

# Carbon-Black-Filled Polyolefine as a Positive Temperature Coefficient Material: Effect of Composition, Processing, and Filler Treatment

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**ABSTRACT:** Polymer-based positive temperature coefficient (PTC) composites are of special interest because they have great potential in temperature-sensitive devices. To obtain a reproducible PTC composite with acceptable PTC intensity, effect of conductive filler content, processing conditions and filler treatment with nitric acid, and titanate coupling agents on room temperature resistivity and PTC intensity of carbon-black-filled low-density polyethylene composites have been described and discussed herein. The results showed that filler arrangement is a key factor influencing the ultimate material performance, which can be tailored in various ways. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 559–566, 1998

**Key words:** carbon black; polyethylene; electrical resistivity; PTC effect; processing

## INTRODUCTION

It has been known that carbon-black (CB)-filled semicrystalline polymers exhibit both percolation phenomenon<sup>1–4</sup> and specific temperature dependence of resistivity.<sup>5–7</sup> The former makes the materials have a wide range of conductivity from insulator to semiconductor, depending on CB concentration. The latter is characterized by either positive temperature coefficient (PTC) effect or negative temperature coefficient. Many models have been proposed for explaining the mechanisms involved in both PTC and negative temper-

ature coefficient phenomena, such as thermal expansion,<sup>8</sup> electron tunneling,<sup>9–11</sup> thermal fluctuation-induced tunneling,<sup>12</sup> cooperative effect of changes in crystallinity and volume expansion,<sup>5</sup> and double percolation.<sup>13,14</sup>

For a polymer-based PTC material of practical value, its volume resistivity increases remarkably by several orders of magnitude when temperature approaches to the melting point of matrix resin. Owing to the commercial significance of such a temperature-activated switch feature for electricity, a composite of this kind plays an increasing role in the polymer production community and serves as self-regulating heaters, self-resetting overcurrent protection elements, microswitches, sensors, etc., with the advantages of excellent formability, moldability, light weight, and flexibility over the conventional inorganic PTC materials.

However, PTC composites suffer from some drawbacks, including unstable electrical repro-

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**Table I** Nomenclature and Characteristics of the Materials Used

Materials	Specifications
LDPE	Density: 0.912 g cm <sup>-3</sup> MFI: 2.0 g 10 min <sup>-1</sup> Melting point: 108°C
Ethylene–vinyl acetate copolymer	VA content: 10–30 wt % Density: 0.930–0.980 g cm <sup>-3</sup> MFI: 2.0–8.0 g 10 min <sup>-1</sup> Melting point: 90–95°C
Conductive CB	Average particle size: 22–24 nm Surface area: 150 ± 5 m <sup>2</sup> g <sup>-1</sup> DBP value: 125 ± 10 mL 100 g <sup>-1</sup> Volatile content: ≤2 wt % True density: 1.90 g cm <sup>-3</sup>
Titanate coupling agent	TC-114 (KR-38S) TM-27 TM-931

MFI, melt flow index; VA, vinyl acetate; DBP, dibutyl phthalate.

ducibility due to irregular structure changes upon heating/cooling cycles during usage, which gradually raises composites resistivity and lower the output power and service life as well. Because composite performance is mostly dominated by starting materials and processing conditions involved in manufacturing,<sup>15,16</sup> effect of CB content, melt mixing conditions, and CB chemical treatment on both room temperature resistivity and PTC characteristics were investigated in the present work by using CB-filled low-density polyethylene (LDPE) composite as model material, in hopes of revealing the fundamentals of property optimization.

## EXPERIMENTAL

### Materials

Conductive CB was obtained from Zigong Institute of Carbon Black, China. Both LDPE and ethylene–vinyl acetate copolymer, the matrix resins for the composites, were supplied by Yanshan Petrochemical Co., China, and Beijing Organic Chemical Factory, China, respectively. Titanate coupling agent was supplied by Nanjing Shuguan Chemical Factory, China. Table I lists the specifications and identification of these materials.

### Treatment of CB

#### Nitric Acid Treatment

First, CB was mixed with nitric acid solution of certain concentration, and 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.

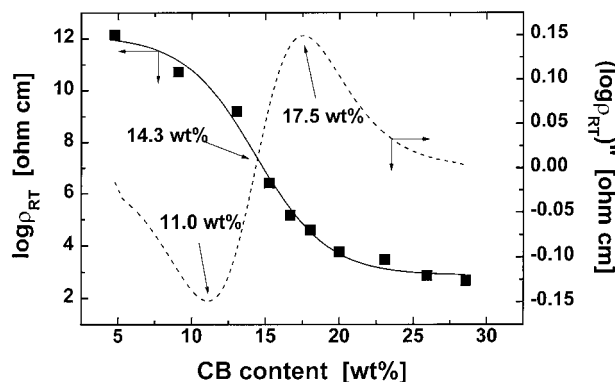
#### Coupling Agents Treatment

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.

#### Sample Preparation

Polymers and CB with different proportions were melt-mixed in a laboratory-size Brabender plastimeter 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 × 45 × 3 mm<sup>3</sup> in size. Sheet samples were rested overnight to release residual thermal stress before the subsequent measurements.

Some of the composite samples were crosslinked by irradiating the plaques with a <sup>60</sup>Co



**Figure 1** Dependence of logarithmic room temperature resistivity  $\log \rho_{RT}$  and its second derivation ( $\log \rho_{RT}'$ ) of CB/LDPE composites on CB content.

$\gamma$ -ray source in air at room temperature. The radiation dose rate was  $0.3 \text{ Mrad h}^{-1}$ , and the radiation dose lay in the range of 10–30 Mrad.

### Characterization

Melt rheological measurements were performed on a piston-type capillary rheometer (Goettfert viscotester model 2002) over a wide range of shear rates ( $11.52\text{--}2880 \text{ s}^{-1}$ ) at  $160^\circ\text{C}$ . The testing samples ( $\sim 20 \text{ g}$ ) were charged into the barrel and preheated for 4 min, and then extruded at a series of piston rates. The capillary diameter was always 1 mm, and the length-to-diameter ratio was 30; therefore, data were not corrected by Bagley. Filler volume fractions at  $160^\circ\text{C}$  were evaluated from the specific weights of the components. Taking account of a thermal expansion coefficient of  $10 \times 10^{-5} \text{ cm}^3/\text{C}$ ,<sup>17</sup>  $1.90 \text{ g cm}^{-3}$  was calculated for CB and  $0.78 \text{ g cm}^{-3}$  was deduced from literature result for LDPE.<sup>10</sup>

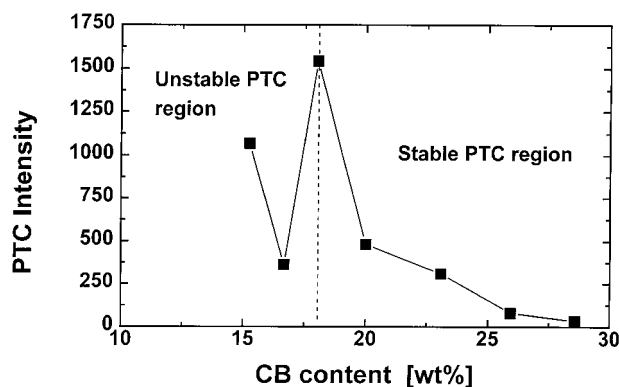
Room temperature volume resistivity was measured with a four-lead system. The temperature dependence of composites resistivity was measured by heating the samples at a rate of  $3^\circ\text{C min}^{-1}$  and cooling with air in an oven. All values of resistivity reported in this work are values of direct current resistivity.

Electron spectroscopy for chemical analysis (ESCA) measurements were conducted with a Vacuum Generators Escalab MK-II using an  $\text{MgK}_\alpha$  X-ray source under a vacuum of  $10^{-8} \text{ Pa}$ . The binding energy was calibrated by means of gold  $4f_{7/2}$  as the internal standard, and quantitative analysis of the surface elements was conducted by taking account of the cross-section and the sensitivity factor.

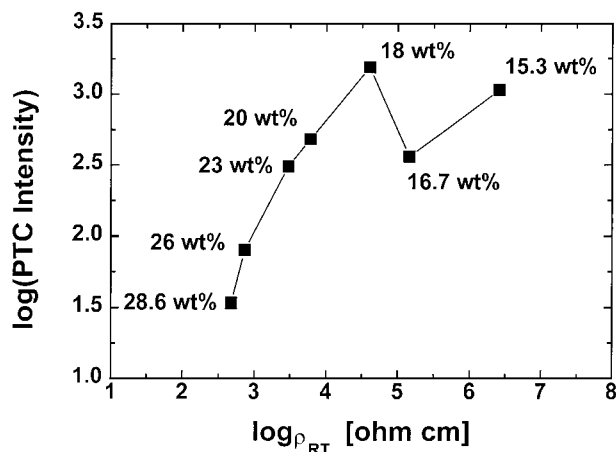
## RESULTS AND DISCUSSION

### Effect of CB Content

Figure 1 shows the composites resistivity as a function of filler content measured at room temperature. To clearly demonstrate the drastic changes in the composite's conductivity, the second derivation of electrical resistivity with respect to CB content is also illustrated, from which the percolation region from 11.0 to 17.5 wt % of CB can be determined, as well as the critical threshold  $\phi_c$  of 14.3 wt %. Accordingly, the PTC intensity, which quantitatively characterizes PTC effect and is defined as the ratio of the maximum resistivity to the room temperature resistivity calculated from the temperature dependence of composite resistivity, is plotted against CB content in Figure 2. Evidently, the highest PTC intensity appears at 18 wt % of CB content. By comparing Figures 1 and 2, it can be concluded that: (1) when CB loading was higher than the upper limit of the percolation region, the CB content dependence of PTC intensity behaved in a similar way to that of resistivity (i.e., the more CB was incorporated, the lower PTC intensity and electrical resistivity, because more and more continuous electric paths throughout matrix had already formed); and (2) PTC effect became irregular when CB content approached the critical fraction so that the corresponding PTC intensity varied disorderly with CB content, which differs from the conventional expectation that PTC intensity increases with decreasing conductive filler loading [like item (1)] and exhibits maximum near the percolation threshold. The metastable nature of the conductive networks established



**Figure 2** PTC intensity of CB/LDPE composites versus CB content.



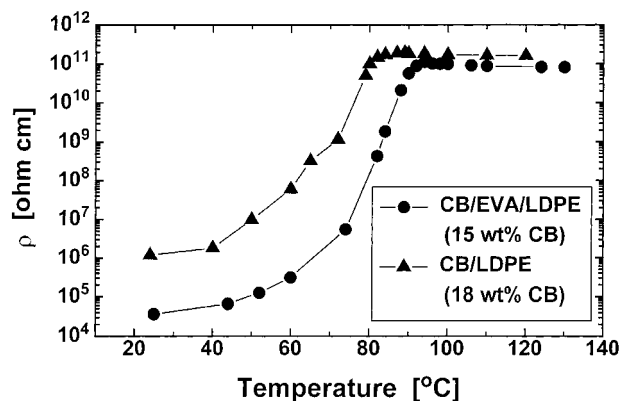
**Figure 3** Plot of PTC intensity against logarithmic room temperature resistivity  $\log \rho_{RT}$  of CB/LDPE composites.

around critical filler loading in the composites should be responsible for the abnormal phenomenon.

Therefore, CB fraction of a reproducible PTC-type composite with acceptable PTC effect should exceed the previously described percolation region (Figure 2). In the case of higher CB content, however, composite's PTC intensity could not be unconditionally raised for purposes of preventing the composite from overheating, while maintaining a relatively low room temperature resistivity so as to ensure sufficient electrothermal output (Figure 3). To solve the problem, polymer blends instead of monopolymer should be used as matrix resin, in which CB might be selectively distributed in one of the blending components and achieve sufficient conductivity at relatively low fraction on the blends basis. Figure 4 shows an example of CB-filled ethylene-vinyl acetate/LDPE blends. Its room temperature resistivity is more than one order lower than that of CB/LDPE, whereas the two composites have similar maximum resistivity between 80 and 90°C. More details related to the effect of polymer blending on PTC behavior will be reported in subsequent articles.

#### Effect of Mixing Time

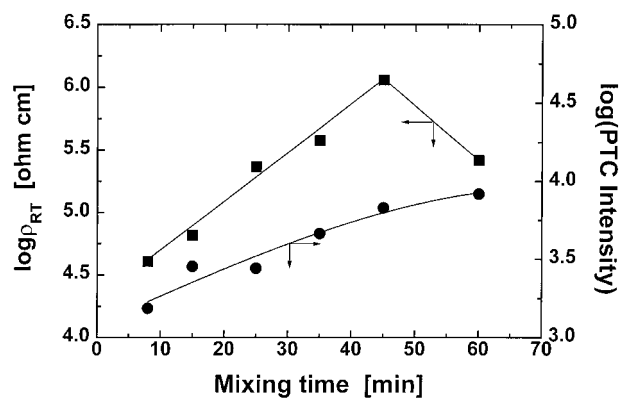
The effect of melt mixing time on room temperature resistivity,  $\rho_{RT}$ , and PTC intensity of the composites is shown in Figure 5. Both  $\rho_{RT}$  and PTC intensity increase with mixing time, but a turning point appears in the  $\rho_{RT}$  curve around 45



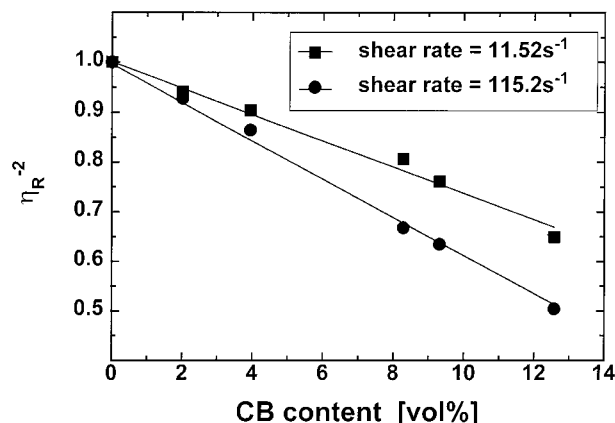
**Figure 4** Temperature dependence of resistivity of CB/LDPE and CB/ethylene-vinyl acetate (EVA)/LDPE composites.

min, which differs from the result of Mather and Thomas.<sup>15</sup>

To explain the phenomena, maximum volume fraction of filler,  $\phi_M$ , is introduced. It is defined as the filler volume fraction of a rigid system with an infinite viscosity, in which all the fillers are arranged in such a way that the interfiller spaces are completely filled with matrix.  $\phi_M$  not only depends on the packing mode, but also varies with filler shape, size distribution, and filler wetting by matrix. Hence,  $\phi_M$  can be used as a gross parameter to characterize morphology and dispersion of CB particles in composites, and CB-CB or CB-polymer interactions.<sup>17,18</sup> From the practical point of view,  $\phi_M$  is correlated to melt rheological measurements as described by the Quemada relationship<sup>19</sup>:



**Figure 5** Typical plots of room temperature resistivity and PTC intensity against mixing time of CB/LDPE composites (CB content = 18 wt %).



**Figure 6** Typical plots of relative viscosity against CB content of CB/LDPE composites (mixing time = 8 min).

$$\eta_R = \eta_B / \eta_P = (1 - \phi_f / \phi_M)^{-1/2} \quad (1)$$

where  $\eta_R$  denotes relative melt viscosity, and  $\eta_B$  and  $\eta_P$  are apparent melt viscosity of filled systems and neat polymer, respectively.  $\phi_f$  denotes filler volume fraction.

Returning to the present composite system, Figure 6 gives the inversed square of relative melt viscosity as a function of CB volume fraction at constant shear rates, from which the  $\phi_M$  values can be calculated in accordance with eq. (1) (Table II).

Like the resistivity curve in Figure 5, Table II indicates that  $\phi_M$  increases as mixing time increases up to 45 min, but decreases in the case of longer mixing time. These results confirm that  $\phi_M$  is directly related to composite conductivity, or in other words, filler arrangement plays a leading role in controlling ultimate material property.<sup>2</sup> Usually, shearing could break CB agglomerates into a few larger fragments at the early stage of dispersion, which is followed by a gradual erosion of small aggregates being continuously detached from the outer surface of these fragments throughout the whole dispersion process.<sup>20</sup> As a result, shear mixing led to (1) smaller size of CB, enhancing the formation probability of conductive networks in favor of lowering composite resistivity, compared with larger particles in the case of the same filler content and arrangement<sup>2</sup>; (2) higher dispersion homogeneity of CB, isolating more fillers from one another and decreasing the apparent melt viscosity; and (3) worse conduction performance of CB due to structure breakdown.

Composite resistivity is the result of competition between these effects. It is believed that the latter two dominated when mixing time was  $\leq 45$  min (Fig. 5, Table II).

On the other hand, slight oxidation cross-linking or branching of matrix resin might take place due to the adsorbed oxygen in the course of prolonged mixing, which could improve CB–polyethylene interaction, so that LDPE chains permeated into the aggregates of CB. Consequently, the size of flowing unit the system increased, and  $\phi_M$  decreased at the mixing time of 60 min (Table II). The well-separated CB partially coagulated again in the melt, and the resistivity of the resultant composite became lower because of such a non-uniform filler arrangement.

With respect to the influence of mixing time on the PTC effect, both interaggregate separation of CB and improvement of filler–matrix bonding facilitate the drastic increase in resistivity around the melting point of LDPE,<sup>21</sup> which accounts for a continuous increase in PTC intensity with a rise in mixing time. Again, Figure 5 gives an example that enables processing condition to be selected for proper conductive performance.

### Effect of CB Treatments

Effects of CB treatment are summarized in Table III. In comparison with the composite filled by untreated CB, the composites' performance exhibits different tendencies of variation with treatment methods: (1) there is a remarkable increase in  $\rho_{RT}$ , but a decrease in  $\phi_M$  due to nitric acid; (2) there is a slight decrease in  $\rho_{RT}$  and increase in  $\phi_M$  due to titanate coupling agents of TC-114 and TM-27; and (3) both  $\rho_{RT}$  and  $\phi_M$  increase due to titanate coupling agent of TC-931.

**Table II**  $\phi_M$  Values of CB/LDPE Composites Deduced from the Quemada Relationship<sup>19</sup> as a Function of Mixing Time

Mixing Time (min)	$\eta_B$ (Pa s)	$\phi_M$
8	4081	0.250
15	4061	0.255
35	3993	0.275
45	3903	0.308
60	3914	0.303

Mixing temperature: 160°C; shear rate: 115.2 s<sup>-1</sup>.

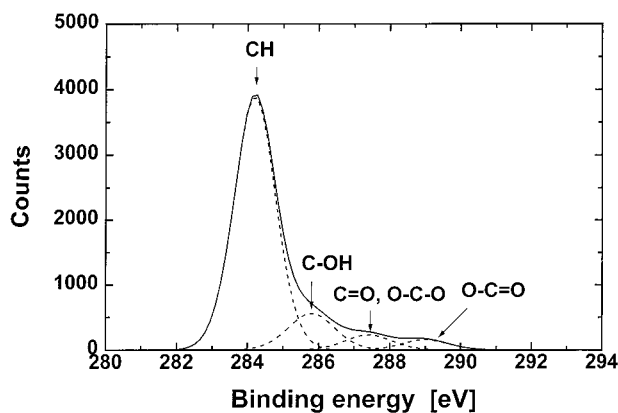
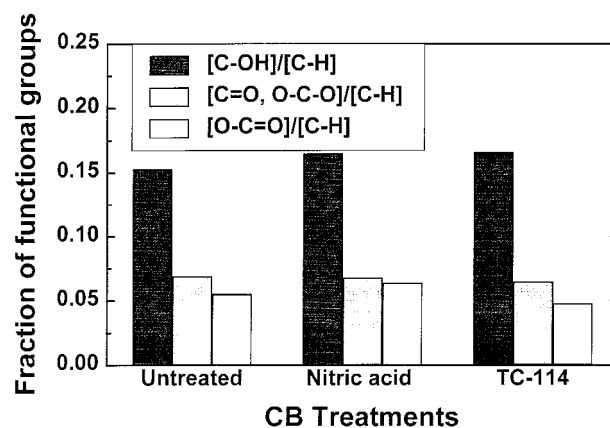
**Table III** Effect of CB Treatment on Composites' Electrical Properties and Maximum Volume Fractions

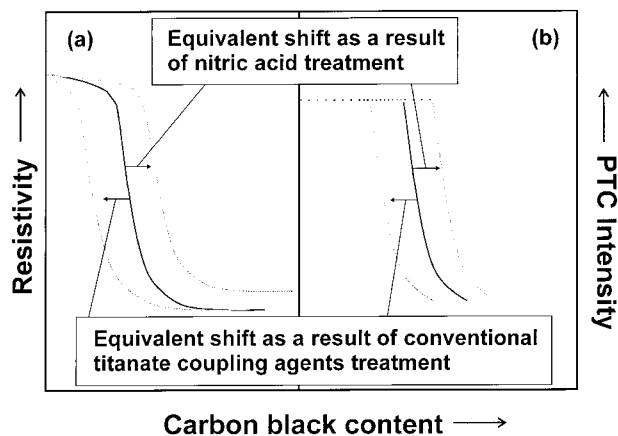
CB Treatment	CB Content (wt %)	$\rho_{RT}$ (ohm cm)	PTC Intensity	$\phi_M$
Untreated	18	$6.54 \times 10^4$	2838	0.255
Nitric acid-treated	18	$2.30 \times 10^{10}$	—	0.215
Nitric acid-treated	20	$3.57 \times 10^7$	750.7	0.215
Titanate coupling agent-treated (TC-114)	18	$3.54 \times 10^4$	115.6	0.257
Titanate coupling agent-treated (TC-114)	20	$2.86 \times 10^4$	86.1	0.257
Titanate coupling agent-treated (TM-27)	18	$6.29 \times 10^4$	154.6	0.257
Titanate coupling agent-treated (TM-931)	18	$1.28 \times 10^5$	952	0.286

To reveal the mechanisms involved, ESCA (electron spectroscopy for chemical analysis) was applied to examine CB surface. The concentration ratios of surface elements were calculated by graphical integration of the related peaks (Fig. 7) and illustrated as a function of treatment methods in Figure 8. It is seen that treatment with both nitric acid and titanate coupling agent increased the fractions of hydroxy, but maintained almost the same amount of the oxygen-containing functional groups C=O and O—C—O. The carboxyl fraction of nitric acid-treated CB was also increased, which factually contributed to a rise in polar components of surface-free energy<sup>22</sup> and formed a striking contrast to the lower value of the titanate coupling agent-treated version. In consideration of the data in Table III, it is evident that carboxyl on CB should be responsible for the previously described variation in  $\rho_{RT}$  and  $\phi_M$ .

Because the oxygen-containing functional groups that had been fixed on surfaces of CB

raised the barrier potential of electrons movement from one aggregate to another, or formed an insulating shield around the particles,<sup>23</sup> the intrinsic resistance of CB aggregates was inevitably increased by oxidation of nitric acid. Thus, the resistivity of composites filled with nitric acid-treated CB became significantly higher (Table III). On the other hand, variation in surface-free energy could also affect filler–matrix interaction and filler arrangement as well. Lower  $\phi_M$  of the nitric acid-treated system is indicative of a stronger CB–LDPE interaction, meaning that more polymers were closely bound to CB aggregates, reducing the formation probability of conductive networks. In the light of phenomenology, the effect of nitric acid treatment is equivalent to a shift of composite resistivity dependence of CB content toward a higher loading direction [Fig. 9(a)]. In addition, the resultant PTC behavior can also be schematically described by a similar drawing [Fig. 9(b)].

**Figure 7** Typical peak resolution for  $C_{1s}$  ESCA spectra of untreated CB.**Figure 8** Effect of CB treatments on the fractions of surface functional groups.



**Figure 9** Schematic illustration of the effect of CB treatment on composite properties. (a) resistivity versus CB content; (b) PTC intensity versus CB content (dotted lines symbolize unstable PTC phenomenon).

In the case of titanate coupling agents, which had better wettability to the filler, composite melt flowability and filler dispersion homogeneity were improved as reflected by the higher values of  $\phi_M$ , whereas the lower contact resistance of CB aggregates due to the reduction of carboxyl groups fraction helped to decrease the ultimate composites resistivity. Therefore, the effect of titanate coupling agents TC-114 and TM-27 is equivalently taken as a shift of both  $\rho_{RT}$  versus CB content and PTC intensity versus CB content toward lower loading regime [Fig. 9(a,b)].

It should be noted that an excessive reduction of filler-resin interfacial free energy originated by modification of CB with titanate coupling agent might lower the interfacial excess energy<sup>24</sup> and thereby hinder CB aggregates from coagulating to form conductive networks in the composite. In fact, this represented an overuniform dispersion of the fillers and resulted in a rise in  $\rho_{RT}$  and  $\phi_M$ , as shown by the effect of TM-931 treatment (Table III).

## CONCLUSIONS

The following statements can be made from the present investigation:

1. Room temperature resistivity and PTC effect of CB-filled LDPE depend to a large extent on CB content, processing conditions,

and surface chemical properties which plays the role of controlling relative arrangement of CB aggregates in the polymer matrix.

2. There is a CB content limit for obtaining stable PTC phenomenon, above which a reproducible PTC material could be made.
3. A composite with relatively low room temperature resistivity and acceptable PTC effect could be available in the case of a blended matrix, rather than a monopolymer system.
4. Maximum volume fraction of filler obtained through melting viscosity measurement is an effective parameter to characterize filler arrangement correlated to composite electrical performance.
5. Modification of CB with nitric acid and titanate coupling agents has completely different influences, which provides a way to tailor composite properties.

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