

# Complicated Resistivity-Temperature Behavior in Polymer Composites

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Received 10 December 2001; accepted 4 March 2002

**ABSTRACT:** The resistivity of different polymer composites is investigated in different temperature-changing processes, which demonstrates more complicated changing behaviors than that usually reported in literatures. The complicated resistivity-temperature (R-T) behaviors cannot be explained by current theories, and the contradictions of them with current theories are presented in this article. With the experiments, a new viewpoint on the R-T behaviors of

polymer composites is proposed, i.e., the resistivity changes are attributed to internal stress generated when the morphology and structure of the composites undergo great changes. Based on this speculation, the complicated R-T behaviors of polymer composites can be well explained. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2217–2221, 2002

**Key words:** morphology; structure

## INTRODUCTION

As is well known, insulating polymers can be changed into conductive or semiconductive materials when mixed with conductive inorganic fillers, which extends polymers into many new application fields such as antistatic materials, electromagnetic interference shields, wire and cable sheathing, and other materials for electronics.<sup>1</sup> Due to the low cost and light weight, carbon black (CB) is the most generally employed conductive filler in industrial applications.<sup>2</sup> These disorderly materials, as typical polymer composites, sometimes show some new mechanical and electrical characteristics, which may completely differ from those of the individual component. This provides a chance to create new functional materials. As one example, the positive-temperature-coefficient (PTC) effect, i.e., positive change in electrical resistivity with temperature, has been known for a long time. Now various industrial devices have been developed and used in great scale utilizing the PTC effect of the polymer composites such as circuit protection device and self-regulating electric heater.<sup>3–5</sup>

Since the PTC effect of polymer composites was first observed by Person in 1939,<sup>6</sup> many experimental and theoretical studies have been done on this R-T behavior of PTC effect. However, the mechanism is still not clear now. Kohler attributed the PTC effect to the thermal expansion of the polymer matrix.<sup>7</sup> In his view-

point, conductive fillers formed conductive networks in polymer matrices at room temperature, and lead to the comparably low resistivity of the composites. When polymer composites are heated, the volume of polymer expands more than the inorganic fillers. Especially at the temperature near the melting point ( $T_m$ ) of the polymer matrix, the polymer expands dramatically due to the phase transition from the crystalline state to the amorphous state. Consequently, the dramatic volume expansion of the matrix separates the adjacent particles that initial connected each other in the conductive networks, and results in the increase of the resistivity.

Ohe and Natio did not agree with the viewpoint that so large a resistivity jump as several orders can be induced only by the volume expansion of the matrix with temperature.<sup>8</sup> Through theoretical calculations and experiments, Ohe and Natio proposed that the conduction mechanism in polymer composites is not ohmic conduction but electron tunneling. With the increase in temperature the increased difficulty of electron tunneling through the separated gaps between conductive particles is thought to be the main reason that causes the increase in the resistivity in polymer composites. The electron tunneling model was modified later by Meyer.<sup>9,10</sup> He assumed that polymer films in the crystalline state have better conductivity for electron tunneling than the corresponding ones in the amorphous state. In polymer composites, the conductive particles in the matrix are thought to be separated by polymer films by about 30 nm. When the composites are heated near the  $T_m$  of the matrix, the polymer films between the conductive par-

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ticles transform from the crystalline state into the amorphous state, which increases the difficulty of electron tunneling in the conductive chains and causes the increase of the resistivity in polymer composites.

Klason and Kubat proposed that the PTC effect is mainly caused by the change of the distribution of conductive fillers in the matrix.<sup>11</sup> With the distribution change of the fillers in the matrix from relatively homogeneous at room temperature into heterogeneous at higher temperature, the resistivity of the composites increases. When the temperature becomes above the  $T_m$  of the matrix, a new homogeneous distribution forms and causes the decrease of the resistivity. Voet developed a more detailed model involving the structure of the crystallizable polymer and the incompatibility of conductive fillers with the polymer crystallite.<sup>12</sup> He proposed CB particles primarily concentrate in the amorphous areas of the polymer composites due to the incompatibility of fillers with the crystallite of the polymer matrix, which results in the relatively low resistivity at normal temperature. When the temperature is up to the  $T_m$  of the matrix, polymer crystallite transfers into amorphous state, and the conductive fillers compressed in initial amorphous areas can diffuse into the new-formed amorphous areas of the primary crystallite. Consequently, the concentration of the fillers in the conductive chains is decreased, with the result of the increase of the resistivity.

In 1993, a new model was proposed by Allak, in which both phase structure and thermal expansion are considered.<sup>13</sup> At room temperature, the crystalline phase and amorphous phase form cocontinuous structure in matrices. Due to the incompatibility of the fillers with the crystalline phase of the polymer, conductive fillers concentrate in the continuous amorphous phase, which lead to the low resistivity of the composites at room temperature. When the composites are heated, the polymer expands; especially the crystalline phase expands largely at the temperature near the  $T_m$ . The continuous structure of the amorphous phase in the matrix is assumed to be destroyed by the great expansion of the crystalline phase. Consequently, the conductive chains in the amorphous area are destroyed as well. When the composite is heated above the  $T_m$ , the migration of the conductive fillers into the new-formed amorphous phase, i.e., the initial crystalline phase, may reestablish the broken conductive chains, which lead to the appearance of the negative-temperature-coefficient (NTC) effect at the temperature above  $T_m$ .

In general, all the theories described above are based on one or both of the two mechanisms. One is volume expansion, and the other is filler migration. Volume expansion has been regarded as a main factor that induced the occurrence of PTC effect in polymer composites for a long time, which is still widely accepted by many people despite no direct evidences

ever being given until now. Lately, the experimental fact that most composites with excellent PTC effect are fabricated with the matrix of crystalline polymer, leads to the proposition of the filler migration mechanism, i.e., the migration of the conductive fillers concentrated in initial amorphous areas into the new-formed amorphous areas causes the steep increase of the resistivity. Recently, volume expansion is always considered simultaneously as another important factor that causes the appearance of the PTC effect when filler migration is employed.

Obviously, previous researches on the R-T behaviors of polymer composites are mostly focused only on the PTC effect due to the huge value in application. However, the R-T behaviors of polymer composites are more complicated than that used to be reported. Therefore, comprehensive investigations on the R-T behaviors of polymer composites are necessary. In this article, the complicated R-T behaviors of three different polymer composites have been studied in heating and cooling processes. The contradictions of the observed R-T behaviors with current theories are discussed, and a new proposal explanation on the R-T behaviors of polymer composites has been explored.

## EXPERIMENTAL

Two high-density polyethylene with the melt index (MI) of 2 g/min and 20 g/min, labeled as PE2 and PE20, respectively, were used as crystalline matrices. PE2 and PE20 were both bought from Qilu Petrochemical Company (China) as commercial products. Polystyrene used as an amorphous matrix in this article was generously provided by Professor Zhang in East China University of Science and Technology (China). Carbon black (CB) made from acetylene with average size about 40 Å was bought from a commercial company. It was used as conductive filler to mix with polymers and labeled as CB in paper.

Different composites with different contents of CB by weight fraction were fabricated by conventional blending techniques. The samples were compression molded into plate films with the thickness of 1 mm, after being mixed for 15 min on two-roll mill at the given temperature, 140°C for PE20 composites, 180°C for PE2 composites, and 170°C for PS composites. Silver paint was painted on the surfaces of the composites to ensure good contact of the samples with the electrodes of the conduction tester. During the measurements, the specimens inevitably deformed when the composites were heated above the  $T_m$  of the polymers. Therefore, the specimens were irradiated by <sup>60</sup>Co- $\gamma$ -ray maintain their shapes during the measurements. A very low dose, only about 20 kGy, has been employed to avoid the severe effect of the radiation on resistivity-temperature behaviors of the composites. The electrical resistivity in the thickness direction was

measured by a digital multimeter when lower than  $2 \times 10^7 \Omega \cdot \text{cm}$  and a ZC-36 type meter when exceeding  $2 \times 10^7 \Omega \cdot \text{cm}$ .

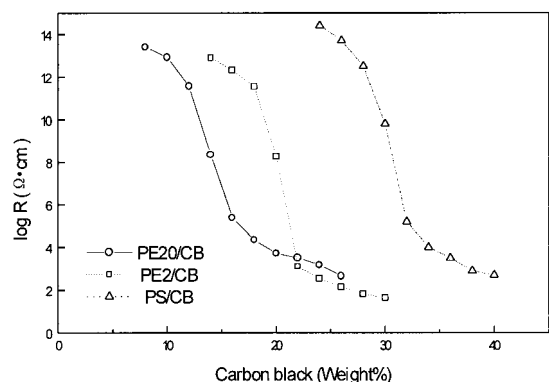
## RESULTS AND DISCUSSION

### The critical content of carbon black in different composites

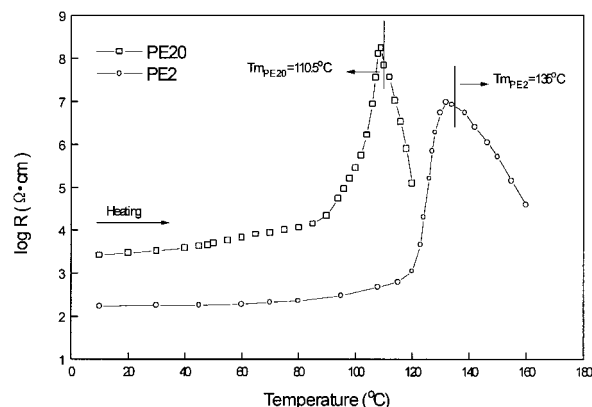
The electrical resistivity of the composites of PE2, PE20, and PS at room temperature as a function of CB content are shown in Figure 1. The electrical resistivity drops at the magnitude of several orders when the filler content exceeds the critical content,  $\Phi_C$ . This is known as percolation threshold,<sup>14,15</sup> i.e., when the content of conductive filler exceeds a critical value, conductive fillers form infinitely conductive network in the composites, which facilitates the electrical current across the composites. The  $\Phi_C$  of different composites is dependent on the composite system, 14% for PE20/CB, 20% for PE2/CB, 30% for PS/CB by weight fraction. The dependence of the  $\Phi_C$  on the melt index of the matrices is consistent with the experiments reported by Tang.<sup>16</sup> He attributed the phenomenon to the different aggregation ability of carbon black in polymer matrices with different melt indices. Conductive fillers are easy to aggregate in a matrix with a higher melt index and to form a more segregated distribution in matrix, which facilitates the formation of conductive network. The  $\Phi_C$  of PS composites is about 30% by weight fraction, much higher than the PE composites, which is attributed to the polarity of PS and the high interfacial energy of PS with carbon black. Detailed investigations on the influence of polymer matrices on the  $\Phi_C$  have been reported by Miyasaka and Sumita.<sup>17,18</sup>

### The R-T behaviors during the heating process

As to polymer composites, the maximum PTC effect generally occurs with conductive filler content that



**Figure 1** The electrical resistivity of the composites of PE20, PE2, and PS at room temperature as function of CB content.

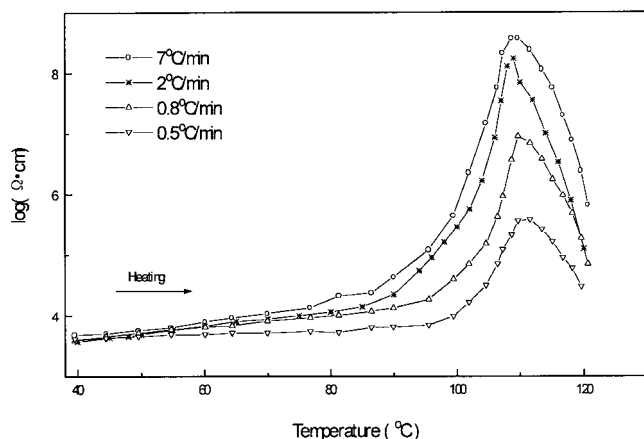


**Figure 2** The resistivity-temperature behavior of the composites of PE20 and PE2 during the heating run.

slightly larger than critical value  $\Phi_C$ . Therefore, the contents of CB were chosen as 22, 26, and 36% for the composites of PE20, PE2, and PS, respectively. The R-T behaviors of the composites of PE during the heating process are shown in Figure 2. It is shown that the composites do demonstrate prominent R-T behaviors. The resistivity increases slightly with the increase of temperature at first, and dramatically jumps with magnitude of several orders near the melting temperature of the polymers, following with the steep decrease of the resistivity when the temperature rises higher. The steep increase of the resistivity near  $T_m$  is the famous PTC effect, which has been extensively investigated and discussed in the literature. As described above, volume expansion and filler migration are usually assumed and accepted as reasonable explanation to the PTC effect of polymer composites for a long time. However, the basic mechanism is still in dispute.

Because of the huge commercial value of PTC effect in application, previous studies are focused on the PTC effect only, other R-T behaviors such as NTC effect are seldom studied in the literature. As shown in Figure 2, the resistivity demonstrates a dramatic drop when the temperature exceeds the  $T_m$ , which is called the NTC effect. This phenomenon is usually followed with the occurrence of the PTC effect in polymer composites, but it can be cut down by crosslinking treatment.<sup>19,20</sup> The appearance of NTC effect is a challenge to current theories.

A new mechanism was proposed by Meyer to explain the NTC effect, i.e., when the composites are heated above  $T_m$ , the diffusion of the conductive fillers into the new-formed amorphous phase forms new conductive chains, which reestablishes the conductive network and leads to the decrease of the resistivity. Anyway, volume expansion mechanism leading to the further increase of resistivity for the continuous expanding of polymer is obviously contracted with the experimental results at the range of the NTC temper-



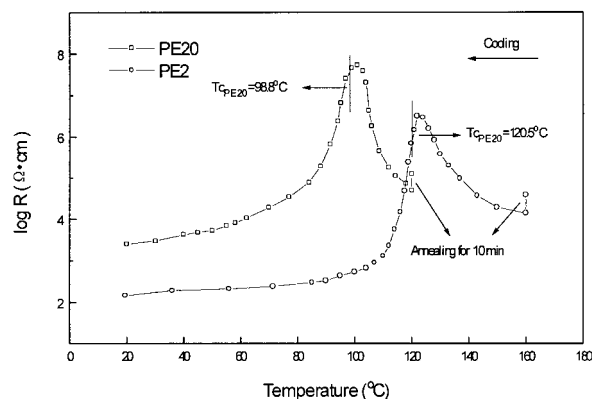
**Figure 3** The resistivity-temperature behaviors of the PE20/CB composites as a function of the heating rate.

ature. The filler migration mechanism cannot be used to explain the NTC phenomenon as well, because only the contrary conclusion can be obtained with the diffusion of conductive fillers into the entire matrix.

Figure 2 shows that the peak in the resistivity of the polymer composites with the change of temperature occurs at the temperature slightly lower than  $T_m$  of the matrices, 109 vs. 110.5°C and 132 vs. 135°C for PE20 and PE2, respectively. It is assumed that the resistivity change somewhat can be attributed to the melting process of the polymer matrix. As we know, the heating rate has a great influence on the melting process of the polymers; it is deduced that the heating rate may have a great influence on this resistivity-changing behavior also. As shown in Figure 3, the R-T behaviors of PE20/CB composites do show great dependence on the heating rates. The resistivity change becomes smaller at the lower heating rate. Similar phenomenon has been observed by Hirano and Kishimoto in the polymer composite of thermoset epoxy.<sup>21</sup> Considering volume expansion of the matrix and diffusion of the fillers should be easier and more sufficient at the lower heating rate, obviously above experimental results cannot be explained by current theories.

### The R-T behaviors during the cooling run

The R-T behaviors of polymer composites during cooling process from higher temperature were seldom reported<sup>11</sup> and never discussed in literatures to our knowledge. Those behaviors are seldom studied for their less importance in application, in addition to the difficulty of being explanation. As shown in Figure 4, the resistivity of the composites of PE20 and PE2 during the cooling run demonstrates similar R-T behaviors with those during the heating run. Nevertheless, all the theories generally used to explain the R-T behaviors during heating run could not be available during the cooling run. With decreasing temperature,

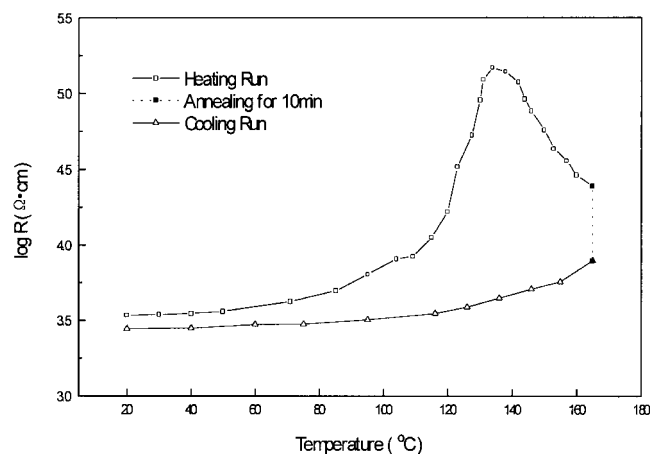


**Figure 4** The resistivity-temperature behavior of the composites of PE20 and PE2 during the cooling run.

the shrinkage of composites should lead to the decrease in resistivity with temperature, which is obviously contrary to the experimental facts. On the other hand, the increased concentration of conductive fillers in amorphous areas by the exclusion of polymer crystallites should result in the resistivity decrease also.

The crystallization temperatures of PE20 and PE2 is 98.8 and 120.5°C, both slightly lower than the temperatures that the resistivity change peak of resistivity occurs, 101 and 122°C for PE20 and PE2, respectively. Therefore, it is assumed that the resistivity change is caused by the crystallization behavior of the polymer matrix. As for the composites of PS, a typical amorphous polymer, there is no distinct resistivity change when the composites are cooled from the melted state, as shown in Figure 5.

As a conclusion, the R-T behavior during heating process, as shown in Figure 2, is attributed to the melting process of the polymer matrix, and R-T behavior during cooling process, as shown in Figure 4, is attributed to the crystallization of the matrix from the melted state.



**Figure 5** The resistivity-temperature behavior of PS/CB composite during the heating run and the cooling run.

### A new suggestion for the R-T behaviors of polymer composites

In the conductive composites made of polymer and inorganic filler, the polymer is the insulating matrix, and the inorganic filler is the conductive substance. When conductive fillers form infinite conductive network in the polymer matrix, the insulating composite transits into conductive. Therefore, conductive network formed by inorganic fillers should be the essential factor that determines the conductivity of the composite. We assume that the morphology and structure of the composites have great influence on the conductive network in matrix.

As we know, internal stress is generally generated when the morphology and structure of materials undergo dramatic changes, including the volume expansion and phase transitions. The generated internal stress may cause some conductive fillers to migrate in position, consequently causing the destruction of some conductive chains and the resistivity increase of the composites. When the morphology and structure changes finish, the generated internal stress fades away due to the relaxation and being absorbed by the matrix. Along with the decay of internal stress, the migrated fillers return to their initial positions under antiferces generated from the spring deformation of the matrix, and the resistivity gradually decreases to its initially low state.

This speculation can well explain the complicated R-T behaviors as shown Figures 2 and 4. The dependence of R-T behaviors on the heating rate can be

explained by the easy relaxation of internal stress at a low heating rate, which leads to weaker intensity of the stress accumulated in the matrix and weaker resistivity change. Detailed work on this speculation is ongoing in our laboratory.

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