Effects of Irradiation on PTC Performance of LDPE/EPDM Blends Filled with Carbon Blacks

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SYNOPSIS

Low-density polyethylene/ethylene–propylene–diene terpolymer/carbon black blends were irradiated in air with a ^{60}Co γ ray or an electron beam accelerator. The absorbed dose ranged from 1-400 Mrad. The influences of irradiation on positive temperature coefficient behavior of the blends were analyzed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Irradiation can produce crosslinking, main chain scission, production, and/or removal of unsaturation, etc. Crosslinking leads to a network, an effect that has extensive technological applications, while scission breaks up the molecules and may eventually degrade them.[1]

When an irradiation technique is used in polymer positive temperature coefficient (PTC) materials, it can improve the PTC intensity and stabilize PTC functions significantly. In our earlier paper,[2] we described the PTC performance of low-density polyethylene/ethylene–propylene–diene terpolymer/carbon black (LDPE/EPDM/CB) blends. The influences of γ-ray and electron beam (EB) irradiation on PTC effects of the blends stated above were studied in more detail, and the variation of crystalline structures analyzed using WAXD and DSC tests.

EXPERIMENTAL

Materials

LDPE with melt index of 2.0 and EPDM were used in this study as the ingredients of the polymer matrix.

CSF CB was used as the conductive filler. Its average size was 70 nm, surface area 230 m^2/g, dibutylphthalate (DBP) value 280 mL/100 g, and pH 7–9.

Sample Preparation

LDPE, EPDM, and CB (3 : 1 : 1) were mixed in a Brabender mixer at 130°C for 5 min, and then the blends were molded under pressure at 160°C for 10 min. The ultimate samples for testing use were 1 mm thick.

Resistivity

The volume resistivity of the sample was measured by a digital multimeter and an insulation resistance tester consecutively at progressively elevated temperatures. The two sides of the sample were bonded with copper foils to reduce the contact resistivity.

Irradiation

Some samples were irradiated with a ^{60}Co γ-ray source in air at room temperature. Radiation dose rate was 0.83 Mrad/h. Others were irradiated by an EB carried out with a 10-MeV dynamitron accelerator at a beam current of 1 mA. Various doses were given from 1 to 400 Mrad.

Characterization

WAXD was obtained with a rotating Cu-anode X-ray source. The intensity curve was measured on

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the 2θ scale, and the crystallinity was evaluated for all samples by comparing the area under the diffraction peaks.

The thermoanalysis of the samples was investigated by differential scanning calorimeter using a Perkin–Elmer DSC-2 instrument at the heating rate of 10°C/min.

RESULTS AND DISCUSSION

Influences of γ-Ray Irradiation

The influences of γ-ray irradiation on PTC performance of LDPE/EPDM/CB blends are shown in Figure 1(a,b). The PTC intensity (expressed by ρ_{max}/ρ_{room}) of the uncrosslinked sample is 3 orders of magnitude, and the transition point at which the negative temperature coefficient (NTC) effects appear is 82°C. With the slight increase of radiation dose, that is, from 1 to 3 Mrad, the PTC intensity increases gradually, and the transition temperatures rises to 100°C, but the samples still have NTC effects. This indicates that although the microcrosslinked networks of the polymer form at low absorbed dose, and thus limit the movement of CB particles to some extent, they cannot prevent the reagglomeration of CB particles in the vicinity of the melting point. Above 4 Mrad, the NTC effect is eliminated and the PTC intensity improves by 4 orders of magnitude compared with that of uncrosslinked sample, illustrating that the crosslinked network is fully formed at this time and thus can stabilize the PTC functions of the material effectively. From 4 to 100 Mrad, the shape and characteristics of the temperature-resistivity curves are very similar.

The samples that received 200 and 400 Mrad doses reappear as an NTC phenomenon, and the transition temperatures decreased to 82°C again. This is probably due to the oxidative degradation that occurred with the polymer matrix being subjected to a lengthy irradiation in air. With the diffusion of oxygen, free radicals were generated by the radiation induced oxidative chain reaction and then formed peroxides that are thermally labile, leading to thermal break down.[3] Break down adds chain ends, hence enhancing the mobility of crosslinked chains as well as CB particles. CB particles tend to flocculate, thus the samples reappeared as NTC effects.

The strength and toughness of the material deteriorated completely above 400 Mrad. There are many reports about the effects of irradiation on mechanical properties of various polymers.[4,5] They were not studied.

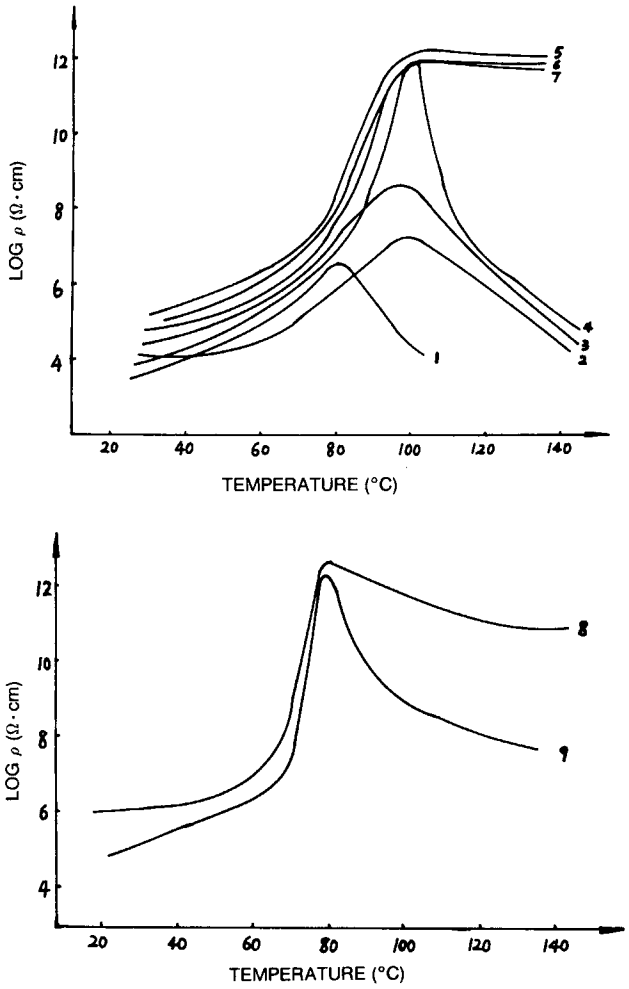

Figure 1 Influences of γ-irradiation on PTC curves of LDPE/EPDM/CB blends. Radiation dose for (a) 1. 0 Mrad, 2. 1 Mrad, 3. 2 Mrad, 4. 3 Mrad, 5. 4 Mrad, 6. 50 Mrad, 7. 100 Mrad, and (b) 8. 200 Mrad and 9. 400 Mrad.

Influences of EB Irradiation

Figure 2 shows the influences of high absorbed dose irradiation on PTC curves. The sample irradiated by 300 Mrad with the EB displays excellent PTC performance; in the mean time, much better mechanical properties are preserved. This difference between the γ ray and EB effect can be explained by the dose rate effect. The mean dose rate of EB is 1,000–10,000 times higher than γ rays. Clearly, for the same dosage a shorter time is required to accomplish the radiation modification of polymers or its composites at a higher dose rate. It was found experimentally that irradiation of polymeric materials in the presence of air almost always results in some damage to their structures and properties, owing to the radiation induced oxidative degradation effect. This effect may be divided into two main

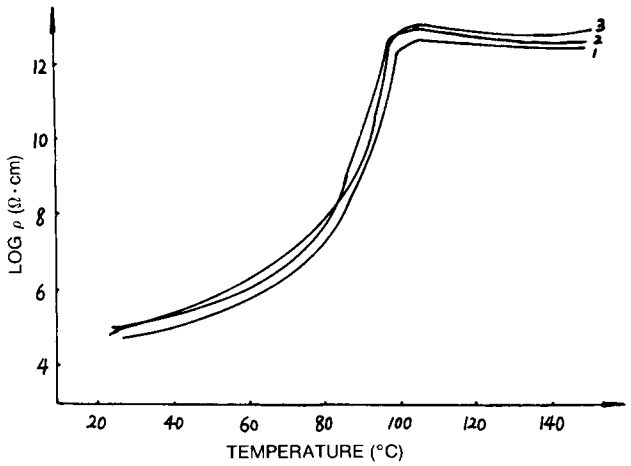

Figure 2 Influences of electron irradiation on PTC curves of LDPE/EPDM/CB blends. Radiation dose for 1. 50 Mrad, 2. 200 Mrad, and 3. 300 Mrad.

steps: diffusion of oxygen and oxidation. Because diffusion of oxygen from the surface layer of the polymer into its inner is a slow process, it is expected that the higher the dose rate, the shorter the radiation time, thus the smaller the radiation induced oxidative degradation effect on the polymers. Therefore, it is reasonable that the γ-ray irradiated sample had an NTC effect at a certain high dose, while the EB irradiated sample did not.

Effect of Irradiation on Crystallinity State

The samples irradiated with different doses first underwent a heating–cooling cycle before WAXD analysis. The wide-angle diffraction patterns are shown in Fig. 3. Note that the observed half-width of the (110) and (200) peaks almost remains unchanged, although the diffraction intensity of the 400-Mrad sample decreased sharply.

According to the Scherrer equation,[6,7]

$$L_{hkl} = \frac{K\lambda}{\beta_{1/2} \cos \theta_{hkl}}, \qquad (1)$$

where L_{hkl} is the mean dimension of the crystallites perpendicular to the planes (hkl), $\beta_{1/2}$ is the half-width of the maximum intensity of the pure diffraction profile in radians, λ is the X-ray wavelength, K is a constant that is usually close to 1, and θ_{hkl} is the Bragg angle. The Scherrer equation can be modified to express the reflection breadth in δS units [$S = 2(\sin \theta)/\lambda$] as follows:

$$L_{hkl} = \frac{K}{[2(\cos \theta)/\lambda]\delta\theta} = \frac{1}{(\delta S)_S}. \qquad (2)$$

Equation (2) can be used to estimate the size of perfect polymer crystals. When the separation of effects due to size and perfection come into consideration, the half-width due to size alone $(\delta S)_S$ is given by eq. (2), that due to lattice distortion $(\delta S)_D$ was given by Wilson in 1949:[8]

$$e = (\delta S)_D/2S \qquad (3)$$

where e is a measure of the maximum lattice distortion, $\delta d_{hkl}/d_{hkl}$. We may use Cauchy profiles to approximate both broadening effects,

$$\delta S = (\delta S)_S + (\delta S)_D = 1/L_{hkl} + 2eS. \qquad (4)$$

We can infer from experimental conditions and results that when the 400-Mrad sample crystallized from the melting state, it had many defects within the crystals, such as peroxide groups, crosslinked points, etc., introduced by the high dose irradiation. Thus the parameter e will increase while the half-width remains unchanged, so L_{hkl} will also increase.

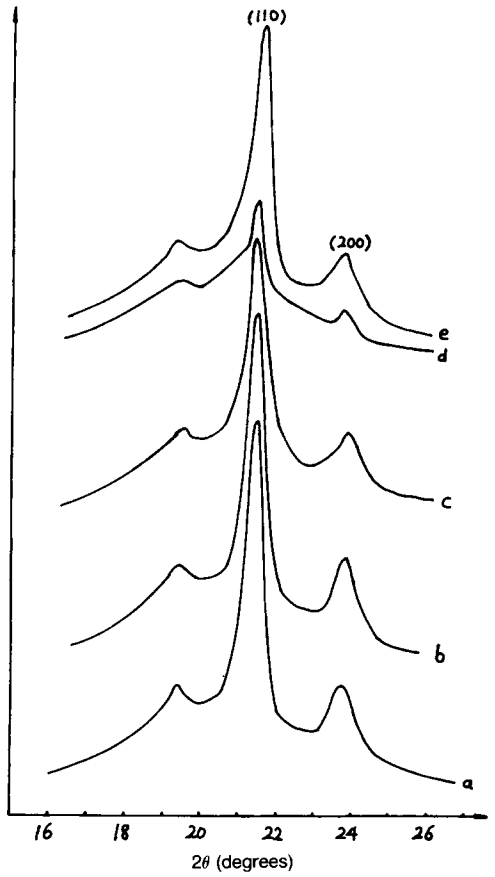

Figure 3 X-ray diffraction patterns of the samples under different doses of γ-ray radiation dose for (a) 0 Mrad, (b) 50 Mrad, (c) 200 Mrad, and (d) 400 Mrad. Electron beam radiation dose for (e) 300 Mrad.

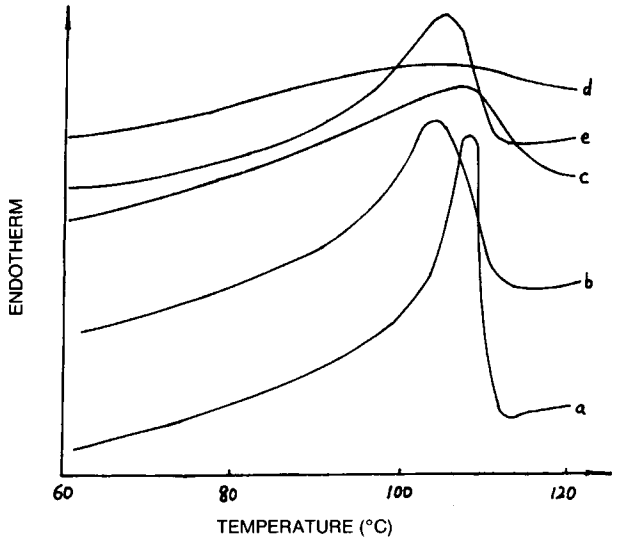

Figure 4 DSC melting endotherms of irradiated samples. γ-Ray radiation dose for (a) 0 Mrad, (b) 50 Mrad, (c) 200 Mrad, and (d) 400 Mrad. Electron beam radiation dose for (e) 300 Mrad.

The increase of L_{hkl} was partially due to the defects formation in the crystal core, making the volume of the crystal expand, and was partially due to the radiation induced degradation of the crosslinked chains, making the mobilities of the chains increase, thus crystallizing them easily.

The apparent decrease of cryatallinity of the 400-Mrad sample as expressed by the area under the crystalline peak in Figure 3(d) is due to the high distortions in its crystals. The crystallinity of the 300-Mrad sample had only a slight decrease compared with that of the 0-Mrad sample because EB irradiation caused little damage in its crystals.

The DSC melting endotherms of different irradiated samples are shown in Figure 4. We can observe that the unirradiated sample has the highest value of melting heat of fusion. With increasing absorbed dose, the endotherm peaks become shorter and broader. This illustrates that crosslinks prevent the perfect folding of polymer chains so that the crystals have more defects, therefore lowering the crystallinity and heat of fusion. In contrast with sample (c) and (d), sample (e) has a relatively narrow DSC peak. This is in agreement with the X-ray diffraction result.

According to two experiments,[1,9] the crystallinity of polyethylene samples fades out at doses above 2,000 Mrad. Under our low radiation doses, the crystallinities of the samples were high enough to guarantee their PTC intensities.

CONCLUSION

γ-Ray irradiated materials have good PTC functions in the dose range of 4–100 Mrad. Beyond that range, the materials have NTC phenomena and bad effects on PTC intensities. In contrast, the materials can endure a dose as high as 300 Mrad by EB.

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REFERENCES

1. A. Keller and G. Ungar, *Radiat. Phys. Chem.*, **22,** 155 (1983).
2. W. Jia and X. Chen, *J. Appl. Polym. Sci.*, **54,** 1219 (1994).
3. R. L. Clough and K. T. Gillen, *Radiat. Phys. Chem.*, **18,** 661 (1981).
4. T. Seguchi, K. Arakawa, M. Ito, N. Hayakawa, and S. Machi, *Radiat. Phys. Chem.*, **21,** 495 (1983).
5. H. Wilski, *Radiat. Phys. Chem.*, **29,** 1 (1987).
6. L. E. Alexander, *X-Ray Diffraction Methods in Polymer Science,* Wiley, New York, 1969, p. 423.
7. B. Wunderlich, *Macromolecular Physics,* Vol. 1, Academic Press, New York and London, 1973, p. 398.
8. A. Wilson, *X-Ray Optics,* Methuen, London, 1949.
9. Y. Luo, G. Wang, Y. Lu, N. Chen, and B. Jiang, *Radiat. Phys. Chem.*, **25,** 359 (1985).

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