11. Radiation Processing (1)

11.1 *Effect of Irradiation on PTC Performances of Carbon Black Filled Polymer Composites

Chen Xinfang, Jia Wentao, Tang Hao and Yang Huali
Institute of Materials Science, Jilin University, Changchun, 130023, China

Li Shuhua
Changchun Institute of Applied Chemistry, Changchun, 130022, China

Abstract The influences of irradiation on Positive Temperature Coefficient (PTC) functions of polymer- carbon black composites are studied systematically, using HDPE, LDPE, PE/EPDM, PE/EEA as polymer matrixes and carbon black as conductive fillers. The results show that under a certain radiation dose, a remarkable improvment of the PTC intensity and the reproducibility of PTC curves of most polymer blends can be achieved,and Negative Temperature Coefficient (NTC) effects are decreased or eliminated. The mechanism of crosslinking structure on improving and stabilizing the PTC functions of polymer blends is also discussed through modern structural analysis methods. In this paper, an interesting and significant phenomenon is discovered. The PTC curve of PE/EPDM/CB composite presents an obvious NTC phenomenon as the dose exceeding 2 MGy.

INTRODUCTION

Polymer composite PTC materials doped with conductive carbon blacks can be used as self- regulating heaters, current limiters and overcurrent protectors, etc.
One fact of great importance in applications of composite PTC materials is their stability under operating conditions. In our earlier work (Yang Huali et al., 1993), the influences of radiation crosslinking on the PTC effects of PE/CB blends have been studied. In this article, the problems on the stability of PTC characteristics of PE/CB, PE/EPDM/CB, PE/EEA/CB blends after radiation crosslinking and the stability mechanism of crosslinking structure on PTC effects are discussed in more detail. We also study the temperature dependence of resistivity of the PTC materials under much higher dose. As the dose exceeds 2MGy, the

NTC effects of PE/EPDM/CB composites have been found after the melting point. This new result is explained reasonably by the mechanism of radiation degradation.

EXPERIMENTS

The structure parameters of polymer matrixes and the specification of carbon black are shown in Tables 1 and 2, respectively. Polymer and carbon black were mixed in a Brabender for 5-6 min., roll- milled for 5-6 min., and compression-molded to about a 1-mm-thick sheet. The mixing and molding temperatures are shown in Table 1.
The samples were irradiated in ^{60}Co- γ-ray at room temperature with a certain dose rate in air. The gel fraction was determined by the method of solvent extraction. The ESR spectra of the irradiated samples were obtained from a Bruker ER 200D EPR.
A digital multimeter was used to measure lower electrical resistivity. When it exceeded $10^8\Omega$, an insulating resistance tester with a programmed temperature controller was used.

Table 1 The Parameters of Polymer Matrixes and Processing Temperature

Polymer	Melting Index (g/10min.)	Density (g/cm^3)	Melting Point (℃)	Processing Temperature	
				Mixing	Molding
HDPE1	1.2	0.954	130.8	150	150
HDPE2	0.2	0.950		150	150
HDPE3	2.0			150	150
LDPE	2.0	0.925	107.1	140	140
EEA	6.0	0.930	89.8	140	140
EPDM	EPT-4050				

Table 2 Physical and Chemical Properties of Carbon Blacks

	Average Size (nm)	Surface Area (m^2/g)	DBP Value (ml/100g)	pH Value
CSF-III	70	230	280	7.0-9.0

RESULTES AND DISCUSSION

The influences of radiation crosslinking on stability of PTC functions

It is clear from Fig.1 and Fig.2 that the stabilities of PTC fuctions of HDPE/CSF and LDPE/EPDM/CSF blends are improved significantly after a certain radiation dose. This can be reflected from two aspects. First, the high reproducibility of polymer blends is obtained undergoing many heating/cooling cycles. Second, the NTC effect is eliminated and the PTC intensity increases.

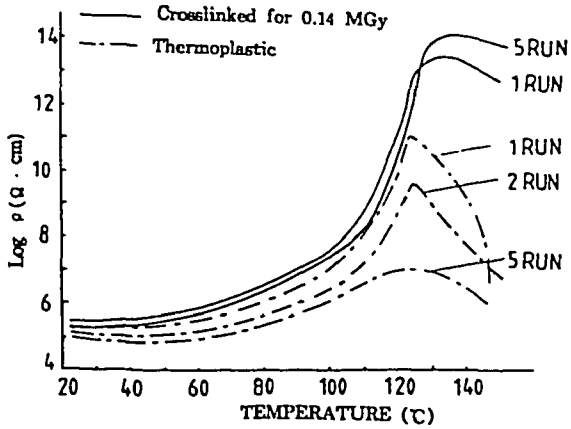

Figure 1 The effect of radiation crosslinking on the PTC intensity and reproducibility of HDPE/CB composite

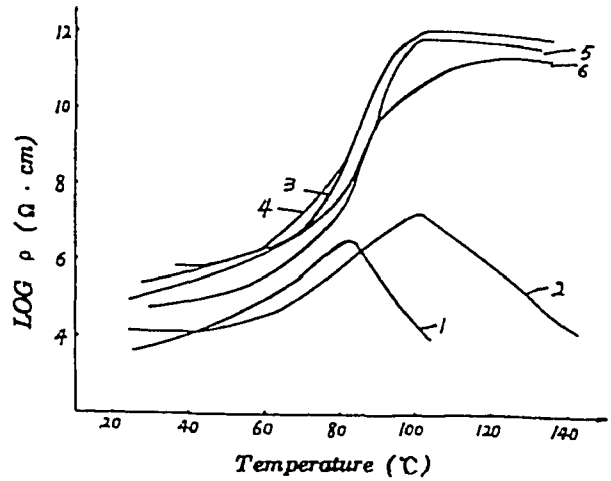

Figure 2 The PTC effect of LDPE/EPDM/CB composite crosslinked for (MGy):(1) 0; (2) 0.01; (3) 0.05 (4) 0.15; (5) 0.5; (6) 0.8

The mechanism of the stability of PTC functions

Though researchers have known earlier that the PTC stability of polymer-CB composite can be improved by radiation croslinking, it has not systematic studies up to date about the micromechanism of how crosslinking structure can affect PTC effects. The authors suggest the crosslinking structure can stabilize the PTC effect of polymer-CB composite from three aspects.

(1) During the croslinking process of linear polymer matrix, CB particles or aggregates participate partly in the crosslinking reactions, thus obviously increase the chemical bindings or physical adsorptions of CB particles on polymer matrix, that is, some CB particles participate directly in the reactions of intermolecular crosslinks, the others agglomerate at the surroundings of these reacted ones, therefore making CB fillers more stable in the polymer networks, and preventing them from reagglomerate at higher temperatures, thus eliminating NTC effects and improving the reversibility of PTC curve.

The experimental results listed below give strong support to this argument.

Table 3 The Effect of Carbon Black on the Gel Content of Polymers

Polymer Matrix (0.14MGy)	*HDPE*			*LDPE*			*EEA*		
CB content (w/w%)	*5*	*10*	*20*	*5*	*10*	*20*	*5*	*10*	*20*
Gel content (%)	*58*	*60*	*70*	*30*	*34*	*42*	*33*	*40*	*67*

Table 3 shows that under the same radiation dose, the gel fractions of three kinds of polymer composites increase with the increase of CB content. It demonstrates that some CB particles participate directly in the intermolecular crosslinking of polymer. This can also be proved by ESR spectra shown in Fig.3. The free radical concentration of HDPE/CSF compound shows considerable decrease compared with that of pure HDPE.

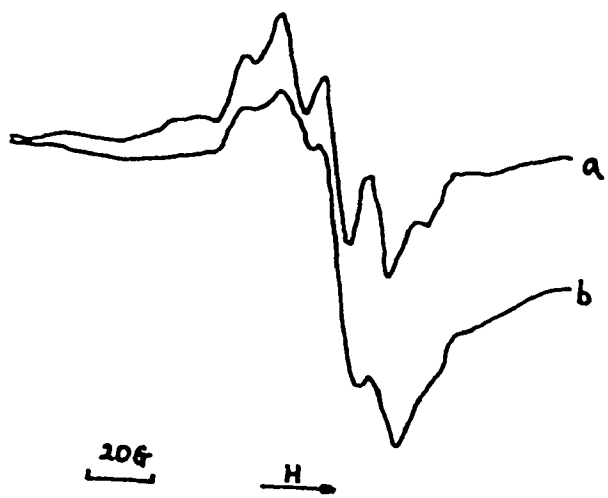

Figure 3 ESR spectra of the samples for crosslinked 0.2 MGy. The weights of the matrixes for all samples were equal. The spectra were obtained 30 min. after irradiation. (a) HDPE; (b) HDPE/CSF-III.

(2) Much more intensive interactions between CB particles and polar polymer segments can be produced due to the hydroxylic, carbonyl or carboxyl groups which may exist at the surfaces of CB particles. So the PTC functions of composite prepared from polar polymer and carbon black are relatively stable. Fig.4 shows the PTC curve of LDPE/EEA/CB composite. All the samples have not NTC effects at temperatures

exceeding melting point. This is due to the intensiveinteractions between the polar groups of CB particles and the ethoxycarbonyl groups of EEA segments. Part CB particles play a role of physical crosslinking bridge through such fairly intensive interactions.

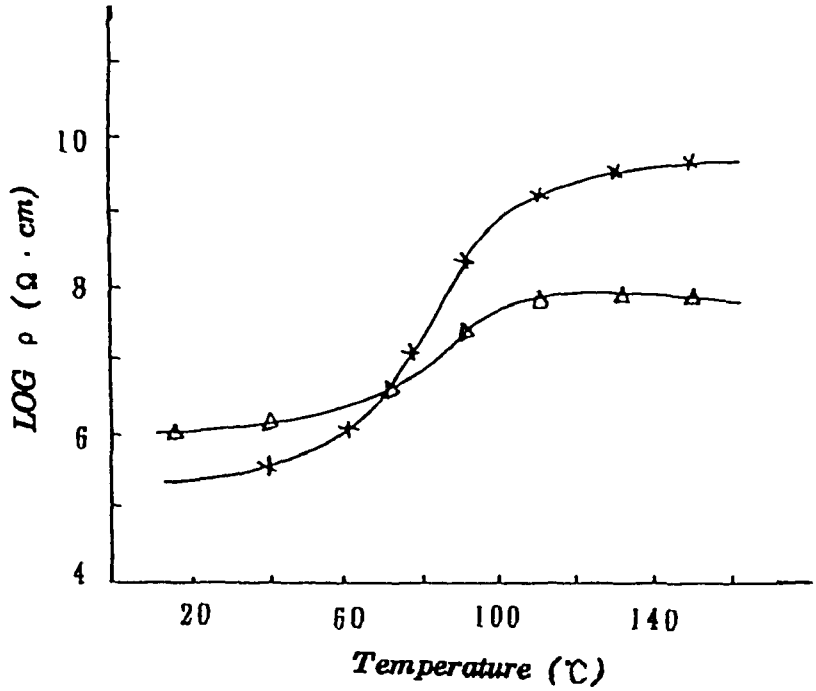

Figure 4 The PTC effect of LDPE/EEA/CSF composite (Δ) thermoplastic; (×) crosslinked for 0.1 MGy

(3) For radiation doses above the critical value for incipient gel formation, the polymeric system breaks into two phases of sol and gel, and the gel fraction increases with the dose. The gel is composed of crosslinked polymers having an infinite tri- dimentional network structure, which no longer melts above the melting temperature of initial linear polymer. Therefore, for the polymer- CB composite subjected to a certain radiation dose, the whole intermolecular movement at high temperatures disappears when the gel fraction exceeds a definite value. For this network system, at the melting temperature region of its initial linear polymers, the relatively stable distribution of CB particles in polymer matrixes remains, and the redistribution or reagglomerate of CB particles can be much weakened or eliminated, resulting in the disappearance of NTC phenomenon and the enhancement of reproducibility. The opinion mentioned above is proved satisfactorily by the experimental results shown in Fig.2.

Effect of Radiation Degradation

It has been observed in Figure 5 that the NTC effects are particularly pronounced in LDPE/EPDM/CB composites irradiated at much larger doses. In the opinion of the authors the reappearance of NTC phenomenon results from oxidative degradation of the main chains of polymer matrixes. Chapiro (Chapiro, 1962) had indicated that when irradiation is carried out in air, some of the polymeric radicals, which would otherwise lead to crosslinking, react with oxygen to form peroxidic structures which eventually decompose and cause oxidative degradation of the main chains.

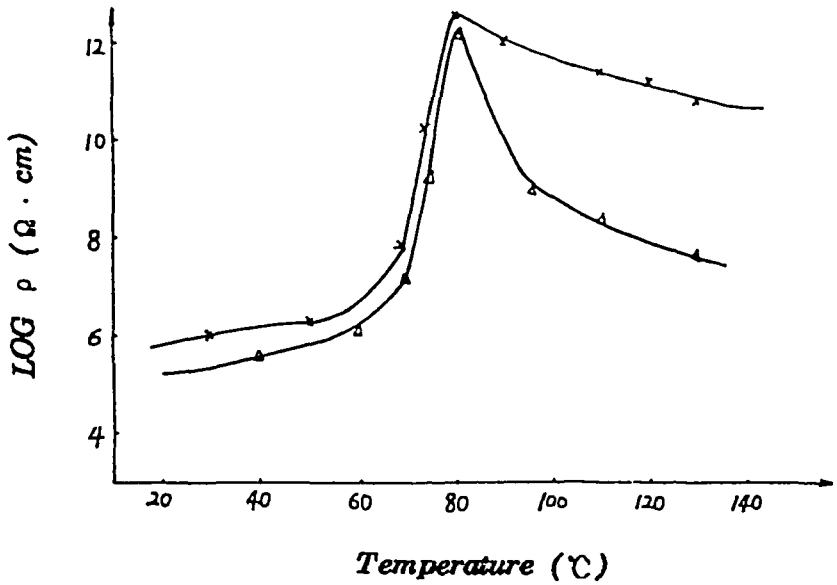

Figure 5 The PTC effect of LDPE/EPDM/CB composite after radiation crosslinking. Crosslinked for:
(×) 2 MGy; (△) 4 MGy.

Because the molecular chains of polymer matrix used contain some structure of polypropylene which can be easily oxidized, the fact that the main chains degradation of LDPE/EPDM polymer matrix occurs under irradiation of the doses higher than 2 MGy is believable. Therefore, the above interpretation on the reproduction of NTC effects of composites under highly radiation dose is reasonable.

REFERENCES

Yang Huali, Tang Hao and Chen Xinfang (1993), Radiat. Phys. Chem., 42 (1-3), 135

Chapiro. A (1962), Radiation Chemistry of Polymeric Systems, P360, John Wiley & Sons, New York, London.

* *The work was supported by National Natural Science Foundation of China*