Resistivity-Temperature Behavior of Carbon Fiber Filled Semicrystalline Composites

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ABSTRACT: Carbon fiber (CF) filled low-density polyethylene (LDPE) composites were prepared by the conventional melt-mixing method. The distribution of CF in the composite was studied by wide-angle X-ray diffraction (WAXD) and scanning electron microscope (SEM) observations. A phenomenological model was proposed to illustrate the resistivity-temperature behavior of CF-filled semicrystalline composites. The effects of the content and aspect ratio of CF on the positive temperature coefficient (PTC) and the room temperature resistivity were elucidated. A balance between the PTC intensity and the room-temperature resistivity can be achieved by using a mixture of CFs with low and high aspect ratios. The negative temperature coefficient (NTC) phenomenon can be effectively eliminated by crosslinking under γ-ray radiation, and the crosslinked composite exhibits a higher PTC intensity and PTC transition temperature than the noncrosslinked counterpart. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1222–1228, 2004

Key words: polyethylene; fibers; irradiation; conducting polymers; WAXS

INTRODUCTION

Intelligent materials are capable of detecting a change in the environment and responding to it by performing both sensing and actuating functions. The usual stimuli are temperature, pressure, electricity, vibration, etc.; the corresponding responses are changes of resistance, heating, mechanical damping, or acoustic damping.[1,2]

One of the most used intelligent materials is the thermistor, or temperature-dependent resistor,[2–4] which can exhibit an abrupt increase in electrical resistance with increasing temperature. The phenomenon of resistivity of a filled polymer composite increasing with temperature is referred to as a positive temperature coefficient (PTC),[2–7] the temperature at which a maximum resistivity is achieved is defined as PTC transition temperature and the ratio of the maximum resistivity to the room-temperature resistivity is referred to as PTC intensity. In general, the PTC phenomenon often occurs at the melting temperature (T_m) of the polymer. Above T_m, however, a more conductive network may be formed and a lower resistivity is observed. This phenomenon is referred to as a negative-temperature coefficient (NTC).[3,6] It is well accepted that the occurrence of PTC phenomenon in a filled semicrystalline composite is mainly due to a large thermal expansion of the polymer in the vicinity of T_m, leading to an increase in the average interfiller particles distance. The NTC behavior following PTC phenomenon is induced by rearrangement of conductive fillers in low viscous polymer melts.[8,9]

Many researchers have studied the PTC/NTC effect of carbon black (CB) filled semicrystalline composites; among which, most[3,4,10] were focused on the composite containing CB and a single semicrystalline polymer, and a few[11–15] were conducted on the PTC/NTC effect of CB-filled immiscible polymer blends. However, few studies[16,17] were conducted on the PTC/NTC effect of carbon fiber (CF) filled semicrystalline polymers.

It is well known that CFs are characterized by a certain aspect ratio, high strength, high modulus, small thermal expansion coefficient, and superior thermal and electrical conductivity. It should be noted that the PTC effect strongly depends on the specific properties[18–20] of a conductive filler such as shape, size, and functional group. Hence, the filler distribution type and formation and deformation of conductive networks for CF-filled composite are probably distinct from those for CB-filled composite. In this work, CF distribution in the composite was studied; a phenomenological model for the resistivity-temperature behavior is proposed, and the effects of CF content, aspect ratio of CF, and crosslinking on the PTC effect are investigated.

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EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) is a commercial resin (18D; Daqing Petrochemical Co., China) with a melt index of 2 g/10 min and a density of 0.921 g/cm^3. CF is high-strength PAN-based carbon fiber (T300; Jilin Carbon Co., China). It is a short fiber with the following characteristics: diameter, 7 μm; density, 1.6 g/cm^3; volume resistivity, 6×10^{-3} Ωcm at 25°C.

Blending of composites

Composites were mixed at polymer melting temperature in a Brabender internal mixer. The mixing procedure involved adding the polyethylene into a preheated rotating mixer and then allowing the addition of CF into melting polymer matrix. These mixtures were further mixed on a two-roll mill at a temperature only slightly above the polymer melting point for short periods. Blends were compression-molded at the vulcanized press, 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.

Irradiation

The sample was sealed in glass tubes under vacuum and irradiated by ^{60}Co γ-rays at room temperature; radiation dose rate was 30 kGy/h and radiation time was 10 h. The sample was held in a vacuum oven at 100°C for 1 day after radiation crosslinking to eliminate postradiation effect.

Resistivity testing

Electrical resistivity was measured with a digital multimeter when it was lower than 2×10^7 Ω, and a high-resistance meter was used when the resistivity exceeded 2×10^7 Ω. Different applied voltages were used on different samples, depending on the level of resistivity of the sample. Highly conductive samples caused short-circuiting of the equipment when the applied voltage was too high. Thus, the voltage was adapted to the resistivity and was 500 V for poorly conductive composites and 50 V for well-conductive composites. According to ASTM D4496 and D257, the resistivity was converted to volume resistivity, ρ_v, by using the formula

$$\rho_v = R_v S/d \tag{1}$$

where S is the surface area of the sample plane, d is the thickness of the sample, and R_v is the measured resistance.
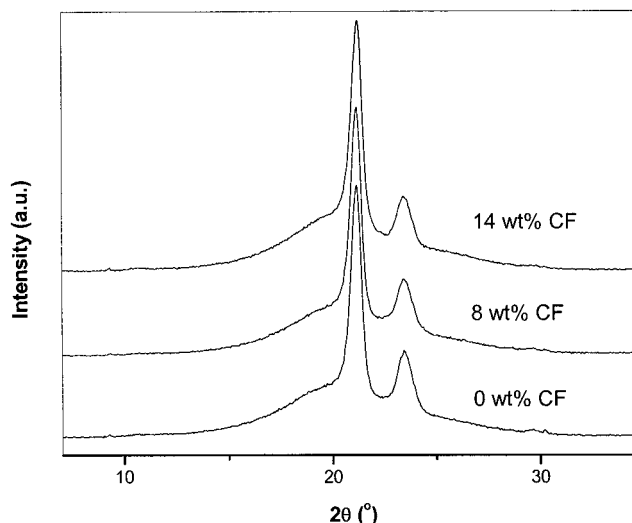

Figure 1 WAXD pattern of CF-filled LDPE composites with various CF contents.

Morphology

The morphology observation of cross-fractured surface was performed with a JSM-5310 scanning electron microscope (SEM), prior to which, the samples were gold-sputtered.

Wide-angle X-ray diffraction (WAXD) measurement was conducted on a Rigaku Denki diffractometer (D_{max}-γA) with a rotating Cu-anode.

Thermal analysis

Linear expansion coefficient measurement was conducted on a Perkin–Elmer thermal analysis system; the heating rate was 5°C/min.

RESULTS AND DISCUSSION

CF distribution

It is seen from the WAXD graph (Fig. 1) that diffraction peaks of LDPE composites filled with 8 and 14 wt % CF, respectively, are similar to those of pure LDPE. It shows that CF is entirely dispersed at the amorphous region and the addition of CF does not influence crystal morphology of the polymer. Carbon fibers are uniformly dispersed in polymer melts; however, during cooling, fibers have been excluded from crystalline region. Thus, CF is selectively localized in the amorphous region, where the conductive paths are established.

Processing the composite in a mechanical mixer causes fiber breakage, the extent of which depends on the initial fiber length, mixing time, and rotating speed of the mixer. Furthermore, the level of fiber breakage is associated with the thickness of the mold. The schematic graph of the sample is presented in Figure 2. If
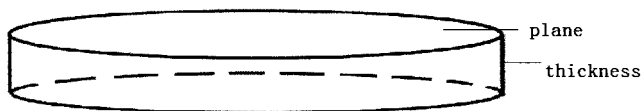
Figure 2 Schematic diagram of the sample with a diameter of 5 cm and a thickness of 1 mm.

the CF length is equal to or slightly larger than the thickness of the mold thickness, CFs have a great tendency to align parallel to the thickness direction of the sample and subsequently fracture when pressure is applied. The longer CF, on the other hand, tends to align in the plane of the sample and is less likely to fracture when pressure is applied. The length of CF used in this study is about 7 mm, which is much larger than the thickness of the sample, which is 1 mm. CFs, thus, have a great tendency to align parallel to the plane of the sample, which is further confirmed by SEM micrographs (Fig. 3).

Phenomenological model for resistivity-temperature behavior

It is thought by many researchers[16,20–24] that high-aspect-ratio CF filler creates a long uninterrupted path for electron hopping or transport, leading to higher conductivity. Jana[24] has performed Hall effect measurements and found that an increase in CF aspect ratio is accompanied by an increase in mobile carrier concentration. Hence, the effect of high carrier concentration interprets the high conductivity achieved in the polymer composite containing high-aspect-ratio CF. Thougruang[23] has reported that the conductivity level of CF-filled polymer composites depends on the CF length at a given loading level. The role of CF in improving electrical conductivity was always focused on the CF aspect ratio,[20–23] because CF easily bridges to form a continuous conductive path in a two-dimensional plane. However, it is worth noting from SEM micrographs (Fig. 3) that the conductive paths along the diameter direction of CF are easily formed because of a small interfiber distance. Therefore, we can deduce that there are two types of conductive pathways formed in the CF-filled semicrystalline composite. The first type is the conductive path along the direction parallel to the sample plane. We refer to it as type P (plane). The second type is the conductive path along the thickness direction of the sample. We refer to it as the type T (thickness). If these two types of conductive paths are connected to each other, a three-dimensional
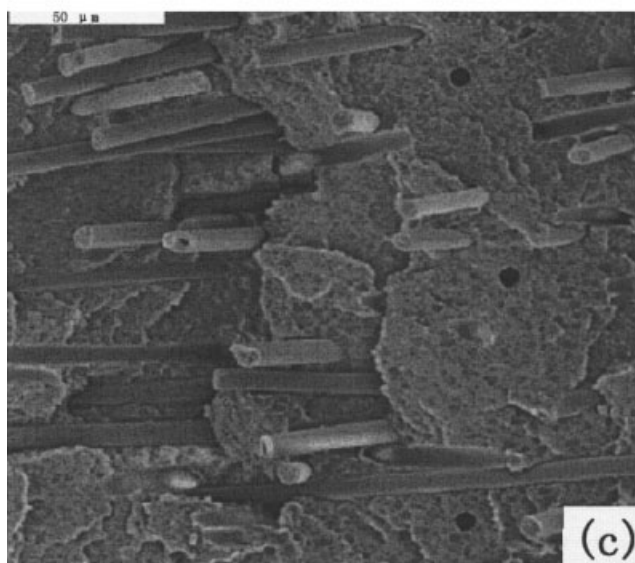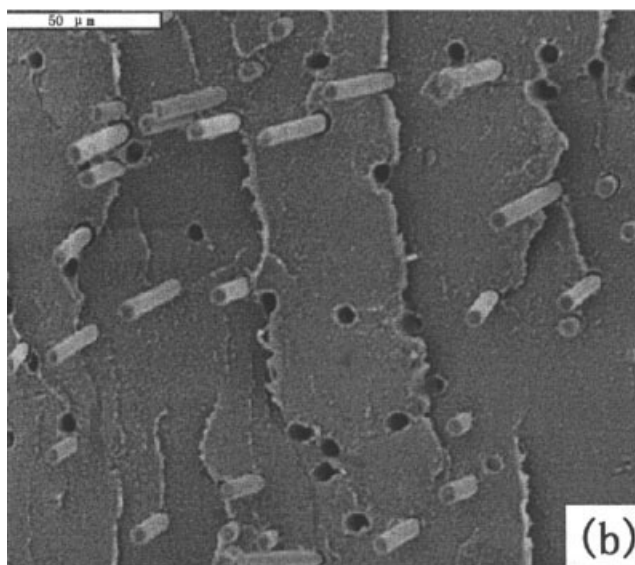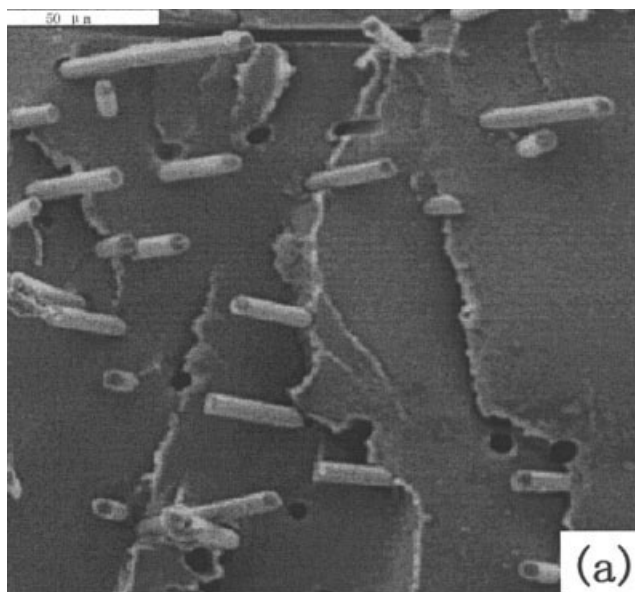

Figure 3 SEM micrographs of cross-fracture surface of the LDPE composite filled with CF. (a) 8 wt % CF; (b) 10 wt % CF; (c) 14 wt % CF.
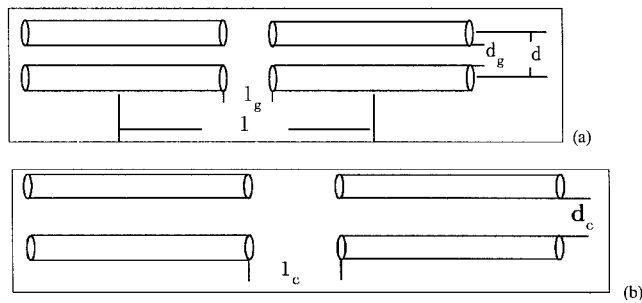
Figure 4 Schematic diagram of two types of conductive pathways in the CF-filled LDPE composite.

conductive network is formed through the entire composite.

Suppose that not all the fibers are in direct contact with each other in the composite (i.e., there is a gap between some of them). Figure 4(a) presents a schematic graph of two types of conductive paths. In the conductive path P, l is the distance between fiber centers along the length direction of CF, and l_g is the gap width. Obviously, $l_g = l - l_0$, where l_0 is the fiber length, assuming that all the fiber lengths are equal. In the conductive path T, d is the distance between fiber centers along the diameter direction of CF, and d_g is the gap width. Obviously, $d_g = d - d_0$, where d_0 is the diameter of CF. If l is equal to or smaller than l_0, or d is equal to d_0, this means that the fibers are in direct contact with each other. The term "direct contact" means that $l_g \leq 0$, and/or $d_g = 0$. In fact, the phenomenon of direct contact is seldom observed, and it is noted from SEM micrographs that a polymer layer exists among the fibers. Especially for the crosslinked composite, the polymer layer could not be squeezed out. It is well known that the expansion and shrinkage coefficients of CF itself are considerably small relative to those of the polymer matrix so that it is considered to be negligible. Therefore, the change in the distances l_g and d_g will mostly depend on the expansion and shrinkage of the polymer layer among the fibers. The polymer matrix shrinks in the course of cooling to room temperature after molding. Hence, we have to consider the residual compressive strain in the sample. Let us consider the contact behavior in the composite during heating. The thermal expansion of polymer matrix in the course of initial heating will compensate the residual strain. Further heating will lead to a separation of fiber. Suppose that there is a critical gap width l_c and d_c [Fig. 4(b)] such that if $l_{(T)} > l_c$, and $d_{(T)} > d_c$, where $l_{(T)}$ and $d_{(T)}$, respectively, represent l_g and d_g values dependent on temperature T; the contacts are broken down. In other words, the electrical conductivity through the contact becomes equal to the polymer conductivity at $l_{(T)} > l_c$ and $d_{(T)} > d_c$. Therefore, the breaking up of type P+T conductive pathways due to a large thermal expansion of the polymer

layer between fibers produces a PTC effect when the temperature reaches the T_m of LDPE.

Resistivity values at room temperature versus fiber content are presented in Figure 5. With increasing the CF content, the average interfiber gap becomes smaller and there is an increase in the number of conductive pathways; thus, the resistivity drops sharply up to a CF content of 9 wt %. Some authors[25] defined the commence of insulator to conductor transition as the percolation threshold, but others[26,27] considered the end of the transition as the percolation threshold. Here, we describe the 9 wt % content of CF (i.e., the end of the transition) as the percolation threshold.

Effects of the content and aspect ratio of CF

Figure 6 displays the log resistivity of CF-filled LDPE composites with various CF contents as a function of temperature. Obviously, the CF content significantly influences the PTC behavior of the composites. The composite containing CF content around the percolation threshold exhibits a higher room temperature resistivity and PTC intensity than the one containing CF content far beyond the percolation value. For the former, the number of conductive pathways formed is smaller (i.e., the number of interfiber contact points is smaller), so the resistivity of the composite is sensitive to even a small decrease in the number of the conductive contacts. For the latter, however, a large number of the conductive pathways or the interfiber contacts are formed within it. Thus only the deformation of a majority of conductive contacts can cause a sharp increase in the resistivity; otherwise, a lower PTC intensity and room temperature resistivity will be achieved.
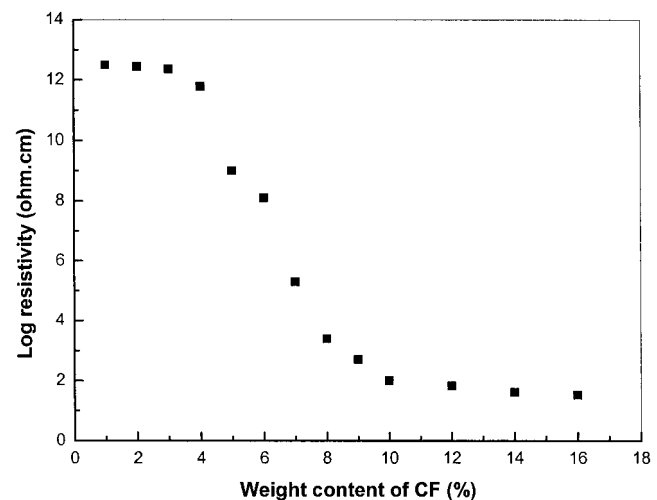

Figure 5 Log resistivity at room temperature as a function of CF weight content.
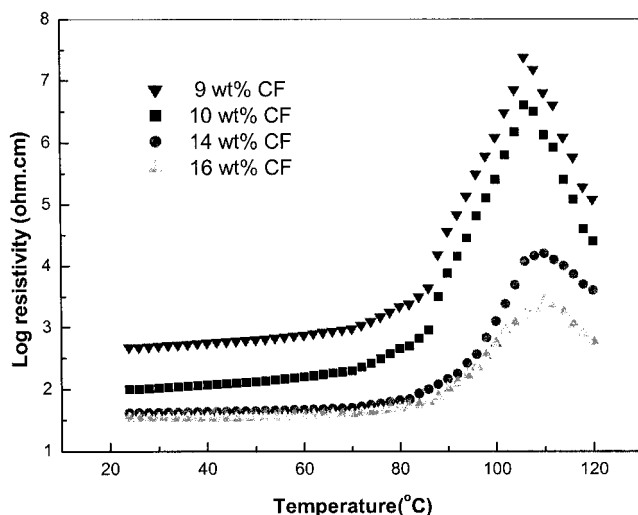
Figure 6 Log resistivity as a function of temperature for CF-filled LDPE composite with various CF weight contents.

Figure 8 Log resistivity as a function of temperature for the CF-filled LDPE composite before and after crosslinking.

The effect of aspect ratio of CF on the PTC behavior would be discussed subsequently. Here, we refer to CF of 7 and 2 mm as CF_1 and CF_2, respectively. Figure 7 shows the temperature dependence of the resistivity in the composites filled with CF_1, CF_2, and mixtures of both at various weight ratios.

It is observed that the 10 wt % CF_1-filled LDPE composite exhibits a lower PTC intensity and room-temperature resistivity than those of 10 wt % CF_2-filled LDPE composite. The differences in the PTC intensity and the room temperature resistivity depend on the interfiber contact ability. This means that high-aspect-ratio CF are better contacted with each other, and their interfiber contacts are difficult to break down at the elevated temperature, and vice versa.
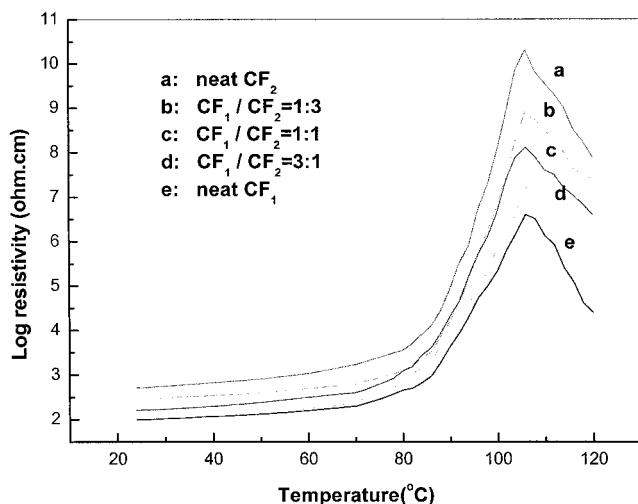

Figure 7 Log resistivity as a function of temperature for the CF-filled LDPE composite containing 10 wt % CF with various ratios of CF_1 to CF_2.
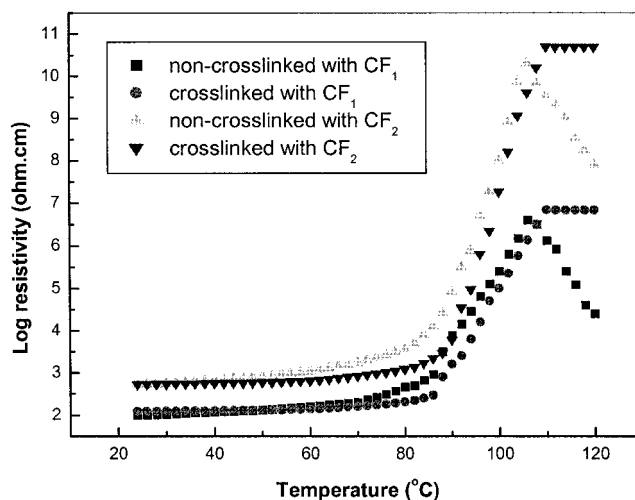
Therefore, composites filled with CF_1 show a lower room temperature resistivity and also a lower PTC intensity, and composites filled with CF_2 show a higher PTC intensity, but a higher room-temperature resistivity. A balance between the PTC intensity and the room temperature resistivity is attempted by using mixtures of CF_1 and CF_2 at various weight ratios. Figure 7 exhibits the effect of the CF weight ratio (CF_1/CF_2) on the PTC behavior and room-temperature resistivity. As predicted, a balance between the PTC effect and room-temperature resistivity can be achieved by varying the weight ratio of CF_1 to CF_2. A higher weight ratio causes a lower room-temperature resistivity and PTC intensity, and vice versa.

Effect of crosslinking by γ-ray radiation

The presence of NTC phenomenon may have an adverse effect[5,28,29] on a desired performance. Structure stabilization and significant reduction of the movements of conductive particles can be achieved by introduction of crosslinks.[29-31] The absence of the NTC effect in the crosslinked semicrystalline polymer composites is attributed to an increase in the viscosity of the polymer matrix, leading to a significant reduction in the mobility of conductive particles in the composites. Crosslinking is thus expected to greatly improve the electrical reproducibility and to effectively eliminate the NTC phenomenon. In the following subsection, the effect of γ-ray radiation on the PTC and NTC behavior is investigated.

Figure 8 shows resistivity-temperature behavior for 10 wt % CF-filled LDPE composite before and after crosslinking by γ-ray irradiation, from which it is noted that the NTC effect has been effectively eliminated after crosslinking. The PTC intensity of the com-

posite after crosslinking is slightly higher than that of the noncrosslinked counterpart, and the PTC transition temperature is shifted to a higher temperature after irradiation crosslinking.

The following two processes are simultaneously operative with an increasing temperature in the noncrosslinked system: (1) The breakdown of existing conductive pathways due to an increase in the gap between fibers, which results from the thermal expansion of the polymer layer between fibers; (2) The formation of new conductive pathways due to the agglomeration of the fibers arising from three factors, as follows: (1) The viscosity of polymer matrix decreases; (2) the adhesion between CF and LDPE is weak, for it is observed in the SEM micrographs (Fig. 3) that there are several holes in the composite formed by pulling carbon fibers out of the polymer matrix. This weak interaction between polymers and filler cannot better prevent the mobility of the conductive particles. (3) The increased thermal energy is obtained by CF with the increase of temperature, inducing their mobility of the conductive particles. The resistivity of the composite with increasing temperature depends on the cooperation of the two processes. Obviously, the former leads to an increase in the resistivity; the latter, on the contrary, leads to a decrease in the resistivity. It is well known that the breakage of conductive paths is much more predominant than the fiber agglomeration and the formation of new conductive paths before the PTC transition temperature, and consequently, the resistivity increases at a fast rate with increasing temperature. Especially in the vicinity of T_m, a maximum resistivity is achieved. On the contrary, the formation of new conductive paths becomes more predominant above T_m, where the polymer becomes more fluid and CFs begin to show considerable migration through the new amorphous region. This could well result in reformation of the conductive paths; consequently, the resistance of the composite will decrease, giving rise to the NTC behavior. For the crosslinked composite, crosslinking mainly occurs at the amorphous region,[29,32,33] where CFs are dispersed as mentioned in the previous subsection. 3 CFs are strongly attached to crosslinked networks, and thus the agglomeration of CF and the NTC effect can be effectively eliminated. For the noncrosslinked composite, however, the effect of polymer thermal expansion on the resistivity is partially counteracted by the agglomeration effect of CF, so the PTC intensity is lower than that of the crosslinked counterpart. The PTC intensity thus is enhanced by the introduction of crosslinks.

It is observed from the linear expansion curves (Fig. 9) that the linear expansion extent of the crosslinked composite is slightly lower than that of noncrosslinked counterpart at the same temperature. That is to say, the deformation extent of the conductive paths for crosslinked sample is lower than that of the
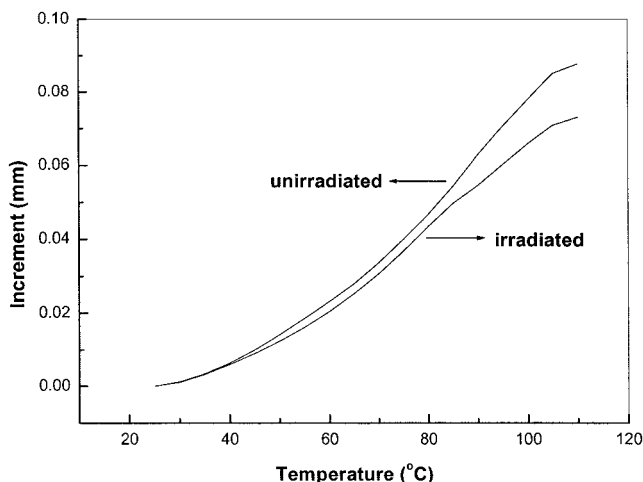

Figure 9 Linear expansion increment with temperature for the irradiated and unirradiated 10 wt % CF_2-filled LDPE composites.

noncrosslinked counterpart at the same temperature. As a result, the conductive pathways are almost broken down and a maximum resistivity is achieved at 106°C for the noncrosslinked composite. For the crosslinked counterpart, however, only at a temperature slightly higher 106°C can the same effect be achieved. Thus, the crosslinked composite exhibits a higher transition temperature than the noncrosslinked counterpart.

CONCLUSIONS

The resistivity-temperature behavior in the LDPE/CF composite was studied in this work. There are two types of conductive pathways formed in the composite. The first one is the conductive path along the direction parallel to the sample plane; the second one is the conductive path along the thickness direction of the sample. These two types of conductive paths are connected to each other. A three-dimensional conductive network is formed through the composite. Around the T_m, the breaking up of these two types of conductive paths due to considerably large thermal expansion of the polymer layer between the fibers causes a PTC behavior.

The content and aspect ratio of CF are the two factors that can significantly influence the PTC intensity and the room-temperature resistivity. The composite containing high-content CF or high-aspect-ratio CF exhibits a lower room temperature resistivity and PTC intensity. However, the composite containing low-content CF or low-aspect-ratio CF exhibits a higher room temperature resistivity and PTC intensity. The composite with CF content around the percolation threshold shows a good PTC effect.

The NTC phenomenon can be effectively eliminated by crosslinking under γ-ray irradiation. The crosslinked composite shows a higher PTC intensity and PTC transition temperature than its non-crosslinked counterpart.

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