PTC Effect in Carbon Black-Filled Ethylene–Propylene–Diene Terpolymer Systems

XIUJUAN HE,[1,2] LIJIE WANG,[1] XINFANG CHEN[1]

[1] Institute of Materials Science, Jilin University, Changchun 130023, People's Republic of China

[2] Department of Materials Science and Engineering, Shenyang Institute of Chemical Technology, Shenyang, 110021, People's Repubic of China

Received 20 December 1999; accepted 13 July 2000

ABSTRACT: The positive temperature coefficient (PTC) effects of carbon black (CB)-filled semicrystalline and amorphous ethylene–propylene–diene terpolymer (EPDM) composites were studied. The semicrystalline EPDM/CB composite exhibited a low PTC effect followed by a pronounced negative temperature coefficient (NTC) effect, while the amorphous EPDM/CB composite exhibited only an NTC effect. By the effect of γ-ray irradiation, not only was the NTC effect of the composites eliminated, but also a high PTC effect appeared. The PTC intensity reached as high as six orders of magnitude even for an amorphous EPDM/CB composite and the PTC transition temperature decreased with the irradiation dose. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1571–1574, 2001

Key words: conducting composite; PTC effect; EPDM

INTRODUCTION

In recent years, polymer positive temperature coefficient (PTC) materials have been drawing more and more attention due to their advantages of relatively lower room-temperature resistivity, easy fabrication, and low cost over that of ceramic ones. Polymer PTC materials are generally composed of conducting particle-filled semicrystalline polymers. For such materials, resistivities increase sharply at the vicinity of the melting temperature of the polymer matrix. Some researchers attributed the PTC effect to the influence of crystalline melting.[1,2] However, PTC effects were also observed in some carbon black (CB)-loaded amorphous polymers.[3–6] But the PTC effects in a CB-loaded amorphous polymer are generally much smaller than are those in crystalline polymers.

In this work, the electrical behavior of carbon black-filled ethylene–propylene–diene terpolymer (EPDM) composites were studied. High PTC effects were developed in both semicrystalline and amorphous EPDM/CB composites by the effect of γ-ray irradiation.

EXPERIMENTAL

Materials

EPDM (EPT 4045) and EPDM (Esprene 505A) were used as polymer matrices. The former has a high ethylene unit content (81 mol %) and is semicrystalline, while the latter has a middling ethylene unit content (55 mol %) and is amorphous. CSF carbon black was used as a conductive filler.

Correspondence to: X. Chen (chenxfmp@public.cc.jl.cn).
Contract grant sponsor: Therm-O-Disc Inc., subsidiary of Emerson Electric.

Journal of Applied Polymer Science, Vol. 80, 1571–1574 (2001)

Its average particle size is 70 nm; surface area, 230 m^2/g; dibutyl phthalate (DBP) value, 280 mL/100 g, and pH value, 7–9.

Sample Preparation and Irradiation

EPDM and CB were mixed in an internal mixer for 5 min at 150°C. The composite was compression-molded at 100 and 120°C for EPT4045/CB and Esprene505A/CB, respectively. The thickness of the sheets was 1 mm. The irradiation of samples was carried out in air at room temperature with a ^{60}Co γ-ray source.

Resistivity, TEC, and DSC Measurements

The volume resistivities of the samples were measured by a digital multimeter for low resistance (<10 MΩ) and an insulating resistance tester for high resistance (≥10 MΩ) consecutively at a progressively elevated temperature. The heating rate was 5°C/min. The two sides of the samples were bonded with metallic foil to reduce the contact resistance.

The thermal expansion coefficient (TEC) of the composites was obtained using a DuPont 9900 thermal analzer at a heating rate of 5°C/min. The differential enthalpy of the sample was determined with a Perkin–Elmer 7 series thermal analysis system. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Electrical Behavior of EPDM/CB Composites

The resistivity–temperature curves of semicrystalline EPDM/CB composites with different CB contents are shown in Figure 1. With the CB content slightly below the percolation threshold, the sample exhibits only a negative temperature coefficient (NTC) effect. With the CB content above the percolation threshold, the sample exhibits a low PTC effect followed by NTC. The DSC curve of semicrystalline EPDM is shown in Figure 2. The endotherm is associated with the melting of crystals composed of ethylene sequences on the EPDM chains.[7] By comparison of Figure 1 with Figure 2, it can be seen that, as is common, the PTC transition region is in the vicinity of the crystalline melting region of the EPDM matrix. Thus, the resistivity increase is attributed to the thermal expansion caused by melting. Figure 3 shows the resistivity–temperature behavior of amorphous EPDM/CB composites for various CB

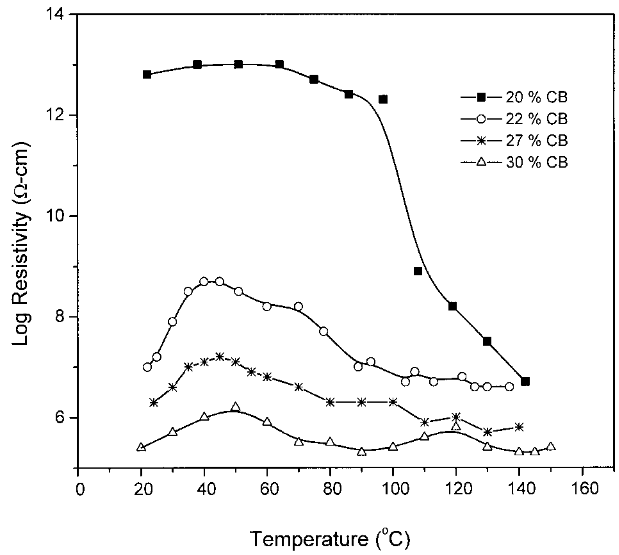

Figure 1 Resistivity–temperature curves of semicrystalline EPDM/CB composites.

contents. Except for some small fluctuations, resistivities decrease with temperature, that is, amorphous EPDM/CB composites exhibit practically only an NTC effect.

Many researchers have studied the NTC effect in CB-filled crystalline polymers above crystalline melting.[8–10] It is generally accepted that the resistivity decrease is due to the agglomeration of CB particles or aggregates, which results in a new CB distribution of better conductivity. Because the movement of CB particles requires polymer segments surrounding them to move correspondingly, the agglomeration of CB could take place only when the polymer segment or chains have sufficient mobility. Semicrystalline EPDM above its melting point and amorphous EPDM above room temperature are both in their rubbery state. Their segments are quite mobile. Therefore, it is presumable that the NTC effect in an EPDM/CB composite results from the agglomeration of CB particles.

PTC Behavior of Irradiated EPDM/CB Composites

The semicrystalline EPDM/CB composites were irradiated with a ^{60}Co γ-ray. Figure 4 shows that when the irradiation dose is 50 kGy the NTC effect of the system is eliminated. By 150-kGy irradiation, another PTC transition appears at a higher temperature and its transition temperature decreases with an increasing dose. Figure 5 shows the influence of the irradiation dose on the PTC behavior of amorphous EPDM/CB. By 50-

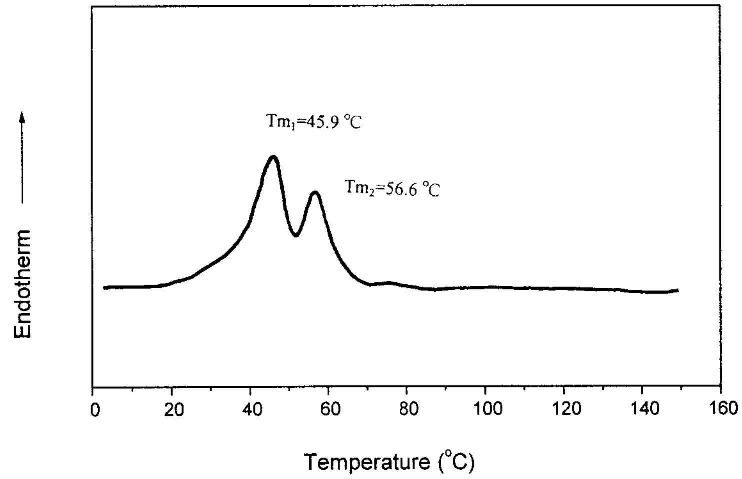

Figure 2 DSC curve of semicrystalline EPDM.

kGy irradiation, not only is the NTC effect eliminated, but also a high PTC appears. With an increasing dose, the PTC transition temperature decreases and the PTC intensity (the ratio of peak resistivity to room-temperature resistivity) reaches as high as six orders of magnitude.

Although the exact mechanism of the PTC effect in polymer composites is not fully understood, it has often been concluded in the literature that the PTC effect resulting from a disturbance in the continuity of the conducting network is principally due to the volumetric expansion of the matrix. The TECs of the amorphous EPDM/0.3CB composite before and after irradiation are compared in Figure 6. Before irradiation, when the temperature is above 50°C, the TEC increases rapidly with increasing temperature, but the resistivities decrease and almost no PTC effects appear. After irradiation, the TEC at high temperature is much lower than that before irradiation and changes little with temperature; however, a high PTC effect appears. This may be attributed to the net result of the two processes having opposite effects: a deagglomeration of CB agglomerates principally caused by the thermal expansion of the matrix which breaks the conducting network and, thus, a resistivity increase, that is, a PTC effect, and agglomeration of CB

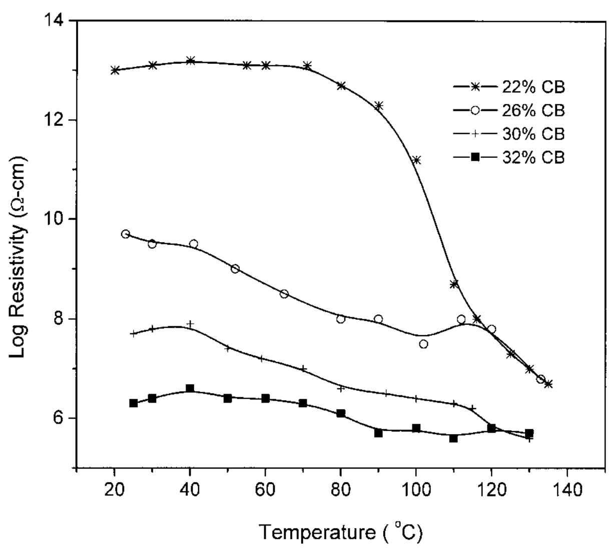

Figure 3 Resistivity–temperature curves of amorphous EPDM/CB composites.

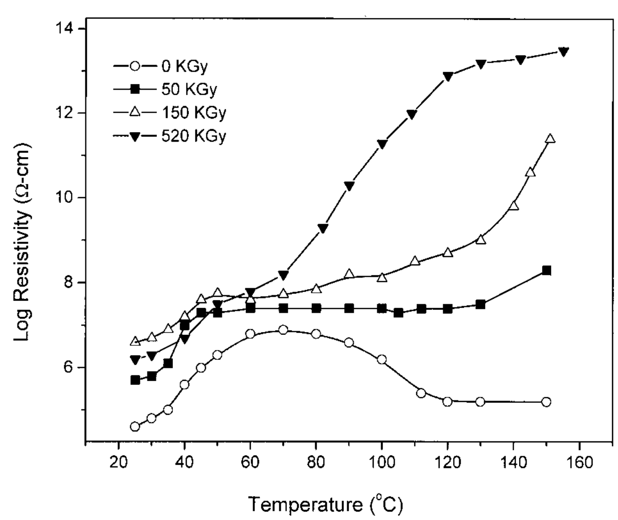

Figure 4 Resistivity–temperature curves of semicrystalline EPDM filled with 26% CB irradiated at different doses. Second heating run.

aggregates accompanied by a resistivity drop, that is, an NTC effect. For amorphous EPDM or semicrystalline EPDM after crystallite melting, the high mobility of the polymer segments facilitates the agglomeration of the CB particles. The increase of resistivity caused by the deagglomeration process could be counteracted or overwhelmed by the drop of resistivity caused by the reagglomeration process. Consequently, only the NTC effect is commonly observed. By irradiation, the EPDM polymer matrices are crosslinked[11] and chemical bonds may form between polymer chains and CBs.[12] The movement of the CB particles is restricted. Thus, the agglomeration of CB particles or aggregates is depressed and the effect of deagglomeration could manifest itself. As a result, the NTC effect is eliminated and a high PTC effect is observed. When the dose is increased, the effect of agglomeration is further weakened. The deagglomeration process could act more effectively on the breakdown of the conducting network. Thus, the PTC transition moves toward a lower temperature.

CONCLUSIONS

The semicrystalline EPDM/CB composite exhibited a small PTC effect in the vicinity of the crystalline melting point of the EPDM matrix followed by a pronounced NTC effect, while the amorphous EPDM/CB composite exhibited practically only an NTC effect. By γ-irradiation, in both systems, NTC effects were eliminated and high PTC effects appeared. This is assumed to have resulted from the depression of agglomeration of CB aggregates by γ-irradiation-induced crosslinking of the EPDM matrices.

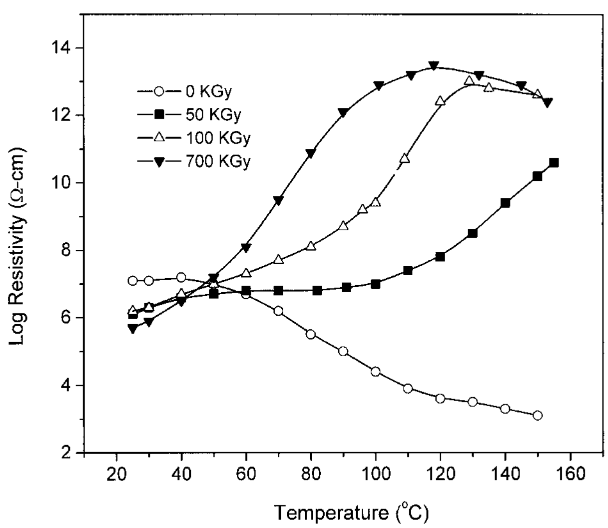

Figure 5 Resistivity–temperature curves of amorphous EPDM/CB composites irradiated at different doses. Second heating run.

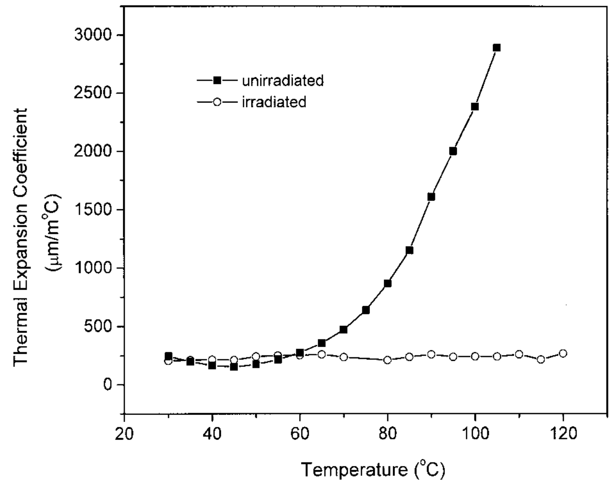

Figure 6 TEC as function of temperature for the EPDM/CB composite.

The authors wish to thank Therm-O-Disc Inc., subsidiary of Emerson Electric, for the financial support of this work.

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