Study on Effect of Carbon Black on Behavior of Conductive Polymer Composites With Positive Temperature Coefficient

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Abstract—Conductive polymer composites showing large positive temperature coefficient (PTC) are made of semi-crystalline polymer as an insulator and a conducting filler, whose concentration is close to the critical volume fraction. In this study, the resistivity and PTC behavior of high density polyethylene (HDPE) filled with different carbon blacks were studied. Among those composites, N660 carbon black filled PE showed the greatest PTC behavior. Carbon black with large particle size, small surface area and small amount of aggregated structure leads to large amplitude of PTC transition (defined as the ratio of maximum resistivity to the resistivity at 25 °C). The great PTC behavior is due to some microscopic mechanism under the macroscopic thermal expansion of polymer matrix during melting of polymer crystal.

Index Terms—Carbon black, conductive polymer composite, HDPE, polyethylene, positive temperature coefficient.

I. INTRODUCTION

CONDUCTIVE polymer composites [1] consisting of a non-conductive polymer matrix and conductive fillers, such as metal powder, carbon powder and oxides of transition metal, have been widely used in electrostatic dissipation and electromagnetic interference shielding. For a polymer filled with conductive particles, there may exist a critical filler volume fraction (percolation fraction). The resistivity of the polymer composite with conductive filler volume fraction above the percolation fraction is several orders of magnitude less than that of the composite with filler volume fraction below the percolation fraction. Conductive polymer composites showing large positive temperature coefficient (PTC) are made with semi-crystalline polymers as insulators and conducting fillers, whose concentration is close to the critical volume fraction. The mechanism for PTC anomaly in semi-crystalline polymer composites is generally attributed to the relatively large change in specific volume of the polymer at its melting temperature [2]–[4]. The PTC amplitude is defined as the ratio of the maximum resistivity ($\rho_{\max}$) to the resistivity at 25 °C. As PTC conductive polymer composite can change from conductor to insulator upon heating or vice versa upon cooling, this kind of material can be used in circuit protection device, temperature sensor and self-regulating heater [5]. For those applications, the PTC conductive polymer composite should have low base resistivity, great PTC amplitude, sharp transition in narrow temperature range and reversibility.

The large PTC anomaly is due to the large thermal expansion of polymer matrix during the melting of polymer crystal. The PTC transition temperature is determined by the melting temperature of the polymer matrix, thus it can be tailored by selecting and compounding the matrix polymer for different applications requiring different transition temperatures. Crystallization during cooling of polymer is the reverse process of melting of polymer crystal during heating. The PTC transition of this kind of PTC conductive polymer composite is reversible. As the recrystallization temperature in cooling cycle is lower than melting temperature of polymer in heating cycle, the PTC transition temperature during cooling cycle is lower than that in heating cycle. Factors affecting the melting and recrystallization behavior, such as pressure, heating and cooling rate, also affect the PTC behavior of conductive polymer composite. Among the PTC conductive polymer systems, the carbon black filled polymer system is the most widely investigated. It has been shown that the PTC amplitude depends on carbon black loading [2]. Electron tunneling or hopping process through the dispersed carbon particles rather than the electron transport through the contact of carbon particles was proposed to be the governing conductive mechanism in the carbon black filled PTC conductive composites [6]. Although the effects of the carbon black structure on the conductivity of the conductive polymer are generally understood [1], their effects on the PTC behavior of conductive polymer have not been systematically studied. This article reports the PTC behavior of polymer composites consisting of different carbon blacks dispersed in high density polyethylene (HDPE) and discusses the relationship between the structure parameters of carbon black (such as particle size, aggregation) and the PTC behavior of the conductive polymer.

II. EXPERIMENTAL

The HDPE (04452N) was supplied by The Dow Chemical Company. It has a melting point of 129–134 °C, a density of 952 kg/m^3 and a melting index of 4.0 g/10 min. Five different carbon blacks were used in this study and their characteristics are listed in Table I. Conductex SC, Conductex 975 and N660 carbon blacks were supplied by Columbia Chemicals Company. Vulcan XC72 and BP-2000 carbon blacks were supplied by Cabot Corporation. The structure of carbon black is generally characterized by tint strength, CTAB (cetyltrimethylammonia bromide)

TABLE I
CHARACTERISTICS OF CARBON BLACKS

Property and [ASTM Method]	CTAB Absorption (m²/gram) [D3765]	Tint strength (% ITRB) [D3265]	DBP absorption (cc/100gram) [D2414]	Iodine absorption (mg/gram) [D1510]	Average particle diameter (nm)
Conductex SC	130	123	115	220	-
Conductex 975	140	87	169	250	-
N660	35	57	90	36	70
Vulcan XC72	143	87	174	253	30
BP 2000	635	163	330	1412	12

absorption, DBP (dibutyl phthalate) absorption, and iodine absorption [7]. Carbon black with small particle size shows high tint strength. Highly-structured carbon blacks contain more void spaces. As a result, a larger volume of DBP is needed to fill the voids between the aggregates. The adsorption of iodine and CTAB serves as the basis for determining the surface area of carbon black.

HDPE and carbon black were mixed in the mixer unit of a Haake Rhecorder at 200 °C, 60 rpm for 20 min, and the equilibrium torque was recorded. The composite was taken out of the mixer after the mixing was complete, and then compression-molded at 200 °C into a sheet with a thickness of 0.5–1.0 mm. A small square specimen with dimension of 2.0 cm in each side was cut from the sheet. The exact thickness of the small specimen was measured and recorded. An electrically conductive adhesive (silver flakes filled epoxy) was applied onto the upper and lower surfaces of the specimen, which were connected to the two probes of a multimeter. The electrical resistivity was measured in the thickness direction of the composite sheet. The samples were put in an oven, and the temperature was raised 5 °C every 5 min in the temperature range below 110 °C, and 3 °C every 3 min when the temperature was above 110 °C. The resistance of the specimen was read for each temperature point at end of each step. The resistivity was then calculated. All the resistivities reported in this work are dc resistivities, and the carbon black concentrations are expressed in weight percentage.

III. RESULTS AND DISCUSSION

A. Effect of Carbon Black on the Processing

During compounding of the composites, the weighed amount of HDPE was first melted in the twin-screw mixer unit at 200 °C, and then the weighed amount of carbon black was added into the mixer. The HDPE and carbon black was mixed for 20 min at 200 °C with rotation speed of the screw at 60 rpm. The torque required to keep the screws rotating at certain speed and temperature was recorded by the machine automatically. The torque reading decreased with the experiment time during first 5 to 6 min of mixing and finally reached an equilibrium value. Fig. 1 shows the equilibrium torque reading of the mixer for different experiments. The equilibrium torque reflects the viscosity of the polymer melt system. The higher torque reading means that the polymer melt system in the mixer has higher viscosity. Without the addition of carbon, the HDPE resin was melted in the mixer under same condition, and the torque reading was about 6.0 Nm. As the carbon black was added into the system, the torque reading increased. This showed that the carbon increased the viscosity of the polymer melt system, which is true for all carbon blacks. However, the extent to which the carbon black affected the viscosity of the melt differed for different carbon blacks. This difference was not so obvious at low loadings, but became more obvious as loading increased. Addition of BP-2000 carbon black increased the torque most dramatically, while the addition of N660 carbon black increased the torque reading the least compared to the other carbon blacks. This difference is directly related to the characteristics of carbon blacks.

As is shown in Table I, BP-2000 carbon black has the highest CTAB adsorption, tint strength, DBP absorption and iodine absorption among all the carbon blacks used in this study. This means BP-2000 carbon black has the smallest particle size (its average particle diameter is 12 nm), highly aggregated structure and highest surface area. These properties contribute to the most obvious torque increase.

N660 carbon black shows lowest CTAB adsorption, tinting strength, DBP absorption and iodine absorption among the five carbon blacks. It has the largest particle size (70 nm), lowest structure and lowest surface area. The addition of N660 carbon black increased the viscosity to the least extent, thus N660 carbon black was the easiest one to disperse.

Vulcan XC72 and Conductex 975 are from different manufactures, but they have similar properties as shown in Table I. Thus they showed similar behavior as showed in Fig. 1. Conductex SC has properties between those of the Conductex 975 and N660, so the torque readings of polymer melt loaded with Conductex SC were between those of polymer melt loaded with Conductex 975 and N660 at same loadings.
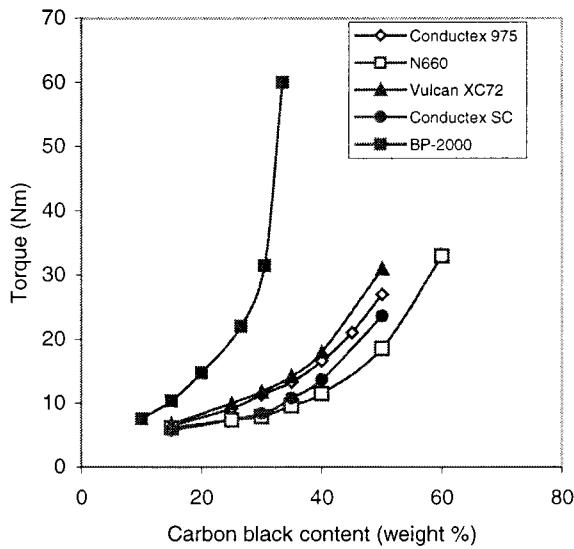
Fig. 1. Torque reading during compounding of the composite at 200°C, 60 rpm.
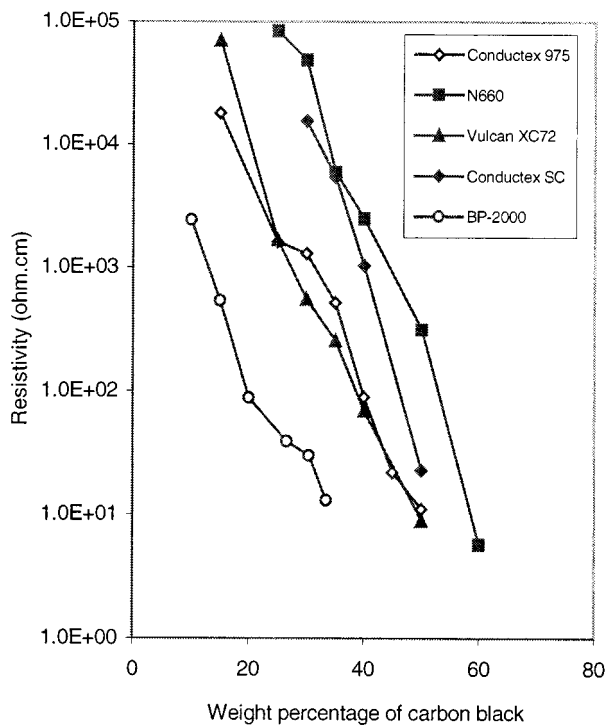

Fig. 2. Resistivity of different carbon black filled HDPE at 25 °C.

Fig. 3. Resistivity of BP-2000 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for each composite).

B. Effect of Carbon Black on the Base Resistivity

Fig. 2 shows the resistivity of the conductive composite at different loadings of carbon blacks at 25 °C. It is not surprising that the resistivity decreases with the increase of carbon black loading; and the trend is true for all carbon blacks. Polymer composite with different carbon black at same loading showed different resistivity, and this is also related to the structure of carbon blacks. As BP-2000 carbon black has the smallest particle size, highly aggregated structure and high surface area, which lead to easy formation of conductive pathway in polymer
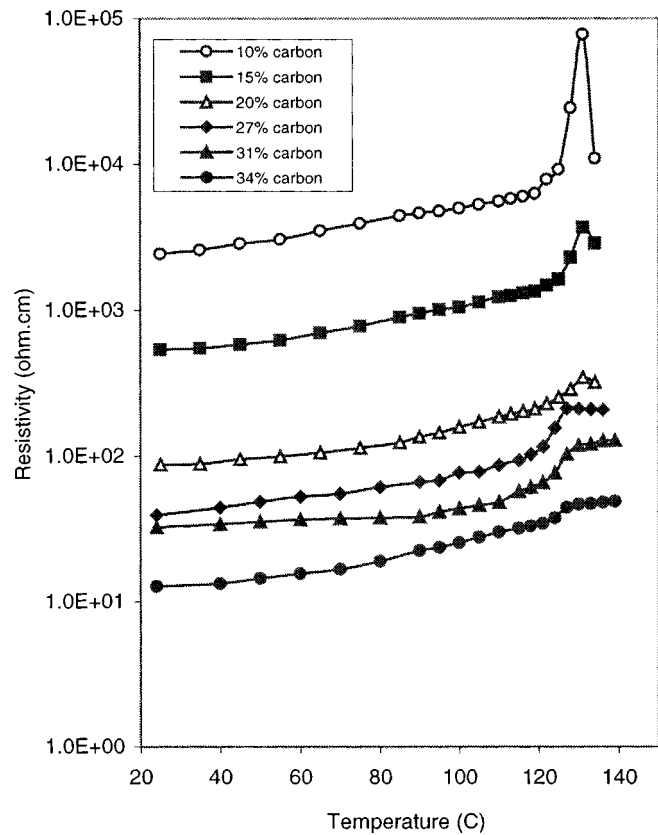
matrix, BP-2000 carbon black filled HDPE showed the lowest resistivity at same amount of loading of carbon blacks. While N660 carbon black has large particle size, the less aggregated structure and surface area, the resistivity of the composite filled with N660 carbon black is higher than those of the composites loaded with other carbon black at same loading. As discussed above, Conductex 975 and Vulcan XC72 have similar structure, thus they showed similar behavior of resistivity versus carbon black loading at 25 °C. The resistivity of Conductex SC carbon black filled HDPE was between that of N660 carbon black filled HDPE and that of Vulcan XC72 carbon black filled one at same loading.

C. PTC Behavior Carbon Black Filled HDPE

The resistivities of those polymer composites filled with different carbon blacks versus temperature are shown in Figs. 3–7.

The resistivities of all the composites at different carbon black loading increased with temperature. The resistivity increased steadily as temperature was raised from 25 °C to 120 °C, and increased more rapidly after 120 °C as the polymer crystal started to melt. The resistivity reached the peak value around 133 °C. The resistivity decreased with further increase of temperature, which is called negative temperature coefficient (NTC) effect. The NTC behavior was very obvious for composite with low carbon black loading, while it was not so obvious for system with high carbon black loading. The PTC anomaly is due to the thermal expansion of polymer matrix during the melting, and
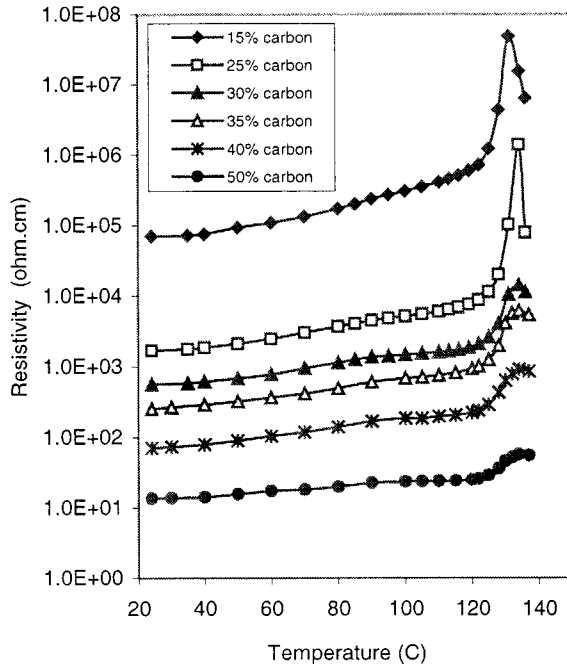
Fig. 4. Resistivity of Vulcan XC72 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for each composite).
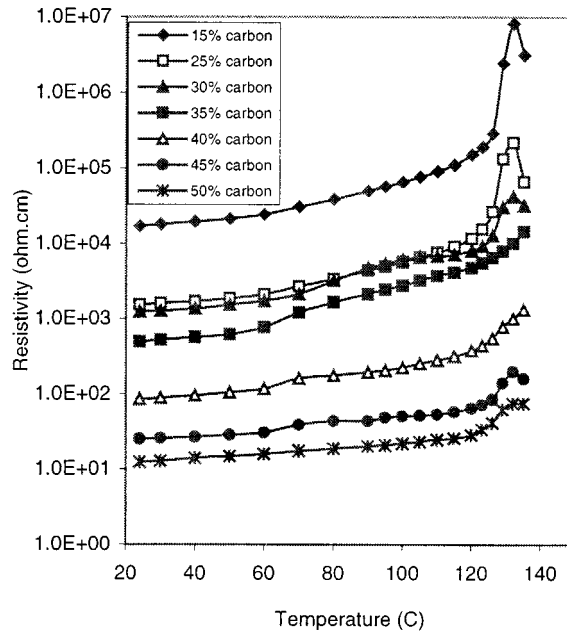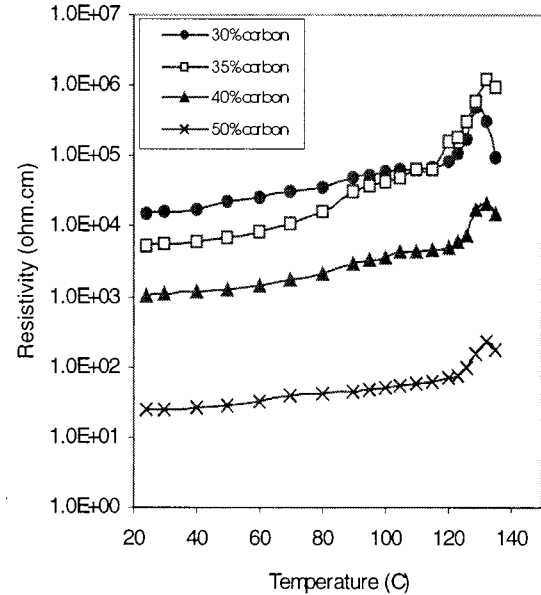

Fig. 6. Resistivity of Conductex SC carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for each composite).
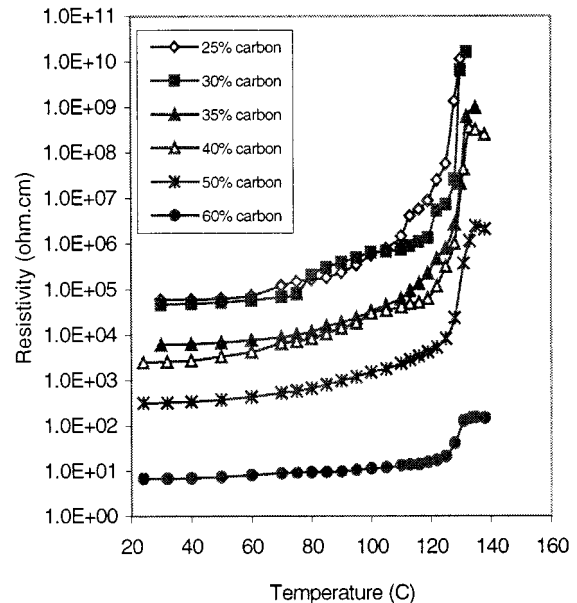

Fig. 5. Resistivity of Conductex 975 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for each composite).

Fig. 7. Resistivity of N660 carbon black filled HDPE versus temperature (The weight percent of carbon black is showed for each composite).

the NTC behavior is due to reorganization of carbon black in the mobile polymer melt phase. This reorganization is easy to occur for composite with lower carbon black loading due to its lower viscosity, while it is difficult for system with high carbon black loading and high viscosity. It has been reported that the NTC behavior can be removed by crosslinking of the polymer network. It was observed by Tang et al. [3] that the PTC intensity

as well as the base resistance decreased with the thermal cycles. The same phenomenon was observed in this study. The specimen always showed lower resistance after being cooled down to room temperature than the same specimen before the resistance versus temperature experiment was carried out.

Different carbon black filled composites did not show exactly the same PTC behavior. For BP-2000 carbon black filled HDPE (Fig. 3), the PTC amplitude is close to $10^{1.5}$ for composite with filler loading of 10%. Further increase of the loading led to the decrease of the PTC amplitude. With loading above 20%, the

PTC amplitude was less than 10, which means that the resistivity of BP-2000 carbon black filled HDPE is insensitive to temperature.

Compared to BP-2000 carbon black filled HDPE, Vulcan XC72 carbon black filled HDPE had greater PTC behavior (Fig. 4). At loading of 15% and 25%, the PTC amplitudes were about 10^3. With further increase of the loading, the PTC amplitude decreased. The PTC amplitude of the composite with 50% carbon black loading is less than 10. The PTC behavior of Conductex 975 carbon black filled HDPE (Fig. 5) and Conductex SC carbon black filled HDPE (Fig. 6) are similar to that of Vulcan XC72 carbon black filled HDPE (Fig. 4).

Among all the carbon blacks tested, N660 carbon black has the largest particle size, lowest surface area and low aggregated structure. Thus the composite filled with N660 carbon black shows the lowest melt viscosity, and highest electrical resistivity compared to other composites at same loading, as mentioned above. However the PTC amplitude of the composite with N660 carbon black (Fig. 7) was the highest compared to those of the composites filled with other carbon blacks. The PTC amplitudes of the composites with carbon black loading of 25%, 30%, 35%, and 40% were all above 10^5. The resistance reading of samples containing 25% and 30% carbon black were beyond the maximum reading (120 MΩ) of the multimeter. Even at carbon black loading of 50%, the PTC amplitude was still as high as 10^4. As the loading increased to 60%, the PTC amplitude dropped to $10^{1.5}$.

From the comparison of PTC behavior of different carbon black filled HDPE, it can be found that carbon black with large particle size, small surface area and small amount of aggregated structure leads to the polymer composite with great PTC behavior. This is because the unaggregated individual carbon black particles can be separated more easily under thermal expansion of polymer matrix, which leads to increase of the distance and decrease of the contact area between the adjacent particles. While, the particles in the aggregated structure are difficult to be separated by thermal expansion of polymer matrix. However, the great PTC behavior can not be simply attributed to the thermal expansion of the polymer matrix, which leads to the conductive filler volume loading fall below the percolation volume fraction as suggested in the literature [2]. As is shown in the PTC behavior of N660 carbon black filled HDPE, the resistivity of the composite with 50% carbon black loading reached 10^6 ohm.cm, which is much higher than the resistivity of the composite with 25%, 30%, 35% and 40% weight loading at room temperature. However, the volume fraction of conductive filler in the composite with 50% weight carbon black loading at the peak resistivity temperature is still higher than that of the composite with loading of 40% weight at room temperature. So the large PTC behavior of N660 carbon black filled polyethylene is due to some microscopic mechanism under the macroscopic phenomenon of large thermal expansion during the melting of the polymer crystal. Although carbon black particles are dispersed homogeneously in the polymer melt during mixing above its melting temperature, carbon particles are pushed out of the crystalline region as impurity in recrystallization process during cooling. Thus, at temperature below melting point of polymer crystal, carbon

particles are dispersed in the amorphous region only. As the crystallite melts when the composite is heated, those carbon black particles re-disperse into the polymer melt, thus the inter-particles distance increases so significantly that electron tunneling between conductive particles is hampered, and resistivity increases greatly.

IV. CONCLUSION

Among the composites filled with different carbon blacks, the N660 carbon black filled HDPE showed the greatest PTC behavior. Carbon black with large particle size, small surface area and small amount of the aggregated structure leads to great amplitude of PTC behavior. The great PTC behavior is due to some microscopic mechanism under the macroscopic thermal expansion of the polymer matrix during the melting of polymer crystal.

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