio produces composites with a lower room resistivity and a lower PTC intensity, and vice versa.

4. Conclusions

Our results indicate that CB-filled PP/UHMWPE composites can be prepared by the conventional melt-mixing method. The PP/UHMWPE weight ratio, CB content and CB particle size are the three factors that can significantly influence the PTC and NTC effects as well as the room temperature resistivity of the composites. For the 10 wt% CB(V-XC72)-filled PP/UHMWPE composites, when the PP/UHMWPE weight ratio is larger than 3/7, the PTC and NTC effects are very similar to those of a CB-filled neat PP composite, but when the PP/UHMWPE weight ratio equals or is smaller than 3/7, the PTC effects of the composites are similar to those of a CB-filled neat UHMWPE composite. The elimination of the NTC effect in CB-filled polymer blend composites can be achieved by using a very high viscosity semicrystalline polymer as one of the components. The double-PTC effect, which can be explained in terms of the two types of conductive pathways in the composites, is clearly observed at low CB contents. A balance between the PTC intensity and the room temperature resistivity can be achieved by using a mixture of large and small CB particles.

Acknowledgements

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