

Research Article

A Numerical Study on Electrical Percolation of Polymer-Matrix Composites with Hybrid Fillers of Carbon Nanotubes and Carbon Black

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The electrical percolation of polymer-matrix composites (PMCs) containing hybrid fillers of carbon nanotubes (CNTs) and carbon black (CB) is estimated by studying the connection possibility of the fillers using Monte Carlo simulation. The 3D simulation model of CB-CNT hybrid filler is established, in which CNTs are modeled by slender capped cylinders and CB groups are modeled by hypothetical spheres with interspaces because CB particles are always agglomerated. The observation on the effects of CB and CNT volume fractions and dimensions on the electrical percolation threshold of hybrid filled composites is then carried out. It is found that the composite electrical percolation threshold can be reduced by increasing CNT aspect ratio, as well as increasing the diameter ratio of CB groups to CNTs. And adding CB into CNT composites can decrease the CNT volume needed to convert the composite conductivity, especially when the CNT volume fraction is close to the threshold of PMCs with only CNT filler. Different from previous linear assumption, the nonlinear relation between CB and CNT volume fractions at composite percolation threshold is revealed, which is consistent with the synergistic effect observed in experiments. Based on the nonlinear relation, the estimating equation for the electrical percolation threshold of the PMCs containing CB-CNT hybrid fillers is established.

1. Introduction

Polymers have been widely used in industrial manufactures, military equipment, and daily life due to their excellent plasticity, lightweight, and low cost. However, most polymers are electrically isolated, which strongly limits their applications in the fields requiring antistatic, electrostatic dissipative, and electromagnetic shielding performances. The inherently conductive polymers are usually expensive and easily aging [1], while adding electrical conductive fillers into polymers can also make them conductive and may improve their mechanical properties as well. Therefore, adding conductive fillers into polymers is an attractive way to enhance conductivity of the polymers [2].

Carbon nanotubes (CNTs) have been considered as an ideal reinforcement phase in composites due to their excellent mechanical and physical properties [3–6]. Especially, their high aspect ratio (over 1000) and high conductivity (up to 10^4 S/cm) enable them to greatly improve the conductivity of

polymer-matrix composites (PMCs) with a very low volume fraction [7–9]. A large number of experiments have been carried out to study the electrical percolation threshold of CNT/polymer composites [4–14]. Meanwhile, theoretical and numerical studies have also been done to estimate the percolation threshold of CNT/polymer composites [15–24], in which excluded volume method [15] and Monte Carlo simulation [17–21] are widely accepted. All these studies indicate that better dispersion, larger aspect ratio, and less waviness of CNTs lead to a lower percolation threshold. However, CNTs with large aspect ratio are easily agglomerated and entangled when dispersing in polymer matrixes [25–27], so it is difficult to get a percolation threshold as low as estimated in simulations. Moreover, the high price of CNTs also limits their application to some extent. Therefore, hybrid filling becomes a good solution to these problems. Carbon black (CB) is one of the most widely used conductive nanoparticles in industrial applications so far and thus considered as a suitable candidate because of its low cost, good dispersion

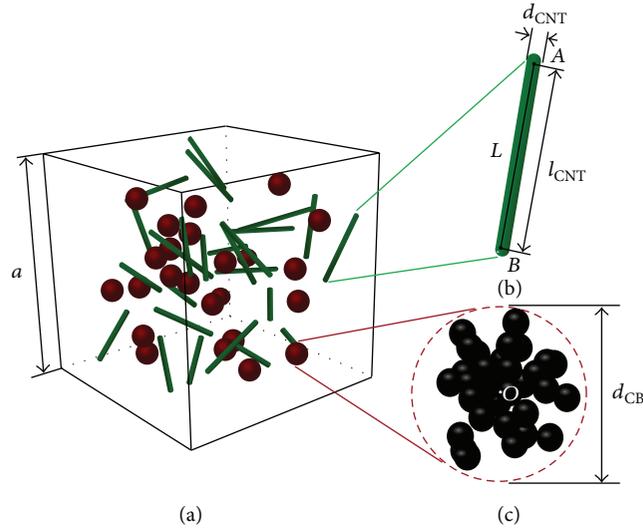


FIGURE 1: Simulation model: (a) representative volume element for CB-CNT/polymer composites, (b) spherocylinder model for CNT filler, and (c) hypothetical sphere model for agglomerated CB particles.

ability, and especially synergistic effect with CNTs which can further improve conductivity and other properties of PMCs. Experimental studies have shown the advantages of the synergistic effect of CB. For example, Socher et al. [1] observed the synergistic effects of CB in multiwalled CNTs (MWCNTs) and CB hybrid nanocomposites regarding maximum conductivity and MWCNT dispersion. Sumfleth et al. [28] found synergistic effects in network formation and in charge transport when they studied conductivity and microstructure of ternary CB/CNTs-epoxy system. Ma et al. [8] also studied CB/CNTs-epoxy composites and found that besides the synergistic effects on conductivity the hybrid fillers improved ductility and fracture toughness of composites more than equivalent CB or CNTs.

However, the experimental studies on the PMC with hybrid fillers are hardly capable of predicting the electrical percolation systematically or quantitatively. According to experiments, researchers can only guess the relation between amount of fillers and electrical percolation of composites and may draw some different, even opposite conclusions. Therefore, it is necessary to develop a theoretical simulation approach to guide the experimental trials. So far, existing numerical and theoretical methods for conductivity and percolation threshold of PMCs are almost all about pure CNT fillers and simulation models are established for the CNT fillers. For the composites with hybrid fillers, as proved in the experiment studies, the fillers can not only combine advantages of different fillers but also improve material properties by synergistic effects. So adding hybrid fillers into PMCs could be potential and promising to enhance the conductivity and other properties of composites.

This paper aims to better understand the synergistic effect and systematically study the effecting factors on electrical percolation threshold of CB-CNT hybrid filler, including CB and CNT volume fractions, aspect ratio of CNTs, and diameter ratio of CB groups to CNTs. A 3D simulation model

for the CB-CNT hybrid filler is set up and a nonlinear law to estimate the percolation threshold is obtained, in which the synergistic effect between CB and CNT volume fractions as well as the effects of geometric dimensions of CB groups and CNTs is taken into account.

2. Numerical Simulation

For PMCs with conductive fillers, the electrical percolation threshold is dominated by the network formation and interactions of the electrical conductive fillers because the conductivity of the polymer matrix is much lower than that of the fillers and can be ignored in the simulation. If the electrical conductive fillers can form conducting pathways to transport electrons, the composite is electrical conductive. With increasing volume fraction of the fillers, the possibility to form these pathways increases. Once the conductive pathway forms, the composite conductivity increases significantly, and this filler volume fraction to form the conductive pathway is called electrical percolation threshold. Therefore, it can be assumed that the electrical percolation threshold is related to the possibility to form the conductive pathway by the fillers. This section will try to estimate the electrical percolation threshold of PMCs with CB-CNT hybrid fillers by calculating the possibility of the pathway formation, and Monte Carlo method is adopted in the numerical simulation.

2.1. 3D Simulation Models for CNTs and CB. For PMCs with CB-CNT hybrid fillers, the simulation models for both CNT and CB are needed in Monte Carlo simulation. In PMCs containing CNT only, the slender spherocylinder model illustrated in Figure 1(b) is commonly used to simulate the CNTs and hence is adopted in this study for the CNT phase. The diameter and length of cylinder model are equal to those of CNT filler, respectively.

A single CB particle is a sphere with diameters from several to tens of nanometers. Agglomerated CB particles always construct intertwined chains, as shown in Figure 1(c). Suppose that the lengths of the intertwined chains are statistically the same in all directions, which means one group of CB particles can connect to any other group of CB particles within the scope of the chain length in all directions in the space, so from the view of pathway connection, a group of CB particles can be equivalent to a hypothetical sphere with the diameter equal to the average chain length, as presented by the dashed circle in Figure 1(c). It should be noted that the hypothetical sphere is not filled with CB only but with both CB and the polymer matrix. The volume fraction of the polymer matrix in the hypothetical sphere is assumed as 70% in this study. This hypothetical sphere model can also be used to simulate intertwined and agglomerated CNT fillers.

It is easy to involve both slender spherocylinder and hypothetical sphere models in Monte Carlo simulation, as shown in Figure 1(a), which presents a 3D cubic representative volume element (RVE) for the simulation of PMCs with randomly distributed CNTs and CB groups. More other shapes/models can be easily taken into account in the simulation, but in this paper, only the two models are used to simulate the two types of fillers, CNTs and CB, which are very promising to be applied in PMCs as mentioned above.

It should be noticed that CNTs are not penetrable to each other in actual composites, but they can superpose on each other in simulations. Berhan and Sastry [18, 19] figured out that the error could exceed 4% for CNTs with aspect ratio less than 400 if impenetrability was not taken into consideration. In this study, the overlapped volume is deducted from the total volume of CNTs to eliminate the error of penetration between CNT models. But for the hypothetical sphere models of agglomerated CB particles, it is reasonable to think they are penetrable because when they are getting close the CB chains in the hypothetical sphere can adjust themselves to avoid penetrating due to the interspaces between the chains, which are taken into account in the volume of the hypothetical sphere model as matrix volume. And for the same reason, when a CNT model penetrates in a CB model, the overlapped volume need not be deducted. In another word, the impenetrability is necessary to be taken into consideration only when the CNTs superpose on each other.

2.2. Numerical Implementation. To form the conductive pathway, the fillers need to make contact with each other first. Here the contact includes not only geometrical contact but also physical contact such as electron tunneling, which means two particles are close enough to let electrons skip although they do not geometrically contact with each other. Whether the pathway exists or not can be determined according to all the contacts between fillers. Repeating the calculation for times can obtain the possibility to form the pathway, which is defined as “connection possibility” in this study. The connection possibility can be used to evaluate the electrical

percolation threshold. The essential steps to calculate the connection possibility of the PMCs containing both CNT and CB fillers are described below.

- (1) Initialize variables: the connection times $N_C = 0$ and the total simulation times $N_T = 0$.
- (2) For given volume fractions and dimensions of CNTs and CB, generate slender spherocylinder and hypothetical sphere models, respectively, in a cubic RVE. The position and direction of the CNT model are totally random and represented by its axial line segment L with two end points A and B , as shown in Figure 1(b). The position of CB model is also random and represented by its center point O , as shown in Figure 1(c).
- (3) According to the positions generated in step 1, evaluate the intersections between every two models by calculating the distances between them, and then build an intersection data matrix. The criterion to evaluate intersection between fillers i and j is

$$D_{ij} \leq \frac{(d_i + d_j)}{2} + d_{\text{tunnel}}. \quad (1)$$

Here d is the diameter of the spherocylinder for CNTs or the hypothetical sphere for CB, d_{tunnel} is the largest distance for tunnel effect and $d_{\text{tunnel}} = 0$ if the tunnel effect is excluded, and D_{ij} is the distance between fillers i and j .

- (4) Check the intersection data matrix to find a pathway from one side to the opposite side of the RVE. This pathway is considered as a route along which electrons can be transported. If the pathway can be found, update the connection times as $N_C = N_C + 1$; otherwise, N_C remains unchanged. The total simulation times N_T are also updated as $N_T = N_T + 1$ no matter the RVE is connected or not.
- (5) Repeat steps 2 ~ 4 for times to determine the connection of the RVEs with the same filler volume fractions and filler dimensions but different random distributions, and then calculate the connection possibility CP as $CP = N_C / N_T$.

2.3. Connection Possibility and Its Sensitivity to RVE Size.

From the procedure in Section 2.2, the connection possibility for given filler volume fraction and filler dimensions is obtained. Changing the filler volume fraction, the relation between the connection possibility and the filler volume fraction can be depicted, as shown in Figure 2. Figure 2(a) shows the simulation result of CNT/polymer composites. The diameter and length of CNT fillers, d_{CNT} and l_{CNT} , are 2 nm and 200 nm, respectively, and the side length of the cubic RVE, a , is set to be 600 nm, 800 nm, and 1000 nm. Figure 2(b) presents the simulation result of CB/polymer composites. The diameter of CB groups, d_{CB} , is 6 nm, and the side length of the RVE, a , is chosen as 60 nm, 120 nm, and 240 nm. The distance for tunnel effect $d_{\text{tunnel}} = 0$ because of the low filler volume fraction.

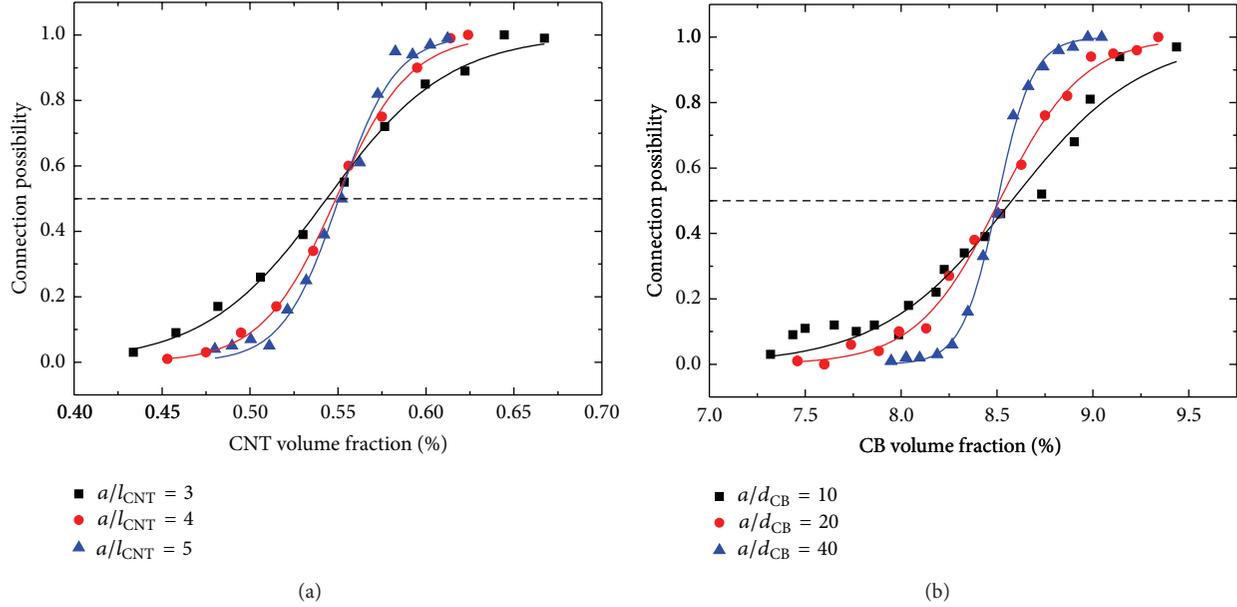


FIGURE 2: Effect of RVE size a on connection possibility for (a) CNT/polymer composites ($d_{\text{CNT}} = 2$ nm, $l_{\text{CNT}} = 200$ nm) and (b) CB/polymer composites ($d_{\text{CB}} = 6$ nm). The solid curves are obtained from fitting of Boltzmann function.

TABLE 1: Parameters of Boltzmann fitting for connection possibilities.

PMCs with CNT only			PMCs with CB only		
a/l_{CNT}	Φ_0 (%)	K	a/d_{CB}	Φ_0 (%)	K
3	0.551	652.36	10	8.68	49.02
4	0.553	1074.46	20	8.53	109.17
5	0.548	1576.61	40	8.50	282.65

TABLE 2: Comparison between Φ_0 and percolation thresholds obtained from excluded volume method [15] for different CNT aspect ratios in CNT/polymer composites.

Aspect ratio	Φ_0	Percolation thresholds	Relative error
300	0.178	0.165	0.0788
500	0.105	0.0993	0.0574
750	0.0687	0.0664	0.0346
1000	0.0495	0.0498	0.0060

Both figures show that the connection possibility first has little response to the filler volume fraction and then suddenly increases sharply with increasing filler volume fraction and saturates quickly. This behavior can be described by Boltzmann function as

$$\text{CP}(\Phi) = A_2 - \frac{A_2 - A_1}{1 + \exp[4K(\Phi - \Phi_0)/(A_2 - A_1)]}. \quad (2)$$

Here A_1 and A_2 are the minimum and maximum values of the function $\text{CP}(\Phi)$, respectively, so for the function of connection possibility, $A_1 = 0$ and $A_2 = 1$. Φ represents the volume fraction of the filler, and Φ_0 is the Φ value satisfying $\text{CP}(\Phi) = (A_2 - A_1)/2$. K is the slope of function $\text{CP}(\Phi)$ at $\Phi = \Phi_0$. Thus, every curve in Figure 2 can be described by Φ_0 ,

the volume fraction for 50% connection possibility, and K , the slope of the curve at Φ_0 , which are listed in Table 1.

Figure 2 also indicates that the simulation results of connection possibility are very sensitive to the size of the RVE. The slope of the curve K depends strongly on the RVE size, becoming steeper with increasing RVE size, as shown in Table 1. So in order to get an accurate result by Monte Carlo simulation, the simulation region must be big enough to contain a large number of fillers.

However, in both Figures 2(a) and 2(b), the curves meet together when the connection possibility is about 50%, which means Φ_0 can be hardly affected by the size of the RVE, as presented quantitatively in Table 1. Therefore, Φ_0 is selected to represent the electrical percolation threshold, so that the RVE size is no longer an influence factor on the result. In this case, it is not necessary to choose a very large simulation region, which absolutely leads to more CPU time in simulations.

Taking into account both accuracy and efficiency, Φ_0 is selected to represent the electrical percolation threshold, and $a/d_{\text{CB}} \geq 30$ and $a/l_{\text{CNT}} \geq 5$ are applied in the following simulations.

2.4. Relation between Connection Possibility and Percolation Threshold. To establish the relation between the electrical percolation threshold and Φ_0 , the filler volume fraction for 50% connection possibility, comparison between simulation results and theoretical values based on excluded volume method [15] for PMCs containing only CNTs is made. In the comparison, the diameter of CNT model is 2 nm, and four different aspect ratios ($l_{\text{CNT}}/d_{\text{CNT}}$) 300, 500, 750, and 1000 are studied. Table 2 shows the comparison between Φ_0 and the electrical percolation threshold estimated by excluded volume method [15]. It can be seen that Φ_0 is very close

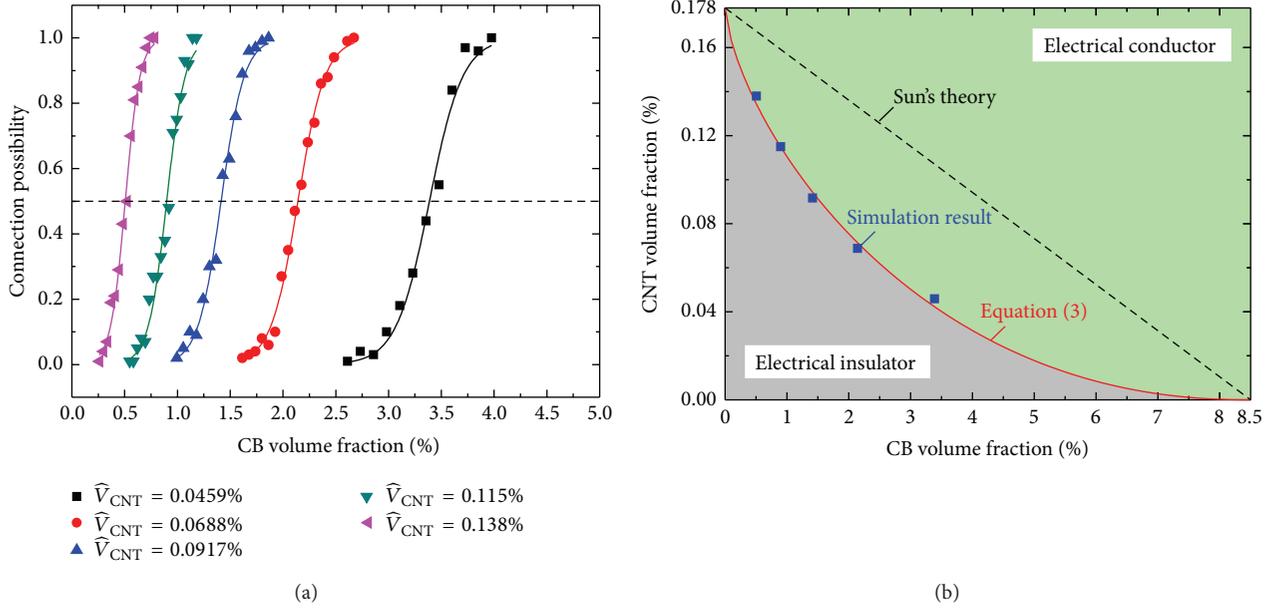


FIGURE 3: Synergistic effect of CB and CNT volume fractions: (a) effect of volume fractions on connection possibility and (b) relationship between volume fractions of CB and CNT at the percolation threshold.

to the theoretical results of percolation threshold, and the error between them becomes smaller with increasing CNT aspect ratio. When the aspect ratio goes beyond 1000, the error becomes less than 0.7%. Even if the aspect ratio is as low as 300, the error is still less than 8%.

Comparing with experimental results, Φ_0 is within the range of the scattered experimental data [9–14] and agrees with some experiments such as researches in [9]. In experiments, the percolation thresholds of CNTs with the same aspect ratio are usually higher than the simulation and theoretical values mainly because of the bad dispersion conditions.

From the comparison, it is revealed that the filler volume fraction for 50% connection possibility (Φ_0) can be considered as the electrical percolation threshold. And this choice is also physically valid, because when the connection possibility is greater than 50%, the pathway has more chance to be formed and the composites are more inclined to be conductive, and when it is less than 50%, the composites tend to be electrically isolated. So the volume fraction corresponding to 50% connection possibility is defined as the threshold at which the electrical conductivity of materials converts.

3. Effects on Electrical Percolation Threshold

When producing PMCs with CB-CNT hybrid filler, what concern us mostly is how much the hybrid filler is needed to transfer isolative polymer matrix into conductor; in other words, the percolation threshold is usually measured by the total volume fraction of CB and CNT hybrid fillers. Generally, the threshold depends on amounts and dimensions of CB and CNTs. So it is necessary to study the effects of volume

fractions of CB and CNT on each other as well as the effects of dimensions of CB and CNT including the diameter of CB groups and the aspect ratio of CNTs.

It has been confirmed that the filler volume fraction for 50% connection possibility (Φ_0) obtained from fitting of Boltzmann function can be used to estimate the electrical percolation threshold. Then effects of CB and CNT on the percolation threshold for PMCs with CB-CNT hybrid fillers can be studied using the numerical method developed in Section 2. Firstly, a basic law for the synergistic effect of CB and CNT volume fractions on the percolation threshold is revealed, and then the effects of CNT aspect ratio and diameter ratio of CB groups to CNTs on the basic law are studied, respectively.

3.1. Synergistic Effect of CB and CNT Volume Fractions. In this study, the diameter and length of CNT models are $d_{\text{CNT}} = 2$ nm and $l_{\text{CNT}} = 600$ nm, respectively, and the diameter of CB models is $d_{\text{CB}} = 60$ nm. Thus, the percolation threshold is $\Phi_0^{\text{CNT}} = 0.178\%$ for PMCs with CNT filler only, and $\Phi_0^{\text{CB}} = 8.50\%$ for PMCs with CB filler only. When the CNT volume fraction $\hat{V}_{\text{CNT}} = 0.25\Phi_0^{\text{CNT}}$, $0.375\Phi_0^{\text{CNT}}$, $0.5\Phi_0^{\text{CNT}}$, $0.625\Phi_0^{\text{CNT}}$, and $0.75\Phi_0^{\text{CNT}}$, the connection possibility of the PMCs with CB-CNT hybrid filler increases with the increasing CB volume fraction, following Boltzmann function, as shown in Figure 3(a). The CB volume fractions at the percolation threshold, denoted by \hat{V}_{CB} , are obtained when the connection possibility is 50%. It is found that the volume fractions of CB and CNT at the percolation threshold follow the relation below as shown in Figure 3(b):

$$\left(1 - \frac{\hat{V}_{\text{CNT}}}{\Phi_0^{\text{CNT}}}\right)^a + \left(1 - \frac{\hat{V}_{\text{CB}}}{\Phi_0^{\text{CB}}}\right)^b = 1. \quad (3)$$

TABLE 3: Exponents a and b for different CNT aspect ratio $l_{\text{CNT}}/d_{\text{CNT}}$.

$l_{\text{CNT}}/d_{\text{CNT}}$	a	b
150	1.445	2.016
200	1.506	2.160
250	1.520	2.150
300	1.478	2.179

Here the exponents a and b are determined by dimensions of CB and CNT, and for the curve in Figure 3(b) they are 1.478 and 2.179, respectively.

If no synergistic effect exists between CB and CNT volume fractions, based on Sun et al.'s study in 2009 [29], the relation equation should be linear as below:

$$\frac{\widehat{V}_{\text{CNT}}}{\Phi_0^{\text{CNT}}} + \frac{\widehat{V}_{\text{CB}}}{\Phi_0^{\text{CB}}} = 1. \quad (4)$$

It can be seen clearly from Figure 3(b) that the CB volume fraction needed to reach the composite threshold is much lower in our simulation than that in Sun's theory [29] (4). This nonlinear behavior and reduced volume fraction imply the existence of synergistic effect, consistent with the experimental observations [1, 30]. It should be pointed out that when $\widehat{V}_{\text{CNT}}/\Phi_0^{\text{CNT}} \ll 1$ or $\widehat{V}_{\text{CB}}/\Phi_0^{\text{CB}} \ll 1$ the difference between Sun's theory [29] and (3) is tiny and negligible, so in [29] and (4) is valid because $\widehat{V}_{\text{CB}}/\Phi_0^{\text{CB}} \ll 1$.

Figure 3(b) also shows that when the CNT volume fraction \widehat{V}_{CNT} is close to Φ_0^{CNT} , increasing CB volume fraction (\widehat{V}_{CB}) can greatly decrease \widehat{V}_{CNT} , which means the CB volume fraction has significant effect on the CNT volume fraction at the percolation threshold. However, if the CNT volume fraction (\widehat{V}_{CNT}) is much lower than Φ_0^{CNT} , adding CB can hardly transform electrically isolating polymers to conductors, until CB volume fraction \widehat{V}_{CB} is very close to Φ_0^{CB} . This conclusion agrees with the experiment results of Socher et al. [1].

3.2. Effect of CNT Aspect Ratio. In (3) of the relation between CB and CNT volume fraction at filler percolation threshold, the parameters a and b are determined by dimensions of CNTs and CB groups. It has been proved that for CNTs the aspect ratio is the dominated factor that affects the percolation threshold in PMCs with only CNT filler [15]; in other words, it affects Φ_0^{CNT} significantly. However, in the PMCs with CB and CNT hybrid fillers, whether the CNT aspect ratio affects the relation between the volume fractions of CB and CNT at the percolation threshold established in (3) and how it affects the exponents a and b of (3) are still unrevealed. So in this subsection, the effect of CNT aspect ratio on (3) as well as the exponents a and b is studied.

In the simulation, the diameters of CB groups and CNTs are set to be $d_{\text{CB}} = 60$ nm and $d_{\text{CNT}} = 2$ nm, respectively. In order to get different CNT aspect ratios, the lengths of CNT in the simulation are $l_{\text{CNT}} = 300$ nm, 400 nm, 500 nm, and 600 nm, corresponding to the aspect ratio of 150, 200,

250, and 300. And for these different aspect ratios Φ_0^{CNT} can be obtained as 0.390%, 0.284%, 0.224%, and 0.178%. CNT volume fractions $\widehat{V}_{\text{CNT}} = 0.25\Phi_0^{\text{CNT}}$, $0.375\Phi_0^{\text{CNT}}$, $0.5\Phi_0^{\text{CNT}}$, $0.625\Phi_0^{\text{CNT}}$, and $0.75\Phi_0^{\text{CNT}}$ are studied, respectively, for every different aspect ratio.

The simulation results of CB and CNT volume fractions at percolation threshold are shown in Figure 4(a). In Figure 4(a), for each CNT aspect ratio, the data can be fitted by (3) very well, as shown by the solid curves. The parameters a and b for each aspect ratio are listed in Table 3. It is found that the aspect ratio of CNT can barely affect a or b . This conclusion can be better illustrated in Figure 4(b), in which the CNT and CB volume fractions are normalized by Φ_0^{CNT} and Φ_0^{CB} , respectively. In Figure 4(b), all the fitted curves are very close to each other especially for those with CNT aspect ratio greater than 200. In practical applications, the aspect ratio of CNTs is usually greater than 1000. So the CB-CNT hybrid filled PMCs with different CNT aspect ratios follow the same threshold rule and the exponents a and b can be considered as unchanged for different CNT aspect ratios. It should be noted that increasing CNT aspect ratio can decrease Φ_0^{CNT} and hence decrease the percolation threshold of composites with hybrid filler, although the CNT aspect ratio has little effect on the parameters a and b .

3.3. Effect of Diameter Ratio. In PMCs with CB-CNT hybrid filler, CB can be very different in size due to the differences in processing, dispersion method, dispersion time, and so forth. The diameter ratio of CB groups to CNT in hybrid filler may affect the composite percolation threshold. Here the diameter and length of CNTs are set to be $d_{\text{CNT}} = 2$ nm and $l_{\text{CNT}} = 600$ nm, respectively, and the CB groups with different diameters (d_{CB}) of 40 nm, 50 nm, 60 nm, 70 nm, and 80 nm corresponding to the diameter ratios ($d_{\text{CB}}/d_{\text{CNT}}$) of 20, 25, 30, 35, and 40 are studied. For each diameter ratio, the volume fractions of CNT and CB at the composite percolation threshold are obtained by studying the connection possibility and presented in Figure 5(a).

From Figure 5(a) it can be observed that for a given CNT volume fraction the CB volume fraction at percolation threshold \widehat{V}_{CB} is reduced by increasing the diameter ratio $d_{\text{CB}}/d_{\text{CNT}}$. And this reduction effect becomes more significant with the decrease of the pre-given CNT volume fraction. So increasing the diameter of CB groups can decrease the composite percolation threshold, especially when the CNT volume fraction is relatively low, but it is not a good way to get low percolation threshold by producing large CB groups for large agglomeration which may lead to decline in other properties of the composites.

It can also be illuminated in Figure 5(a) that relation between the volume fractions of CB and CNT follows the rule of (3), as shown by the fitted solid curves in Figure 5(a). The parameters a and b of these five fitting curves are exhibited in Figure 5(b). It is found that the exponent a is almost not affected by the diameter ratio while the exponent b increases with increasing diameter ratio. Furthermore,

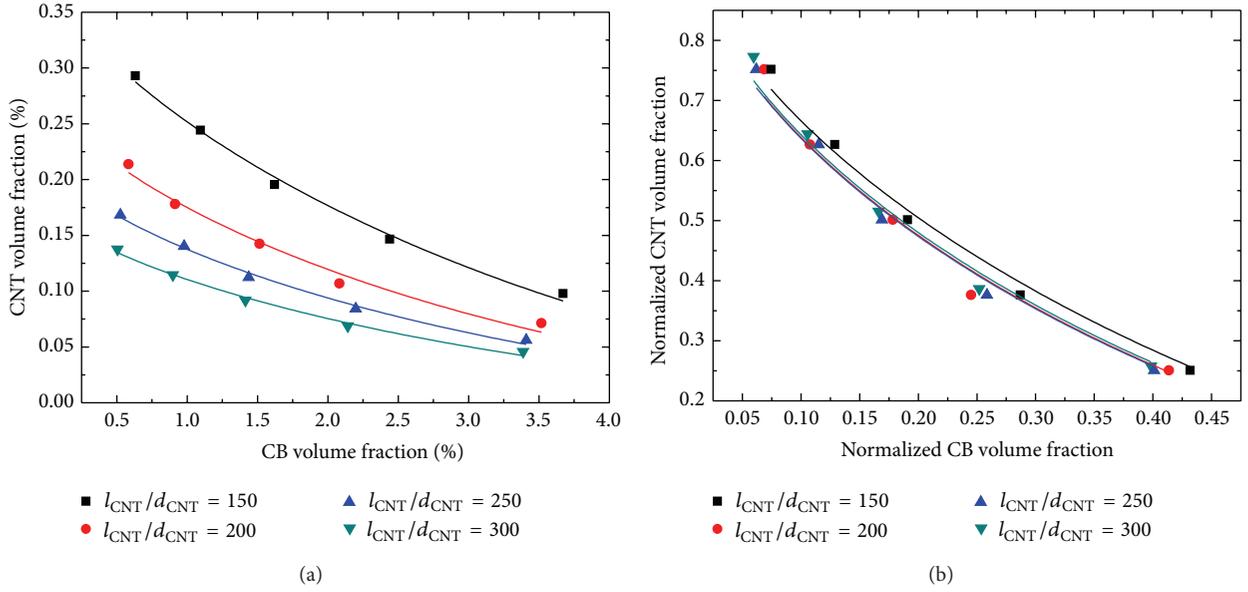


FIGURE 4: Relation between CB and CNT volume fraction at filler percolation threshold for different CNT aspect ratios: (a) volume fractions of CB and CNT and (b) CB and CNT volume fractions normalized by Φ_0^{CNT} and Φ_0^{CB} , respectively.

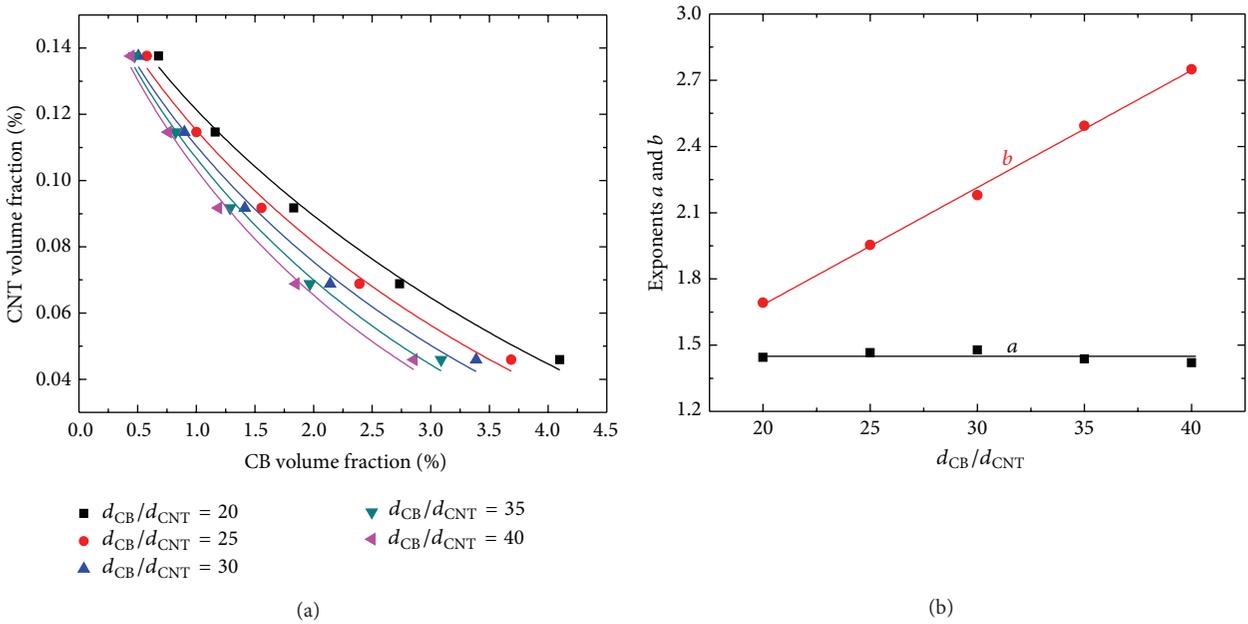


FIGURE 5: Effect of diameter ratio: (a) relation between CB and CNT volume fractions at filler percolation threshold for different diameter ratios of CB to CNT and (b) relation between exponents a and b and diameter ratio of CB to CNT.

it is reasonable to consider that the relation between exponent b and the diameter ratio d_{CB}/d_{CNT} is linear following the equation below:

$$b = 0.622 + 0.0531 \frac{d_{CB}}{d_{CNT}}. \quad (5)$$

Thus (3) can be rewritten by replacing a by its average value and b by (5) as below:

$$\left(1 - \frac{\widehat{V}_{CNT}}{\Phi_0^{CNT}}\right)^{1.449} + \left(1 - \frac{\widehat{V}_{CB}}{\Phi_0^{CB}}\right)^{0.622+0.0531(d_{CB}/d_{CNT})} = 1. \quad (6)$$

4. Estimation on Electrical Percolation Threshold

It has been revealed above that in PMCs with hybrid fillers the relation between volume fractions of CB and CNT at percolation threshold depends on their own percolation threshold in PMCs with single filler and their volume fractions as well as their diameter ratio. The CNT aspect ratio can only affect the percolation threshold in PMCs with only CNTs Φ_0^{CNT} . Therefore, the composite percolation threshold $\Phi_0^{\text{CB\&CNT}}$, which is defined as the volume fraction of both fillers when the electrical conductivity of the composites converts, can be estimated by replacing \widehat{V}_{CNT} by $(\Phi_0^{\text{CB\&CNT}} - \widehat{V}_{\text{CB}})$ as

$$\Phi_0^{\text{CB\&CNT}} = \Phi_0^{\text{CNT}} \left\{ 1 - \left[1 - \left(1 - \frac{\widehat{V}_{\text{CB}}}{\Phi_0^{\text{CB}}} \right)^{0.622+0.0531(d_{\text{CB}}/d_{\text{CNT}})} \right]^{0.690} \right\} + \widehat{V}_{\text{CB}}. \quad (7)$$

Similarly, $\Phi_0^{\text{CB\&CNT}}$ can also be estimated by the CNT volume fraction \widehat{V}_{CNT} as

$$\Phi_0^{\text{CB\&CNT}} = \Phi_0^{\text{CB}} \left\{ 1 - \left[1 - \left(1 - \frac{\widehat{V}_{\text{CNT}}}{\Phi_0^{\text{CNT}}} \right)^{1.449} \right]^{d_{\text{CNT}}/(0.622d_{\text{CNT}}+0.0531d_{\text{CB}})} \right\} + \widehat{V}_{\text{CNT}}. \quad (8)$$

In (7) and (8), the percolation thresholds of PMCs with single filler, Φ_0^{CNT} and Φ_0^{CB} , can be obtained by many existing methods, such as excluded volume method and Monte Carlo simulation, and the diameters and volume fractions of CB and CNTs are determined by material processing.

5. Conclusions

The electrical percolation threshold of PMCs with hybrid filler system of CNT and CB is studied by Monte Carlo simulation on the connection possibility of the fillers. In the simulation, CNTs are modeled as slender spherocylinders and agglomerated CB particles are modeled as hypothetical spheres with interspaces. The overlapped volume is deducted to deal with the impenetrability among CNTs. The following conclusions can be drawn in this study.

- (1) The electrical percolation threshold can be defined as the filler volume fraction at 50% connection possibility, which is not only physical valid but also verified by theoretical and experimental results.
- (2) The synergistic effect exists in PMCs with CB-CNT hybrid filler system, and the CB and CNT volume

fractions at composite percolation threshold follow the nonlinear relation in (6).

- (3) Adding CB into CNT composites can decrease the CNT volume needed to convert the composite conductivity only when the CNT volume fraction is close to Φ_0^{CNT} , the threshold of PMCs with only CNT. If the CNT volume fraction is very low, adding CB is not a good way to make the conversion.
- (4) The electrical percolation threshold can be decreased by increasing CNT aspect ratio, as well as increasing the diameter ratio of CB groups to CNTs, but the latter is not an effective way because large agglomeration of CB particles may lead to decline in other properties of the composites.
- (5) In practice applications, the percolation threshold of PMCs with CB-CNT hybrid filler can be estimated formularily by (7) (or (8)) if CB (or CNT) volume fraction is required.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publishing of this paper.

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