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PTC effect of carbon fiber filled EPDM rubber composite

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Abstract Conductive ethylene-propylene-diene (EPDM) rubber composites filled with carbon fiber (CF) and carbon black (CB) were prepared by the conventional melt-mixing method. Optical microscope was used to observe the formation of the conductive pathways in the CF-filled composite. A model based on thermal expansion and electron tunneling theory was proposed to explain the PTC effect of CF-filled composite. The resistivity-temperature behavior of filled EPDM composites depended on the shape of carbonaceous fillers, CF/EPDM composite showed a positive temperature coefficient (PTC) effect, while CB/EPDM composite showed a negative temperature coefficient (NTC) effect.

1 Introduction

In recent years, polymer positive temperature coefficient (PTC) materials have been paid more and more attention and used in a wide variety of industrial applications such as sensors, self-regulating heaters, over-current, and over-temperature protection devices and switching materials [1, 2]. Up to now, there is no comprehensive theory to describe the PTC phenomenon, but many models, such as thermal expansion [3], electron tunneling [4], double percolation [5, 6] and cooperative effect of changes in crystallinity and volume expansion [7], have been established to explain it. All of these models suggest that the volume expansion plays an important role in the PTC behavior.

The main feature of PTC materials is that with heating, the conductive system displays an abrupt increase in resistivity at the melting temperature of a semicrystalline polymer. Above this temperature, a decrease in the resistivity is sometimes observed. This phenomenon is called a negative temperature coefficient (NTC) effect. The NTC effect, which usually arises from the agglomerate of filler in polymer matrix, is the main disadvantage for the application of PTC materials. If the agglomerate of filler is restricted, the NTC effect would be eliminated. According to this consideration, researchers have proposed and developed many methods of eliminating the NTC effect, such as crosslinking the polymer composite [8], modifying the surface of conductive fillers [9], and using a very high viscosity polymer as one component in a composite [10, 11]. However, few studies [12, 13] were focused on the resistivity-temperature behavior of high viscous rubber composites filled with conductive filler. In this work, EPDM rubber composites filled with carbonaceous fillers, i.e., carbon fiber (CF) and carbon black (CB), were prepared, and the resistivity-temperature behavior of composites was investigated.

2 Experiment

Ethylene-propylene-diene (EPDM) rubber (4640, Dupont Co., USA) was used as polymer matrix. A high-strength PAN-based carbon fiber (T300, Jilin carbon Co., China) and super conductive carbon black powder (HG1P, Linzi Huaguang Chemical Engineering Factory, China) were used as conductive filler. Their characteristics were listed in Table 1 and Table 2, respectively.

Ethylene-propylene-diene rubber and conductive filler were mixed in a Brabender for 15 min at 140 °C, then

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Table 1 Characteristics of carbon fiber

Precursor	Diameter (μm)	Density (g/cm^3)	Volume resistivity (Ω cm)
Polyacrylonitrile (PAN)	7	1.6	6×10^{-3}

Table 2 Characteristics of super conductive carbon black

Particle size (nm)	CTAB[a] surface area (m^2/g)	DBP[b] value (mL/g)	PH value	Specific resistivity (Ω cm)	Iodine absorption value (mg/g)
33	828	5.86	6.5	0.27	944

[a] Cetyl trimethyl ammonium bromide

[b] Dibutyl phthalate

kneaded on two-roll mill for 5 min at 100 °C. Compounds were compression-molded at the vulcanized press at 140 °C for 10 min, then cooled down in air to room temperature, and made into sheets with a radius of 2.5 cm and a thickness of 1 mm. In this study, all the ingredients are in phr (grams per hundred grams of rubber).

The samples were placed in a vacuum oven to measure the resistivity, and the oven was heated at a heating rate of 2 °C/min. The resistivities of the composites were measured by a digital multimeter (Model VC-9808) when it was lower than 2×10^7 Ω; a high-resistance (ZC-36) was used when the resistivity exceeded 2×10^7 Ω. According to ASTM D4496 and D257, the resistivity was converted into volume resistivity, ρ (Ω cm), by the following formula

$$\rho = RS/t \tag{1}$$

where R is the measured resistance (Ω), S is the surface area of the sample plane (cm^2), and t is the thickness of the sample (cm).

Optical micrograph was obtained by a polarizing optical microscope (Leica) equipped with a camera (Leica) operating at the transmission mode. Prior to our observations, the samples were made into sheets with a thickness of 0.06 mm.

Thermal expansion coefficient of composite was performed using a thermal analyzer (DuPont 9900) at a heating rate of 5 °C/min.

3 Results and discussion

Figure 1 shows the log resistivity of CF-filled EPDM composites with different CF contents as a function of temperature, from which it is noted that: (1) all composites exhibit an increase in resistivity with the increase of temperature, namely, PTC effect. (2) The composite containing CF content in the percolation region (7–10 phr) shows a stronger PTC effect than the one containing CF content out of the percolation region. (3) The resistivity of composites shows a slight increase following a rapid increase when the content of CF equal to or is higher than 10 phr.

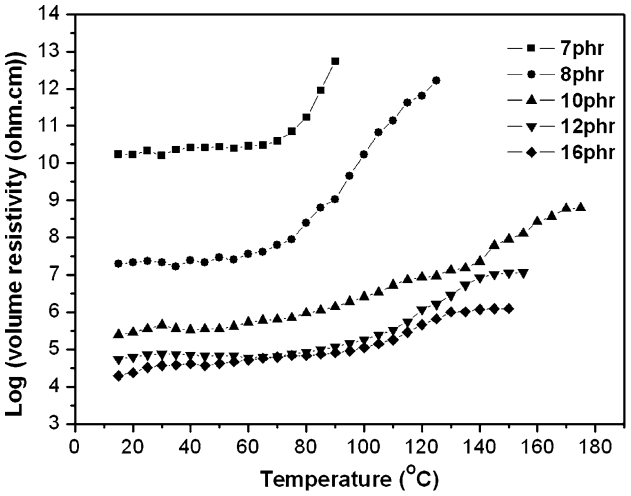

Fig. 1 Log resistivity as a function of temperature for CF-filled EPDM composite with different CF contents

The effect of temperature on the resistivity is associated with the change in spatial arrangement of conductive elements. Figure 2 shows the optical micrograph of CF-filled composite at room temperature. It can be obviously seen from this micrograph that a large number fibers contact each other with a small gap, forming a continuous conductive network in the matrix. According to electron tunneling theory [4], when the gap between conductive particles is small enough, charge transport takes place. In fact, the resistivity of composite depends not only on the gap between the fibers, but also on the number of inter-fiber contact points. The more the number of contact points, the lower the resistivity of composite, since each contact point can be regarded as a channel for charge transport. During heating, the polymer matrix undergoing volume changes due to thermal expansion can move the filler particles. We can deduced from Fig. 2 that two processes breaking down the conductive network occur at the same time during heating: (1) The adjacent fibers remove along the diameter direction of CF, as seen in Fig. 3a; (2) The contacted fibers remove along the direction parallel to the surface of the sample, as seen in Fig. 3b. The former results in an increase in the gap between the fibers, and the latter results in a decrease in the number of inter-fiber contact points. The cooperative effect of these two processes results in the reduction of the possibility of electron tunneling, consequently, the resistance of the composite will increase, giving rise to the PTC effect.

The PTC effect is associated with the CF content. The composite with CF content in the percolation region

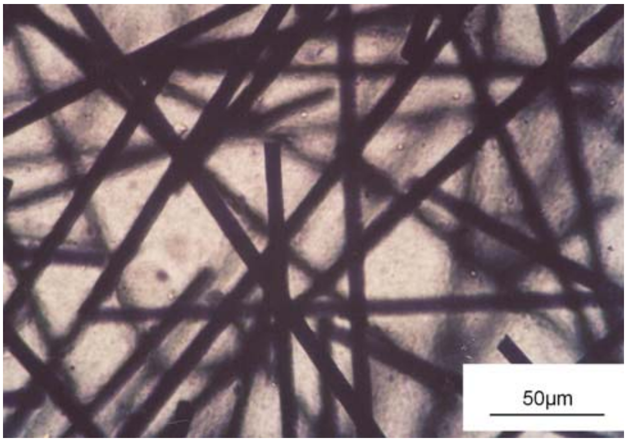

Fig. 2 Optical micrograph of 10 phr CF-filled EPDM composite

(7–10 phr) shows a stronger PTC effect. This is because the conductive pathways formed in this region can be completely broken down by the thermal expansion of polymer matrix. For composites with low CF content (lower than 7 phr), the number of conductive pathways formed is smaller, so the resistivity of the composites is very high and the PTC effect is weak, whereas for composite with high CF content (higher than 10 phr), a large number of conductive pathways or the inter-fiber contacts are formed within it, in this case, not all the conductive pathways are destroyed, and thus leading to a weaker PTC effect.

It is worth noting that the resistivity of composites shows a slight increase following a rapid increase when the content of CF equal to or is higher than 10 phr. This change may be associated with the polymer thermal expansion. It can be seen from thermal expansion curve (Fig. 4) that polymer matrix exhibits a slight expansion above 120 °C. That is to say, the ability of polymer matrix to break down conductive network gradually reduces, so the resistivity of composites is not sensitive to temperature changes, consequently, a slight increase in resistivity is observed.

According to our earlier report [14], for CF-filled semicrystalline composite, the NTC effect following PTC phenomenon is observed above the melting point of polymer, which induced by agglomerate of conductive fillers in low viscous polymer melt. However, in this study the resistivity-temperature behavior of CF-filled EPDM rubber composites is different from that of CF-filled semicrystalline polymer composite. This difference is mainly attributed to the high viscosity of rubber matrix and the high-aspect-ratio of conductive filler. It is well known that EPDM rubber is a noncrystalline polymer and their polymer chains are regarded as an anomalous clew configuration. With the increase of temperature, the viscosity of polymer matrix has not a remarkable reduce. On the other hand, CF possesses a certain aspect ratio, and it is regarded as a rigid and conductive chain formed by many CB particles. Therefore, when the fibers are dispersed in the rubber matrix, they may be entangled by the polymer chains, and thus the viscosity of composites is further increased, in this case, the agglomeration of these fibers is restricted, so the resistivity of composite has no decrease.

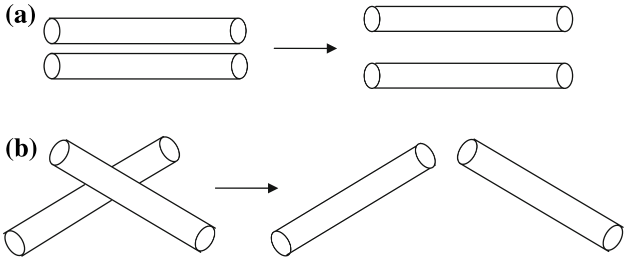

Fig. 3 Schematic diagram of the influence of thermal expansion on the conductive pathways formed in the CF/EPDM composite

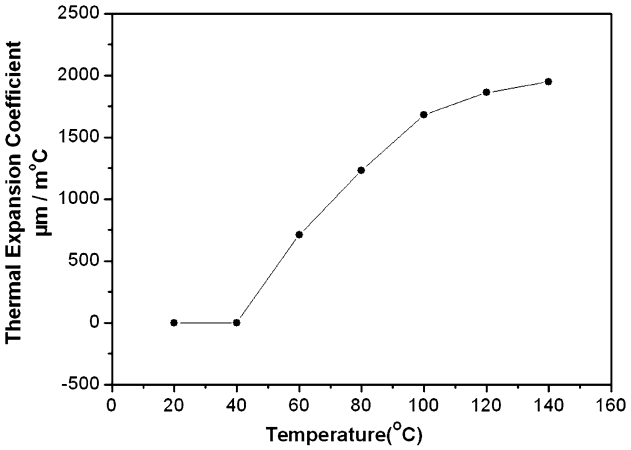

Fig. 4 Thermal expansion coefficient curve for 10 phr CF-filled EPDM rubber composite

In order to establish the effect of filler shape, the CB, which has a small particles size (33 nm), is filled with the EPDM composites. Figure 5 shows the log resistivity of CB-filled EPDM composites with different CB contents as a function of temperature. It is found that the temperature dependence of the composite containing carbon black is just the opposite to that of CF-filled composites, i.e. the resistivity of the composite decreases with increasing temperature. When the temperature is raised, the polymer chains become very active, the free movement of CB particles induced by the movement of polymer chains takes place, so CB particles agglomerate because of their tendency to aggregate, and new conductive pathways are reestablished, the ability of the electric conduction of the CB-filled composites is thus increased. Although the thermal expansion effect of the polymer matrix can break down the conductive network formed by CB particles, the rate of

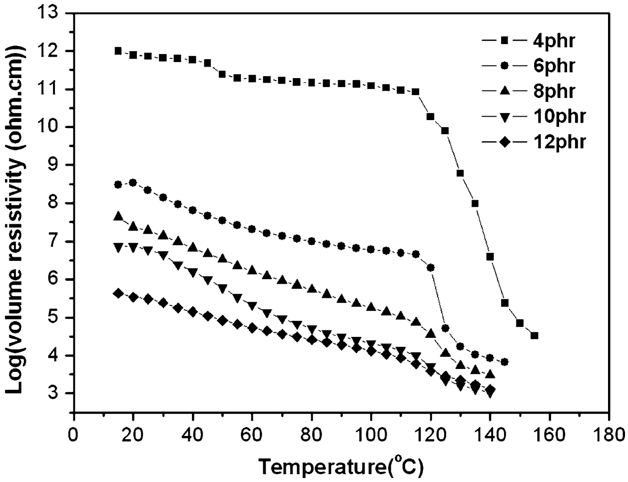

Fig. 5 Log resistivity as a function of temperature for CB-filled EPDM composite with different CB contents

breakage of the conductive network is lower than that of formation of the conductive network, hence the CB-filled composites exhibit a NTC effect in the whole range of temperatures investigated, especially, a deep decrease in resistivity occurs near 120 °C, where the polymer matrix shows a slight expansion. He et al. [15] researched CSF carbon black (70 nm) filled EPDM rubber composites, they found that all the composites showed a NTC effect. This indicates that the NTC effect of the EPDM rubber composites cannot be changed by increasing the size of CB particles. In fact, the shape of conductive filler can assuredly influence the resistivity-temperature behavior of EPDM rubber composites.

4 Conclusions

Carbon fibers can form a bridged conductive pathway structure. Due to the thermal expansion of the polymer matrix during heating, the gap width between fibers increased and the number of inter-fiber contact points decreased. The cooperative effect of these two factors resulted in the breakdown of the bridged conductive pathways, thereby giving rise to a PTC effect. The composite containing CF content in the percolation region showed a stronger PTC effect than the one containing CF content out of this region. The resistivity of composites shows a slight increase following a rapid increase when the content of CF equal to or is higher than 10 phr. The shape of carbonaceous filler can influence the resistivity-temperature behavior of EPDM rubber composites.

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