

Special Electrical Conductivity of Carbon Black-Filled Two-Phased Thermoplastic Vulcanizates

Hongchi Tian,¹ Ming Tian,^{1,2} Hua Zou,¹ Zhimin Dang,^{1,2} Liqun Zhang^{1,2}

¹Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

²Key Laboratory of Ministry of Education on Preparation and Application of Nano materials, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT: The electrical properties of carbon black (CB)-filled two-phased thermoplastic vulcanizates (based on ethylene-propylene-diene copolymer and polypropylene, TPV) were investigated in this article. The results showed that the composites had a singularity in electrical conductivity compared with CB-filled polypropylene composites. Both the loading of CB and the concentration of rubber phase in TPV had the remarkable effect on electrical property of composites. The rubber particles in TPV presented unique and competitive effects in constructing CB electrical conducting network, namely exclusion and block effects. The percolation threshold value of composites apparently decreased with rubber phase content. However, percolation behavior of composites was weakened when rubber phase content was very high. The percolation behavior of composites with loading of CB is weakened appa-

rently by rubber particles. When annealing the composites in the melt state, the resistance-time dependence of composites was strongly affected by the pressure of mold annealing. Although air aging had a negligible effect on the electrical properties, the microstructure of the CB/TPV composites had changed during air aging. CB/TPV composite only exhibited the negative temperature coefficient behavior even though the temperature was in the melting region of polypropylene, which was mainly attributed to the exclusive effect brought by the thermal expansion of rubber particles. The special electrical properties of CB/TPV can find potential application in many fields. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 691–699, 2010

Key words: thermoplastic vulcanizate; electrical conductivity; composite; NTC; PTC

INTRODUCTION

Most polymers have excellent electrical insulating properties. However, some level of electrical conductivity is required for antistatic, semiconductive, and electromagnetic interference applications.^{1,2} This need is usually satisfied by the filling of a polymer matrix with conductive particles.

It is well known that the carbon black (CB)/polymer composites have two characteristics affecting the electrical conductivity, namely percolation behavior and strong positive temperature coefficient (PTC) or negative temperature coefficient (NTC).³ The former is the common characteristics of polymer composites filled by electrical conductive fillers; with an increase of conductive filler content, the resistivity of the composite will decrease gradually and then drop dramatically close to the percolation threshold.^{4,5} Because of the PTC or NTC effect, thermoplastic CB composites suffer from two main drawbacks,^{6–12} making them of little potential use in

applications where their switching properties are important. In practice, there are three important issues in filled conductive polymer materials, which are (1) achieving high conductivity; (2) reducing the content of conductive filler; and (3) controlling the conductivity of polymer composites in percolation region and PTC and NTC behavior. However, it is not capable of touching above goals only adjusting the conductive filler and single polymer matrix. To obtain the low percolation threshold value, some researchers had even tried to achieve preferred dispersion of CB in polymer blends by using two or more polymers with different affinity with CB.^{13–15}

Thermoplastic vulcanizate (TPV), as a kind of important thermoplastic elastomers, has been extensively investigated in the past years because this kind of material exhibits some specific characteristics, such as its special morphological structure, excellent physical and mechanical property, and unique production process (dynamic vulcanization).^{16–22} Figure 1 was the sketch of morphological structure of TPV, where crosslinked rubber phase dispersed in polymer matrix as particles. Normally, the rubber is ethylene-propylene-diene copolymer (EPDM) and the plastic is polypropylene (PP). It is

Correspondence to: H. Tian (hongchicwj@yahoo.com.cn).

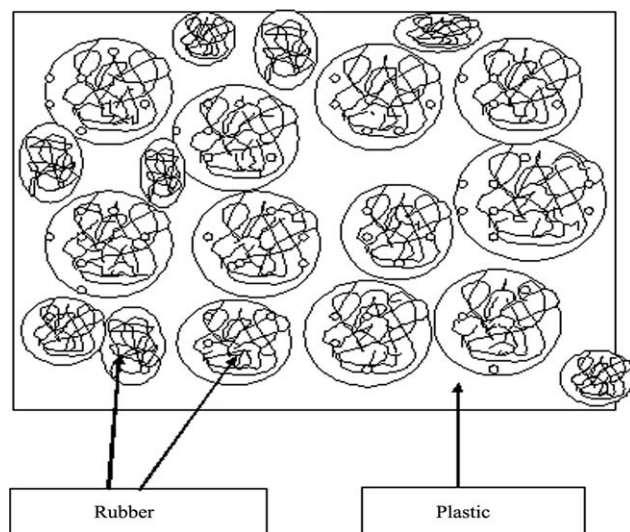


Figure 1 Sketch of TPV.

very interesting to investigate the electrical conductivity of the TPV blended with CB because the conductive CB particles can only be dispersed into the PP phase and not into already crosslinked rubber phase during blending. A natural question aroused up automatically, which is whether incorporating very little amount CB into TPV could get the excellent electrical composites? It was also suggested that the crosslinked rubber phase might have two effects on the CB fillers dispersed in TPV, i.e., exclusion effect and block effect. The exclusion effect would benefit the formation of conductive filler network, whereas the block effect would be harmful to the conductivity through interrupting the filler network. Which effect would play a more important role in determining the electrical conductivity of the CB/TPV composites? Hitherto, there are very few reports regarding the percolation behavior and PTC/NTC effect of CB/TPV composite. In this article, the dependence of electrical conductivity of CB/TPV composites on the CB content, rubber/plastic ratio of TPV, and heat annealing condition was studied for the first time. The electrical conductivity as a function of temperature was also investigated. Many interesting phenomena were explored and some results are valuable to develop the high performance conductive polymer materials.

EXPERIMENT

Materials

The TPVs (EPDM/PP) with different R/P ratio (R = EPDM; P = PP) were supplied by Shandong Dawn_BH Elastomer Co. Ltd., China. The size of rubber particles are about 2 μm . Before use, the TPV

was dried in an oven at 80°C for 4 h. The conductive CB, with about 50 nm particle diameter, DBP 380 ml/100 g, N2 1000 m²/g, electric resistivity 0.2–0.4 $\Omega\cdot\text{cm}$, was supplied by Beijing Caron Black Co. Ltd., China.

Sample preparation

PP or TPV was mixed with CB at 180°C for 15 min in two rolls mill with 6-inch roll diameter. The material was cooled in air after blending, and then the CB/PP or CB/TPV mixtures were pressed into 2-mm thick sheet on a hot presser at 180°C for 5 min by means of a special mold. A round sample (disk) with 2.6 mm (for low-resistivity samples) and 50 mm (for high-resistivity samples) diameter was cut from the sheet for electrical property test.

Electrical property tests

For the electrical characteristics, all surfaces were cleaned with ethanol to remove dust and any other contaminates and dried in air. Copper films with conductive adhesive were fasted on both sides of the CB/TPV or CB/PP sample to serve as electrodes. DC conductivity measurement was done using a QJ 36 double-arm electrical bridge (Shanghai XinXin Electronic Instrument Co. Ltd., China). A model ZC36 electrometer (SPSIC Huguang Instruments & Power Supply Branch, China) was used for high-resistivity samples with 50-mm diameter and 2.0-mm thickness. The above experiments are using five samples, finally take average.

The bulk receptivity of the samples can be expressed as following equation

$$\rho = \frac{E \cdot A}{I \cdot h}$$

where E is the voltage across the samples, I the electrical current, and A , h are the area and thickness of the samples. The dimension of the samples is 2-mm thick, with 2.6 mm (for low-resistivity samples) and 50 mm (for high-resistivity samples) diameter.

Transmission electron microscopy

Transmission electron microscopy(TEM) micrographs were taken from ultrathin section with an H-800-1 transmission electron microscope (Hitachi, Japan), using an acceleration voltage of 200 kv.

Air aging

Air aging of the sample was performed by a 401-A air aging oven (Shanghai Instrument Factory), according to ISO-188-1998.

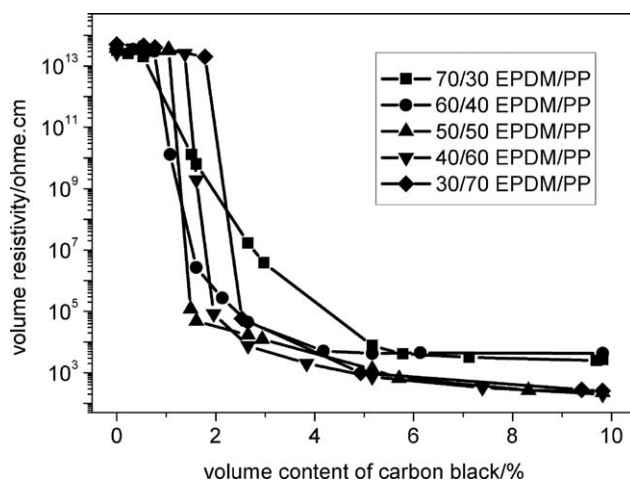


Figure 2 Effect of CB content on the resistivity of CB-TPV composites.

Heat treatment

The CB/PP and CB/TPV composites with different CB contents were preheated in a compression molder for 5 min under minimum pressure at 180°C, subjected to five pressure-release cycles to remove air bubbles, and kept under a pressure of 10 MPa for different long time. All specimens were immediately cooled in air, unless otherwise specified.

NTC/PTC experimental

The CB/PP and CB/TPV composites were put in the oven with digital display and temperature control system, and the heating rate was 2°C/min. When the temperature rises to 180°C, keep the temperature at 180°C for 60 min. Record resistivity every 10 min. Finally, with 5°C/min cooling, and regularly record the resistivity.

RESULTS AND DISCUSSION

Effect of CB content on electrical property of CB/TPV composites

Figure 2 shows the effect of CB content on the resistivity of CB/TPV composites on the condition of different R/P ratio TPV systems. As shown in Figure 2, just like most conductive filler/polymer composites, the bulk resistivity of the CB/TPV composites drops dramatically with an increase of CB content when the R/P ratio in TPV systems is below 70/30 (such as 60/40, 50/50, 30/70).

More important and interesting, percolation threshold value of composites apparently decreases when R/P ratio increases, as shown in Table I. ρ as a function of CB content for the different R/P CB/TPV composites is shown in Figure 2. ρ of a dispersion of conductive particles in an insulating matrix

at and above the percolation threshold is generally described by a power law relationship²³:

$$\frac{1}{\rho} \propto \left(\frac{V - V_c}{1 - V_c} \right)^t \quad (1)$$

where V is the volume fraction of the filler, V_c the volume fraction of the filler at the percolation threshold, and t the power law exponent that characterizes the strength of the transition. The fits of eq. (1) are included in Figure 2, and the corresponding parameters are given in Table I. In most CPC system, t was assumed to depend only on the dimensionality of the system and for a three-dimensional system is 2 according to classical lattice percolation theory or 3 according to continuum percolation theory.²⁴ In most cases, t was in the range 2–3. However, in CB/TPV composites, results showed that the percolation threshold depended strongly on the different R/P (Table I). CB/TPV composites with relatively high rubber content had the lowest values of V_c . This phenomenon strongly supports the exclusion effect and is very useful for the preparation of conductive elastomer composites with low usage of CB. Namely, a percolation does happen in the CB/TPV composites when R/P ratio is 70/30. However, the resistivity of CB/TPV composites with an R/P ratio 70/30 reduces slowly with increasing the CB content. From this result it is found that, although CB particles only distribute in the plastic phase and around the rubber phase, which is named as the exclusion effect of the rubber particles, the experiment results of the CB/TPV composites with the R/P 70/30 in TPV system imply that the block effect of rubber particles plays a role in addition to exclusion effect, that is double percolation. When R/P ratio is higher than a certain level, it becomes more difficult to form an electrical pathway as sketched in Figure 3. Therefore, one more tool is available for adjusting the electric conductivity of the composite beside CB level and this is investigated in the next section. Figure 2 also demonstrates a valuable result for application. It is well known that the polymer materials with 10^5 – 10^6 Ω ·cm resistivity cannot be easily achieved by the method of compounding conductive filler and polymer because of the strong percolation behavior occurring in composites. However,

TABLE I
Power Law Parameters for the Resistivity of CB/TPV Composites with Different RP

R/P	V_c (vol%)	t
70/30	0.53	9.1
60/40	0.76	6.3
50/50	1.05	2.1
40/60	1.38	2.2
30/70	1.78	2.3

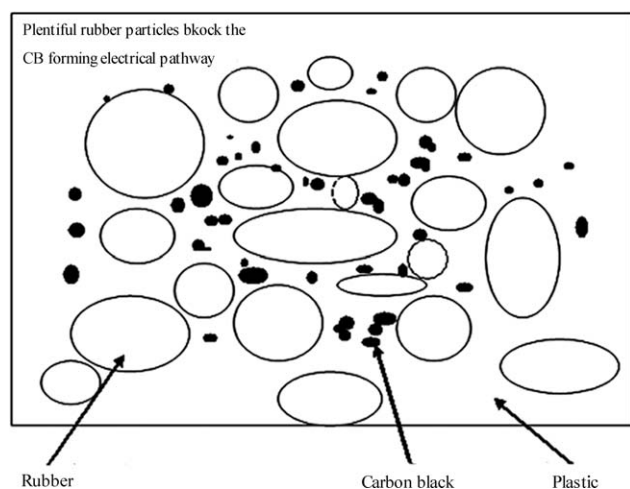


Figure 3 Sketch of rubber particles block CB forming electrical pathway.

the composites based on TPV with high R/P ratio (such as 70/30) illustrate the more controllable decrease in resistivity, which is a very useful characteristic for preparing materials with 10^5 – 10^6 Ω -cm resistivity.

Effect of rubber content on electrical property of CB/TPV composites

Effect of rubber content on electrical property of CB/TPV composites is shown in Figure 4. The elec-

trical resistivity of the CB/TPV composites with all kinds of CB contents tends to drop when the R/P ratio changes from 30/70 to 50/50. A marked drop in the resistivity can be noted in the low CB content composites. However, the resistivity rises up with an increase of R/P ratio after the R/P ratio reaches 50/50. This novel result indicates that two effects, which are exclusion and block effect originated from crosslinked rubber particles, work at the same time in the CB/TPV composites. CB concentration in the plastic phase increases because of the exclusion of rubber particles under a lower R/P ratio. Therefore, an electrical pathway might be formed in the CB/TPV composites and the resistivity drops. However, the block effect can play an important role in higher R/P ratio composites, in which crosslinked rubber particles contact each other to interrupt the formation of CB network. Therefore, the electrical resistivity increases with a rise of rubber content when the R/P ratio is higher than 50/50. In addition, as shown in Figure 4, the law of the resistivity of the CB/TPV composites with the rubber content was affected in return by the content of CB. At the low CB content, such as the content of 3 wt %, the resistivity of the composite was high and the function of the exclusion was obvious. However, at the high CB content, the resistivity of the composite was low and the function of the exclusion was weakened because CB networks already formed or became strong. For the same reason, the block effect expressed the same operation regulation with CB content.

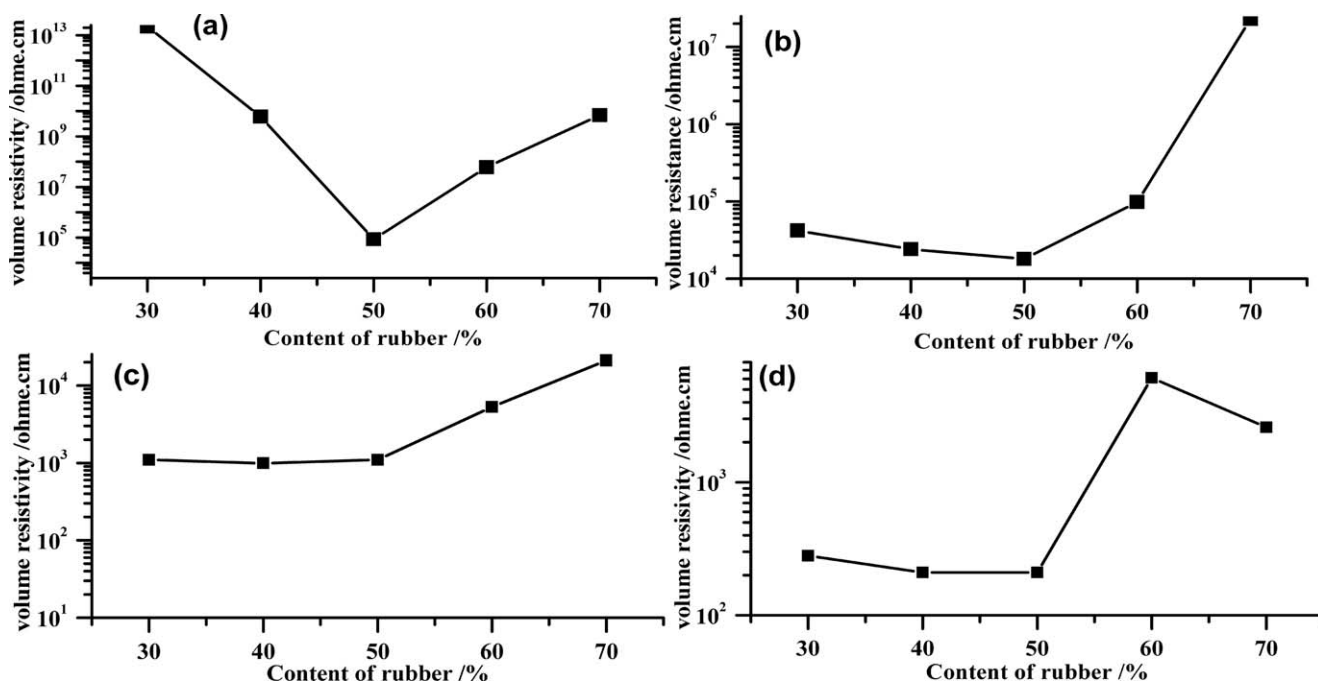


Figure 4 Effect of rubber content on electrical property of CB-TPV composites (a) 3 wt% CB, (b) 5 wt% CB, (c) 10 wt% CB, and (d) 20 wt% CB.

TABLE II
Effect of Aging on Electrical Property of CB/TPV Composites

CB Content		30/70	40/60	50/50	60/40	70/30
3 wt % CB	Before aging	4.2×10^{13}	9.8×10^9	1.0×10^6	1.8×10^5	8.5×10^9
	After Aging	$\pm 2.1 \times 10^{13}$ 4.1×10^{15} $\pm 3.3 \times 10^{15}$	$\pm 4.8 \times 10^9$ 1.2×10^{12} $\pm 2.8 \times 10^{12}$	$\pm 3.1 \times 10^6$ 6.2×10^9 $\pm 3.6 \times 10^9$	$\pm 2.3 \times 10^5$ 3.5×10^8 $\pm 2.6 \times 10^8$	$\pm 5.9 \times 10^9$ 4.3×10^{13} $\pm 3.2 \times 10^{13}$
6 wt% CB	Before aging	2.2×10^5	6.6×10^4	1.8×10^4	2.5×10^5	1.3×10^8
	After Aging	$\pm 1.1 \times 10^5$ 4.5×10^6 $\pm 1.6 \times 10^6$	$\pm 8.1 \times 10^3$ 1.1×10^6 $\pm 1.7 \times 10^6$	$\pm 7.6 \times 10^3$ 1.6×10^6 $\pm 1.5 \times 10^6$	$\pm 2.3 \times 10^5$ 1.2×10^7 $\pm 2.7 \times 10^7$	$\pm 3.4 \times 10^8$ 1.1×10^{10} $\pm 3.3 \times 10^{10}$
10 wt % CB	Before aging	6.0×10^3	6.0×10^3	6.0×10^3	7.5×10^3	5.3×10^5
	After Aging	$\pm 8.5 \times 10^2$ 2.1×10^3 $\pm 7.1 \times 10^2$	$\pm 6.1 \times 10^2$ 4.0×10^3 $\pm 7.8 \times 10^2$	$\pm 7.5 \times 10^2$ 8.2×10^3 $\pm 8.6 \times 10^2$	$\pm 4.4 \times 10^2$ 8.7×10^3 $\pm 5.2 \times 10^2$	$\pm 3.2 \times 10^5$ 9.5×10^5 $\pm 2.4 \times 10^5$
20wt % CB	Before aging	2.3×10^2	2.1×10^2	2.2×10^2	1.1×10^4	5.1×10^3
	After Aging	± 50 2.0×10^2 ± 48	± 38 2.1×10^2 ± 45	± 32 1.7×10^2 ± 36	$\pm 5.2 \times 10^3$ 1.2×10^4 $\pm 6.3 \times 10^3$	$\pm 4.6 \times 10^2$ 6.8×10^3 $\pm 5.2 \times 10^2$

In a word, above experiment results illustrate that the resistivity of the CB/TPV composites can be controlled by changing CB content and R/P ratio, which are very interesting results for application.

Effect of air aging on electrical property of CB/TPV composites

TPV has an excellent antiaging property as reported in Ref. ²⁵. It can keep its original mechanical property and elasticity even after aging at 100°C for 30 days. However, it was found that the extrusion flow ability of aged TPV after long time became worse and extrude surface became coarse. This result was attributed to the agglomeration of crosslinked rubber particles during the air aging. Does this agglomeration prevent CB particles from forming the electrical pathway and therefore affect the electrical resistivity of the CB/TPV composites? Table II summarizes the effect of aging (100°C for 7 days) on the electrical property of CB/TPV composites. The resistivity of the CB/TPV (R/P = 30/70) composites with 3 wt % CB content rises about two orders in magnificent. However, the resistivity of composites almost keeps the same level at high CB content., the other R/P composites also have the same effect. The increase of the resistivity of composites with low CB content is ascribed to a strong block effect generated by agglomeration of rubber particles during aging. However, at high CB content, the conductive filler network density is high. Rubber particles movements during aging break some filler conductive lines because of block effect, but help to construct some new conductive lines in new areas due to the exclusion effect. In summary, the TPV composites with high CB content possess the steady electrical property, which is also interesting discovery for application.

Effect of heat treatment on electrical property of CB/TPV composites

When polymer matrix was in melt state the self-diffusion capability of polymer matrix was greatly strengthened and the aggregation of inorganic particles dispersed in it also greatly enhanced. Observing the evolution of electrical property of CB/TPV composites in melt state is an interesting research. Thermal annealing was also used to study the aggregation of inorganic particles in polymer matrix and to improve the conductivity of composites.²⁶⁻²⁸

To get a clear mechanism, CB/PP and CB/TPV composites were studied in comparison. The CB/PP and CB/TPV composites with different CB contents were treated in the mold by hot pressor at 180°C (above the melting point of PP) for different time under 10 MPa pressure, respectively.

It can be seen from Figure 5 that the electrical conductivity of the CB/PP composite with 3 wt % CB content first dramatically increases with the heat treatment time and then approaches a balance. The

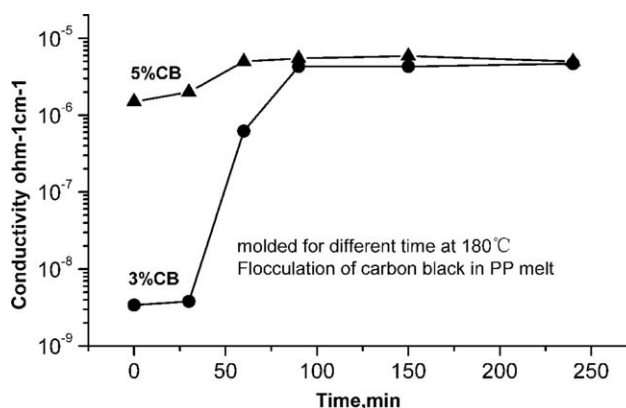


Figure 5 Effect of heat treatment on electrical property of CB-PP composites.

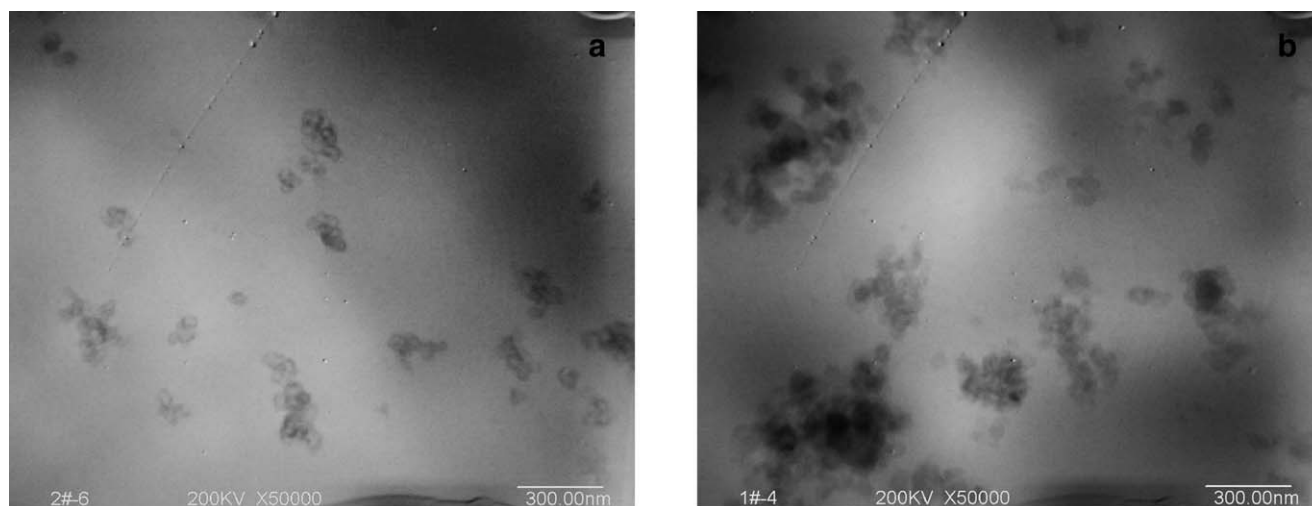


Figure 6 (a) TEM photographs showing the effect of heat treatment on the condition of melting and press (before the heat treatment), (b) TEM photographs showing the effect of heat treatment on the condition of melting and press (after heat treatment 30 min at 180°C).

CB/PP composite transforms into a semiconductor after heat treatment for 80 min from an insulator. This result can be reasonably explained that an electrical conducting network is formed in the CB/PP composite because of the aggregation of CB particles in the PP melt, which is thermodynamically driven by the difference of surface tensions between CB particles and PP melt.²⁶ Figure 6 shows the TEM photos of the CB/PP composite with 3 wt % CB content before and after heat treatment. As shown in Figure 6(a), before the heat treatment, the conducting network of CB particles does not form in the composite, and CB particles are dispersed in PP as CB aggregates (i.e., fused primary particles and chemically bonding together). However, from Figure 6(b), it can be seen that CB particles aggregating definitely occurs. It is believed that a three-dimensional network generated in space. Figure 5 also displays that the conductivity of CB/PP composite with 5 wt % CB content with thermal annealing time obeys the same rule as that expressed by composite with 3 wt % CB. However, the resistivity change is not so much, which is because that an electrical conducting network already formed in composites due to a higher CB content.

Inconceivably, a different rule is presented by CB/TPV composite and shown in Figure 7. The electrical conductivity of the CB/TPV composite with 3 wt % CB content reduces with an increase of heat treatment time. This result is contrary to that of the CB/PP composite. At the same time, the electrical conductivities of the CB/TPV composite with higher CB content do not change with an increase of heat treatment time. It is believed that the aggregation of CB particles in TPV still occurred, which benefited conducting property. Therefore, a suggested mechanism

is put forward here and sketched by Figure 8. The spherical rubber particles of TPV would be transformed into ellipse-shaped particles by pressure at 180°C. The ellipse-shaped rubber particles would restore to original spherical shape because of their elastic characteristic when the thermal treatment finished and mold pressure was released. As a result, the conducting network strengthened by aggregating of CB was destroyed again (at least part of the network) by this release process, and the CB particles distribute again around the rubber particles as shown in Figure 8. In addition, accompanying with the aggregating of CB particles, the crosslinked rubber particles also aggregate in melt state of TPV, which is already mentioned before. The block effect of rubber particles was probably strengthened by aggregating of rubber particles, which also decreased the conductivity of the CB/TPV composites. Further investigation will be conducted.

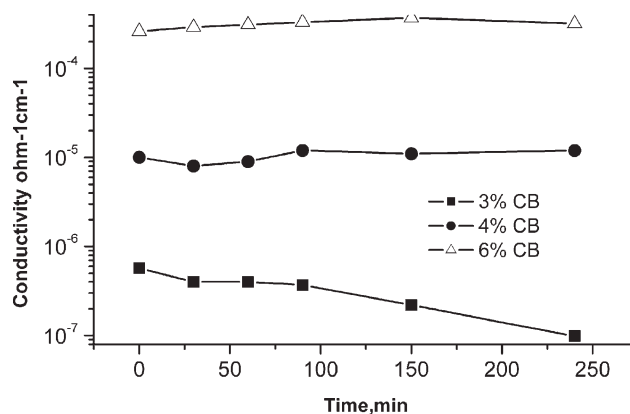


Figure 7 Effect of heat treatment on electrical property of CB-TPV composites.

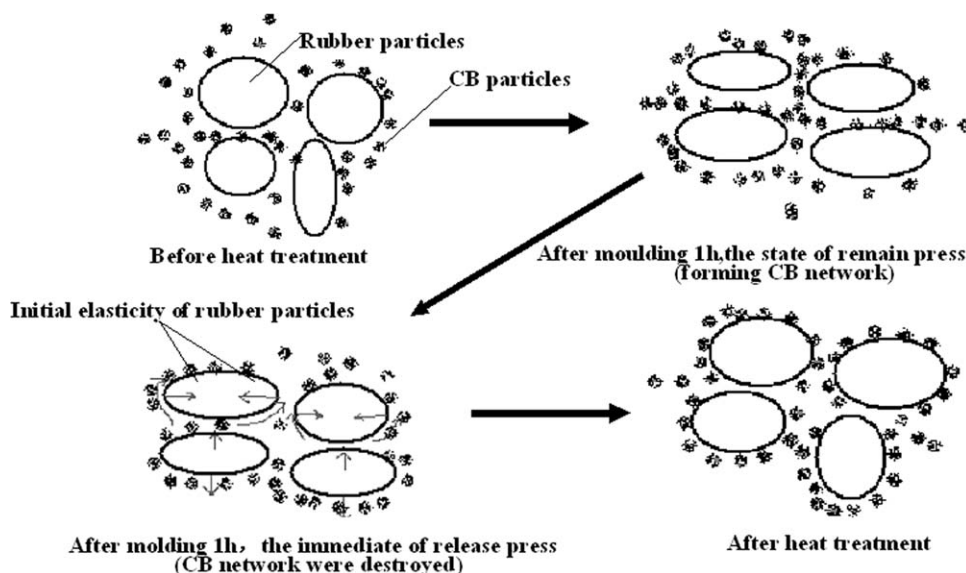


Figure 8 Sketch of the course of heat treatment on the composite.

NTC effect of CB/TPV composites

Some research results showed that the CB-filled polymer matrix composites had PTC and NTC effect,²⁹⁻³² which was the resistivity of the CB/polymer composites changed with an increase in temperature and generally ascribed to the destruction and construction of conductive network because of the thermal expansion and shrinkage of polymer matrix with temperature, especially in temperature-volume transition region, such as melt region and glassy transition region. PTC effect is very remarkable in many composites with the electrical conducting fillers. Figure 9 shows the PTC effect taken place in the CB/PP composite. It can be seen that the resistivity of the composite gradually increases with a rise in temperature from 20 to 140°C, which is attributed to a normal heat expansion of the composite. The resistivity of composite rapidly increases when temperature increases from 140°C to 170°C because the volume expansion becomes strong due to melting of matrix. However, the resistivity drops rapidly when the composite is kept at 190°C for 10 min, which is because strong aggregating of CB particles in melt state strengthens the conducting network. This strengthened new network even prevents composite from further change (generally decrease) of resistivity with temperature decreasing. However, the resistivity of composite displays a special and weak increase and decrease around 110°C. When temperature was lowered to 110°C, PP melt would crystallize. On one hand, the produced lamellar crystals possibly cut off the conductive network and increased the resistivity, and on another hand, the volume shrinkage brought by crystallization would make CB particles move closely and decreased the

resistivity of composite. It was assumed that this competitive effects resulted in this change of resistivity around 110°C.

Different from the result reflected by Figure 9, Figure 10 (the first heating/cooling cycle) demonstrates that all the CB/TPV composites exhibit the NTC effect, i.e., the resistivities of the CB/TPV composites decline with temperature increasing from 30 to 180°C. During the heating stage, both plastic phase and rubber phases expand. However, the expansion of the rubber phase is stronger than that of the plastic phase, so no PTC effect is observed with CB/TPV. CB particles that disperse around rubber particles are easy in connection with each other because of the strong expansion effect of rubber phase, which therefore decreases the resistivity of composite. However, in a comparison with the CB/PP composite, CB/TPV composites keep relatively stable resistivities even if the CB/TPV composites are kept

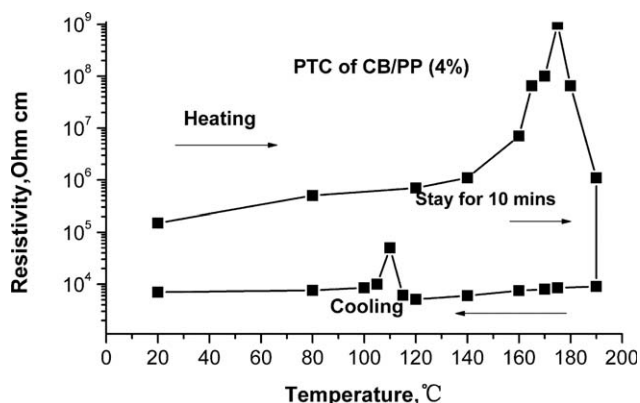


Figure 9 The PTC and NTC behavior of CB-PP composite.

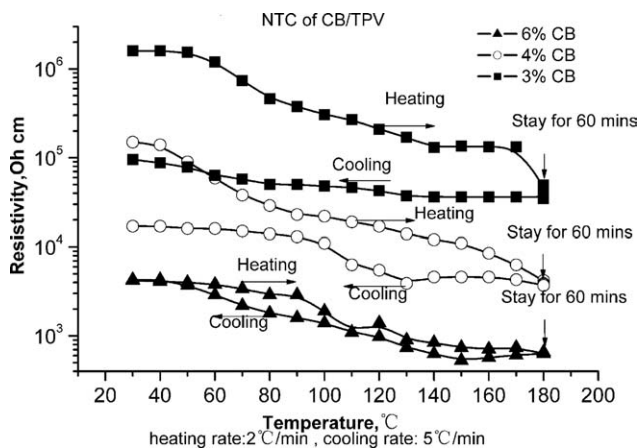


Figure 10 The NTC effect of CB-TPV composite.

at 180°C for 60 min. Different from CB/PP composites, CB particles would not only aggregate in PP of TPV but also crosslinked rubber particles aggregate in PP of TPV. The aggregation of CB in PP melt favors the improvement of conductivity, whereas the aggregation of rubber particles increases resistivity. The relatively stable resistivity of TPV composite in melt region is the result brought by two competitive aggregations. When temperature decreases from melt point to room temperature, the resistivities of CB/TPV composites gradually increase. The resistivity of the CB/TPV composite with high CB content even recovers the original value. This novel recovery still comes from higher thermal shrinkage of rubber phase (than that of plastic phase) and crystallization of PP. Because the content of PP in TPV is low, the small peak corresponding to crystallization does not appear in Figure 10. The good recovery of resistivity of conductive TPV composite might be found potential application in electrical field.

CONCLUSIONS

1. The content of CB has a remarkable influence on the electricity performance of the CB/TPV composites. With the CB amount increasing, the resistance of the CB/TPV composites reduces greatly. However, the content of rubber phase of TPV also strongly affects the resistivity of composites. The percolation threshold value of composites apparently decreased with rubber phase content. However, percolation behavior of composites was weakened when rubber phase content was very high. Therefore, both R/P ratio and CB content can be used to adjust the electric conductivity of the composite. Therefore, it is possible to get the polymer composites with steady antistatic property or conductive polymer composites with lower CB content base on TPV.

2. Although air aging has a negligible effect on the electrical properties, the microstructure of the CB/TPV composites has changed during air aging. In the melting state, the heat treatment favors the CB particles forming the network structure, thus enhances the electric conductivity of the CB/PP composite. However, for the CB/TPV composite, the ellipse-shaped rubber particles by high pressure would restore to original spherical shape because of their elastic characteristic when the thermal treatment finished and mold pressure was released. Therefore, the conducting network strengthened by aggregating of CB was destroyed again (at least part of the network) by this release process. As a result, the conductive property of CB/TPV composite was less affected.
3. The CB/TPV composites exhibit typical NTC effect, i.e., as the temperature increasing, the resistance of the composite decrease. At the same time, the CB/TPV composites display unique characteristics, which is the resistance change is very small in the melting condition. It is valuable for developing new conductive material in the future.

References

1. Li, F. K.; Qi, L. Y.; Yang, J. P.; Xu, M.; Luo, X. L.; Ma, D. Z. *J Appl Polym Sci* 2000, 75, 68.
2. Olivero, D. A.; Radford, D. W. *J Reinforced Plast Compos* 1998, 17, 674.
3. Adriaanse, L. J.; Reedijk, J. A.; Teunissen, P. A. A.; Brom, H. B.; Michels, M. A. J.; Brokken-Zijp, J. C. M. *Phys Rev Lett* 1997, 78, 1755.
4. Dang, Z. M.; Shen, Y.; Nan, C. W. *Appl Phys Lett* 2002, 81, 4814.
5. Dang, Z. M.; Shen, Y.; Fan, L. Z.; Cai, N.; Nan, C. W. *J Appl Phys* 2003, 93, 5543.
6. Narkis, M.; Ram, A.; Stein, Z. *J Appl Polym Sci* 1980, 25, 1515.
7. Gubbles, F.; Jerome, R.; Teyssie, P.; Vanlathem, E.; Deltour, R.; Calderone, A.; Parente, V.; Bredas, J. L. *Macromolecules* 1994, 27, 1972.
8. Calberg, C.; Blacher, S.; Gubbels, F.; Brouers, F.; Deltour, R.; Jerome, R. *J Phys D: Appl Phys* 1999, 32, 1517.
9. Breuer, O.; Tchoudakov, R.; Narkis, M.; Siegmann, A. *Polym Eng Sci* 2000, 40, 1015.
10. Lagreve, C.; Feller, J. F.; Linossier, I.; Levesque, G. *Polym Eng Sci* 2001, 41, 1124.
11. Wu, T. M.; Cheng, J. C. *J Appl Polym Sci* 2003, 88, 1022.
12. Feller, J. F. *J Appl Polym Sci* 2004, 91, 2151.
13. Wang, N.; Zhang, X. X.; Yu, J. G.; Fang, J. M. *Polym Int* 2008, 57, 1027.
14. Cheah, K.; Forsyth, G. P. *J Polym Science: Part B: Polym Phys* 2000, 38, 3106.
15. Zhang, C.; Yi, X. S.; Hiroshi, Y.; Shigeo, A.; Masao, S. *J Appl Polym Sci* 1998, 69, 1813.
16. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53, 141.
17. Choudhury, N. R.; Bhowrnick, A. K. *J Mater Sci* 1990, 25, 161.
18. Radusch, H. J. *Kautsch Gummi Kunschl* 1991, 44, 1125.
19. Toshio, I. *J Appl Polym Sci* 1994, 54, 709.
20. Kim, Y. K.; Cho, W. J.; Ha, C. S.; Kim, W. *Polym Eng Sci* 1995, 35, 1592.

21. Wiessner, S.; Michael, H.; Mennig, G. *Kautsch Gummi Kunstst* 2003, 56, 514.
22. Zribi, K.; Feller, J. F.; Elleuch, K.; Bourmaud, A.; Elleuch, B. *Polym Adv Technol* 2006, 17, 727.
23. Lux, F. *J Mater Sci* 1993, 28, 285.
24. Heaney, M. B. *Phys Rev* 1995, 52, 12477.
25. Tian, H. C.; Wu, S. M.; Han, J. B. *China Synth Rubber Ind* 2004, 27, 34.
26. Yu, J.; Zhang, L. Q.; Rogunova, M.; Summers, J.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 2005, 98, 1799.
27. Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. *Polym Bull* 1991, 25, 265.
28. Miyasaka, K.; Watanabe, K.; Jojima, E.; Aida, H.; Sumita, M.; Ishikawa, K. *J Mater Sci* 1982, 17, 1610.
29. Aminabhavi, T.; Cassidy, P.; Thompson, C. *Rubber Chem Technol* 1990, 63, 451.
30. Voet, A. *Rubber Chem Technol* 1981, 54, 42.
31. Mckenna, G. B.; Zapas, L. J. *Rubber Chem Technol* 1981, 54, 718.
32. Meinecke, E.; Maksin, S. *Rubber Chem Technol* 1981, 54, 857.