

# Preparation of Carbon Black/Polypropylene Nanocomposite with Low Percolation Threshold Using Mild Blending Method

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**ABSTRACT:** A new approach, mild blending method, to prepare carbon black (CB) filled polypropylene (PP) nanocomposite using CB aqueous suspension was reported in this study. In this compounding process, the CB particles were first dispersed in aqueous suspension by using an ultrasonic irradiation. Subsequently, the CB suspension was blended with melting PP using an extruder with low shear strength screw configuration, followed by removing the vapor from the vent by vacuum. The morphological observation showed that the CB particles were dispersed at a nanometer level in the nanocomposites as they were in

aqueous suspension and distributed homogeneously in PP matrix. The CB/PP nanocomposite prepared by this method exhibited a very low percolation threshold, i.e., 2.49 vol %, and a high-critical resistance exponent  $t$  ( $t = 5.82$ ). These phenomena, which deviated from the classical percolation theory, were likely to come down to the homogeneous distribution of CB particles and the tunneling conduction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2629–2634, 2010

**Key words:** carbon black; polypropylene; nanocomposite; percolation threshold

## INTRODUCTION

In recent years, inorganic nanoparticle-filled polymer composites have attracted great interest from researchers and the industrial world because of the remarkable improvement in mechanical, thermal, electrical, and magnetic properties compared with pure polymers. Because the nanocomposites combine the merits of polymer and inorganic nanoparticles, they have potential applications in diverse areas such as chemistry, physics, electronic, optics, material science, and biomedical science.<sup>1–7</sup>

The results of numerous studies have indicated that the effects of nanoparticles on the mechanical and other properties of the composites strongly depend upon the dispersion state of nanoparticles and the interactions between filler and polymer matrix.<sup>8–12</sup> However, the main challenge encountered in preparing inorganic nanoparticle-filled polymer composites via melt mixing is that the nanoparticles cannot be dispersed in polymer matrix at nanoscale by general processing techniques, because of the

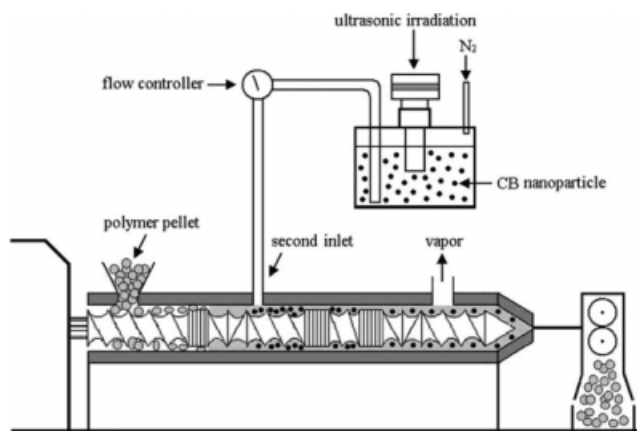
high surface energy of the particles and chemical incompatibility between nanoparticles and polymers.<sup>10–13</sup> When the size of the particle aggregations diminished to certain degree, the external force applied to the aggregations would become too small to offset the mutual attraction among the particles in aggregations, i.e., the nanoparticles could not be distributed in polymer matrix uniformly in the form of primary particles by enhancing the shear of screw.

A new approach, mild blending method that can facilitate continuous preparation of true nanocomposites through twin-screw extruder and actualize good dispersion of nanoparticles to the size of primary particles was brought forward in this work. It was conceived that the CB particles were first dispersed at the nanoscale in aqueous suspension by ultrasonic irradiation. Subsequently, the CB suspension was blended with melting PP using an extruder with low shear strength screw configuration, followed by removing the vapor from the vent by vacuum, and the CB particles were located in the PP matrix almost as they were in suspension. In this process, the key point is that the CB particles were uniformly dispersed in aqueous suspension by ultrasonic irradiation and fixed into the polymer matrix without aggregation.

It is well known that the electrical properties of CB-filled conductive polymers composites usually depend on the features of both polymers (such as

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**Figure 1** Schematic figure depicting the compounding process for preparing the CB/PP nanocomposite using mild blending method.

degree of crystallinity, melt viscosity, and surface tension) and CB (such as species, surface area, chemical groups, and dibutyl phthalate (DBP) absorption values).<sup>14–18</sup> For a certain sort of CB, the distribution of CB particles in the material, to a great degree, affects many properties of the composites significantly, especially, the percolation threshold. Up to now, there have been many investigations on reducing the percolation threshold by manipulating the distribution of CB particles, such as multipercolation,<sup>19–22</sup> segregated distribution,<sup>14,17,23</sup> and electrical field-induced method,<sup>24</sup> etc. Multipercolation is an effective technology through melt mixing method. It can be achieved by locating CB particles in one phase of a continuous multiphase blend selectively and greatly reduced the percolation threshold of conductive polymer composites.<sup>19–22</sup> However, for single percolation system, the phenomenon of controlling percolation threshold is uncommon because of the difficulty of distributing the particles uniformly at the nanoscale in polymer matrix in the traditional processes. Therefore, it was worthwhile researching the electrical properties of composites with CB dispersion as primary particles and comparing the electrical mechanism with universal percolation theory.

## EXPERIMENT

### Materials

The polymer used in this study was isotactic PP (T30S; powder, melt flow rate = 4.1 g/10 min at 230°C, exerting a load of 21.6 N) from Petroleum Chemical Co., Wuhan, China. The filler was electrically conductive CB (ECP-CB-1; N<sub>2</sub> surface area = 954 m<sup>2</sup>/g; DBP value = 280 mL/100 g; mean particle diameter = 40 nm) from Tebao Electric Conductive Powders R & D Center, Beijing, China.

### Preparation of nano-CB aqueous suspension

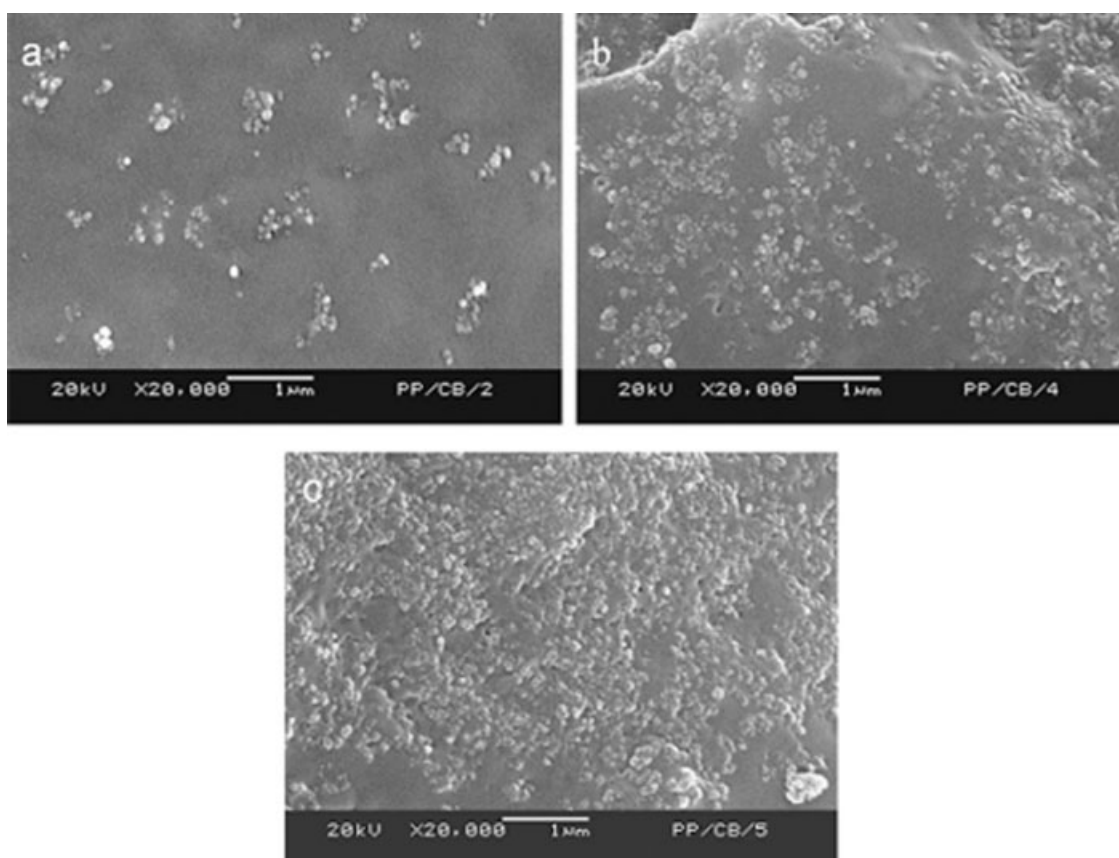
Absolute ethyl alcohol was used to infiltrate into CB powder by using a stirrer for 10 min. Then the CB suspension was prepared by dispersing the infiltrated CB powder into deionized water using a VCF-1500 ultrasonic irradiation instrument (Sonics & Materials, Inc, USA) for 10 min, power output 1050–1200 W, and frequency 20 kHz. The CB aggregate structure was broken apart, and the CB particles were dispersed into the suspension as their original size. The primary particle state of CB was preserved temporarily by soluble cellulose HPMC (Luzhou North Chemical Industry Co., Ltd., China). The CB content in the aqueous suspension was 10 g/L.

### Preparation of CB/PP nanocomposite using mild blending method

The intermeshing corotating twin-screw extruder (SHJ-20; screw diameter = 21.7 mm; screw length = 700 mm) from Nanjing Giant Machinery Co. Ltd was used to prepare the nanocomposites. Figure 1 was an illustration depicting a compounding process for preparing the nanocomposite. PP was put into the extruder and melted at 170°C in the kneading blocks at the end of feeding section. The CB suspension was pumped into the second inlet of the extruder and compounded with the melting PP in the compounding zone composed of specific kneading blocks and screw elements at 200°C. A pair of reversed kneading blocks was used to increase filling factor of melting PP and prevent vapor from flowing back to the hopper. The water of the CB suspension was removed from the vent by vacuum to obtain the nanocomposite consisted of PP and CB nanoparticles. Both the extrusion velocity of PP and perfusion velocity of the CB suspension were controllable, and so nanocomposites with different CB content would be prepared. For comparison, the common CB/PP composite was also prepared. The extruding conditions were the same as mild blending method (130, 170, 200, and 200°C from hopper to die), but PP and CB powder were high-speed mixed before introduced into the extruder. The strands were pelletized and dried under vacuum at 60°C and then compression molded into 100 × 100 × 2 mm<sup>3</sup> board at 200°C for 10 min with a pressure of ca. 10 MPa. All the sheets were cooled to room temperature by cold compression molding for 5 min.

### Electrical property testing

The volume electrical resistivity was measured by a high resistivity meter when the volume resistivity of the samples was beyond 10<sup>6</sup> Ω·cm. When the volume resistivity of the samples was below 10<sup>6</sup> Ω·cm, it



**Figure 2** SEM micrographs of the common CB/PP composites. The volume fraction content of CB is 2 vol % (a), 7 vol % (b), and 10 vol % (c), respectively.

was measured by a four-probe method (ASTM D-991) using two multimeters and a voltage supply, which could effectively avoid the contact resistance and therefore have adequate precision of the measurement. The specimen dimensions for high and low resistivity measurements were  $2 \times 100 \times 100 \text{ mm}^3$  and  $2 \times 10 \times 100 \text{ mm}^3$ , respectively.

### Morphological observation

The morphology of the nanocomposites was observed by a JEOL JSM-5900LV scanning electron microscope (SEM). All samples were fractured after immersion in liquid nitrogen for about 1 h. The fracture surfaces were sputter coated gold and examined at an accelerating voltage of 10 kV.

## RESULTS AND DISCUSSION

### Dispersion of nano-CB particles in PP matrix

Figure 2 was SEM micrographs of the common CB/PP composite. It showed that most particles were aggregated together and the aggregation detached from each other [Fig. 2(a)]. With increasing CB content, close contact between the aggregations was observed [Fig. 2(b)]. In contrast, at a higher CB con-

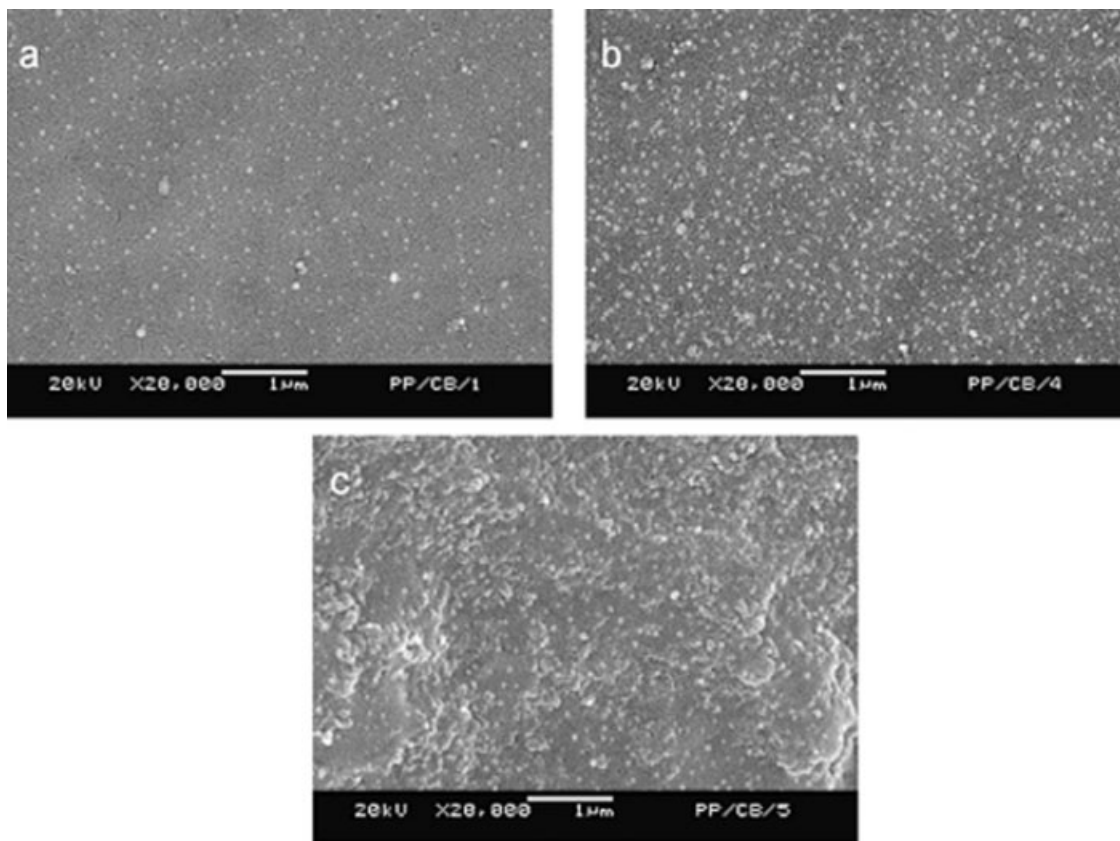
tent, the scale of aggregations increased which was caused by the connection of CB aggregations [Fig. 2(c)].

The morphological features of the CB/PP nanocomposite using mild blending method, as depicted in Figure 3, exhibited a different structure from conventional CB/PP composite. It was observed evidently that CB particles were detached from each other at nanometer level [Fig. 3(a)], with a homogeneous distribution in PP matrix [Fig. 3(b)]. When the CB content increased, the nanoparticles dispersed reasonably well, although there were still aggregated particles forming clusters [Fig. 3(c)].

### Electrical properties of the conductive in CB/PP composite

Figure 4 showed the correlation between the volume resistivity and CB loading for the CB/PP nanocomposite using mild blending method. For comparison, the CB/PP composite prepared by melt blending was also shown in this figure. The CB/PP nanocomposite using mild blending method was found to percolate at a threshold of about ca. 2.49 vol % (calculated based on the measured data<sup>25</sup>), whereas the common CB/PP composite had a percolation

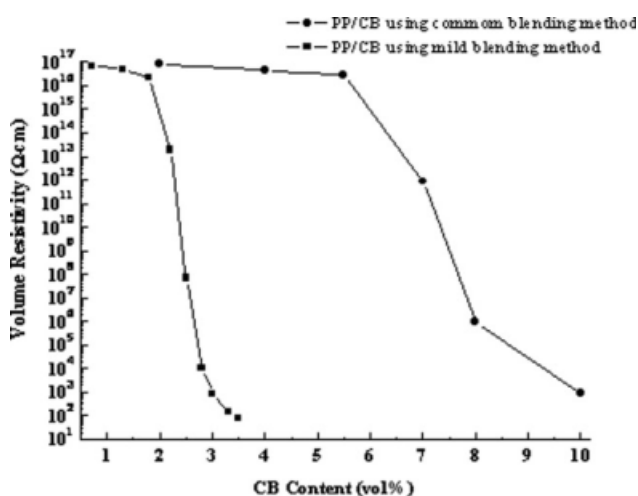




**Figure 3** Morphological features of the CB/PP nanocomposite using mild blending method. The volume fraction content of CB is 0.7 vol % (a), 2.5 vol % (b), and 3.5 vol % (c), respectively.

threshold of about ca. 7.66 vol %. The difference in percolation thresholds between the two CB/PP composites could be explained in light of the dispersion and distribution of the carbon black particles.

At the low CB content, most particles were aggregated together in common CB/PP composite, and the aggregation detached from each other. For com-



**Figure 4** Correlation between the volume resistivity and CB loading for the CB/PP nanocomposite and common CB/PP composites.

posites greater than the threshold, close contact between the aggregations, which were finally combined to the conductive networks, was observed. In contrast, at a higher CB content, the amount of conductive paths increased by more conductive contact between CB aggregations so a significant decrease in volume resistivity with rising levels of CB was exhibited. However, in the CB/PP nanocomposite using mild blending method, most of CB particles which did not contact closely with each other could be observed, and the interparticle (centers of particles) distance between the two adjacent CB particles could be measured by using image analyzing software, as shown in Figure 5. With increasing content of CB, the distance between the adjacent particles reduced significantly, from  $10^2$  nm scale to 10 nm scale. It was expected that the conducting mechanism was different from classic percolation theory.

#### Electrical mechanism of the conduction in CB/PP nanocomposite using mild blending method

In an attempt to analyze the conductive mechanism of the CB/PP nanocomposite using mild blending method, the relationship between nanocomposite conductivity and the percolation threshold was examined. According to the universal percolation

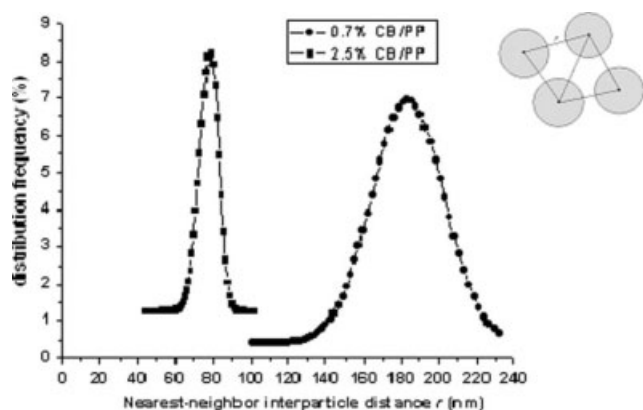
theory, the electrical conductivity beyond the percolation threshold could be expressed as a universal law:<sup>26,27</sup>

$$\sigma \propto (v - v_c)^{-t}$$

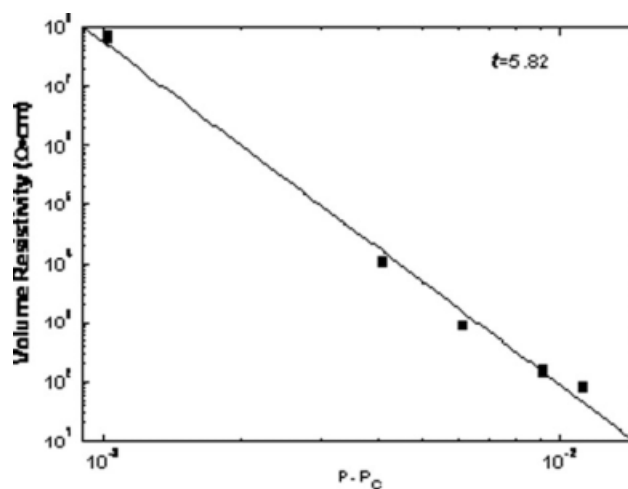
where  $\sigma$  was the conductivity of the mixture with different filler contents,  $v$  was the volume fraction of the filler,  $v_c$  was the volume percolation concentration, the critical exponent  $t$  governed the scaling behavior in the region of  $v_c$  and was used to predict the mechanism of electrical network.

The  $t$  value could be estimated from the slope of the line in a  $\log(P - P_c)$  vs.  $\log \sigma$  plot, and the experimental  $P$  and  $P_c$  were defined as  $v/(1 - v_c)$  and  $v_c$ , respectively.<sup>28</sup> Percolation threshold models depended on the  $t$  value. For single percolation, the critical exponent depended solely on the dimensionality of the system and followed a power-law dependence of approximately 1.6-2.0 in three dimensions.<sup>26</sup> The resistivity of the CB/PP nanocomposite using aqueous suspension as a function of the proximity to the percolation threshold  $P - P_c$  was presented in Figure 6. The experimental data exhibited a good linearity, and the  $t$  value of the nanocomposite was estimated to be ca. 5.82. Hence, both  $v_c$  and  $t$  of the special CB/PP nanocomposite were found to deviate from the universal percolation theory that predicted the values  $v_c = 12$  vol % and  $t = 2.0$ .<sup>29</sup>

Balberg and coworkers proposed and confirmed the existence of the comprehensive percolation tunneling model in low structure CB-filled polymer composites.<sup>28,30</sup> In their study, the exponent  $t$  of the CB/polyvinyl chloride composite was about 6.4, which greatly deviated from the theoretical predictions of the universal model. This case was ultimately attributed to the nonrandom dispersion of the particles in these systems. It was similar to the



**Figure 5** The distance between the centers of nearest two CB particles in CB/PP nanocomposite using mild blending method with different CB content.



**Figure 6** The electrical conductivity as a function of excess concentration  $P - P_c$  for electrically conductive in a particular CB/PP nanocomposite.

result of this study that on account of the nanoscale dispersion and homogeneous distribution, a very low percolation threshold (2.49 vol %) was obtained with a high-critical resistance exponent  $t$  (5.82).

The percolation tunneling mechanism was effective to explain the observations of this work. In the CB/PP nanocomposite, the CB particles were dispersed as primary particle state, located apart from each other and enclosed by the PP, an excellent insulator, which satisfied the requirement of tunneling conduction.<sup>31</sup> It could be presumed that formation of conductive network was based on tunneling conduction theory when CB particles were dispersed at the nanometer scale in the composite.<sup>30,32</sup> Concerning the conductive mechanism, if the separation distance between two CB particles was not close enough, which was larger than the sum of their effective tunneling distances, the tunneling conduction could not occur. When the CB content reached the percolation threshold, the effective tunneling zone of the nearest-neighbor particles overlapped, and tunneling conduction would come into being between spheres in the matrix. This was the dominant conducting element in this CB/PP nanocomposite using mild blending method to make a high exponent  $t$  and also made the system deviate from the theoretical prediction of the universal law.

### CONCLUSIONS

The PP nanocomposites have been successfully fabricated by compounding PP with nano-CB aqueous suspension using twin-screw extruder. The morphological observation showed that the CB particles were dispersed at nanometer level in the

nanocomposites as they were in aqueous suspension, and distributed homogeneously in PP matrix.

The percolation threshold of the CB/PP nanocomposite by mild blending method was only ca. 2.49 vol %, showing a considerable decrease of percolation compared with that of the common CB/PP composite. The critical resistance exponent  $t$  of this nanocomposite was estimated, i.e., ca. 5.4. This high value indicated that the system did not obey the prediction of the universal percolation theory. The homogeneous distribution of CB particles and the tunneling conduction could be the possible origin of the high  $t$  value.

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