

Electrical Properties and Morphology of Polypropylene/Epoxy/Glass Fiber Composites Filled with Carbon Black

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ABSTRACT: The volume resistivity and percolation thresholds of carbon black (CB) filled polypropylene (PP), PP/epoxy, and PP/epoxy/glass fiber (GF) composites were measured. The morphology of these conductive polymer composites was studied with scanning electron microscopy (SEM). The effects of the GF and epoxy contents on the volume resistivity were also investigated. The PP/epoxy/GF/CB composite exhibited a reduced percolation threshold, in comparison with that of the PP/CB and PP/epoxy/CB composites. At a given CB content, the PP/epoxy/GF/CB composite had a lower volume resistivity than the PP/CB and PP/epoxy/CB composites. SEM micrographs showed that CB aggregates formed chainlike structures and dispersed homogeneously within the PP matrix. The addition of the epoxy resin to PP resulted in the preferential

location of CB in epoxy, whereas in the PP/epoxy/GF multiphase blends, because of the good affinity of CB to epoxy and of epoxy to GF, CB particles were located in the epoxy phase coated on GF. The decreased percolation threshold and volume resistivity indicated that conductive paths existed in the PP/epoxy/GF/CB composite. The conductive paths were probably formed through the interconnection of GF. Appropriate amounts of GF and epoxy should be used to decrease the volume resistivity and provide sufficient epoxy coating. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1142–1149, 2005

Key words: morphology; poly(propylene) (PP); conducting polymers; blends

INTRODUCTION

The electrical resistivity of insulating polymers can be decreased by the incorporation of conductive fillers, such as metal powder or fiber,^{1,2} carbon black (CB),^{3–5} and carbon fiber,^{6,7} into the polymer matrix. The critical amount of the conductive filler to form continuous conductive paths or networks and cause a dramatic resistivity decrease is known as the percolation threshold. CB is the most widely used conductive filler because of its light weight, low cost, and permanent conductivity. The volume resistivity of CB is about 0.1 Ω cm. The percolation threshold of CB for imparting conductivity to polymers varies from polymer to polymer and is usually in the range of 10–20 wt %. The relatively high CB loading has a negative effect on the processability and mechanical properties.⁸ In highly filled CB compounds, CB particles tend to slough and cause contamination in a clean room environment.^{8,9} Also, because of the steepness of the percolation curve, it is difficult to precisely control the desired intermediate conductivity levels for electrostatic dissipative (ESD) applications.^{8,9}

Recently, special interest has been shown in the conductive polymer composites based on CB-filled immiscible polymer blends. The heterogeneous distribution of CB in such ternary or multiphase composites makes the percolation threshold and resistivity values of the blend lower than those depicted for the corresponding CB-filled individual polymers.^{8,10–20} The CB distribution mainly depends on the interaction of CB with either polymer, which is affected by the surface tension^{11,21} or interfacial free energy;²² it also depends on the polymer crystallinity,¹⁰ viscosity,^{20,23,24} and processing.^{10,16,25} There are two types of CB distributions that favor electrical conduction. One is the selective or preferential location of CB in one polymer phase. When the CB concentration reaches the percolation level in the continuous CB-rich phase, double percolation is achieved, and the percolation threshold is lowered.^{10–15} The other is the location of CB at the interface of cocontinuous immiscible polymer blends, which can obtain the lowest percolation threshold.^{10,16–18} The enhanced conductivity of polymer blends and CB composites makes them suitable for versatile applications, such as ESD and conductive composites,^{10–16} positive temperature coefficient materials,^{23,24} liquid or chemical vapor sensors,^{26,27} and electromagnetic interference shielding.²⁸

In this work, a new type of CB-filled polypropylene (PP)/epoxy/glass fiber (GF) conductive polymer com-

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posite with a reduced percolation threshold was prepared by a melt-mixing method. The relationship between the electrical properties and the morphology of the composites was studied. The effects of the GF and epoxy contents on the volume resistivity were also investigated.

EXPERIMENTAL

Materials

The polymers were PP (melt flow index = 25 g/10 min; M1600, Hyundai Petrochemical Co., Ltd., Seoul, Korea) and diglycidyl ether of bisphenol A resin (weight-average molecular weight = 4500 g/mol; Shanghai Resin Co., Ltd., Shanghai, China). Short GFs (average length = 3.4 mm, average diameter = 10 μm ; Jushi Group Co., Ltd., Tongxiang, China) were treated with a silane coupling agent. Electrically conductive CB (Dibutylphthalate absorption = 168.6 mL/100 g; V-XC72, Cabot Co., Pampa, TX) was used as the conductive filler.

Sample preparation

Before the blending, all materials were dried at 80°C *in vacuo* for about 8 h. The composites were prepared by the melt mixing of the dry-blended components in a Haake (Karlsruhe, Germany) RC90 rheometer at 190°C and 30 rpm for about 10 min. The composites were subsequently compression-molded to form plaques 1 or 4 mm thick.

Measurements

For samples with resistivity higher than $10^8 \Omega \text{ cm}$, the volume resistivity measurements were carried out with 1-mm plaques with a ZC36 high-resistance meter (Shanghai Electrical Meter Factory, Shanghai, China) according to ASTM D 257. For moderately conductive samples with resistivity lower than $10^8 \Omega \text{ cm}$, the 4-mm plaques were cut into specimens 90 mm long and 10 mm wide. The volume resistivity was measured according to ISO 3915 with a set of low-resistance measurement apparatus, which consisted of current electrodes, potential electrodes, a power supply, a digital ampere meter, and a voltage meter.

The microstructure of the conductive CB (V-XC72) was observed with a JEOL (Tokyo, Japan) JEM100-CX transmission electron microscope.

The composites were fractured in liquid nitrogen, and the morphology of the freeze-fractured surfaces was observed with a Hitachi (Tokyo, Japan) S-2150 scanning electron microscope. All samples were gold-sputtered before observation.

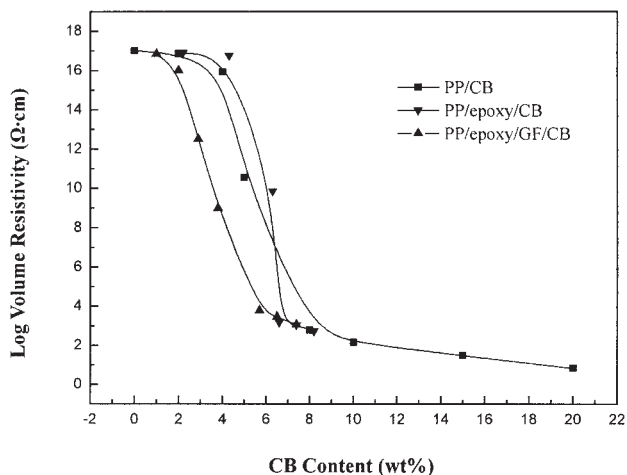


Figure 1 Volume resistivity versus the CB content of CB-filled PP, PP/epoxy (89/11), and PP/epoxy/GF (80/10/10) composites.

RESULTS AND DISCUSSION

Electrical properties

Figure 1 depicts the volume resistivity of CB-filled PP, PP/epoxy (89/11), and PP/epoxy/GF (80/10/10) composites as a function of the CB content. All the composites exhibit typical characteristics of percolation. At low CB loadings, little or slight changes in the volume resistivity can be observed because the distances between the CB particles are large. Increasing the CB content makes CB more crowded, leading to the slow decrease of the volume resistivity. In the vicinity of the percolation threshold, the volume resistivity decreases drastically, and the transition from insulating materials to conductive materials occurs. This indicates that CB particles come into contact with one another or close up enough to allow electron hopping by tunneling, thus forming continuous conductive paths or network. Once the percolation is reached, additional CB loading does not greatly reduce the volume resistivity because the conductive network has already formed.

The three conductive polymer composites have different percolation thresholds. The percolation threshold of PP/CB is about 7.5 wt % CB. PP/epoxy/CB has a slightly lower percolation threshold of about 6.5 wt % CB. The PP/epoxy/GF/CB composite has the lowest percolation threshold of about 5.0 wt % CB. It is perceptible until 8 wt % CB that the volume resistivity of the PP/epoxy/GF/CB composite is lower than that of the PP/CB and PP/epoxy/CB composites. For example, with 4 wt % CB, the volume resistivity of the PP/epoxy/GF/CB composite is $9.48 \times 10^8 \Omega \text{ cm}$, and the composite is antistatic or ESD, whereas the volume resistivity of PP/CB and PP/epoxy/CB with 4 wt % CB is 8.56×10^{15} and $5.80 \times 10^{16} \Omega \text{ cm}$, respectively,

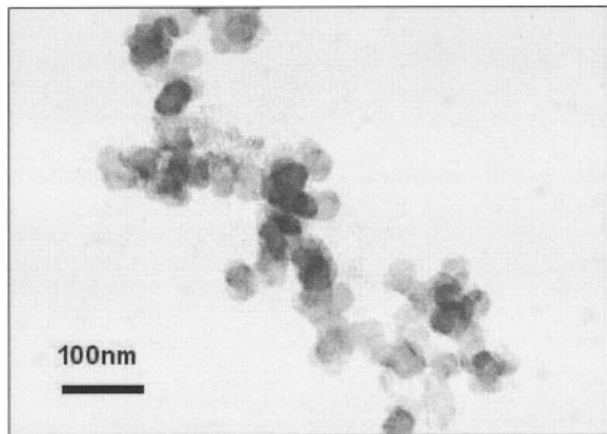


Figure 2 TEM micrograph of the V-XC72 conductive CB.

and the composites are highly insulating. Therefore, the electrical conductivity of the PP/epoxy/GF/CB composite is the highest.

Morphology

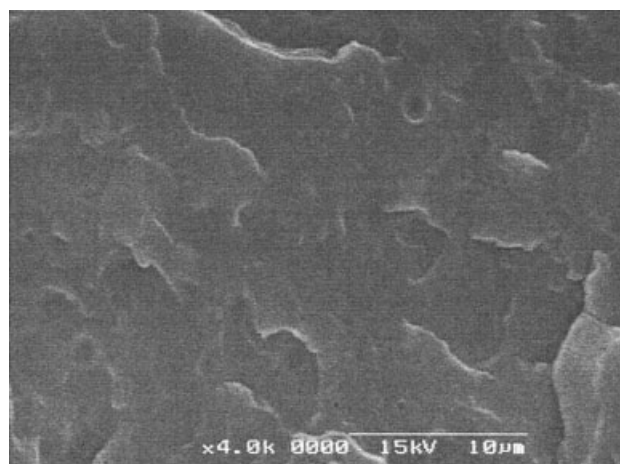
It is well established that the resistivity and percolation threshold of CB-filled single polymers or polymer blends depend greatly on the interaction of the polymer and CB and the CB distribution.^{5,10-22} The difference in the percolation thresholds of the PP/CB, PP/epoxy/CB, and PP/epoxy/GF/CB composites can be explained by the morphological differences.

Figure 2 shows the microstructure of the V-XC72 conductive CB. V-XC72 is a high-structure CB. The aggregate is chainlike, with a few branches. Figure 3 shows the scanning electron microscopy (SEM) micrographs of freeze-fractured surfaces of PP and the PP/CB (90/10) composite. CB forms a chainlike structure within the PP matrix in the form of aggregates rather than individual particles. The distribution of CB in PP is relatively homogeneous. This uniform distribution results in the comparatively high percolation threshold of the PP/CB composite.

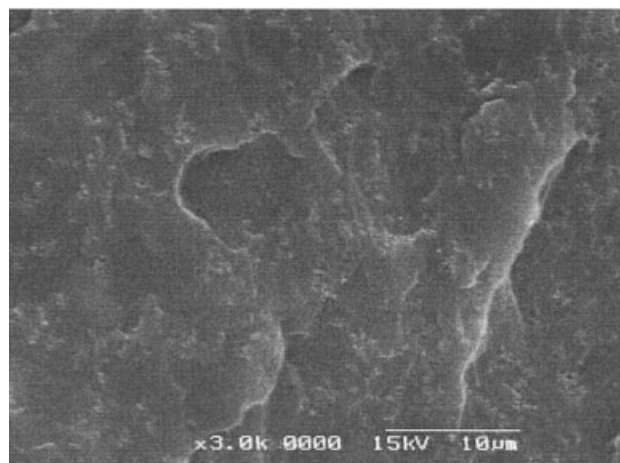
The morphologies of PP/epoxy (89/11) and PP/epoxy/CB (89/11/4) are shown in Figure 4. PP forms the continuous phase. The epoxy resin disperses in PP and forms spherules 1–4 μm in diameter. After the addition of CB to PP/epoxy, the preferential location of CB in the epoxy phase can be observed. Previous studies^{8,22,29} have shown that the uneven distribution of CB in immiscible polymer blends is mainly due to the affinity of CB with one polymer phase. Usually, this phase has higher surface tension and polarity.¹¹⁻¹³ In this work, the selective location of CB in epoxy is consistent with the results of those studies. PP is a nonpolar polymer, whereas epoxy resin is a polar resin with epoxy, hydroxyl, and ether groups. The higher polarity of epoxy makes it easily wet the CB

surface; that is, CB has a stronger affinity to epoxy than PP. Furthermore, at the processing temperature of 190°C, epoxy has a lower melt viscosity than PP, and this also favors CB incorporation. Thus, in PP/epoxy/CB composites, CB is preferentially dispersed in epoxy.

However, epoxy forms the dispersed phase in the continuous PP phase. The distances between the epoxy spherules are large, and CB cannot form conductive paths through double percolation because the epoxy phase is not continuous. As shown in Figure 1, when the CB concentration is lower than 5 wt %, the volume resistivity of the PP/epoxy/CB composite is beyond $10^{14} \Omega \text{ cm}$, and the composite remains insulating. At a low CB concentration, the volume resistivity of the PP/epoxy/CB composite is also higher than that of PP/CB. This is because CB particles are distributed in isolated epoxy spherules and cannot come into contact with one another. After CB reaches

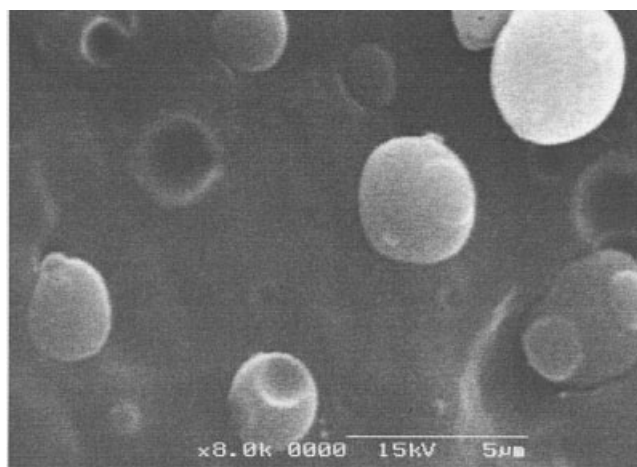


(a)

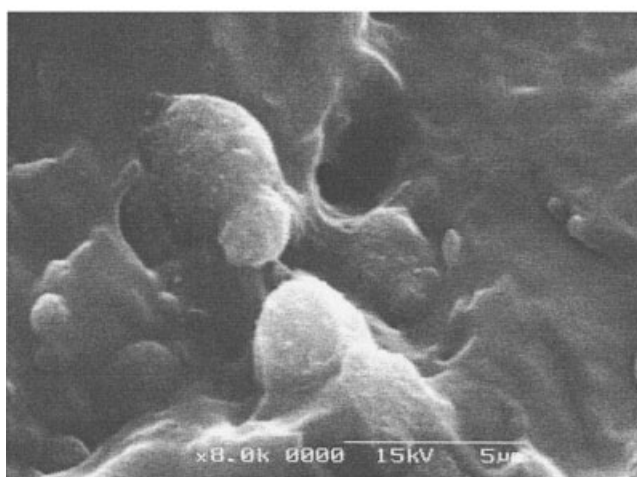


(b)

Figure 3 SEM micrographs of freeze-fractured surfaces of (a) PP and (b) the PP/CB (90/10) composite.



(a)



(b)

Figure 4 SEM micrographs of freeze-fractured surfaces of (a) PP/epoxy (89/11) and (b) PP/epoxy/CB (89/11/4) composites.

the percolation level in the preferred phase, additional CB can be observed to locate at the interface or in the other phase.³⁰ Mironi-Harpaz and Narkis²⁰ reported that for a PP/ultrahigh-molecular-weight polyethylene (UHMWPE)/CB composite, the extremely high viscosity of UHMWPE prevented CB penetration. Because of the stronger affinity of CB to PE, CB initially formed conductive networks in the dispersed UHMWPE phase, and this was followed by distribution in the PP matrix; thus, the CB-covered UHMWPE particles were interconnected. This CB distribution resulted in a reduced percolation threshold. A study on poly(4-methyl pentene-1)/UHMWPE/CB composites got a consistent conclusion.²⁴ Similarly, increasing the CB content in our study could result in the location of additional CB in the PP matrix after CB percolates in epoxy and the interconnection of the CB-rich epoxy

spherules. This kind of CB distribution can decrease the volume resistivity more effectively than a uniform distribution in PP/CB. A reduced percolation threshold of the PP/epoxy/CB composite (ca. 6.5 wt % CB) has also been obtained, in comparison with that of the PP/CB composite (ca. 7.5 wt % CB). Beyond the percolation threshold, the volume resistivity of PP/epoxy/CB is a little lower than that of PP/CB (Fig. 1).

A study of the morphology of PP/epoxy indicates that the blend can become cocontinuous when the PP/epoxy ratio approaches 40/60. The percolation threshold of the CB-filled PP/epoxy (40/60) composite is about 7 wt % CB, slightly lower than that of the PP/CB composite. This further proves that CB preferentially distributes within the epoxy phase. If CB locates in PP or at the interface, the percolation threshold should be greatly reduced. Furthermore, increasing the epoxy content to form a continuous phase is not a practical strategy for lowering the CB loading. Because the epoxy resin is a thermoset oligomer with a comparatively low molecular weight, its high proportion in the PP/epoxy blend will severely damage the mechanical properties and increase the final cost.

Narkis et al.^{8,31} reported new ESD PP/polyamide (PA)/GF/CB composites. The composites formed an electrically conductive network of PA-coated GF, with CB particles located at the PP/PA interface and within PA. This morphology was attributed to the strong affinity of PA to GF and CB. The addition of GF to PP/PA/CB actually led to the spontaneous *in situ* formation of conducting fibers.⁸ In the composites, there existed a triple-percolation morphology of a continuous GF network, a continuous PA phase, and continuous CB pathways.

On the basis of the aforementioned studies, GF was added to PP/epoxy/CB to investigate its effect on the volume resistivity. Figure 1 shows that a reduced percolation threshold of the PP/epoxy/GF/CB composites has been achieved. This is probably due to the structure of the composites and the CB location.

In the PP/GF (90/10) composite, there is little PP on the surface of GF, as shown in Figure 5(a,b). Figure 5(c,d) shows that GF is coated with a relatively even and smooth polymer matrix in the PP/epoxy/GF (80/10/10) composite. Figure 5(e,f) shows that the addition of CB to the PP/epoxy/GF (80/10/10) composite leads to its preferential distribution in the phase coated on GF. CB appears to have a coarsening effect on the morphology of that phase. From the morphological change presented in Figure 5, it can be deduced that the epoxy resin coated on the GF surface during the melt mixing. This is due to the good affinity between them. Because epoxy can coat on the GF surface, epoxy will easily become a continuous phase at a low concentration. When added to the PP/epoxy/GF composite, CB distributes in the epoxy phase coated on GF because of the high polarity of epoxy. The

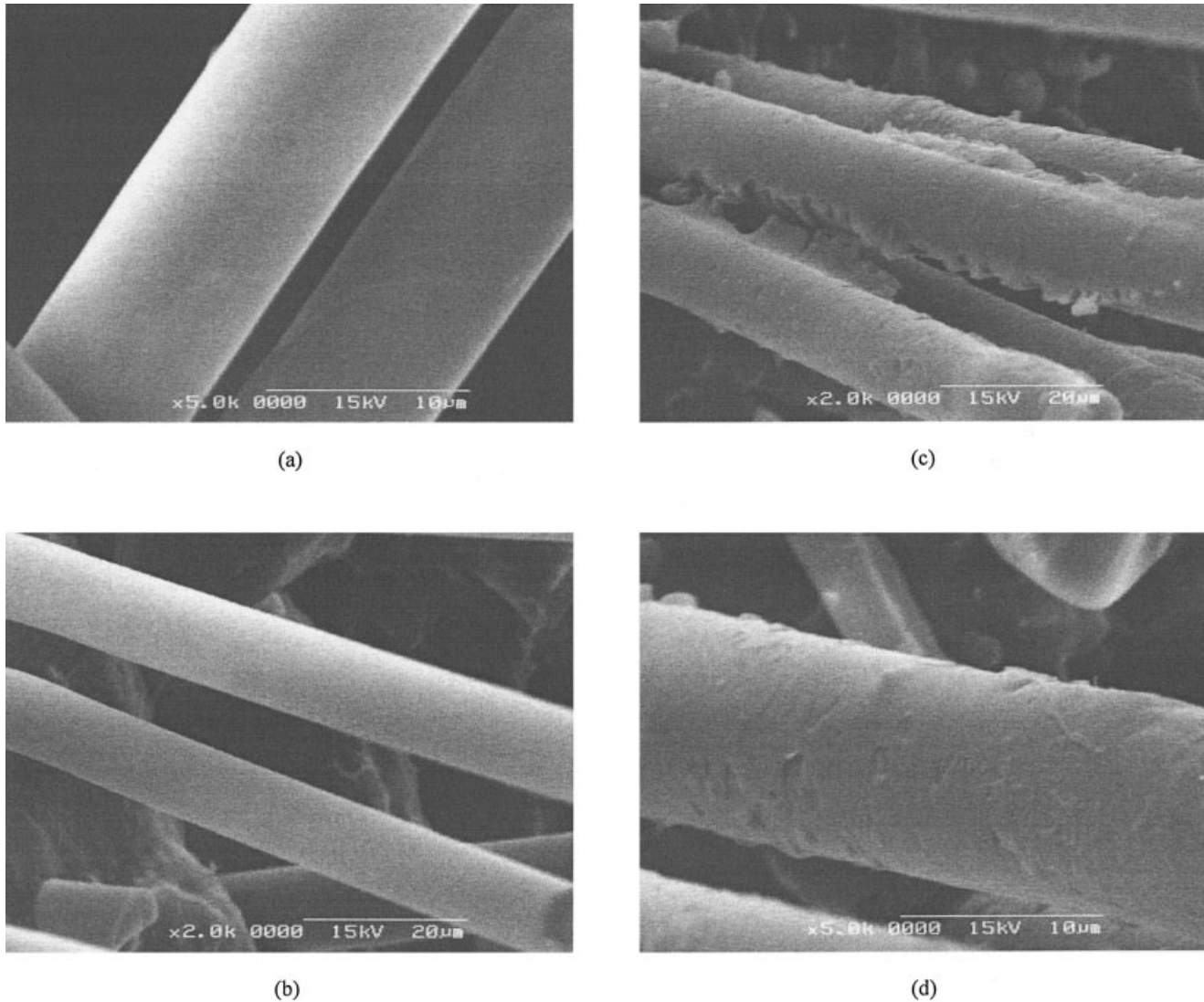


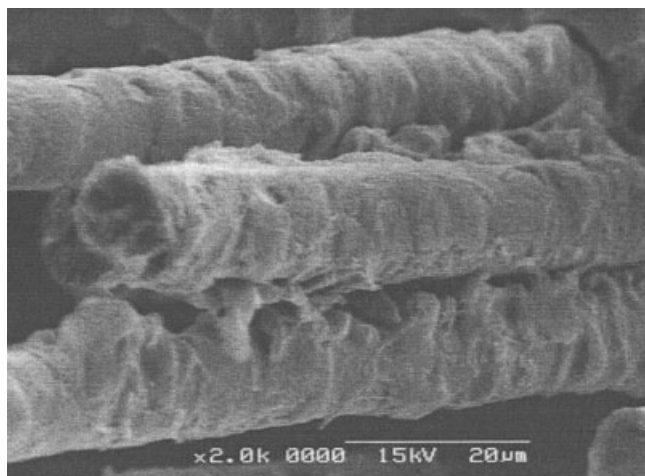
Figure 5 SEM micrographs of (a) GF and freeze-fractured surfaces of (b) PP/GF (90/10), (c,d) PP/epoxy/GF (80/10/10) at two magnifications, and (e,f) PP/epoxy/GF/CB (80/10/10/4) at two magnifications.

coarsening effect of CB on the morphology of epoxy probably occurs because the addition of CB increases the viscosity of epoxy.

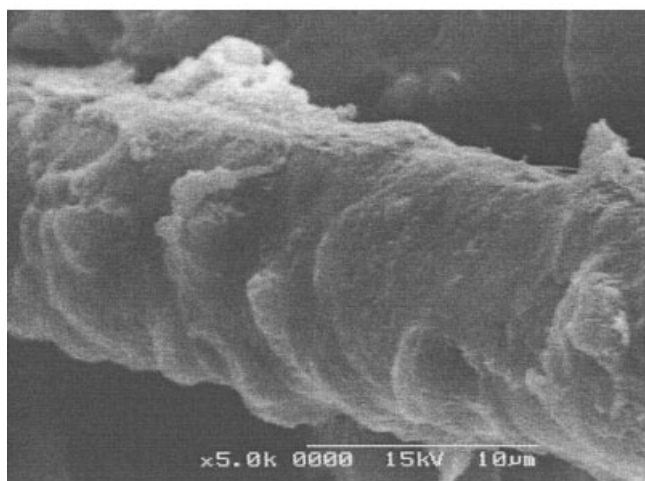
The data in Figure 1 show that the percolation threshold of the CB-filled PP/epoxy/GF (80/10/10) composite is approximately 5 wt % CB, which is lower than that of the PP/CB and PP/epoxy/CB composites. It is perceptible until 8 wt % CB that the PP/epoxy/GF/CB composite has a lower volume resistivity than the PP/CB and PP/epoxy/CB composites. The decreased percolation threshold and volume resistivity suggest that conductive paths exist in the PP/epoxy/GF/CB composite, which has a unique structure of epoxy-coated GF and the preferential location of CB in the continuous epoxy phase. According to the studies on PP/PA/GF/CB composites,^{8,31} the conductive paths are probably formed through the interconnection of GF.

Effects of the GF and epoxy contents on the volume resistivity

At a given composition of PP/epoxy/CB (80/10/4), the volume resistivity of the PP/epoxy/GF/CB composite varies with increasing GF content, as shown in Figure 6. The volume resistivity has a tendency to decrease with increasing GF content. When the PP/epoxy/GF ratio is 80/10/10, the composite filled with 4 wt % CB has a minimum volume resistivity. At a higher GF content, the volume resistivity increases slightly. At a low GF content, because GF can hardly interconnect, the volume resistivity of the composites will remain high. Figure 7(a) shows that in the PP/epoxy/GF/CB (80/10/5/4) composite, GF disperses disorderly in the matrix and apart from each other. This makes the composite insulating with a volume resistivity of $1.20 \times 10^{14} \Omega \text{ cm}$. Increasing the GF



(c)



(f)

Figure 5 (Continued from the previous page)

content will improve the interconnection. Figure 7(b) shows that in the PP/epoxy/GF/CB (80/10/10/4) composite, GF forms effective interconnections, which lead to the decrease of the volume resistivity to $9.48 \times 10^8 \Omega \text{ cm}$. The PP/epoxy/GF/CB (80/10/15/4) composite exhibits a slightly higher volume resistivity. This may be explained by the fact that the same amount of epoxy coated on more GF and the continuity of the epoxy coating became less complete. In PP/epoxy/GF, 10 wt % GF appears to be sufficient to decrease the volume resistivity. This is consistent with the studies of the PP/PA/GF/CB composite,^{8,31} in which 10 wt % GF was sufficient to generate continuity of the PA/CB-coated GF within the continuous PP matrix.

At a given composition of PP/GF/CB (80/10/4), the effect of the epoxy content on the volume resistivity of the PP/epoxy/GF/CB composite is shown in

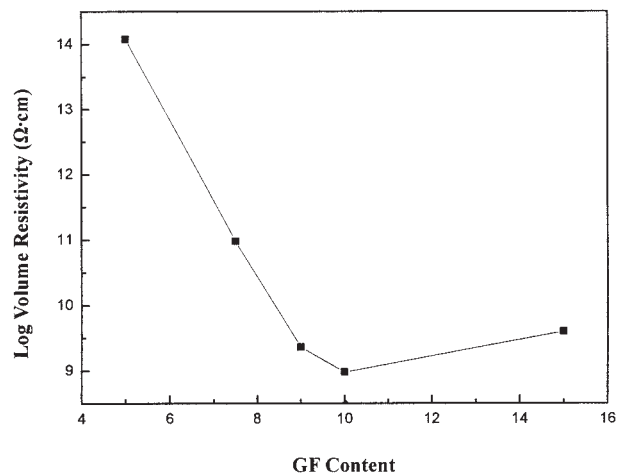
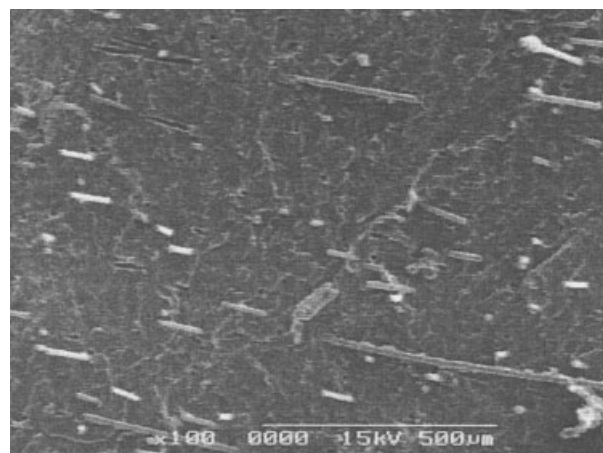
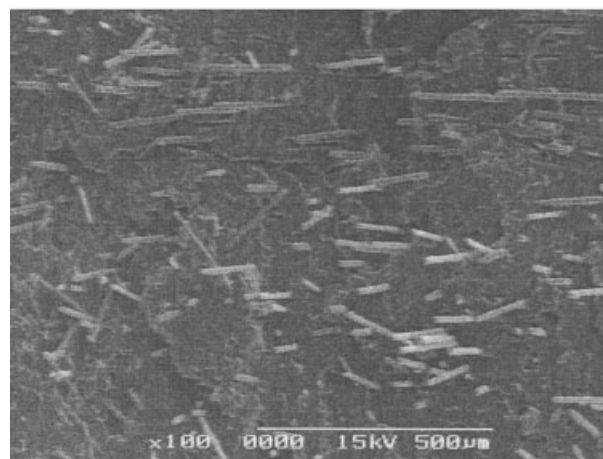


Figure 6 Volume resistivity versus the GF content of PP/epoxy/GF/CB (80/10/x/4) composites.



(a)



(b)

Figure 7 SEM micrographs of freeze-fractured surfaces of (a) PP/epoxy/GF/CB (80/10/5/4) and (b) PP/epoxy/GF/CB (80/10/10/4) composites.

Figure 8. The volume resistivity decreases with increasing epoxy content. The minimum volume resistivity of the composite filled with 4 wt % CB is obtained when the PP/epoxy/GF ratio is 80/10/10. A higher epoxy content results in a slight increase in the volume resistivity. A low epoxy content is insufficient to form a continuous coating on the GF surface. Figure 9 shows that in the PP/epoxy/GF/CB (80/5/10/4) composite, CB distributes in the discontinuous epoxy phase coated on GF. Because CB cannot form conductive paths, the volume resistivity of the composite is as high as $6.65 \times 10^{14} \Omega \text{ cm}$. An increase in the epoxy content will improve the epoxy coating. Figure 5(e,f) shows that in the PP/epoxy/GF/CB (80/10/10/4) composite, epoxy coats GF sufficiently. The slight increase in the volume resistivity at a higher epoxy content can be attributed to the decrease in the CB concentration in more epoxy.

The optimal composition of PP/epoxy/GF is fixed at 80/10/10. Filled with about 3–7.5 wt % conductive CB, the composites show a volume resistivity of 1×10^{12} to $1 \times 10^3 \Omega \text{ cm}$, respectively (Fig. 1). The composites are suitable for antistatic or conductive applications.

CONCLUSIONS

Conductive polymer composites exhibiting a reduced percolation threshold have been successfully prepared by the incorporation of CB and GF into immiscible PP/epoxy blends. The CB-filled PP/epoxy/GF (80/10/10) composite exhibits low electrical resistivity. The composite has a percolation threshold of 5.0 wt % CB, which is lower than that of the PP/CB and PP/epoxy/CB composites. The PP/epoxy/GF (80/10/10) composites filled with 3–7.5 wt % CB show volume resistivity of 1×10^{12} to $1 \times 10^3 \Omega \text{ cm}$ and can be used

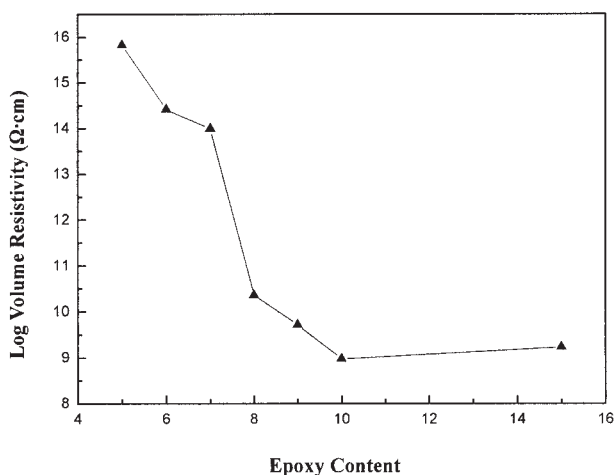


Figure 8 Volume resistivity versus the epoxy content of PP/epoxy/GF/CB (80/x/10/4) composites.

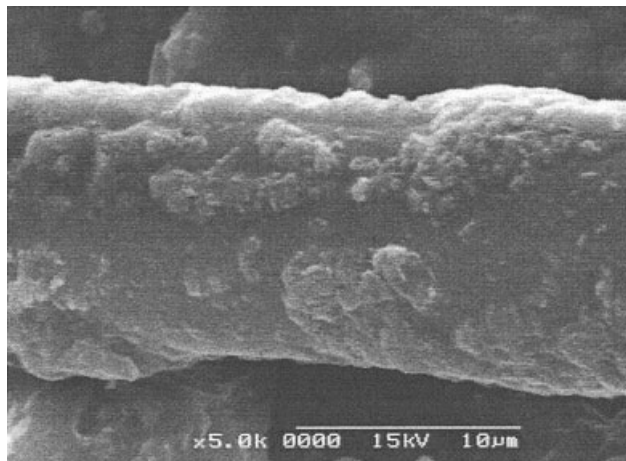


Figure 9 SEM micrograph of the freeze-fractured surface of the PP/epoxy/GF/CB (80/5/10/4) composite.

as antistatic or conductive materials. In the composites, CB preferentially distributes in the epoxy phase because of the high polarity and low melt viscosity of the epoxy resin. The strong affinity between epoxy and GF leads to the formation of epoxy-coated GF. The reduced percolation threshold and volume resistivity suggest that conductive paths exist in the PP/epoxy/GF/CB composite. The conductive paths are probably formed through the interconnection of GF. The GF and epoxy contents have significant effects on the volume resistivity. The GF content should be high enough to decrease the volume resistivity. The epoxy content should be sufficient to provide a complete epoxy coating.

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