

Carbon Black-Filled Immiscible Polypropylene/Epoxy Blends

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ABSTRACT: Carbon black- (CB) filled immiscible thermoplastic/thermosetting polymer blends consisting of polypropylene (PP) and epoxy resin were reported in this paper. The PP/epoxy/CB blends with varied compositions and different processing sequences were prepared by melt-mixing method. The CB distribution and the relationship between morphology and electrical properties of the PP/epoxy/CB blends were investigated. Scanning electron microscopy (SEM), optical microscopy, and extraction experimental results showed that in PP/epoxy blends CB particles preferentially localized in the epoxy phase, indicating that CB has a good affinity with epoxy resin. The incorporation of CB changed the spherical particles of the dispersed epoxy

phase into elongated structure. With increasing epoxy content, the elongation deformation of epoxy phase became more obvious and eventually the blends developed into cocontinuous structure. When CB was initially blended with PP and followed by the addition of epoxy resin, the partial migration of CB from PP to the epoxy phase was observed. When the PP/epoxy ratio was 40/60, the percolation threshold was reduced to about 4 phr CB, which is half of the percolation threshold of the PP/CB composite. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 461–471, 2006

Key words: polypropylene; blends; conducting polymers; morphology

INTRODUCTION

Conductive fillers, such as metal powder,^{1,2} carbon black (CB),^{3–5} and carbon fiber⁶ have long been used to decrease the electrical resistivity of insulating polymers and fabricate conducting polymer composites (CPCs). The critical amount of conductive filler required to form continuous conducting paths and to impart electrical conductivity to the polymer matrix is called percolation threshold. CB is the most widely used conductive filler because of its abundant source, low density, permanent conductivity and low cost. For CB-filled CPCs, it is desirable to decrease the percolation threshold as low as possible. High CB concentration increases the melt viscosity and decreases the impact resistance, thus the processability and mechanical properties of the composites were lost.^{7,8} In highly filled CB compounds, CB tends to slough and cause contamination in clean room environment.⁸ Increasing CB concentration also increases the final product cost.

In recent years one promising method on the basis of CB-filled immiscible polymer blends has been developed to decrease the percolation threshold of CPCs. In such ternary or multiphase composites, the heterogeneous distribution of CB makes the percolation threshold and resistivity values of the composites

lower than those of the corresponding CB-filled individual polymers.^{8–20} Electrical conduction can be achieved via double percolation, i.e., CB preferentially distributes in one continuous polymer phase and the CB concentration reaches the percolation level in that phase.^{9–14} The more beneficial case is the preferential localization of CB at the interface of the cocontinuous immiscible polymer blends, which can remarkably decrease the percolation threshold.^{9,15–17} Several factors determine the CB distribution in the polymer blends, such as polarity or surface tension,^{10,18} polymer crystallinity,⁹ melt viscosity,^{19,20} flexibility of polymer chains,²¹ and processing.^{9,15} CB-filled immiscible polymer blends with low percolation threshold and enhanced conductivity have found application in conductive or antistatic materials,^{8–17} positive temperature coefficient (PTC) materials,^{19,20} liquids or chemical vapor sensors,^{22,23} and electromagnetic interference (EMI) shielding.²⁴

All the reported work about CB-filled immiscible polymer blends is based on nonpolar/nonpolar,^{9,18} nonpolar/polar,^{10,15} polar/polar thermoplastics,²⁵ or plastic/rubber and rubber/rubber blends.^{16,24} In this paper, CB-filled immiscible thermoplastic/thermosetting polymer blends consisting of polypropylene (PP) and epoxy resin were investigated for the first time. The PP/epoxy/CB blends with varied compositions and different processing sequences were prepared by melt-mixing method. The CB distribution in the blends and the relationship between the morphology

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and the electrical properties of the blends were studied.

EXPERIMENTAL

Materials

PP, M1600, was produced by Hyundai Petrochemical Co., Ltd. (Korea), with a melt flow index of 25 g/10 min. Diglycidyl ether of bisphenol A resin (DGEBA, M_w : 4500 g/mol) was produced by Shanghai Resin Co., Ltd. (China). Electrically conductive CB (V-XC72) was provided by Cabot Co., Ltd. (USA), with DBP absorption of 168.6 mL/100 g.

Sample preparation

Prior to blending, all materials were dried at 80°C in vacuum for about 8 h. Unless otherwise specified, the PP/epoxy/CB blends were prepared by melt-mixing of the dry-blended components in a Haake RC90 Rheometer (Germany) simultaneously at 190°C and 30 rpm for 10 min. The epoxy/CB/PP blends were prepared by initially melt-blending the CB with epoxy, followed by the addition of PP. The PP/CB/epoxy blends were prepared by initially melt-blending the CB with PP, followed by the addition of epoxy resin. All blend ratios described is related to percentage by weight. The resultant blends were subsequently compression-molded at 190°C to form plaques of 1 or 4 mm thickness.

Measurements of volume resistivity

For samples with electrical resistivity $>10^8 \Omega \text{ cm}$, the volume resistivity measurements were carried out using 1-mm plaques with a ZC36 high resistance meter (Shanghai Electrical Meter Factory, China), according to ASTM D 257. For moderately conductive samples with resistivity $<10^8 \Omega \text{ cm}$, 4-mm plaques were cut into specimens of 90 mm length and 10 mm width. And the volume resistivity was measured according to ASTM D 4496 with a set of low resistance measurement apparatus, consisting of current electrodes, potential electrodes, a power supply, a digital ampere meter, and a voltage meter.

SEM and optical microscopy analysis

The blends were fractured in liquid nitrogen and the freeze-fractured surfaces were observed with a Hitachi S-2150 scanning electron microscope (Japan). To analyze the morphology clearly, some freeze-fractured samples were etched in dichloromethane for 30 min to remove the epoxy phase on the surfaces. All samples were gold-sputtered prior to observation.

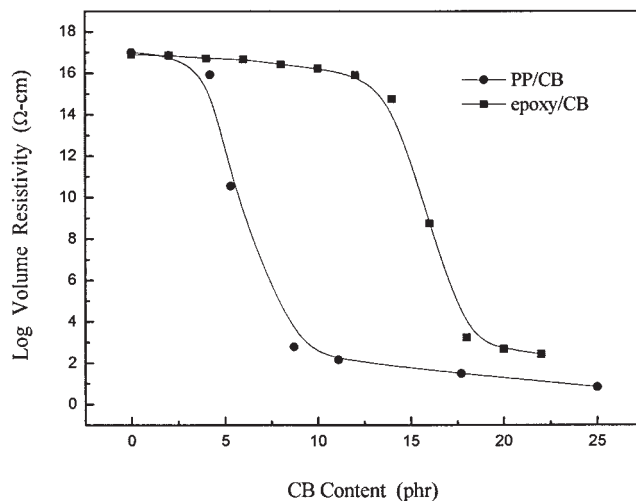


Figure 1 Volume resistivity versus CB content of CB filled individual PP and epoxy matrix.

Optical microscopy analysis was performed on thin films by a Leica DMLPI optical microscope (Germany).

Extraction experiments and thermogravimetric analysis

The selective extraction of PP and epoxy phases in the blends was carried out with a Soxhlet extractor by xylene and dichloromethane, respectively, until the left samples were of constant weight.

The thermogravimetry of the extracted samples were studied with a PerkinElmer TGA7 (Wellesley, MA) to analyze the CB content in the insoluble component. The samples were scanned from 30 to 600°C in nitrogen atmosphere and 600–850°C in oxygen atmosphere, at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Individually filled polymers

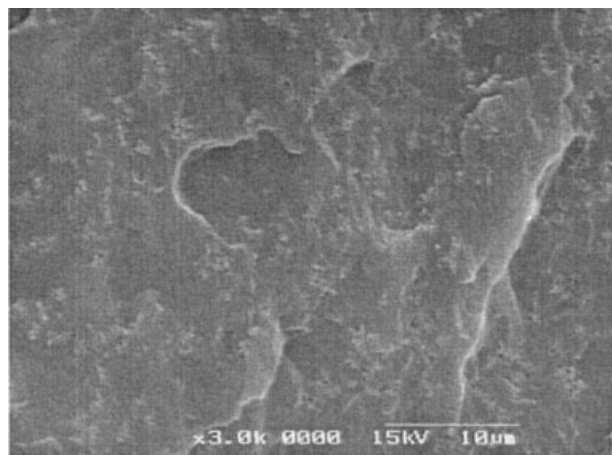
Figure 1 depicts the volume resistivity of CB-filled individual polymers as a function of CB content. Both PP/CB and epoxy/CB composites exhibit typical characteristics of percolation. At low CB loadings, a little change in volume resistivity can be observed because the distances between CB particles are large enough. Increasing the CB content makes CB more crowded, leading to the slow decrease of volume resistivity. In the vicinity of the percolation threshold, the volume resistivity decreases markedly by several orders of magnitude and a transition from insulating to conductive materials occurs. This indicates that the CB particles came into contact with each other or closed up enough to allow the electron hop by tunneling, thus forming continuous conducting paths or net-

work. Once the percolation was reached, additional CB loading could not greatly reduce the volume resistivity because of the formation of conducting paths.

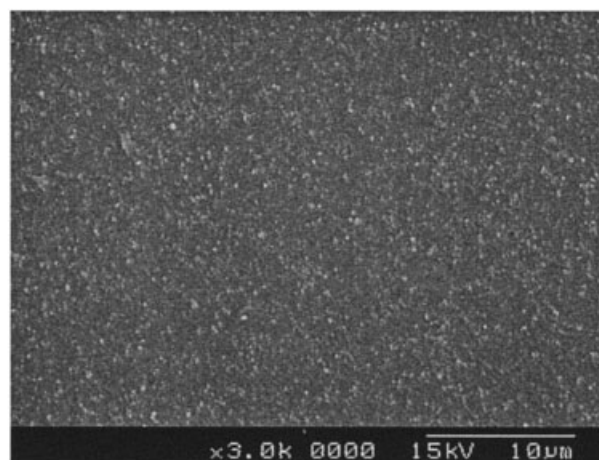
The percolation threshold of PP/CB composite is about 8 phr CB, less than half of the value of epoxy/CB composite, which is about 17 phr CB. The significant difference in percolation threshold can be explained by the crystallinity and polarity of the polymer matrix. For crystalline polymers, CB particles would be ejected from the crystalline regions and localized in the amorphous phase.^{7,9} Previous studies showed that the polymer polarity or surface tension played an important role in the formation of conducting paths in CB-filled CPCs.^{5,10} The larger the polarity or surface tension of a polymer matrix, the higher the percolation threshold is.^{5,10} Because the polymer with higher polarity (larger surface tension) can readily wet CB and disperse the CB particles more uniformly, thus requiring higher concentration to achieve percolation. However, in the case of poor wetting of the CB surface by the polymer, CB/CB interface is preferred, leading to the formation of chain-like structure of CB agglomerates.¹⁰ PP is a highly crystalline polymer in which CB can only distribute in the amorphous phase. This selective distribution of CB in the amorphous phase is equivalent to increasing the effective concentration of CB in the PP matrix. In contrast with PP, epoxy is an amorphous and polar resin with epoxy, hydroxyl, and ether groups. The high polarity of epoxy resin makes it easily wet the CB surface and CB particles disperse more uniformly in epoxy. As a result, the percolation threshold of epoxy/CB composite is much higher than that of PP/CB composite. The morphological observation shown in Figure 2 demonstrates clearly the difference in the interaction of CB particles with the PP or epoxy matrix. In the PP/CB (100/11) and epoxy/CB (100/20) composites CB has reached the percolation level. CB forms chain-like structure within the nonpolar PP matrix in the form of agglomerates rather than individual particles because of the poor wetting of CB. The CB distribution in PP is relatively heterogeneous, as a result of the selective localization in the amorphous phase. However in epoxy resin, CB particles disperse rather uniformly because of the good wetting by the epoxy matrix with higher polarity. The chain-like structure of CB can hardly be seen. This comparatively uniform CB distribution results in the high-percolation threshold of epoxy/CB composite.

CB distribution in PP/epoxy blends

Figure 3 shows the scanning electron micrographs of PP/epoxy (70/30), PP/epoxy/CB (70/30/6) blends and their etched samples. In the PP/epoxy (70/30) blend, epoxy resin disperses in the continuous PP matrix and forms spherical particles of 3–20 μm diameter, as shown in Figure 3(a). Figure 3(b,c) shows the



(a)



(b)

Figure 2 SEM micrographs of freeze-fractured surface of (a) PP/CB (100/11) and (b) epoxy/CB (100/20) composites.

addition of CB to PP/epoxy blend, which is accompanied by its preferential localization in the epoxy phase. It should be noted that the incorporation of CB changes the blend morphology significantly. Only a few spherical dispersed epoxy particles can be seen and more elongated dispersed phase structure appears, in which CB accumulates. To observe the morphology clearly, the freeze-fractured surface of the above-mentioned samples was etched by dichloromethane to remove the epoxy resin. The scanning electron micrographs of the etched sample are shown in Figure 3(d,f). For comparison, samples of PP and PP/CB composite were etched under the same condition, and the results show that the etching has little influence on their morphology. Figure 3(d) indicates the epoxy phase in the PP/epoxy (70/30) blend, which is completely removed by the solvent extraction, leaving spherical cavities of $<20 \mu\text{m}$ diameter in the PP

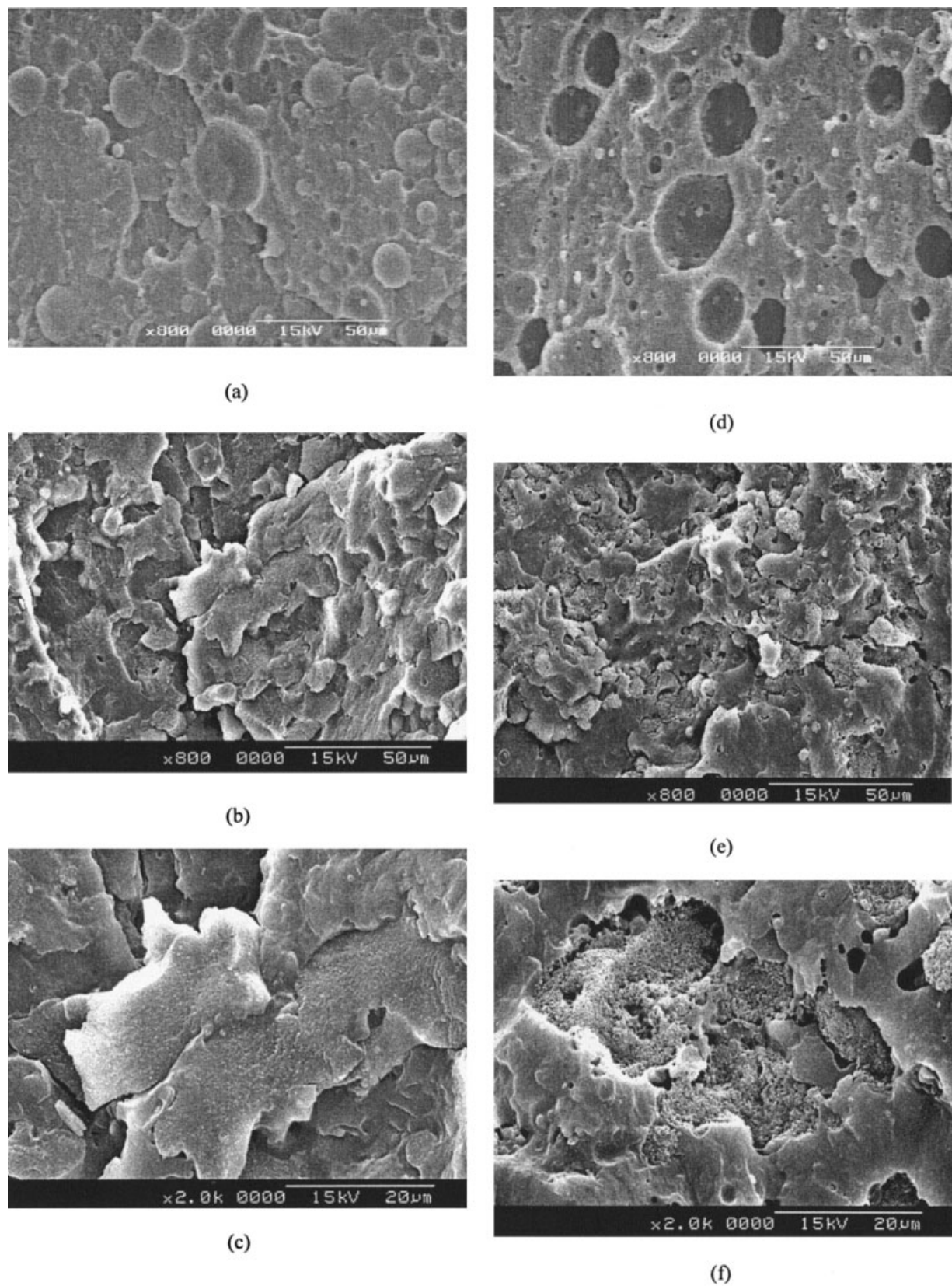


Figure 3 SEM micrographs of freeze-fractured surface of (a) PP/epoxy (70/30), (b),(c) PP/epoxy/CB (70/30/6) at two magnifications, (d) PP/epoxy (70/30, etched), and (e), (f) PP/epoxy/CB (70/30/6, etched) at two magnifications.

matrix. However, for the PP/epoxy/CB (70/30/6) blend, the etching is incomplete. Judged from the shape and size, the etched phase corresponds to the CB-rich domains, i.e., the epoxy phase. The incomplete etching of epoxy phase is found in CB-filled immiscible PP/epoxy blends with varied compositions, manifesting the existence of strong epoxy/CB interaction that prevents the epoxy phase from being etched.

The preferential localization of CB in epoxy can be attributed to the high polarity and low melt viscosity of the epoxy phase. Previous studies show the heterogeneous distribution of CB in immiscible polymer blends, which is mainly due to the good affinity of CB with one phase of the polymer blends, usually the phase with higher polarity or surface tension, and accordingly high percolation threshold.^{10–12,18} In the present work, the preferential localization of CB in epoxy is consistent with the results of those studies. PP is a nonpolar polymer, whereas epoxy resin is a polar resin. The high polarity of epoxy resin makes it easily wet the CB surface (i.e., CB has a stronger affinity with epoxy than PP), and the percolation threshold of epoxy/CB is much higher than that of the PP/CB composite. Furthermore, at the processing temperature of 190°C, epoxy has a lower melt viscosity than PP, which also favors the CB incorporation into epoxy.

The formation of elongated dispersed phase structure due to the addition of CB has been previously reported.^{11,15,22} Breuer et al.¹¹ thought that the friction between the CB-coated dispersed particles and the matrix caused deformation, leading to the elongated structures. Cheah et al.¹⁵ explained the elongation of the dispersed phase as the result of the interfacial activity of CB, i.e., the incorporation of CB into the blend decreased the interfacial tension between the immiscible binary polymers. Segal et al.²² attributed the elongated deformation of the dispersed phase to the intrinsic interfacial activity of CB particles as well as the interphase friction. The cause of the formation of elongated structure of the dispersed epoxy phase in our work needs further investigations.

Figure 4 shows the optical micrograph of PP/epoxy/CB (70/30/6) composite. The dispersed epoxy resin mainly forms elongated structure accompanied with some spherical particles, shown as the dark domains in the micrograph, because of the CB incorporation, whereas the continuous PP phase is rather transparent. For the PP/CB blend with the same CB content, dark and opaque films are obtained. Thus the optical microscopy also confirms the preferential localization of CB in the epoxy phase.

The CB distribution in immiscible polymer blends is usually studied with scanning electron microscopy (SEM), transmission electron microscopy (TEM), or optical microscopy in the reported literatures. In our

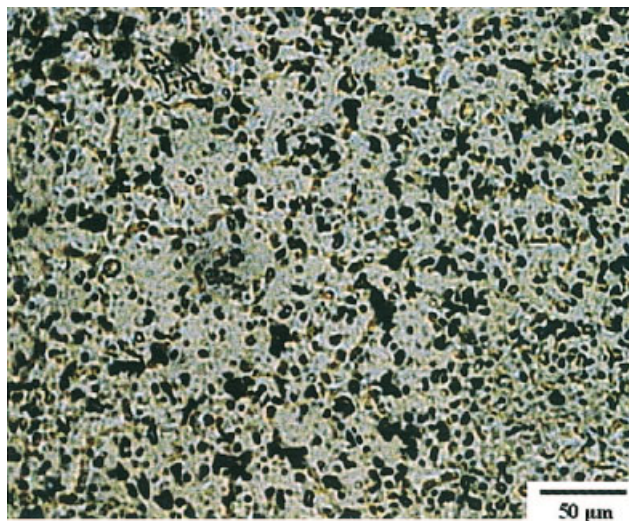


Figure 4 Optical micrograph of the PP/epoxy/CB (70/30/6) blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

work, the CB distribution in the PP/epoxy/CB (70/30/6) composite was also studied using extraction experiments and TGA. The composite was selectively extracted by xylene to remove PP and the insoluble component was analyzed with TGA. For comparison, the epoxy resin used in this work was also analyzed with TGA. The CB content in the PP and epoxy phase was calculated according to the mass loss after extraction and the TGA curve, respectively. After extraction, there was little CB in the solvent. The weight fraction of the extracted component is 65.1%. In the PP/epoxy/CB (70/30/6) composite, the weight fraction of PP is 65.8%. Considering the experimental error, it can be deduced that the extracted component was PP and little CB distributed in the PP phase. The weight loss corresponding to epoxy and CB in the insoluble component was determined according to the TGA curves, which are 83.2% and 16.8%, respectively. Accordingly, the CB content in epoxy is calculated to be 20.2%. In the PP/epoxy/CB (70/30/6) composite, the ratio of CB/epoxy is 20.0%. The results of both the extraction and TGA methods showed that nearly all the CB particles distribute in epoxy resin, which is in agreement with the preferential localization of CB in epoxy observed with SEM and optical microscopy.

Relationship between the morphology and the electrical properties

Figure 5 depicts the volume resistivity of CB-filled PP/epoxy blends with varied compositions as a function of CB content. An exceptional phenomenon is found in the electrical properties of CB-filled PP/epoxy blends with 70/30 and 60/40 PP/epoxy ratios. For the PP/epoxy (70/30) blend, at low CB content (<4

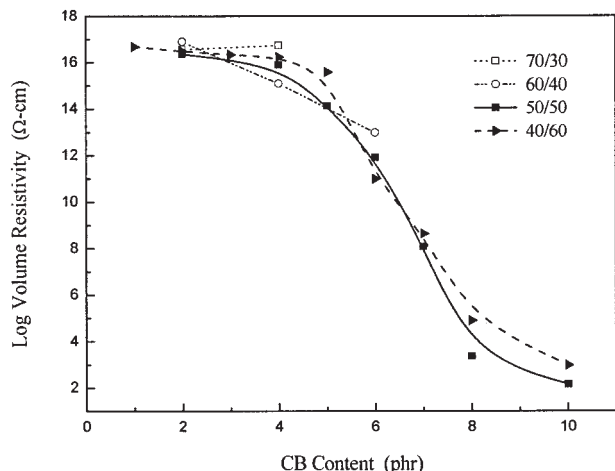


Figure 5 Volume resistivity versus CB content of PP/epoxy/CB blends with various PP/epoxy ratios.

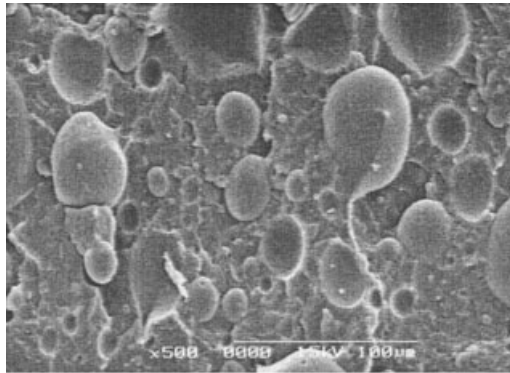
phr) the volume resistivity was very high, over 10^{16} Ω cm. In the vicinity of 6 phr CB or higher, the volume resistivity was about 10^{14} Ω cm, tested under a voltage of 10 V. But when the voltage of 100 V was applied, the volume resistivity was beyond the measuring range of the high resistance meter, i.e., $<10^8$ Ω cm. A similar phenomenon occurred in the CB-filled PP/epoxy (60/40) blend when the CB content was 8 phr or higher. The volume resistivity was about 10^{12} Ω cm when tested with 10 V, whereas it was lower than 10^8 Ω cm with 100 V. The significant fluctuation in the electrical resistivity obtained with different applied voltage makes it difficult to determine the reliable volume resistivity, thus this type of data is not presented in Figure 5. For the PP/epoxy/CB blends with PP/epoxy ratios of 50/50 and 40/60, stable and reproducible volume resistivity data were obtained. Accordingly the percolation thresholds of CB-filled 50/50 and 40/60 PP/epoxy blends were about 7.5 and 8 phr, respectively, which are close to the percolation threshold of PP/CB composite.

It has been well established that the electrical resistivity and the percolation threshold of CB-filled immiscible polymer blends depend greatly on morphology.^{8-22,26} The difference in the electrical behavior of various PP/epoxy/CB blends can be explained by the morphological difference. The scanning electron micrographs in Figure 3 shows that CB preferentially localizes in the dispersed epoxy phase in the PP/epoxy (70/30) blend. Although the epoxy phase is not continuous, there are narrow gaps between the adjacent CB-rich epoxy domains. At low CB content, CB does not percolate in epoxy, resulting in the very high volume resistivity. When CB content is in the vicinity of 6 phr, CB has reached the percolation level in epoxy resin (the percolation threshold of epoxy/CB is about 17 phr). However, conducting paths cannot be formed via double percolation because of the discontinuity of

the epoxy phase, leading to the relatively high volume resistivity when tested with 10 V. In CB-filled conducting polymers and polymer blends, a higher applied electric field can excite electrons and maintain a higher kinetic and potential energy level, which allows electrons to proceed in the "tunneling process" or "jump" through the gap.⁷ This well explains the significant decrease in volume resistivity when the voltage of 100 V was applied for PP/epoxy (70/30) blends with 6 phr or higher CB content. The tunneling effect between the CB clusters in adjacent epoxy domains is the dominant conduction mechanism at this high voltage, reducing the volume resistivity of the blends remarkably.

The similar electrical behavior of CB-filled PP/epoxy (60/40) blend can also be explained by the morphology. Figure 6 shows the scanning electron micrographs of the PP/epoxy (60/40) blend and its CB-filled composite. Epoxy disperses in the continuous PP matrix, forming spherical particles, as shown in the scanning electrons micrograph of the 70/30 samples. Likewise, addition of CB results in its preferential localization in the epoxy phase. The elongated structure of dispersed epoxy phase in PP/epoxy/CB (60/40/10) is also observed, and the elongation is more obvious than in the CB-filled 70/30 blends. Etching of the freeze-fractured surface helps to analyze the morphology clearly. As shown in Figure 6(d), the dispersed epoxy phase is elongated to a great extent. Although the epoxy phase is incompletely continuous, the gaps between some adjacent CB-rich epoxy domains are very small. In certain regions, the morphology seems to approach the onset of a cocontinuous structure. The volume resistivity of the blends with low CB loading remains high because CB cannot reach the percolation threshold in epoxy. Increasing the CB content results in the gradually slow decrease of volume resistivity due to the increased CB concentration in the partially continuous epoxy phase. When the CB content is close to or higher than the percolation level of 8 phr in epoxy, the incomplete continuity of epoxy phase makes the blends impossible to achieve electrical conduction through double percolation. Thus the volume resistivity tested with 10 V is relatively high. Similarly, when the higher voltage (100 V) is applied, the tunneling effect between the adjacent CB clusters dominates the conduction process and thus the volume resistivity is significantly decreased, compared with the results obtained with 10 V.

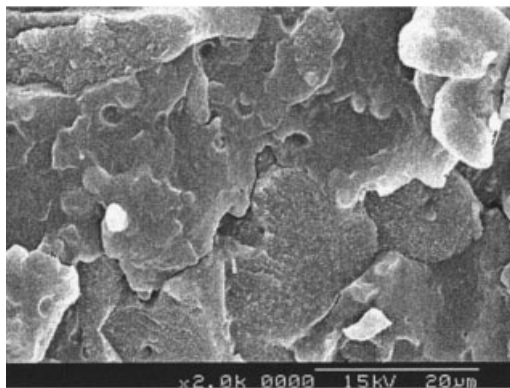
The scanning electron micrographs of the PP/epoxy/CB (50/50/8) blend are presented in Figure 7. CB preferentially distributes in the epoxy phase, as observed in the 70/30 and 60/40 blends. Seen from Figure 7(b), PP and epoxy resin are in cocontinuous phases in the CB-filled PP/epoxy (50/50) blend. When CB reaches the percolation concentration in the epoxy phase, double percolation can be achieved and the blend is imparted electrical conductivity. The cocon-



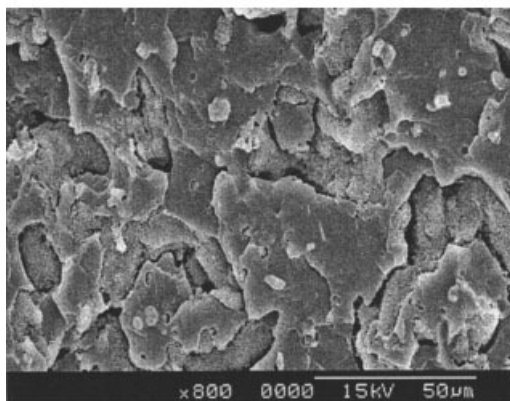
(a)



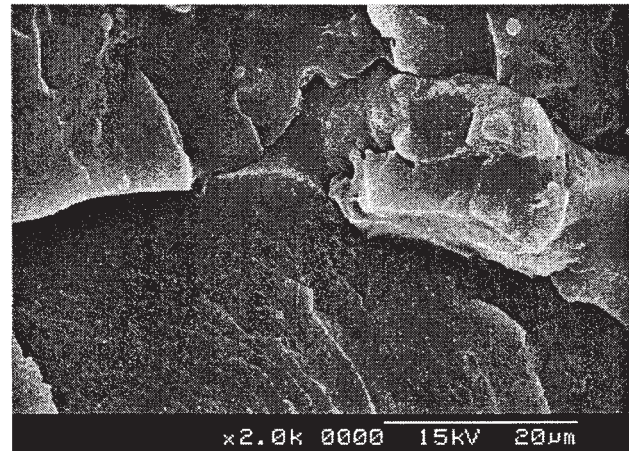
(b)



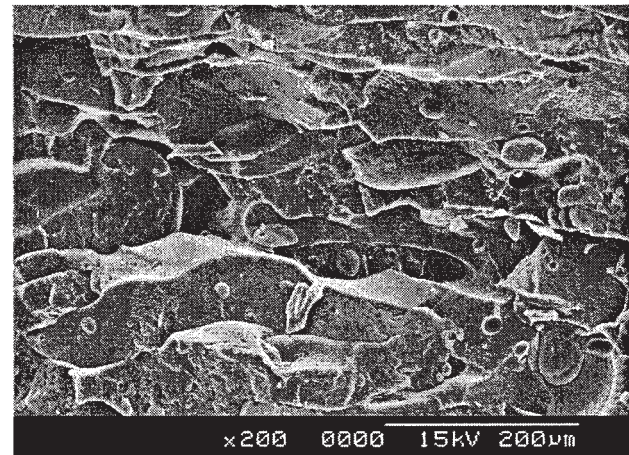
(c)



(d)



(a)



(b)

Figure 7 SEM micrographs of freeze-fractured surface of PP/epoxy/CB (50/50/8) at two magnifications.

tinuous structure results in the stable volume resistivity with good reproducibility. Because of the high critical CB content required to percolate in epoxy, the percolation threshold of CB-filled PP/epoxy (50/50) blend is about 7.5 phr, which is not greatly reduced in comparison with that of the PP/CB composite.

For CB-filled PP/epoxy (40/60) blend, the morphological studies also show that the PP and epoxy phases are cocontinuous, and CB localizes in the epoxy phase (not shown). Increasing the CB content causes the volume resistivity of the blend to decrease. Finally the

Figure 6 SEM micrographs of freeze-fractured surface of (a) PP/epoxy (60/40), (b), (c) PP/epoxy/CB (60/40/10) at two magnifications, (d) PP/epoxy/CB (60/40/10, etched).

TABLE I
Volume Resistivity of PP/epoxy/CB (70/30/6) and PP/epoxy/CB (40/60/4) Blends with Different Processing Sequences

Sample composition	Processing sequence	Volume resistivity (Ω cm)
PP/epoxy/CB (70/30/6)	Simultaneously melt-blended	About 10^{14} (10 V) < 10^8 (100 V)
	Epoxy/CB/PP	About 10^{14} (10 V) < 10^8 (100 V)
	PP/CB/epoxy	4.87×10^9
PP/epoxy/CB (40/60/4)	Simultaneously melt-blended	1.72×10^{16}
	Epoxy/CB/PP	7.75×10^{16}
	PP/CB/epoxy	1.66×10^4

blend can become conductive through double percolation. Compared with the 50/50 blend, the 40/60 PP/epoxy blend requires a higher critical CB content to percolate in epoxy, resulting in the slightly higher percolation threshold of about 8 phr CB. This value is nearly equal to the percolation threshold of PP/CB composite. At a given CB content, the volume resistivity of CB-filled PP/epoxy (40/60) blend is higher than that of the CB-filled 50/50 blend, as shown in Figure 5. This is because the given amount of CB disperses in more epoxy phase in the PP/epoxy (40/60) blend, and the CB concentration in epoxy is actually decreased.

Effect of processing sequence on the electrical properties

It has been reported that the processing sequence is one of the important factors that influence the electrical properties of CB-filled various binary polymer blends.^{9,10,15} In those blends CB particles preferentially distribute in the phase that has a good affinity with CB, i.e., the phase compatible with CB. When CB is initially blended with the phase less compatible or incompatible with it, followed by the addition of the other phase, the migration of CB from the incompatible phase to the compatible phase is observed. By this means the CB distribution can be controlled and the volume resistivity is decreased, lower than that of the simultaneously melt-blended samples.

In this work, the effect of different processing sequence on the electrical properties was investigated. In addition to the simultaneously melt-mixing blends, epoxy/CB/PP and PP/CB/epoxy blends were prepared by premelt-blending the CB with epoxy resin (or PP), followed by the addition of PP (or epoxy resin). Table I shows the volume resistivity of PP/epoxy/CB (70/30/6) and PP/epoxy/CB (40/60/4) blends with different processing sequence. For the PP/epoxy/CB (70/30/6) blends, the volume resistivity of the simultaneously melt-blended and the epoxy/CB/PP samples is alike. When 10 V is applied the volume resistivity is about 10^{14} Ω cm, whereas the

higher applied voltage of 100 V results in the significantly decreased volume resistivity, < 10^8 Ω cm. The volume resistivity of the PP/CB/epoxy samples is comparatively stable and reproducible, which is 4.87×10^9 Ω cm. For the PP/epoxy/CB (40/60/4) blends, the volume resistivity of the epoxy/CB/PP samples is nearly the same as that of the simultaneously melt-blended samples, which is about 10^{16} Ω cm, indicating the blends are insulating. However, the volume resistivity of the PP/CB/epoxy samples is much lower, being 1.66×10^4 Ω cm.

The processing sequence affects not only the volume resistivity of the blends, but also the CB distribution and the morphology. Figure 8 shows the scanning electron micrographs of the epoxy/CB/PP (30/6/70) and PP/CB/epoxy (70/6/30) blends, which can explain the difference in volume resistivity presented in Table I. Figure 8(a) reveals that CB localizes in the epoxy phase in the epoxy/CB/PP blend, as in the simultaneously melt-blended samples. Because of the good affinity between epoxy resin and CB, the migration of CB from the epoxy phase to PP could not be observed. The epoxy phase exhibits a dispersed morphology similar to that in Figure 3(b,c). The epoxy particles are elongated but not continuous, leading to the similar electrical behavior as in the simultaneously melt-blended PP/epoxy/CB (70/30/6) samples, i.e., the significant fluctuation of the volume resistivity obtained with different applied voltage. Figure 8(b,c) demonstrates the discrepant morphology of the PP/CB/epoxy (70/6/30) blend. The migration of CB particles to the dispersed epoxy phase is clearly shown. It could be the good affinity of epoxy with CB and the strong epoxy/CB interaction that drive CB to interact with the epoxy phase and transfer to it. However the CB particles migrate only partially and accumulate mainly on the surface of the epoxy phase. CB particles are also observed in the PP matrix. This is probably due to the low melt viscosity of epoxy resin at the processing temperature that exerts weak shear stress on CB particles. Thus CB is less likely to migrate from the high viscosity PP phase to the epoxy phase. Since

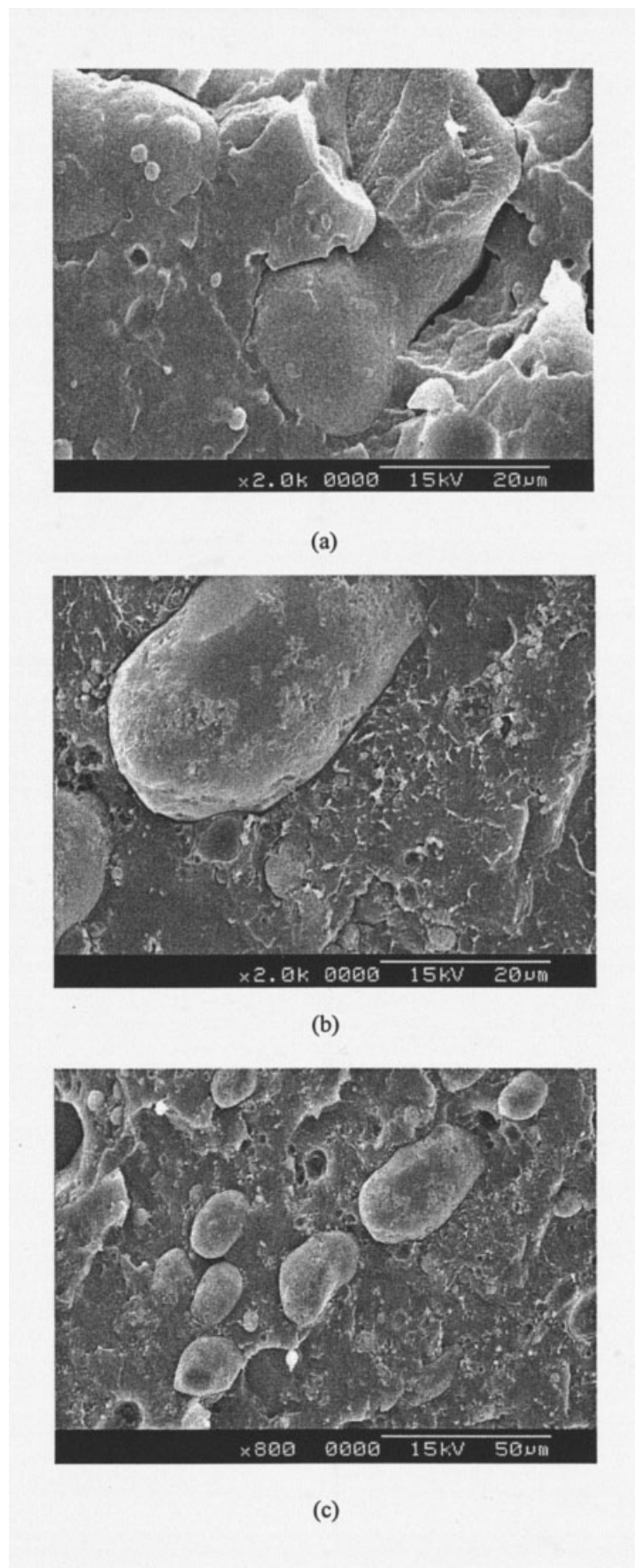


Figure 8 SEM micrographs of freeze-fractured surface of (a) epoxy/CB/PP (30/6/70), (b), (c) PP/CB/epoxy (70/6/30) at two magnifications.

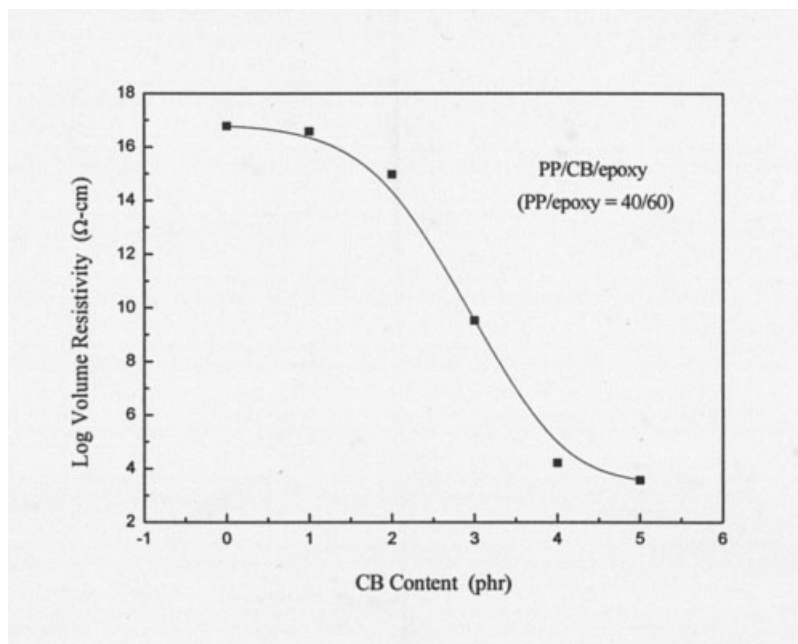


Figure 9 Volume resistivity versus CB content of the PP/CB/epoxy blend (PP/epoxy = 40/60).

a small amount of CB transfers to epoxy resin, CB could not greatly change the morphology of the dispersed epoxy phase, resulting in the spherical epoxy particles rather than the elongated structure. Before the addition of epoxy phase, the CB content in PP/CB (70/6) has reached the percolation level and the PP/CB blend is conductive. Addition of epoxy into PP/CB will cause the CB particles to partially migrate to the epoxy phase, reducing the CB concentration in the continuous PP matrix. Accordingly, the volume resistivity is increased to $4.87 \times 10^9 \Omega \text{ cm}$.

Similarly, in the epoxy/CB/PP (60/4/40) blend, CB particles localize in the continuous epoxy phase, as in the simultaneously melt-blended samples. But the CB concentration in the epoxy phase is much lower than that of the percolation level and the conducting paths could not be formed. As a result, the volume resistivity of the epoxy/CB/PP (60/4/40) blend is as high as that of the simultaneously melt-blended samples, over $10^{16} \Omega \text{ cm}$. However, in the PP/CB/epoxy (40/4/60) blend, CB also partially migrates from PP to the epoxy phase, as observed in the 70/3/30 blend. Before the addition of epoxy resin, the CB content in PP/CB (40/4) is well beyond the percolation level and the volume resistivity is $<10^3 \Omega \text{ cm}$. The partial migration of CB to the epoxy phase because of the addition of epoxy into PP/CB decreases the CB concentration in the PP phase. After the selective extraction of epoxy resin, the shape of the insoluble component was kept unchanged, indicating the continuous phase of PP. Thus the majority of the CB particles left in the continuous PP phase after migration can maintain the conducting paths. The decreased CB concentration in

PP results in a slightly higher volume resistivity of $1.66 \times 10^4 \Omega \text{ cm}$. The PP/CB/epoxy processing sequence offers the possibility to control the CB distribution and obtain a reduced percolation threshold. Figure 9 shows the volume resistivity of the PP/CB/epoxy (PP/epoxy = 40/60) blend as a function of CB content. The volume resistivity decreases with increase in CB content. The percolation threshold is about 4 phr CB, which is greatly reduced, being half of the percolation threshold of the PP/CB composite.

CONCLUSIONS

The percolation threshold of epoxy/CB composite (17 phr) is much higher than that of the PP/CB composite (8 phr). This could be due to the high polarity and surface tension of epoxy resin, which requires high CB content to percolate. SEM, optical microscopy, and extraction experiments show that in the PP/epoxy blends, CB preferentially localizes in the epoxy phase as a result of the good affinity between CB and epoxy. The incomplete etching of the CB-rich epoxy phase indicates the strong CB/epoxy interactions. The addition of CB changed the morphology of the epoxy phase significantly. In the CB-filled 70/30 and 60/40 PP/epoxy blends, the dispersed epoxy phase changed from the spherical particles into the elongated structure, resulting in the very narrow gaps between the adjacent epoxy domains. With increasing epoxy content, the epoxy phase became a continuous phase. Conducting paths can be formed via double percolation. However the percolation threshold of the PP/epoxy/CB blends with PP/epoxy ratio of 50/50 and

40/60 is about 7.5 and 8 phr CB, respectively. The percolation thresholds are almost not reduced in comparison with that of the PP/CB composite, as a result of the high percolation threshold of the epoxy/CB composite. Processing sequence has an important effect on the volume resistivity and morphology of the CB-filled PP/epoxy blends. When CB was initially blended with epoxy and followed by the addition of PP, CB preferentially distributed in the epoxy phase, the same as in the simultaneously melt-blended composites. When CB was initially blended with PP and followed by the addition of epoxy resin, CB particles partially migrated from PP to the epoxy phase. The majority of CB particles left in the continuous PP phase could maintain the conducting paths when CB was sufficient in amount. With a PP/epoxy ratio of 40/60, the blend exhibited a reduced percolation threshold of about 4 phr CB, which is much lower than that of the individually CB-filled PP and epoxy resin composites and the simultaneously melt-blended composites.

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