Effect of Filler Treatment on Temperature Dependence of Resistivity of Carbon-Black-Filled Polymer Blends

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ABSTRACT: Polyblends prove to be able to provide more possibilities for tailoring conductive polymer composites in comparison with individual polymer systems. Accordingly, ethylene-vinyl acetate—low-density polyethylene (EVA-LDPE) filled with carbon black (CB) was prepared in this study as a candidate for positive temperature coefficient (PTC) material. In consideration of the fact that CB distribution plays the leading role in controlling a composite's conduction behavior, chemical treatment of CB was applied to reveal its influence on percolation and the PTC effect. It was found that titanate coupling agent treatment facilitated sufficient distribution of CB in LDPE phase, leading to lower resistivity and a squarer PTC curve. Composites filled with nitric-acid-treated CB exhibited specific temperature dependence of resistivity as a result of the heterogeneous dispersion of CB at the interface of EVA-LDPE, which might provide the materials with a new function. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 489-494, 1999

Key words: carbon black; polymer blends; electrical conductive composites; chemical treatment; positive temperature coefficient

INTRODUCTION

Inherently insulating polymers can be made conductive with the incorporation of electrically conducting fillers, which is usually attributed to percolation effect.¹ One of the desired properties of these conductive polymer composites lies in its positive temperature coefficient (PTC) behavior characterized by a drastic rise in resistivity when the temperature approaches the melting point of the matrix.^{2–4} According to such a temperatureactivated switch feature for electricity, polymerbased self-regulating heaters, sensors, and microswitches, coupled with excellent formability, moldability, and flexibility, can be manufactured.

In order to achieve a balanced property profile and to improve performance reproducibility, polymer blends instead of individual polymer are employed as matrix resin in PTC-type composites,⁵ which brings about new possibilities for material design because of the effects of double percolation and two-step percolation (the latter describes the loading dependence of conductive polyblends' resistivity consisting of two subsequent Z-shaped transitions and flattening midway at a higher conductive filler loading region prior to the

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achievement of equilibrium resistivity that approaches the value of filler itself.⁶ Appearance of such a terrace-like part on a percolation curve provides a wider processing window for composite manufacturing.). It is believed that effective concentration of filler in the filler-rich phase, structural continuity, and melting behavior of this phase determine the PTC effect of conductive polyblends. By changing thermodynamic and kinetic factors, including interfacial energy, melt viscosity matching, blending ratio, melt mixing time, and sequence of blending, as well as filler concentration, the composites' PTC performance can be tailored. In fact, it can be found that all these factors are rooted in the filler distribution. Therefore, surface treatment of conductive filler, which might affect the ultimate dispersion status of the filler,⁷ should be an effective way to control composite properties.

The present work is focused on the effect of filler chemical treatment on the temperature dependence of resistivity of carbon-black-(CB)-filled ethylene-vinyl acetate—low-density polyethylene (EVA-LDPE) composites in hopes of revealing the fundamentals of property optimization.

EXPERIMENTAL

Low-density polyethylene (LDPE) and ethylenevinyl acetate (EVA) with an identical melting flow index of 2.0 g/10 min were employed as matrix resins in this work. An electrically conductivegrade CB was used as a conductive filler.

Nitric acid and titanate coupling agent treatments for CB were carried out as follows, respectively. Firstly, CB was mixed with nitric acid solution of certain concentration, then the solution was refluxed for purposes of oxidation. The CB slurry was thoroughly washed with distilled water after filtration to ensure that all traces of the acid were removed. Finally, the treated CB was allowed to air-oven-dry before use. On the other hand, titanate coupling agent was added to CB as petroleum ether solution under high-speed stirring while being heated by boiling water. The amount of the coupling agent was controlled to give a constant fraction of titanate on the filler basis. The liquid was then removed under vacuum in an oven.

Polymers and CB with different proportions were melt mixed in a laboratory size Brabender plasticorder model XB20-80 under standard conditions of the experiment in each case at 160°C and 20 rpm for 15 min. CB was added when the polymers were melted. Having been removed and granulated, the blends with pre-embedded electrodes were compression-molded at 140°C, and then cooled down in air to room temperature, making sheets about $65 \times 45 \times 3 \text{ mm}^3$ in size. The sheet samples were rested overnight to release residual thermal stress before the subsequent measurements.

All the composite samples were crosslinked to eliminate a negative temperature coefficient phenomenon by irradiating the plaques with a 60 Co γ -ray source in air at room temperature. The radiation dose rate was 0.3 Mrad/h, and the radiation dose was 25 Mrad.

Volume resistivity was measured with a fourlead system. The temperature dependence of composites resistivity was measured by heating the samples at a rate of 3°C/min and cooling with air in an oven. All values of resistivity reported in this work are values of dc resistivity.

The contact angle of CB was measured by means of filler column method at 20°C using *n*decane as the spreading liquid based on the relationship between wicking height and time of various wetting liquids proposed by Washburn.⁸ Surface-free energies of CB–polymer systems were then calculated by using the harmonic-mean method and the geometric-mean method.⁹

RESULTS AND DISCUSSION

Percolation Behavior

Figure 1 gives the dependence of room temperature resistivity on CB content for different CB treatments. It can be seen that there are shifts for the percolation curves of both CB-LDPE and CB-EVA-LDPE composites toward the lower loading side when CB was treated by a titanate coupling agent. According to the previous electron spectroscopy for chemical analysis (ESCA) and rheological study of the CB–LDPE system,⁷ titanate treatment was found to be able to reduce carboxyl groups fraction fixed on CB surface, which lowered the contact resistance of CB aggregates as a result, and to enhance melt flowability of the composite due to better wettability of the coupling agent to the filler. That is, the coupling agent increases the probability of electrical network formation throughout the matrix and decreases the percolation threshold. A comparison between Figure 1(a) and (b) reveals that in the blends of



Figure 1 Typical dependence of room temperature resistivity ρ_{RT} on CB content: (a) CB–LDPE; (b) CB–EVA–LDPE (EVA–LDPE = 20/80).

EVA–LDPE, titanate-treated CB performs in a manner similar to the case of CB–LDPE,⁷ and the majority of the treated CB was still distributed in LDPE phase as the untreated version.⁵

Surprisingly, nitric acid treatment led to opposite trends of variation in the percolation behavior of CB-LDPE and CB-EVA-LDPE (Fig. 1). As evidenced in Yu et al.,⁷ the carboxyl content contained in nitric-acid-treated CB was increased, which inevitably increased the intrinsic resistance of CB and improved filler-matrix interaction, leading to higher resistivity of CB-LDPE composite, as compared with the original CBfilled LDPE at the same filler concentration [Fig. 1(a)]. With respect to the result shown in Figure 1(b), however, the percolation threshold of nitricacid-treated CB-filled EVA-LDPE is 1.24 wt % lower than the untreated version, suggesting nitric acid treatment of CB exerted different influence on composite performance due to the addition of EVA. Evidently, this abnormal phenomenon should be a reflection of the heterogeneous characteristics of CB distribution in the blends.



Figure 2 Effect of nitric acid treatment of CB on composites' room temperature resistivity ρ_{RT} versus CB content.

From Figure 2, it can be seen that the percolation threshold of nitric-acid-treated CB-filled EVA–LDPE is even lower than the value of the dotted curve calculated on the assumption that CB was completely dispersed in the LDPE phase in analogy to the situation of untreated CB-filled EVA–LDPE.⁵ In other words, the higher conductivity of the present composites manifests the fact that the oxidized CB were not fully distributed in LDPE.

In order to reveal the mechanism involved, surface properties of CB–EVA–LDPE system should be analyzed (Tables I and II). The data listed in Table II show that both the harmonic-mean method and the geometric-mean method give the same trend of variation in interfacial-free energies as a function of material couples. Therefore, the following discussion will proceed on the basis of the results from the former method.

Having been treated with titanate coupling agent, the interfacial free energy $\gamma_{CB-LDPE}$ de-

Table ISurface-Free Energies (γ) and TheirComponents at 160°C

Samples	γ (mJ/m ²)	γ^d (mJ/m ²)	γ^p (mJ/m ²)
LDPE	25.9	25.9	0
EVA	26.6	25.0	1.6
CB (untreated)	42.2	41.9	0.3
CB (titanate-treated)	40.7	40.7	0
CB (nitric-acid-treated)	44.0	41.5	2.5

 $\gamma = \gamma^d + \gamma^p$, γ^d : dispersion component. γ^p : polar component. The γ values of LDPE and EVA at 160°C were obtained by using the relation of temperature dependence: $-d\gamma/dT = 0.067$ and 0.054, respectively.

Substances		$\gamma_{12} (mJ/m^2)$		
1	2	Harmonic-mean method	Geometric-mean method	
LDPE	CB (untreated)	4.1	2.2	
LDPE	CB (nitric-acid-treated)	6.1	4.3	
LDPE	CB (titanate-treated)	3.3	1.7	
EVA	CB (untreated)	5.2	2.7	
EVA	CB (nitric-acid-treated)	4.3	2.2	
EVA	CB (titanate-treated)	5.4	3.5	
LDPE	EVA	1.6	1.6	

Table II Interfacial-Free Energies (γ_{12}) at 160°C

creased, but $\gamma_{\rm CB-EVA}$ increased (Table II), indicating that $\gamma_{\rm CB-LDPE}$ became much lower than $\gamma_{\rm CB-}$ EVA in comparison with the untreated version. As a result, CB was more sufficiently dispersed in LDPE because of this favorable thermodynamic condition, and the composite exhibits better conductivity. When CB was treated by nitric acid, Table II indicates that there is a remarkable increase in $\gamma_{\rm CB-LDPE}$ and a decrease in $\gamma_{\rm CB-EVA}$ so that $\gamma_{\rm CB-LDPE} > \gamma_{\rm CB-EVA}$. The affinity of nitricacid-treated CB for EVA surpasses that for LDPE. In consideration of the fact that EVA acts



Figure 3 (a) Typical temperature dependence of resistivity ρ of nitric-acid-treated CB–EVA–LDPE; (b) typical DSC heating traces of CB–EVA–LDPE at different polymer blending ratios.

as the dispersed phase in the blends at the current blending ratio of 20/80 and has a higher melt viscosity (the apparent viscosity of LDPE and EVA at current processing conditions are 1156 and 1210 Pa s, respectively¹⁰), the competition between the thermodynamic and kinetic factors brought about a preferential distribution of CB at the interface of EVA-LDPE and/or in EVA phase as well.⁶ Obviously, electrical paths at the interface of two polymers are more effective than in the bulk,¹¹ leading to a shift of the percolation curve toward low filler content regime (Fig. 1). Filler concentration and arrangement, rather than resistivity of the filler (that became higher after nitric acid treatment), make a dominate contribution to the composite conduction in this case.

Temperature Dependence of Resistivity

Electrical resistivity of the composite consisting of nitric-acid-treated CB-filled EVA–LDPE is shown in Figure 3(a) as a function of temperature.



Figure 4 Schematic drawing of conventional PTC behavior.

Since CB contents of these composites exceed the upper limit of percolation region, stable PTC phenomena can be observed. Both PTC intensity (defined as the ratio of the maximum resistivity to the room temperature resistivity calculated from the temperature dependence of resistivity) and room temperature resistivity decrease with a rise in CB content, as usual.⁷ However, a careful analysis of the shape of the curves illustrated in Figure 3(a) reveals that they are different from the conventional PTC curves reported in literature (Fig. 4), that is, the composite resistivity increases with increasing temperature first, but slightly decreases after a maximum, and then keeps on increasing again. Clearly, this should be attributed to the thermal response of aforesaid uneven distribution of treated CB in the matrix because the interface of the polymers occupying a rather small volume fraction are much more sensitive to temperature than bulk.

When temperature approaches to the melting point of EVA [Fig. 3(b)], conduction networks formed by CB located at the polymers' interface are damaged due to partial melting of EVA crystallites, and, hence, composite resistivity increases drastically. The improved flowability of matrix resin makes CB reaggregate with a further rise in temperature, resulting in limited recovery of the conducting paths. As temperature keeps on increasing, the crystalline region of LDPE phase begins to melt. The newly established conducting paths in the interface and those already existing in LDPE are broken down. Composite resistivity increases again. Since CB aggregates are restricted within the amorphous phase by crosslinking processing and the interface of EVA–LDPE fully expands due to the subsequent melting of crystallites of EVA and LDPE, the damaged networks at the interface could not be recovered, and composite resistivity continues to increase with a rise in temperature.

In the case of higher CB loading, 19 wt %, for example, the influence of EVA melting is not highlighted, as expected in accordance with the regularity that the PTC effect is an inverse measure of conducting filler content, so that melting of LDPE crystallites becomes significant (Fig. 3).

The above discussion can be supported by the effect of blending sequence shown in Figure 5.⁵ It has been recognized that CB is selectively dispersed in LDPE phase in the case of (LDPE + CB) + EVA but transfers from EVA to LDPE for (EVA + CB) + LDPE. Because the present melt mixing



Figure 5 Comparison of temperature dependence of resistivity of CB (untreated)–EVA–LDPE composites as a function of sequence of ingredients' incorporation (CB content = 18 wt %; EVA–LDPE = 20/80). (EVA + LDPE) + CB: addition of CB to the polymer blends. (CB + LDPE) + EVA: CB compounding with LDPE followed by EVA addition. (CB + EVA) + LDPE: CB compounding with EVA followed by LDPE addition. (Specimens appearing in other figures of this article were prepared according to the first sequence.)

time (15 min) is not sufficient for a complete redistribution of CB, a certain amount of CB may stay at the interface of EVA–LDPE, and the corresponding plot of resistivity against temperature has an appearance similar to the curves in Figure 3(a). With respect to (LDPE + EVA) + CB, its turning point on the PTC curve is around 80°C, which is close to the value of (EVA + CB) + LDPE but 10°C lower than that of (LDPE + CB) + EVA, reflecting the influence of EVA and the existence of CB at EVA–LDPE interface.

The influence of different CB treatments on PTC behavior of the composites are summarized in Figure 6, which factually reflects the difference in heterogeneous CB distribution. From the practical point of view, the more square a PTC curve, the better the switching effect. Evidently, titanate coupling agent ensures sufficient distribution of CB in LDPE and provides the composite with the squarest curve in a manner similar to (LDPE + CB) + EVA (Fig. 5). In addition, PTC intensity of titanate-treated CB-filled EVA-LDPE achieves the order of magnitude of 10⁵ at a CB content 3 wt % lower than that needed for CB-LDPE.^{5,7} Of course, the ever-increasing PTC curve shape offered by nitric acid treatment of CB has the outstanding advantage of overcurrent protection, being superior to conventional ones, as shown in Figure 4.



Figure 6 Comparison of temperature dependence of resistivity of CB–EVA–LDPE composites as a function of CB treatment (CB content = 15 wt %; EVA–LDPE = 20/80).

CONCLUSION

Filler surface treatment is an effective way to tailor performance of polyblend-based conductive composite. Unlike the case of CB–LDPE, both the titanate coupling agent and nitric acid can reduce the percolation threshold and result in a lower room temperature resistivity of CB–EVA–LDPE. Besides, the curve shape of the temperature dependence of resistivity is a function of filler treatment and content of the treated filler. A PTC curve with ever-increasing characteristics can be obtained by using nitric-acid-treated CB.

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