

Effect of Polymer–Filler Interactions on PTC Behaviors of LDPE/EPDM Blends Filled with Carbon Blacks

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Received 18 February 1997; accepted 17 March 1997

ABSTRACT: The dependence of electrical resistivities on the temperature of different polymer systems (including rubbers and plastic/rubber blends) loaded with carbon blacks (including oxidized and normal carbon blacks) were studied. We found that polymer–carbon black interactions could greatly influence the electrical resistivity and temperature relations of the polymer composites. The polymer blends filled with oxidized carbon black, or the elastomer which has polar functional groups filled with carbon black, have a very weak negative temperature coefficient (NTC) effect, which is due to the strong polymer–filler interactions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1885–1890, 1997

INTRODUCTION

The positive temperature coefficient/negative temperature coefficient (PTC/NTC) phenomena of carbon black filled polymers have drawn our interest for years. In our previous work,¹ we studied the PTC effect of LDPE/EPDM blends filled with carbon blacks. In polymers, the carbon black aggregates are loosely associated in a reversible secondary network held together by van der Waals forces. We assumed that the carbon black network undergoes two processes upon increase in temperature: one is breakdown and the other is reagglomeration. The ultimate PTC behavior of the composite is the competitive result of the two processes. Many factors can influence these processes, such as the properties of fillers and the polymer matrix, filler content, and processing conditions. In this article, the effect of carbon black–polymer (including rubbers, crystalline plastics, and their compounds) interactions were mainly studied. As far as carbon black interactions are concerned, there are many reports on this topic.^{2–6}

Polymer–carbon black interactions include (1) multicontact of polymer chains on to the surface of carbon black (physicosorption), (2) reactions of carbon black with polymers (chemisorption), and (3) mechanical chain entanglements and covalent carbon–carbon crosslinks in the polymer matrix. These interactions will obviously influence the relations between the electrical resistivity of the composites and the temperature.

EXPERIMENTAL

Low-density polyethylene (LDPE) with a melt index of 2.0, ethylene–propylene–diene terpolymer (EPDM), and chlorosulfonated polyethylene (CSPE, 37% chlorine and 1.2% sulfur) were selected as the polymer matrices in this work. The carbon black (CB) was of the CSF3 type obtained from the Changchun Institute of Applied Chemistry. Its average size is 50–70 nm; surface area, 230 m²/g; DBP value, 280 mL/100 g; and pH value, 7–9. One partial carbon black was oxidized by immersing it in nitric acid for 24 h. Nitric acid was then washed away and the oxidized carbon black was dried at 50°C.

The carbon black and polymers were mixed in

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Table I Elemental Analysis

	C%	H%	N%	O%
Normal CB	96.91	0.27	1.60	1.22
Oxidized CB by HNO ₃	88.15	0.27	1.56	10.02

an internal mixer for 5 or 15 min. The masterbatches were then molded under pressure at 160°C for 10 min. The resulting samples were cooled in air and were 1 mm thick.

The volume resistivities of the samples were measured using a digital multimeter and an insulating resistance tester consecutively at progressively elevated temperatures. The heating rate was 5°C/min. The two sides of the samples were bonded with copper foils in order to reduce the contact resistivity.

Elemental analysis of the two types of carbon blacks was carried out on a 240C EA instrument, made by the PE Co., U.S.A. The outcome is listed in Table I. It is shown that the oxygen content of

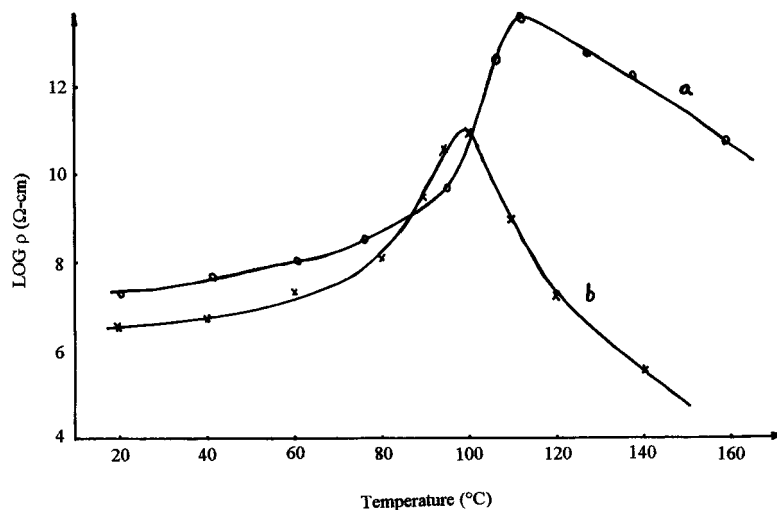


Figure 1 Variations of electrical resistivity versus temperature of LDPE/EPDM blends filled with (X) 14 phr normal CB and (O) 14 phr oxidized CB. The mixing time of the compounds was 5 min.

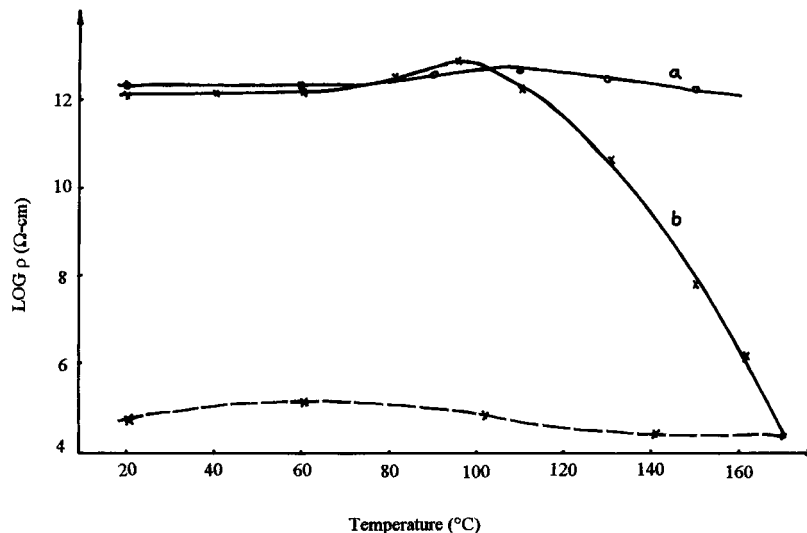
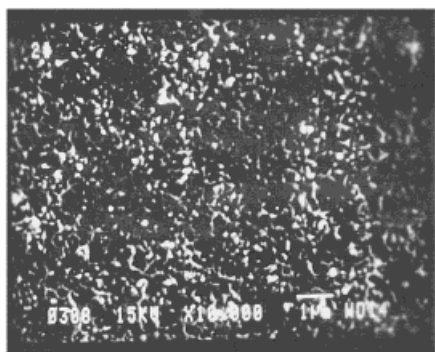
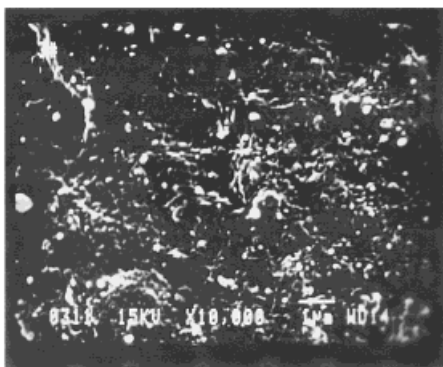


Figure 2 Variations of electrical resistivity versus temperature of LDPE/EPDM blends filled with (X) 14 phr normal CB and (O) 14 phr oxidized CB. The mixing time of the compounds was 15 min.



(a)



(b)

Figure 3 Scanning electron micrograph of LDPE/EPDM blends filled with CB: (a) initial sample; (b) sample after a heating-cooling cycle.

carbon black after oxidizing by nitric acid increases greatly.

Dynamic mechanical analysis was carried out on a DuPont 9900 instrument with a heating rate of 3°C/min. Viscosities were measured at 190°C on a Rheomat 120 made in Switzerland.

RESULTS AND DISCUSSION

Different Types of Carbon Black Fillers in Polymer Blends

The variations of the electrical resistivity with temperature of LDPE/EPDM blends (the proportion is 3 to 1) filled with two types of carbon blacks are shown in Figure 1. The mixing time of the compounds is 5 min. In comparison with a normal carbon black filled compound (curve b), LDPE/EPDM blends filled with oxidized carbon black (curve a) exhibit higher room-temperature re-

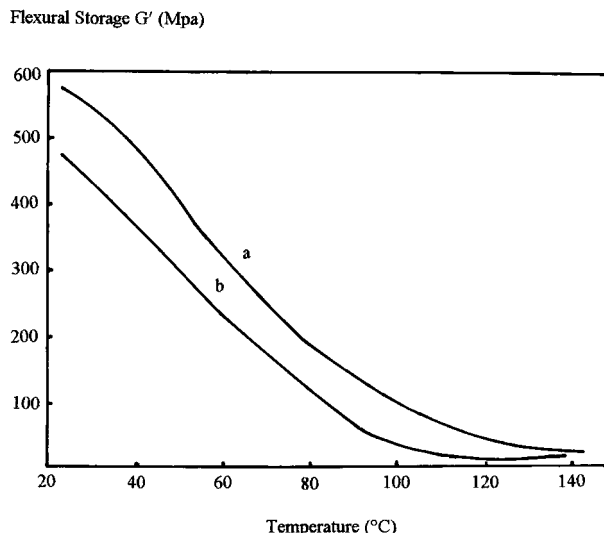


Figure 4 Flexural storage modulus G' versus temperature of LDPE/EPDM blends filled with (a) 14 phr oxidized CB and (b) 14 phr CB.

sistivity due to the reduced conductivity of CB after oxidizing, higher PTC intensity ($\rho_{\max}/\rho_{\text{room}}$), weaker NTC effect (the decrease of resistivity with temperature is slow), and higher PTC/NTC transition temperature. These are mainly attributed to the strong interactions between carbon black and polymer chains. Among the three methods of polymer-filler interactions described above, chemisorption plays a very important role for polymers filled with oxidized carbon blacks. The surface functional groups of CB such as quinones, carboxyls, phenols, and lactones may react with polymer free radicals during mastication,³ fixing the polymer molecules to their surface. Many authors⁷⁻¹² have studied this kind of reaction using the electron spin resonance method. The strong

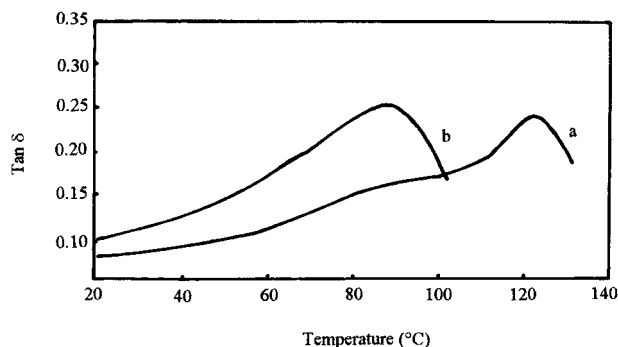


Figure 5 Loss tangent correlation with temperature for two compounds described in Figure 4.

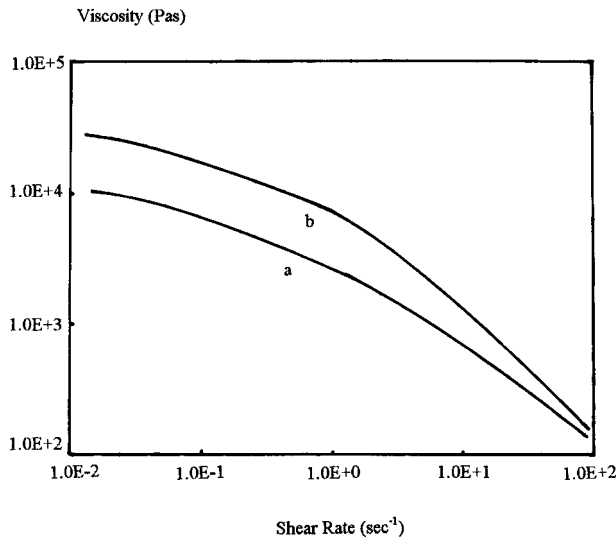


Figure 6 Viscosity versus shear rate of three compounds described in Figure 4.

polymer–filler interactions can partly prevent the flocculation of carbon black aggregates during temperature increase. Therefore, the compound has a higher PTC intensity and a weaker NTC effect (it cannot eliminate it completely).

The restraint of flocculation of carbon black aggregates by polymer–filler bondings can also be explained by another experiment. The mixing time of the samples used in this experiment is 15 min. Their resistivities versus temperature are shown in Figure 2. Because the mixing time of the samples is relatively long, carbon black particles are better dispersed in this case. The network structure of the carbon blacks disappears, thus

giving the samples very high room-temperature resistivities. When the increasing temperature exceeds the melting point of the polymer matrix, the sudden reduced viscosity makes the normal carbon black particles move freely, leading to flocculation or agglomeration. We can see from curve a that the resistivity of polymer blends filled with oxidized carbon black remains almost unchanged, which is due to the strong polymer–filler interactions. The resistivity of the polymer blend filled with normal carbon black (curve b) drops rapidly as the temperature increases above 100°C, due to the agglomeration of CB aggregates. Agglomeration will enlarge the average size of the CB aggregates, and the enlarged CB aggregates will then be preserved as the sample is cooled to room temperature (see dotted line in curve b: the resistivity is almost unchanged as the sample is cooled). The agglomeration of CB aggregates can be demonstrated by the SEM of the sample (shown in Fig. 3). Figure 3(a) represents the CB dispersion of the sample, and 3(b) represents that of the sample after a heating–cooling cycle. The latter shows a larger CB aggregate dispersion.

The flexural storage modulus G' and $\tan \delta$ of the two compounds plotted against temperature are shown in Figures 4 and 5, respectively. The compound filled with oxidized carbon black gives a higher G' and $\tan \delta_{\max}$ appears at higher temperature. The cause is that the strong interaction between polymer and filler increases the strength of the composite. Only at much higher temperature, shown as 120°C, do the reduced polymer–filler interactions and polymer chain slippage contribute to the maximum hysteresis.

The viscosities of the two compounds versus

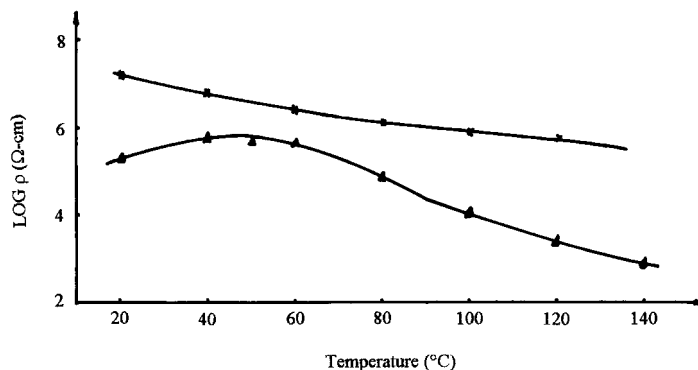


Figure 7 Plots of electrical resistivity against temperature for rubbers filled with carbon blacks: (X) CSPE/30 phr CB; (Δ) EPDM/30 phr CB.

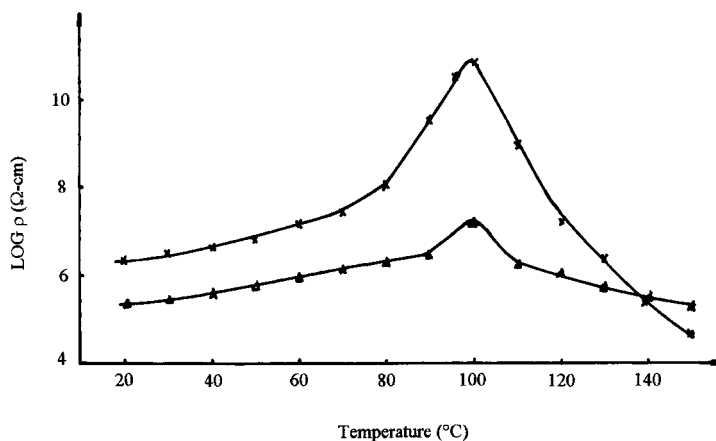


Figure 8 Plots of electrical resistivity against temperature for (X) LDPE/EPDM/14 phr CB and (Δ) LDPE/CSPE/14 phr CB.

shear rate are plotted in Figure 6. It can be seen that the normal carbon black filled compound gives higher viscosity. This indicates that at a very high test temperature (190°C) the strong interactions of interaggregates of normal carbon black make them reform the three-dimensional network structure and therefore enhance the friction resistance of molecular slippage and give the high viscosity of the system.

Carbon Black Filled Rubbers

In this study, two rubber systems CSPE and EPDM were selected, both filled with 30 phr carbon blacks. The plots of electrical resistivity versus temperature of the two compounds are shown in Figure 7. The electrical resistivity of the CSPE/CB compound decreases gradually with temperature increase. For the EPDM/CB compound, the resistivity first increases and then decreases very rapidly.

Roychoudhury et al.¹³ reported the crosslinking of CSPE by carbon black. They postulated two reaction schemes of CSPE crosslinked by the hydroxyl groups on carbon black and concluded that the hydroxyl groups play a major role in the elastomer/filler reaction. The chemical bondings between the CSPE rubber and filler prevent the motions of carbon black as well as rubber chains; therefore, the resistivity does not change much with temperature.

The interaction between EPDM and CB is rather weak; their compound displays a low PTC effect. When LDPE is mixed with EPDM or CSPE

rubber and carbon blacks (the proportion is 3 : 1 : 1), it is quite evident that the LDPE/CSPE/CB blends have a much weaker NTC effect than that of the LDPE/EPDM/CB blends, as shown in Figure 8. The lower PTC intensity of the LDPE/CSPE/CB blends is due to the smaller thermal expansion coefficient of CSPE rubber than that of EPDM rubber.

CONCLUSION

The variations in electrical resistivity of polymer blends filled with carbon blacks at elevated temperatures can be greatly influenced by polymer-carbon black interactions. The strong interactions between polymers and oxidized carbon black improve the PTC intensity and weaken the NTC effect compared to that of normal carbon black filled polymer. Rubbers containing functional groups can also strongly interact with carbon black by chemical reactions. This results in the small change of electrical resistivity with temperature.

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