Percolation threshold and morphology of composites of conducting carbon black/polypropylene/EVA

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Conducting carbon black (CB), one of the intrinsic semi-conductors, was added into matrix polypropylene (PP) to prepare conducting composites by means of the melt processing method. Another component EVA was mixed into the composites in order to lower the percolation threshold. The percolation threshold of the ternary CB/PP/EVA composites was merely 3.8 vol%, while it was up to 7.8 vol% for the binary CB/PP composites without EVA. The conductivity of the ternary CB/PP/EVA composites was up to 10^{-2} S/cm when the CB percentage was 5 vol%, while that of the binary CB/PP was lower than 10^{-2} S/cm when the CB percentage was up to 10 vol%. DSC thermograms of the CB/PP/EVA composites showed that the melting peak shifted to low temperature with increasing CB content. The addition of CB and EVA resulted in the decrease of the crystallinity of PP in the ternary composites. The mechanical properties are also discussed. SEM and TEM were employed to study the morphology of the blend system. The results indicated that CB existed in the form of aggregations in the blend system. The smallest unit that formed a percolation network was grape-like aggregates with some small branches, which consisted of some CB particles, rather than the individual particles. This distribution was very valuable for forming conducting paths and for lowering the percolation value.
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1. Introduction
During the past few decades, electrically conductive polymer materials have found use in a variety of applications. They are divided into two types: one is intrinsically conducting polymers (ICPs) such as polypyrrole, polyaniline, polythiophene; and the other is conducting composites in which some conducting fillers, such as carbon black, graphite, short carbon fibers, etc., are added. Unlike general polymers and conducting fillers, the relatively low thermal stability and environmental stability of ICPs result in their poor processability, although they have been considered potentially suitable for applications in various fields such as light emitting diodes, batteries, electromagnetic shielding, antistatic coating or fibers, gas sensor, corrosion protection and activators [1–5].

Electrically conductive composites with thermoplastic matrices are considered to be an important group of relatively inexpensive materials for special applications. Binary composite systems, consisting of conducting fillers (e.g., carbon black, graphite, metal powder, short carbon fibers) in a polymer matrix, may create materials that are tough and flexible with high electrical conductivity [6, 7]. These unique materials are

ideally suited for antistatic layers, electromagnetic interference shielding, chemical vapor sensors and thermal resistors [8–10]. In spite of a growing number of potential applications, these composites are plagued by a serious drawback. The amount of conductive filler required to achieve a sufficient level of electrical conductivity often leads to processing difficulty [11]. Many simple binary composites have a percolation threshold around 15 vol% fillers [12, 13] as would be predicted by classical percolation theory for a random system [14]. Lowering the percolation threshold of a composite system appears to be an effective way to reduce the amount of filler required to produce adequate conductivity and thereby minimize problems with mechanical properties.

The percolation threshold has already been successfully reduced using ternary composite systems in which carbon black has been incorporated into a mixture of two immiscible polymers [15–21]. Sumita and coworkers [12, 17] reported that matrix blends were able to significantly reduce the percolation threshold. Carbon black was found to aggregate at the interface of the two polymers, which led to more efficient formation of the conductive pathways. The surface energies of the two

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polymers seemed to determine where the carbon black will localize. The critical volume fraction required to reach the percolation threshold was now determined by a "double percolation" effect. Double percolation resulted from the dependence of electrical conductivity on both the connectivity of carbon black within a given polymer and the connectivity of that polymer within the blend. Tchoudakov *et al.* [18] have studied the electrical resistivity and the morphology of polypropylene/nylon (PP/Ny) immiscible blends incorporated with carbon black (CB). They found carbon black was preferentially located in the nylon phase or upon the PP/Ny interface. Due to the "double percolation" effect, blends with a co-continuous phase morphology displayed especially low resistivity values. A study by Gubbels *et al.* [22] showed two-phase semicrystalline polyethylene (PE) favored a decrease in the percolation threshold down to 5 wt%, in agreement with the selective localization of CB particles in the amorphous phase of PE,
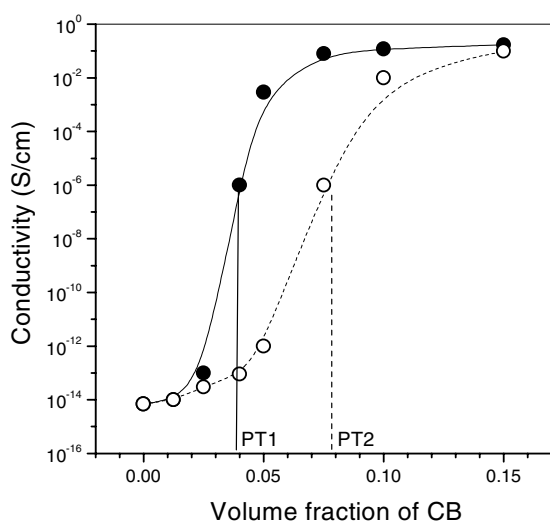
and increasing the degree of crystallinity of PE was a potential way of decreasing further the percolation threshold.

Presently, conducting composites of CB/PP/EVA were prepared by the melt blending method. The purpose of adding EVA into the composites was to lower the percolation threshold. The thermal properties of the blend system were studied by means of DSC and the morphology was observed by means of SEM and TEM.

2. Experimental
2.1. Materials
The matrix polymer used to prepare the ternary blend composite was polypropylene with the melt flow index of 26 g/10 min, which was purchased from Shanghai Petrochemical Co. Limited, China. EVA, an ethylene—vinyl acetate copolymer (1:1), was supplied by the Shanghai representative of BASF Co. The density of EVA was $1,000 \, kg/m^3$. Carbon black, used as a conducting component in the composites, was Vulcan XC-72 obtained from the Cabot (Shanghai) Corporation. Its surface area was 254 m^2/g, DBPA (dibutyl phthalate absorption) value was 178 cm^3/100 g, and the density was about 1900 kg/m^3.

Figure 1 The dependence of conductivity of the CB/PP/EVA composites on the volume fraction of CB. Solid line represents the ternary CB/PP/EVA blend system and dotted line represents the binary CB/PP blend system.
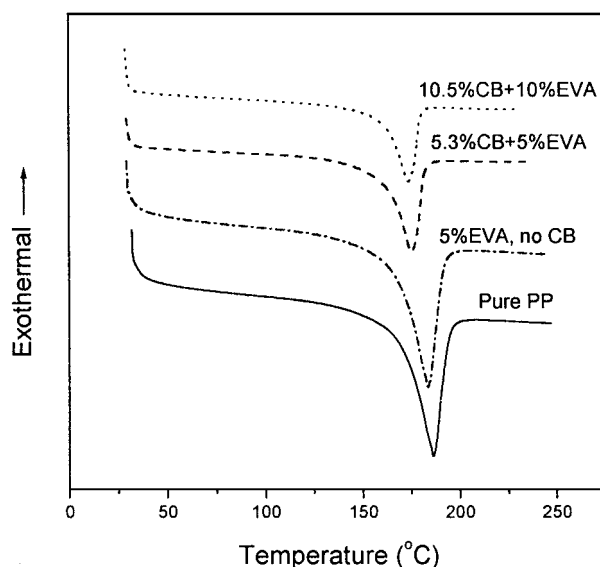
2.2. Preparation of conducting composites
CB-filled PP/EVA conducting composites were prepared using a Haake Rheocord 90 made in Germany. The three components of CB, PP and EVA were added into the mixer at the same time and were blended at a temperature of 185°C, at a rotating rate of 40 rpm and for a mixing time of about 10 min. When the torque did not change with time for 5 min, the blend processing was stopped.

2.3. Characterization
Prior to a measurement, the composites obtained above were further compressed into about 1 mm thickness sheets by a hot press at 190°C. The electrical conductivity of the conducting composite films is measured with a four-probe technique. For any one sample, five points were measured and averaged for the conductivity.

The thermal properties of the conducting composite films were measured using a Mettler 822^e DSC with a heating rate of 10°C/min.

The measurement of the mechanical properties was conducted on a Shimadzu AGS-500ND instrument made in Japan. The composites were compressed into sheets with the thickness of 3 mm.

A Comscan-4 scanning electron microscope (SEM) and a Hitachi H-800 transmission electron microscope (TEM) were employed to study the CB distribution and the morphology of the ternary composites. The samples were broken in liquid nitrogen and were gold-sputtered, and then the cross-section was observed in the SEM at an accelerating voltage of 10 kV. The samples were embedded in epoxy resin and were microtomed on a Reichert–Fung Ultracut. Then, the observation of the thin films with the thickness of 90 nm could be performed by TEM at an accelerating voltage of 250 kV.

Figure 2 DSC thermograms of PP and CB/PP/EVA composites.

3. Results and discussion
3.1. Conductive property

Percolation can be defined as a phase-transition at which a dramatic change occurs at one sharply defined parametric value, as this parameter is continuously changed [23]. In the case of polymer composites filled with carbon black, the electrical conductivity changes by many orders of magnitude at a precise volume fraction of filler. The concentration of carbon black that marks this insulator—conductor transition is often referred to as the percolation threshold. This sudden jump in conductivity is attributed to the formation of the first "infinite" agglomerate pathway that allows electrons to travel a macroscopic distance through the composites [24].

The changes of conductivity of the composites with the volume fraction of CB were illustrated in Fig. 1. Apparently, for either the ternary CB/PP/EVA composites (solid line in Fig. 1) or the binary CB/PP (dash line), the conductivity increased dramatically when the CB content reached close to the percolation threshold. When the content was less than the percolation value, the conductivity of the composites was low and gradually increased with increasing CB content. When the CB content was up to the vicinity of the percolation value, it rapidly increased by many orders of magnitude and then gradually increased with further increasing CB content in the blend system. Interestingly, the addition of EVA in the conducting composites dramatically affected the percolation threshold. The value of
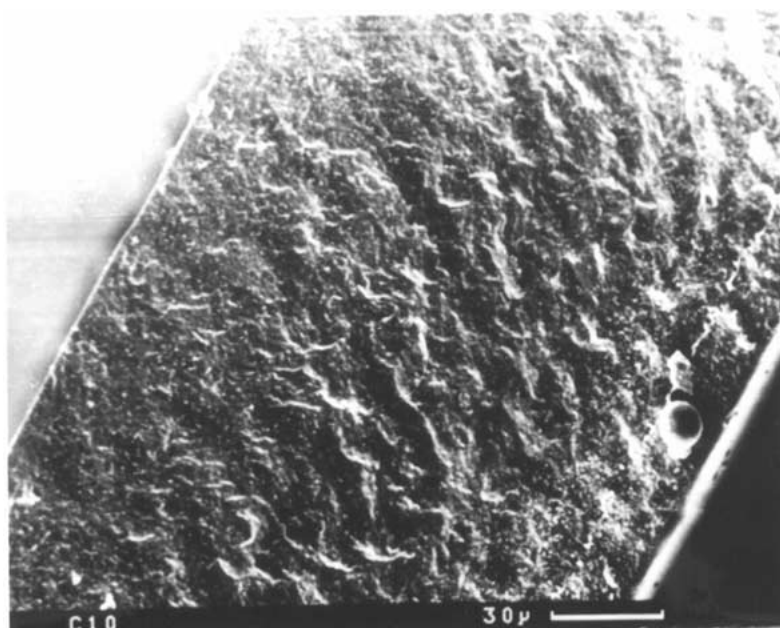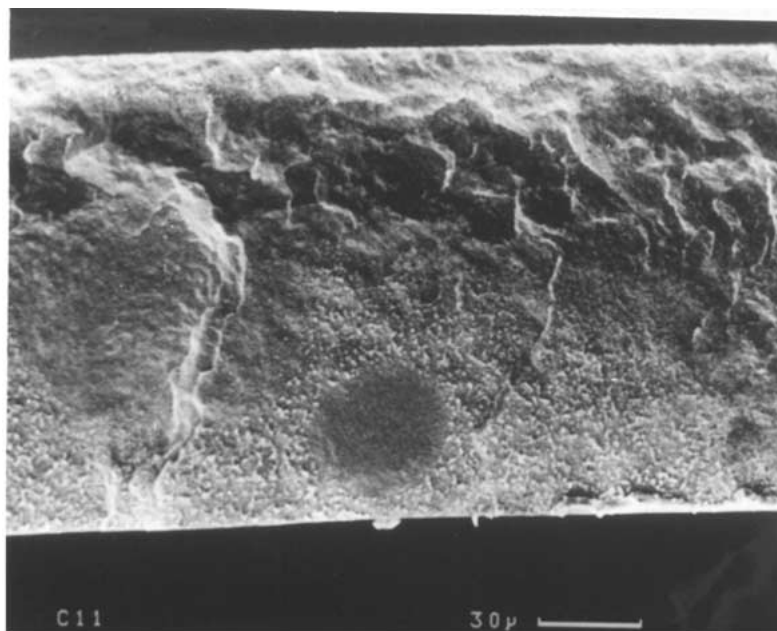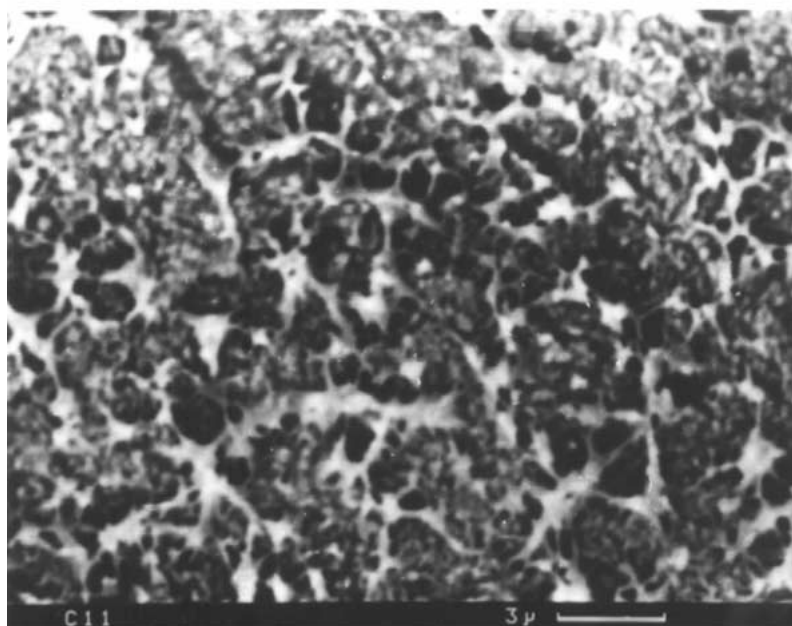

(a)
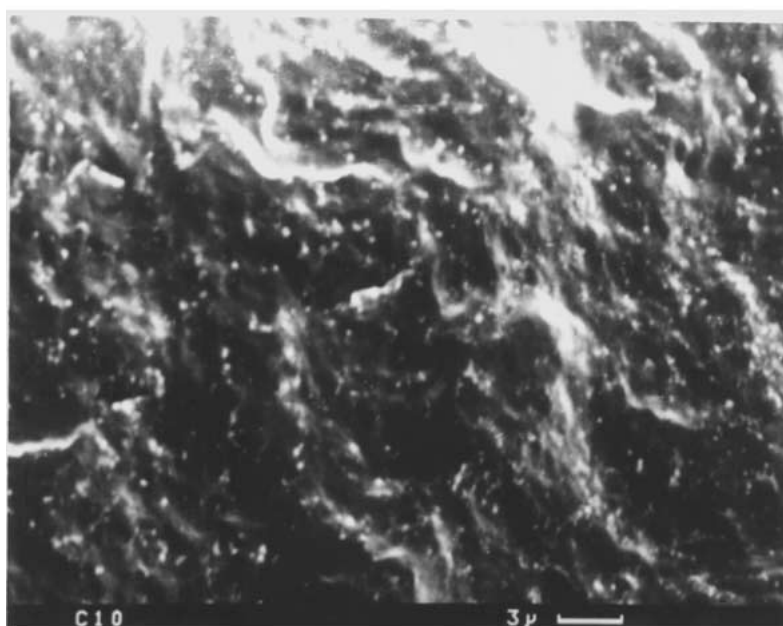
(b)

Figure 3 SEM micrographs of the cross section of the composites with CB content of 2.7 vol% (a and b, different magnification) and 5.3 vol% (c and d).   (*Continued*)

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(c)

(d)

Figure 3 (Continued).

CB/PP/EVA composites was about 3.8 vol% marked PT1 in Fig. 1, while the value of CB/PP composites was up to 7.8 vol% marked PT2. As expected, EVA in the conducting composites was valuable for forming the conducting paths. Lowering percolation threshold, which meant less CB added into the composites with a good conductive property, not only reduced the cost of the materials, but also improved the processability and the mechanical properties.

The CB/PP/EVA composites had higher conductivity than the binary CB/PP. When the volume fraction of CB was 0.05 and 0.1 respectively, the conductivity of the CB/PP/EVA composites was 10^{-2} and 10^{-1} S/cm, respectively. However, it was merely 10^{-12} and 10^{-2} S/cm, respectively, for the binary CB/PP composites without EVA. Therefore, the addition of

EVA in the conducting composites not only lowered the percolation threshold but also increased the conductivity.

3.2. Thermal property

DSC thermograms of some samples with different volume percentage of CB were illustrated in Fig. 2. Contrasting the three DSC curves, it was shown that the melting peaks of these samples shifted to lower temperature and the melting enthalpy changed with the addition of CB. The detailed data listed in Table I indicated that the addition of EVA and CB had an influence on the melting peak of PP. When the content of EVA was 5 vol%, the melting peak of PP decreased by 2.6°C. Meanwhile, when the volume percentage of
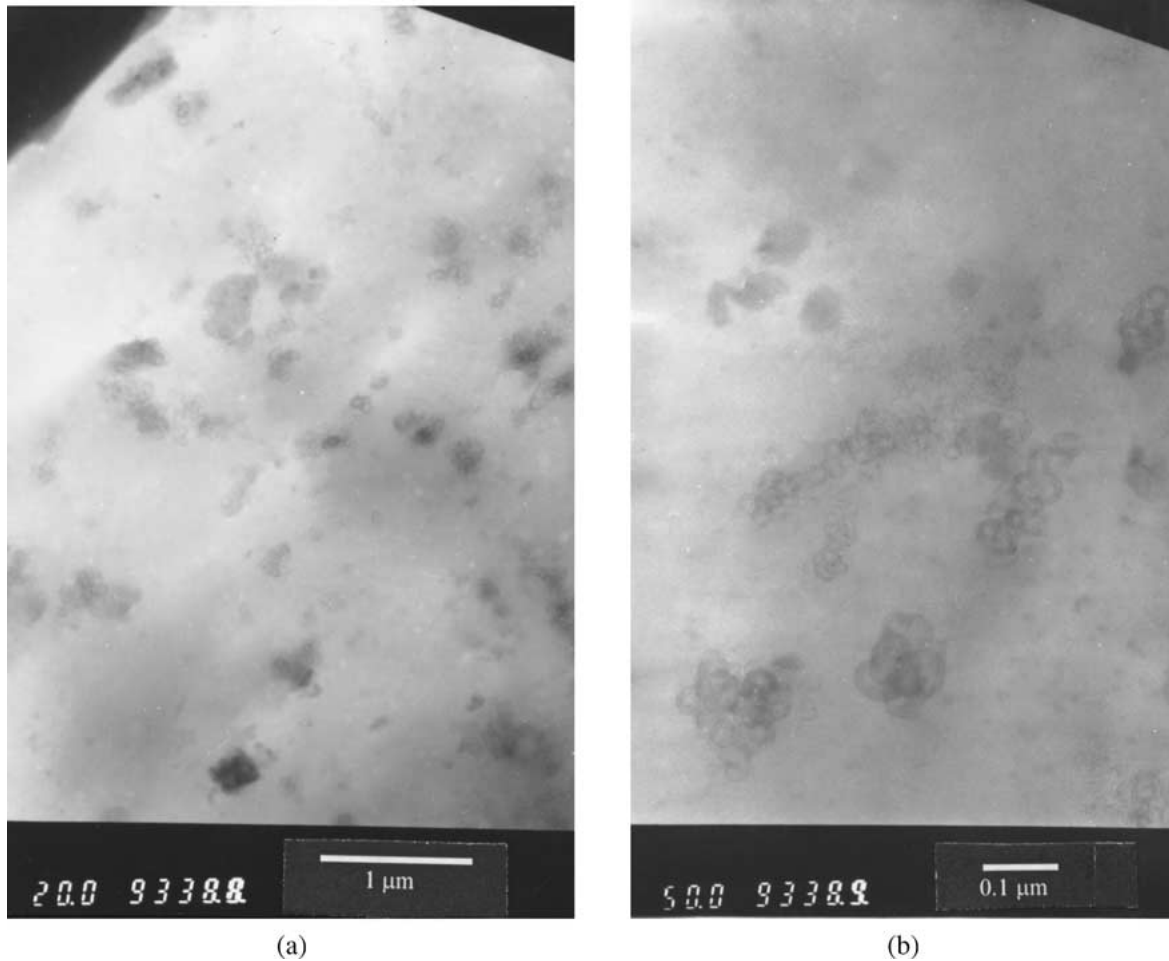
Figure 4 TEM micrographs of CB/PP/EVA composites with 5.3 vol% CB: (a) ×20,000 and (b) ×50,000.

CB increased from 0 to 10.5%, the melting peak of the composites decreased from 177.3 to 166.6°C and the melting enthalpy decreased from 85.1 to 65.9 J/g. Consequentially, the crystalline property was affected. The crystallinity of a pure polymer can be calculated by Equation 1 [25]:

$$X_{DSC} = \frac{\Delta H_m}{\Delta H_0} \times 100\% \qquad (1)$$

where, ΔH_m is melting entropy of a sample, ΔH_0 is that of a crystal of the polymer. However, the conducting composites are multi-component polymers, whose crystallinity cannot directly be calculated by Equation 1. So, the equation must be modified as Equation 2:

$$X_{DSC} = \frac{1}{[PP]} \times \left(\frac{\Delta H_m}{\Delta H_0}\right) \times 100\% \qquad (2)$$

TABLE I DSC data of CB/PP/EVA composites

CB/PP/EVA (w/w/w)	T_m (°C)	ΔH_m (J/g)	X_{DSC} (%)[a]
Pure PP	177.3	90.5	67.1
0/95/5	174.7	85.1	66.4
5.3/89.7/5	167.4	79.8	65.6
10.5/79.5/10	166.6	65.9	61.4

[a]Calculated according to Equation 2, only related to the crystallinity of PP.

where, ΔH_0 is melting entropy of crystal of PP of 134.9 J/g [25], and [PP] is the weight fraction of PP in the ternary composites. It should be noted that the crystallinity merely refers to the PP content and does not include that of EVA because EVA is an amorphous polymer with a mild endothermic peak at 103°C, which did not appear in Fig. 2. Therefore, the equation was divided by a factor of the weight fraction. Apparently, the addition of CB and EVA changed the crystalline characteristics of PP. In order to minimize the effect of processing procedure on the crystallinity of the samples, pure PP was also processed in the same way as the composites. The data in Table I showed that the crystallinity of pure PP was 67.1%, while that of the sample with the CB content of 10.5% decreased to 61.4%.

3.3. Mechanical properties of the composites

The mechanical properties of the CB/PP/EVA and blank samples were measured. The process of the samples was performed in the same way in order to avoid the influence of the processing procedure on the mechanical properties. The data listed in Table II indicated that the addition of CB had an obvious influence on the properties. The increase of CB in the composites resulted in the decrease of the tensile

TABLE II Mechanical properties of CB/PP/EVA composites

CB/PP/EVA (w/w/w)	Tensile strength (MPa)	Elongtion (%) at room temperature
Pure PP	43	25
0/95/5	41	28
5.3/89.7/5	34	13
10.5/79.5/10	28	5.8

strength and the elongation to break. Therefore, the addition of CB improved the electrically conductive property, whereas, on the other hand, it had a negative influence on the mechanical properties of the blend materials. The addition of EVA in PP caused a decrease of the tensile strength, however, it caused an increase of the elongation. EVA in PP played a role of plasticizer and resulted in the increase of the elongation.

3.4. Morphology of CB/PP/EVA composites
The morphology of CB/PP/EVA composites is observed using SEM and the micrographs of the cross section are shown in Fig. 3. The micrograph (a) with the CB content of 2.7 vol% indicated that the cross section was a fragile fracture. The micrograph (c) with 5.3% CB also indicated that the fragile fracture was further obvious because of more CB content. The increase of fragility meant the decrease of the elongation of the composites, which has been discussed in the last section. In Fig. 3b and d with a large magnification, the light area represented CB and the dark area represented PP and EVA phase. The micrograph with 2.7 vol% CB, shown in Fig. 3b, indicated that the distribution of CB in the blend system was in the form of particles instead of an obvious network because the CB content was less than the percolation value (3.8 vol%). However, Fig. 3d with 5.3 vol% CB indicated that CB was in form of fibril and formed an obvious network, which was very useful for forming the conducting paths and improving the conductivity.

To further study the morphology of CB/PP/EVA blend composites, TEM was employed to observe the distribution of CB in the blend system. TEM micrographs in Fig. 4 provided further information. The micrographs with different magnification showed a typical CB morphology in the composites. Grape-like CB particle aggregates in the blend polymers were clearly observed. Among these grape-like CB aggregates, there were many branch-like CB conducting paths even though the aggregates did not touch each other. It was also found from these micrographs that either the size of the grape-like CB aggregates or the size of the branch-like conducting paths were much larger than the size of individual CB particles with an average diameter of tens of nanometers. The smallest unit that formed a percolation network was the close-packed aggregates rather than the individual particles. This morphology of the CB was very valuable for forming conducting paths and for lowering the percolation threshold.

4. Conclusion
CB/PP/EVA conducting composites were prepared by blending the three components. Contrasting with the binary CB/PP composites, the CB/PP/EVA composites had lower percolation threshold and higher conductivity. The thermal property measured using DSC indicated the addition of CB and EVA reduced the melting temperature and the crystallinity of PP. The measurement of mechanical properties showed that the tensile strength and elongation of the samples decreased with the increase of CB content. A fragile fracture was observed by SEM micrographs. TEM micrographs indicated that the grape-like CB particle aggregates consisting of many individual CB particles were distributed in the ternary composites. Obviously, the morphology of the CB was valuable for improving the conductivity and for lowering the percolation threshold. However, some properties of the ternary composites and the mechanism of forming grape-like CB should be further investigated. These studies will improve the processability and broaden the application of the composites.

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