

Electrical Properties and Morphology of Carbon Black-Filled HDPE/EVA Composites

Quan-Quan Yang, Ji-Zhao Liang

School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

Received 19 October 2009; accepted 16 January 2010

DOI 10.1002/app.32117

Published online 5 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The sensitive effect of weight ratio of the high-density polyethylene (HDPE)/ethylene-vinylacetate copolymer (EVA) on the electrical properties of HDPE/EVA/carbon black (CB) composites was investigated. With the EVA content increasing from 0 wt % to 100 wt %, an obvious change of positive temperature coefficient (PTC) curve was observed, and a U-shaped insulator-conductor-insulator transition in HDPE/EVA/CB composites with a CB concentration nearby the percolation threshold was found. The selective location of CB particles in HDPE/EVA blend was analyzed by means of theoretical method and scanning electron micrograph (SEM) in order to explain the U-shaped insulator-conductor-insulator transition, a phenomenon different from

double percolation in this composite. The first significant change of the resistivity, an insulator-conductor transition, occurred when the conductive networks diffused into the whole matrix due to the forming of the conductive networks and the continuous EVA phase. The second time significant change of the resistivity, a conductor-insulator transition, appeared when the amorphous phase is too large for CB particles to form the conductive networks throughout the whole matrix. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1998–2002, 2010

Key words: polyethylene; EVA; carbon black; conductive composite; electrical property

INTRODUCTION

It has been known that the composites consisting of conductive fillers and an insulating polymer become electrically conductive as the filler content exceeds a certain critical value. Carbon black (CB) is the most frequently used filler in these composites. However, using CB as an additive to obtain electrical conductivity usually requires a concentration so high that it will decrease the processability and mechanical properties of the composites.^{1–6} One of the recent trends is to use polymer blends as the matrix resin to reduce the amount of conductive fillers in the composites.^{7–11} The critical value corresponding to resistivity transition of these composites might change to a lower loading than theoretically expected due to the multiple percolation resulting from selective distribution of conductive fillers in one phase of the polymer blends and/or at the interface of the polymers. Many studies have focused on the electrical properties of these composites and the factors that influence the distribution of CB in the blends, such as the affinity of CB to different polymers, the interfacial tension between polymers, and viscosity ratio of the polymer components,^{12–15} how-

ever, very few of them have taken notice of the electrical properties of the composites with a filler concentration a bit lower or higher than the percolation threshold. According to Xu et al.,¹² the composites in which CB particles locate at the interface of two polymer components have higher electric conductivity when the content of the two polymers is near to 1 : 1. Cheah et al.¹⁴ found that the percolation threshold was dramatically reduced by the isolation of the CB particles at the cocontinuous interface of a binary polystyrene and poly(styrene-co-acrylonitrile) matrix. In the region that the filler concentration is a bit lower or higher than the percolation threshold, the electrical properties of these composites is variable and sensitive to the ratio of polymers, and their resistivity may present an evident insulator-conductor-insulator transition at a certain filler concentration.

In this article, the effect of high-density polyethylene (HDPE) and ethylene-vinyl acetate copolymer (EVA) weight ratio on electrical properties of HDPE/EVA/CB composites with a CB concentration nearby the percolation threshold is investigated. Distribution state of CB particles in the HDPE/EVA blends is analyzed by means of theoretical analyses and scanning electron micrograph (SEM), to explain the U-shaped insulator-conductor-insulator transition, a phenomenon different from double percolation, in this composite.

Correspondence to: J.-Z. Liang (scutjzl@sohu.com).

TABLE I
The Data of Surface Tension for Various Components

Material	$\gamma \times 10^3$ (N/m)	$\gamma^d \times 10^3$ (N/m)	$\gamma^p \times 10^3$ (N/m)
HDPE	27.7	27.7	0
EVA	26.5	25.2	1.3
CB	34.4	28.8	5.6

EXPERIMENTAL

Materials

CB (Vulcan XC-72), used as a conductive filler, was provided by Cabot Co. Its average diameter, BET surface area and DBP value were 30 nm, 254 m²/g, and 178 mL/100 g, respectively. HDPE (5000S) with a melting index of 0.9 g/10 min (190°C, 2.16 kg) was supplied by PetroChina Co. Ltd. EVA(14-2) with a VA content of 14 wt % was supplied by Beijing Eastern Petrochemical Co., Ltd, China.

Sample preparation

Polymers and carbon black with desired proportions were melt mixed in a Brabender mixer (plasti-corder) at 155°C and 40 rpm for 8 min. The polymers were added in the mixer all together and then the carbon black was added when the polymers were melted. The blends were then compressed into sheets with a thickness of 2 mm by compression modeling at 160°C under a pressure of 10 MPa for 10 min.

Mesurement of electrical properties

When the volume resistance of the sample is below 10⁸ Ω, the volume resistivity was measured by a four-probe method (ASTM D-991) using two multi-meters and a voltage supply. The four-probe method can effectively avoid the contact resistance which may affect the precision of the measurement. A high resistance meter was used when the volume resistance of the sample is beyond 10⁸ Ω. The relationship between the temperature and resistivity was measured progressively by elevated temperature with the heating rate of 1°C/min.

Morphological observation

As a convenient approach to directly observe the CB-polymer interactions, the selective location of CB in two chemically different polymers was observed by means of a Hitachi S-550 SEM. All the specimens were fractured after frozen in liquid nitrogen and then gold-sputtered.

RESULTS AND DISCUSSION

Selective distribution of CB Particles in HDPE/EVA blend

When CB is added into an immiscible polymer blends, it is not distributed homogeneously in polymer blends but predominately located in one phase or at the interface, depending upon its affinity to the polymer components.¹⁶ Sumita et al.¹⁷ have suggested that the dispersion state of CB particles in polymer blend can be predicted qualitatively from the value of the wetting coefficient, ω_{A-B} , which is defined as follows.

$$\omega_{A-B} = (\gamma_{CB-B} - \gamma_{CB-A})/\gamma_{A-B} \quad (1)$$

where γ_{A-B} , γ_{CB-B} , and γ_{CB-A} are the interfacial tension between polymer A and polymer B, between CB and polymer B, and between CB and polymer A, respectively. The following distribution is predicted:

$\omega_{A-B} > 1$ CB particles distribute in phase A.

$-1 < \omega_{A-B} < 1$ CB particles distribute at the interface.

$\omega_{A-B} < -1$ CB particles distribute in phase B.

Wu's harmonic mean average equation can be used to estimate the interfacial tension between two phases¹⁸:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (2)$$

where γ is the surface tension, $\gamma = \gamma^d + \gamma^p$, γ^d is the dispersion component of surface tension, and γ^p is the polar component. The surface tension of the materials and interfacial tension between materials are listed in Table I¹⁸ and Table II, respectively.

From the calculations, we obtained $\omega_{HDPE-EVA} = 1.9 > 1$. The result suggests that CB particles tended to be dispersed in the EVA phase. On the other hand, CB particles prefer to selectively locate in the lower melt viscosity phase in a multi-phase blend. Therefore, in the view of the thermodynamics, CB particles have stronger tendency to locate in EVA than HDPE. The fact that there are many functional polar groups on the surface of CB is also a factor affecting the selective distribution of CB particles.¹⁹ As to HDPE/EVA/CB composite, EVA has a very high polarity, while the HDPE is a nonpolar

TABLE II
The Data of Interfacial Tension Between Various Components

Component 1	Component 2	$\gamma_{12} \times 10^3$ (N/m)
HDPE	CB	5.62
EVA	CB	2.92
HDPE	EVA	1.42

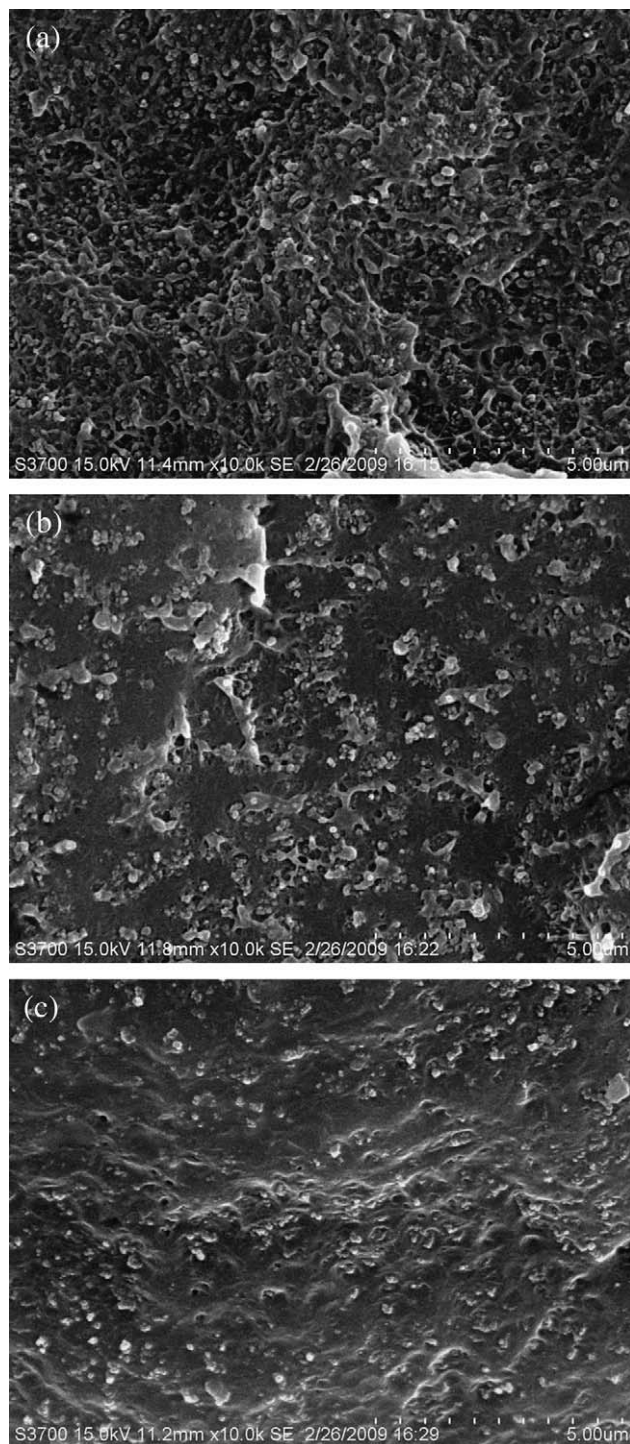


Figure 1 SEM photographs of HDPE/EVA/CB composites with a CB content of 12 wt %. HDPE/EVA weight ratios: (a) 95/5; (b) 40/60; (c) 0/100.

polymer. The interaction between EVA phase and CB particles is, thus, stronger than the interaction between HDPE phase and CB particles. In other words, CB particles have a priority to locate in the EVA phase.

To verify the analysis above, typical SEM observation of HDPE/EVA/CB composites with a CB con-

tent of 12 wt % was carried out (Fig. 1). It can be seen that in the case of a lower EVA content [5 wt %, Fig. 1(a)] which is not enough to influence the morphology of polymer blend, CB particles are homogeneously located in the polymer blend. Conductive networks throughout the whole matrix have not formed yet at this time. The EVA phase is translated into continuous phase when the weight ratio of HDPE/EVA is 40/60 [Fig. 1(b)]. On the other hand, the tendency of CB to locate in the EVA phase makes its concentration high enough to form conductive networks in the EVA phase. Both the forming of continuous EVA phase and conductive networks in the EVA phase make the conductive networks diffuse into the whole matrix. When the content of EVA is 100 wt % [Fig. 1(c)], the conductive networks throughout the whole matrix can not be formed due to the homogeneous distribution and insufficient content of CB particles.

U-shaped transition of resistivity

Figure 2 shows the relationships between EVA content and room temperature resistivity of HDPE/EVA/CB composites with a CB content of 12 wt %. A U-shaped insulator-conductor-insulator transition with the increase of EVA content can be seen clearly in Figure 2.

When the EVA content is lower than 10 wt %, the density of the conductive networks is increased due to the migration of CB particles to EVA phase which the CB particles are inclined to locate in. However, although the concentration of conductive networks in the EVA phase may exceed the percolation threshold, complete conductive networks throughout the matrix have not form due to the uncontinuous EVA phase. The increase of EVA weight fraction results in the forming of HDPE/EVA cocontinuous

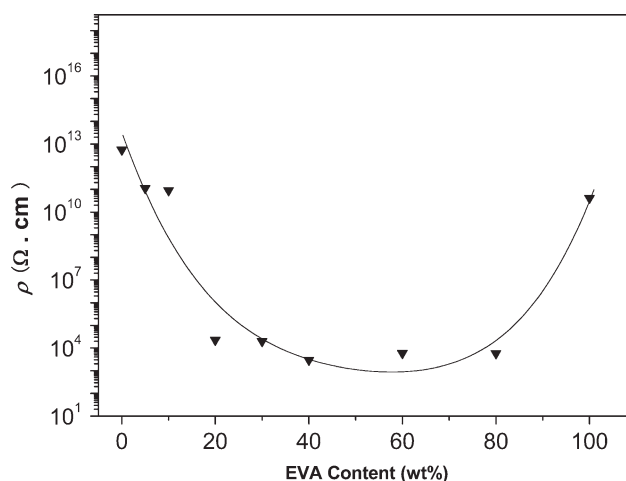


Figure 2 Influence of EVA content to room-temperature resistivity of composites.

phase. The transition of EVA phase from uncontinuous phase to continuous one makes the conductive networks diffuse into the whole blend, thereby, results in a sharp decrease of room temperature resistivity of the composites. This is an insulator-conductor transition, the first transition of the U-shaped transition. With a further rise in EVA content, the change of resistivity is very little until the EVA content exceeds 80 wt %. The reasons may be, on the one hand, the migration of CB particles from HDPE to EVA phase makes up the dilution of CB concentration resulting from enlargement of amorphous phase, on the other hand, the interaction between the EVA molecular and the polar functional groups on the surface of CB particles prevent the agglomeration of the CB aggregate. When the EVA content exceeds 80 wt %, conductive networks throughout the whole matrix can not be formed because there are not enough CB particles to supply the enlarged amorphous phase, results in a sharp increase of room temperature resistivity of the composites. This is a conductor-insulator transition, the second transition of the U-shaped transition.

PTC characteristics of HDPE/EVA/CB composites

The dependence of positive temperature coefficient (PTC) characteristic on EVA content of HDPE/EVA/CB composites with a CB content of 18 wt % is illustrated in Figure 3, from which we can observe that the temperature corresponding to peak value of the PTC curves remain unchanged when the EVA content is lower than 60 wt %. However, when the EVA content exceeds 60 wt %, this temperature moves towards lower temperature direction with increasing EVA content.

After our careful observation to Figure 3, we found that the PTC curves of HDPE/EVA/CB composites, unlike that of the HDPE/CB composites,

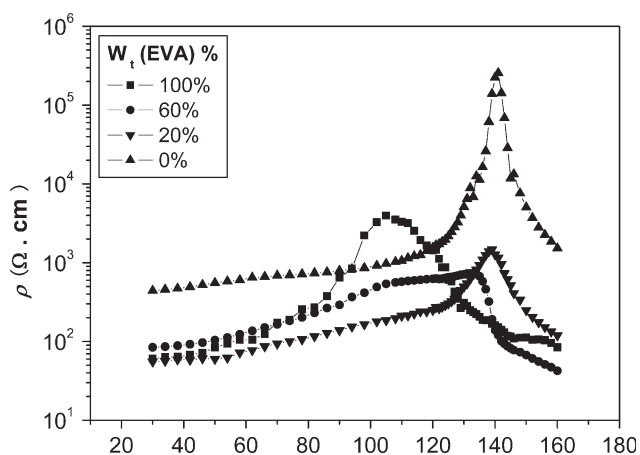


Figure 3 Resistivity-temperature curve of HDPE/EVA/CB composites with different content of EVA.

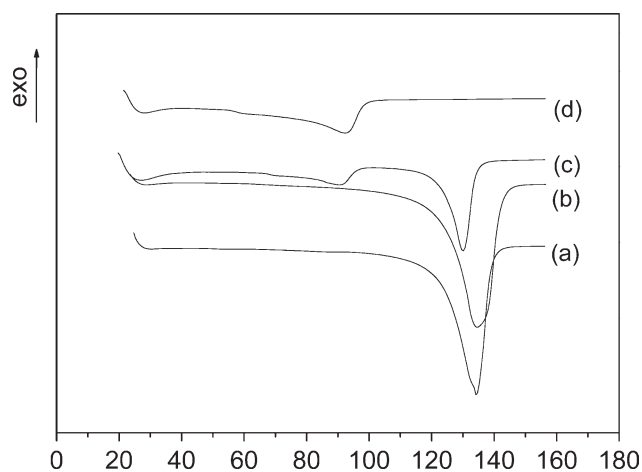


Figure 4 DSC curves of HDPE/EVA/CB composites weight fraction of EVA: (a) 0%, (b) 20%, (c) 60%, (d) 100%.

increase slightly when the temperature is higher than 60°C. The immanent cause of the slight increase may be the low melting temperature of EVA component. The destructive effect of volume expansion of EVA phase increases when the temperature rises to 60°C, however, this kind of effect is blocked to a certain degree due to the restrict of continuous HDPE phase. Thus, the restrict of HDPE component will be weaker as the increase of EVA content, and the rising trend of resistivity will be more and more obvious, which can be confirmed from Figure 3.

Unlike the sharp PTC curve of HDPE/CB composites, there is a section of relatively smooth curve between the melting temperature of EVA and HDPE in the PTC curve of HDPE/EVA/CB composites when the EVA content is 60 wt %. This is because NTC effect of EVA phase and PTC effect of HDPE phase are added together.

From Figures 3 and 4, we can find that the PTC curves have a good consistence with DSC curves of HDPE/EVA/CB composites. The content of EVA has a slight influence to the temperature corresponding to peak value of the PTC curves, and there is no melting peak in the DSC curves when EVA content is smaller. When EVA content is 60%, in the PTC curve, there is a section of relatively level curve produced by superposition of NTC and PTC effect, meanwhile there are two melting peak appear in the DSC curve.

CONCLUSIONS

All the factors affecting the distribution of CB particles in an immiscible blend, including interfacial tension, melt viscosity, and functional groups on the surface of CB particles, are in favor of the migration of the CB particles from HDPE phase to EVA phases. An U-shaped insulator-conductor-insulator

transition for HDPE/EVA/CB composites with a CB content of 12 wt % appears with the increasing EVA content. When the EVA content increases from 0 wt % to 20 wt %, the resistivity of HDPE/EVA/CB composites rapidly decreases by 9 orders of magnitude and a transition from insulator to conductor occur. When the EVA content increases from 20 wt % to 80 wt %, the change of composites resistivity is very little. When the EVA content exceeds 80 wt %, a sharp increase of room temperature resistivity of the composites and a conductor-insulator transition occur.

References

1. Wu, G. Z.; Asai, S.; Sumita, M. *Macromolecules* 2002, 35, 945.
2. Huang, J. C. *Adv Polym Technol* 2002, 21, 299.
3. Dai, K.; Xu, X. B.; Li, Z. M. *Polymer* 2007, 48, 849.
4. Zheng, Q.; Shui, B.; Shen, L. *Polym Mater Sci Eng* 2006, 22, 15.
5. Zhang, M. Q.; Yu, G.; Zeng, H. M.; Zhang, H. B.; Hou, Y. H. *Macromolecules* 1998, 31, 6724.
6. Zhou, P.; Yu, W.; Zhou, C. X. *J Appl Polym Sci* 2007, 103, 487.
7. Zhang, Q. H.; Cheng, D. J. *J Mater Sci* 2004, 39, 1751.
8. Li, Y.; Wang, S. F.; Zhang, Y.; Zhang, Y. X. *J Appl Polym Sci* 2006, 99, 461.
9. Tchoudakov, R.; Breuer, O.; Narkis, M.; Sieqmann, A. *Polym Eng Sci* 1996, 36, 1336.
10. Sun, F.; Xu, W.; Liu, P. B. *Polym Mater Sci Eng* 2005, 21, 287.
11. Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Brouers, F.; Teyssie, P. *Macromolecules* 1995, 28, 1559.
12. Xu, Z. B.; Zhao, C.; Gu, A. J.; Fang, Z. P.; Tong, L. F. *J Appl Polym Sci* 2007, 106, 2008.
13. Lee, B. *Polym Eng Sci* 1992, 32, 36.
14. Cheah, K.; Forsyth, M.; Simon, G. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 3106.
15. Feng, J. Y.; Chan, C. *Polymer* 2000, 41, 4559.
16. Shemesh, R.; Sieqmann, A.; Tchoudakov, R.; Narkis, M. *J Appl Polym Sci* 2006, 102, 1688.
17. Sumita, M.; Sakata, K.; Asai, S.; Et, A. *Polym Bull* 1991, 25, 265.
18. Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker Inc: New York, 1982.
19. Zoldan, J.; Sieqmann, A.; Narkis, M. *Polym Eng Sci* 2006, 46, 1250.