Modeling of the Electrical Percolation of Mixed Carbon Fillers in Polymer-Based Composites

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Introduction

Polymer composites containing carbon-based fillers have recently received considerable attention in both academic research and industry because of their high conductivity, low weight, ease of processing, and so on.[1−8] They are widely used in a variety of applications including conductive material, antistatic material, electromagnetic shielding material, and so on.[9−11] There are mainly four types of carbon fillers: carbon black (CB), graphite (G), carbon fibers (CFs) and carbon nanotubes (CNTs), and each type of carbon filler has its own characteristics. For example, G is cheap, but its percolation threshold is usually high, which could lead to distortion of some properties (e.g., the mechanical properties). Although the percolation threshold of CNTs is very low because of their inherent conductivity and high aspect ratio, the high cost hinders their large scale application. The use of a combination of different carbon fillers would be a good way to get balanced properties and cost. In fact, some polymer-based composites containing two different carbon fillers (e.g., CFs and CB) have been investigated, and a dramatic increase in electrical conductivity has been reported.[12−17] It is commonly believed that the two types of carbon fillers can form cosupporting conductive networks in which the fibrous filler CFs act as long distance charge transporters and the particulate filler CB or G serves as an interconnection between the fibers by forming local conductive paths.[12,13]

Modeling of the electrical conductivity of carbon-filler-filled polymer composites is very important for predicting the conductive behavior of the materials and for material design. Various models have been proposed for single-conductive-filler-filled systems.[18−28] However, to the best of our knowledge, there has not yet been any appropriate model for mixed-carbon-filler-filled systems. In an ongoing project aimed at the preparation of conductive polymer composites using mixed conductive fillers, we found that the addition of a small amount of multiwalled carbon nanotubes (MWCNTs) (which alone cannot make the materials conductive) to CB- or G-filled polymers considerably lowers the percolation thresholds. A model is proposed on the basis of the excluded volume theory. An equation is developed to predict the percolation threshold of the mixed fillers and is analyzed with the experimental data.

Experimental Section

Materials. The MWCNTs used in this work were supplied by Tsinghua University, China. The purity was >95% in weight base. The diameter of the MWCNTs ranged from 3 to 20 nm with the statistic average diameter of 10 nm, and the length was several micrometers. G, with an average particle size of ~15 μm, and CB (VXC-605), with a primary particle diameter of 25 nm, a dibutyl phthalate (DBP) absorption of 1.48 cm^3/g, and an iodine absorption of 90 mg/g were purchased from Shanghai Colloid Chemical Factory and Cabot (Shanghai), respectively. Polypropylene (PP, S1003), with a density of 0.905 g/cm^3 and a melt flow index of 3.2 g over 10 min, and polyoxymethylene (POM, F2002), with a density of 1.41 g/cm^3 and melt flow index of 9.0 g over 10 min, were purchased from China SINOPEC Yanshan Chemical and Mitsubishi, respectively.

Sample Preparation. Polymer/single filler composites were prepared by melt mixing in a torque rotational rheometer for 10 min. We prepared polymer/mixed-filler composites by first melt mixing the polymer with one filler, PP/CB and polymer/MWCNT (in cases where G was used as the other filler), for 5 min; then, the second filler was added, and the mixing was continued for another 5 min. For mixed filler systems, the MWCNT contents were kept constant (1 and 0.5 wt %) for PP- and POM-based composites, respectively. The mixing temperatures were 200 and 180 °C for PP- and POM-based composites, respectively. The rotation rate was 60 rpm.

Measurement of the Volume Resistivity. Prior to the electrical resistivity measurements, the composites were compressed into plates under a pressure of 8 MPa for 5 min using a hot press at temperatures of 230 and 210 °C for PP- and POM-based composites, respectively. Disk samples with a diameter of 30 mm and a thickness of 2.5 mm or a diameter of 75 mm and a thickness of 0.38 mm were prepared for low- and high-resistivity measurements, respectively.

Samples with electrical resistivity of $>10^8$ Ω·cm were measured by the ZC-36 resistivity test (Shanghai Cany Precision Instrument). The principle of the test is based on the formula $\rho_v = (R_v \pi d^2)/(4L)$, where L is the thickness of the sample (0.38 mm), d is the diameter, and R_v is the measured volume resistance. For more conductive samples ($<10^8$ Ω·cm), the electrical resistivity was measured using a four-point test fixture. (i.e., Silver wire was used as electrode material, and silver paint was used to ensure good contact of the sample surface with the electrodes to reduce the contact resistance.) Data from four measurements were averaged, and the mean values are plotted in Figure 1. The standard deviation relative to the mean value was <10%.

Field Emission Scanning Electron Microscopy (FESEM). FESEM was performed on a JEOL model JSM-7401 apparatus with an operating voltage of 1.0 kV to investigate the morphology of the cryofractured surfaces of the composites.

Results and Discussion

Electrical Percolation in Two-Filler-Containing (MWCNTs + CB or MWCNTs + G) Composites. Figure 1 shows the electrical resistivities of PP and POM filled with different kinds of single fillers and mixed fillers at various filler contents. In the case of the mixed fillers, MWCNT content is fixed at either 1 or 0.5 wt %, a value that is insufficient for the formation of a conductive network. The common feature of the three cases is as follows: The curve with MWCNTs is always on the left, and that with CB or G is always on the right, indicating that the percolation threshold of MWCNTs is lower than that of CB or G. The curve with mixed fillers (either MWCNTs + CB or MWCNTs + G) is always in the middle, indicating a decrease in the percolation threshold compared with the cases in which single CB or G is used. This feature reveals the participation of MWCNTs in the formation of conductive CB or G networks, because the neither the amount of MWCNTs nor the amount of CB (or G) alone can make the material conductive at percolation of mixed fillers.

The formation of cosupporting conductive networks of MWCNTs and CB (or G) can also be evidenced by comparing

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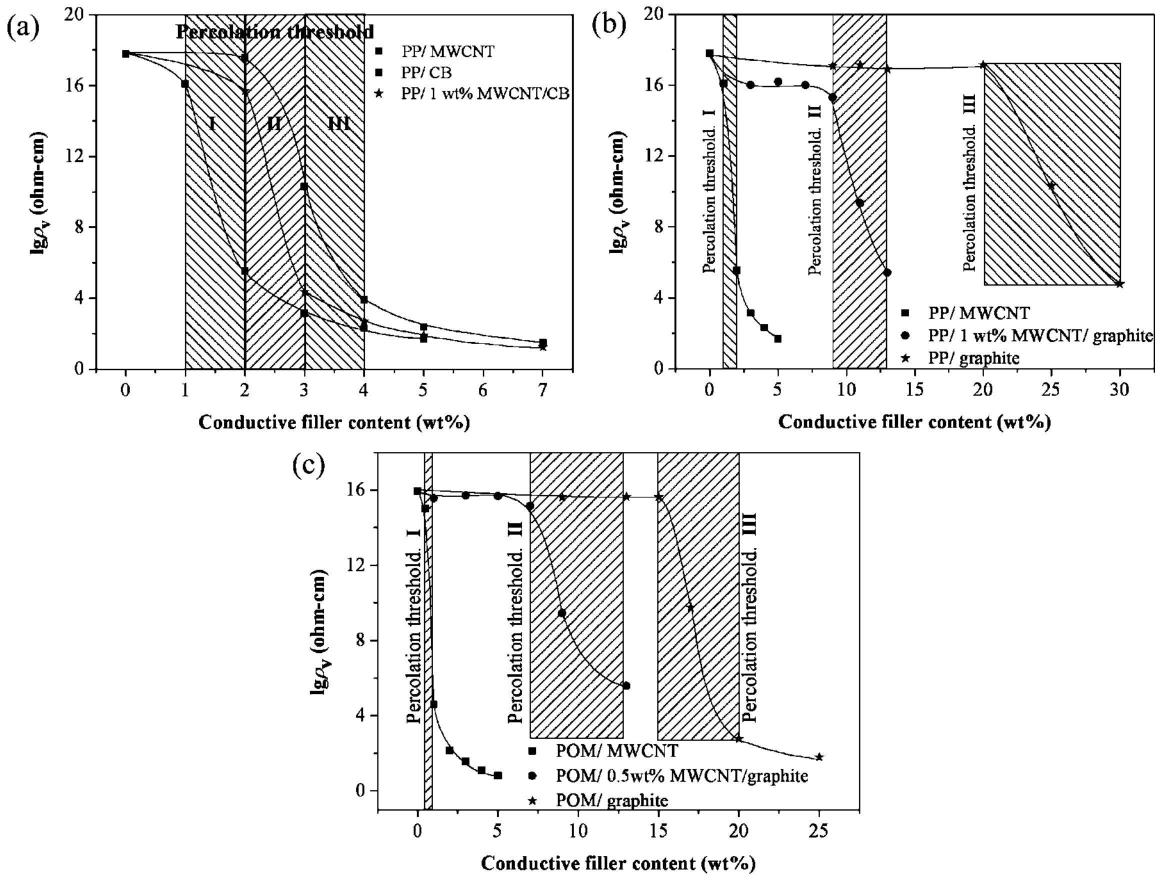

Figure 1. Electrical resistivity as a function of filler concentration for (a,b) PP- and (c) POM-based composites. The curves are model fits for eq 10.

the electrical resistivities of mixed-filler systems with the sum of the electrical resistivities of the corresponding single-filler systems at fixed total filler contents. For example, in Figure 1a, the electrical resistivity of PP/MWCNT composite at 1 wt % MWCNTs and that of PP/CB composite at 2 wt % CB is about 10^{16} and 10^{18} Ω·cm respectively, whereas the resistivity of PP/MWCNT/CB composite at 3 wt % filler content (1 wt % MWCNTs + 2 wt % CB) is 10^4 Ω·cm, a decrease of over 12 orders of magnitude from the sum of the values obtained with 1 wt % MWCNTs and 2 wt % CB.

The cosupporting networks of mixed carbon fillers are illustrated in Figure 2 using MWCNT/CB system as an example. As shown in the FESEM photos (Figure 2a,b), both CB agglomerates (with a size of about 30−900 nm) and MWCNTs disperse homogeneously in the polymer matrix. Similar to the previously reported case of CB/CF mixed fillers, the MWCNTs with long aspect ratio serve to connect CB agglomerates. As a result, cosupporting CB/MWCNT conductive paths are formed (Figure 2c).

Modeling of the Electrical Percolation. On the basis of the fact that the two carbon fillers form cosupporting conductive networks, a model was proposed by extending the excluded volume theory, which was originally proposed by Balberg et al.[21,29] for systems containing one type of object, to systems containing two types of fillers. The excluded volume is the volume around the object into which the center point of an identical object is prohibited if the two are not to overlap. According to the excluded volume theory, the number of objects per unit volume at percolation, q_p, is inversely proportional to the excluded volume $V_{\langle ex\rangle}$ of one of the objects, that is

$$q_p \propto \frac{1}{V_{\langle ex\rangle}} \tag{1}$$

The excluded volume theory has been used for single-filler-filled systems to predict the percolation thresholds of CB,[30] G,[21] and CNTs[25] where the three conductive fillers were considered to be sphere, disk, and spherocylinder. For systems containing two types of fillers with different shapes, a model can be built starting from eq 1.

Here we define V_{unit} as the unit volume, N_c as the number of objects in the unit volume V_{unit} at percolation, and k as the proportionality constant that shows the relationship between N_c/V_{unit} and $1/V_{\langle ex\rangle}$, that is, the inverse proportional relationship between the number of objects per unit volume at percolation versus the excluded volume of the object, which is related to the shape and arrangement of the object. The proportionality constant k becomes unity when the aspect ratio of the object is long and randomly oriented.[19] According to eq 1, we may have

$$N_c = k\frac{V_{unit}}{V_{\langle ex\rangle}} \tag{2}$$

If there is only one type of conductive filler, then we may assume that the unit volume V_{unit} is divided into N_c much smaller equivalent volumes (called small volumes thereafter), and each small volume is $V_{\langle ex\rangle}/k$. When a conductive filler object exists in each small volume, percolation occurs, and we have $N_cV_{\langle ex\rangle}/k = V_{unit}$, which is equivalent to eq 2.

Therefore, if there is only CNT-type filler, then according to eq 2, we may assume that the averaged excluded volume of one CNT object (single or cluster depending on its dispersion

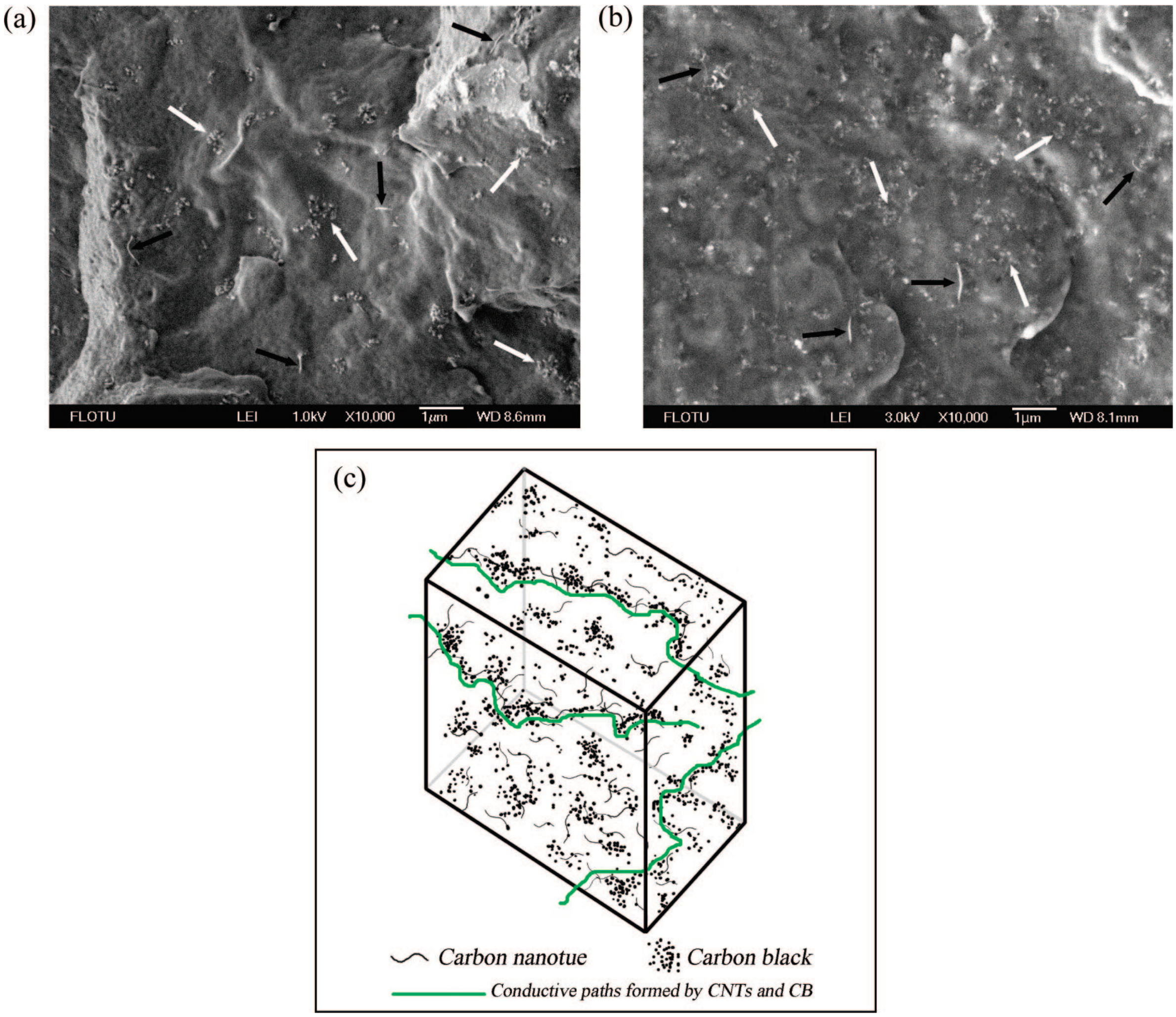

Figure 2. FESEM micrographs of cryofractured surfaces of PP/MWCNT/CB composites at 10 000× magnification for (a) PP/1 wt % MWCNT/2 wt % CB and (b) PP/1 wt % MWCNT/6 wt % CB. The black arrows in a and b point to MWCNT, whereas the white arrows points to CB agglomerates. (c) Model of the formation of cosupporting MWCNT/CB conductive paths, where CNTs with long aspect ratio act as long-distance charge transporters, and the particulate filler CB serves as an interconnection between the tubes by forming local conductive paths.

and average size in the most probable case of coexisting of single and clusters) is $V_{\langle CNT\rangle}$ and the corresponding constant is k_{CNT}; then, the small volume is $V_{\langle CNT\rangle}/k_{CNT}$, and when one CNT object occupies one small volume ($V_{\langle CNT\rangle}/k_{CNT}$), percolation occurs, as illustrated in Figure 3a. Similarly, if there is only CB-type filler, then we may assume that the averaged excluded volume of one CB object (average size of clusters) is $V_{\langle CB\rangle}$ and the corresponding constant is k_{CB}; then, the small volume is $V_{\langle CB\rangle}/k_{CB}$, and when one CB object occupies one small volume, percolation occurs, as illustrated in Figure 3b.

For a system containing two types of conductive fillers such as CNTs and CB, the unit volume can be divided into two types of small volumes, $V_{\langle CNT\rangle}/k_{CNT}$ and $V_{\langle CB\rangle}/k_{CB}$, which are not drawn in the real random mixing state shown in Figure 3c because of the difficulty in drawing, but an extreme case is drawn in Figure 3d for a better understanding. When all of the small volumes are filled, percolation occurs. Therefore, we have the following equation

$$V_{unit} = N'_{CNT}\frac{V_{\langle CNT\rangle}}{k_{CNT}} + N'_{CB}\frac{V_{\langle CB\rangle}}{k_{CB}} \tag{3}$$

where N'_{CNT} and N'_{CB} are the numbers of CNT and CB objects, respectively.

Because the number of CNT (or CB) objects is proportional to the volume fraction of CNTs (or CB) in a given volume, we have

$$N'_{CNT} = \frac{V_{CNT}}{\phi_{c,CNT}}N_{CNT} \tag{4}$$

$$N'_{CB} = \frac{V_{CB}}{\phi_{c,CB}}N_{CB} \tag{5}$$

where V_{CNT} and V_{CB} are the actual volume fractions of CNT and CB objects, $\varphi_{c,CNT}$ and $\varphi_{c,CB}$ are the percolation concentrations of CNTs and CB expressed in volume fraction if the unit volume is filled with CNTs or CB alone, and N_{CNT} and N_{CB} are the numbers of CNT and CB objects at the corresponding percolation concentrations.

Entering eqs 4 and 5 into eq 3

$$V_{unit} = \frac{V_{CNT}}{\phi_{c,CNT}}N_{CNT}\frac{V_{\langle CNT\rangle}}{k_{CNT}} + \frac{V_{CB}}{\phi_{c,CB}}N_{CB}\frac{V_{\langle CB\rangle}}{k_{CB}} \tag{6}$$

Entering eq 2 into eq 6, we may get

$$V_{unit} = \frac{V_{CNT}}{\phi_{c,CNT}}V_{unit} + \frac{V_{CB}}{\phi_{c,CB}}V_{unit} \tag{7}$$

That is

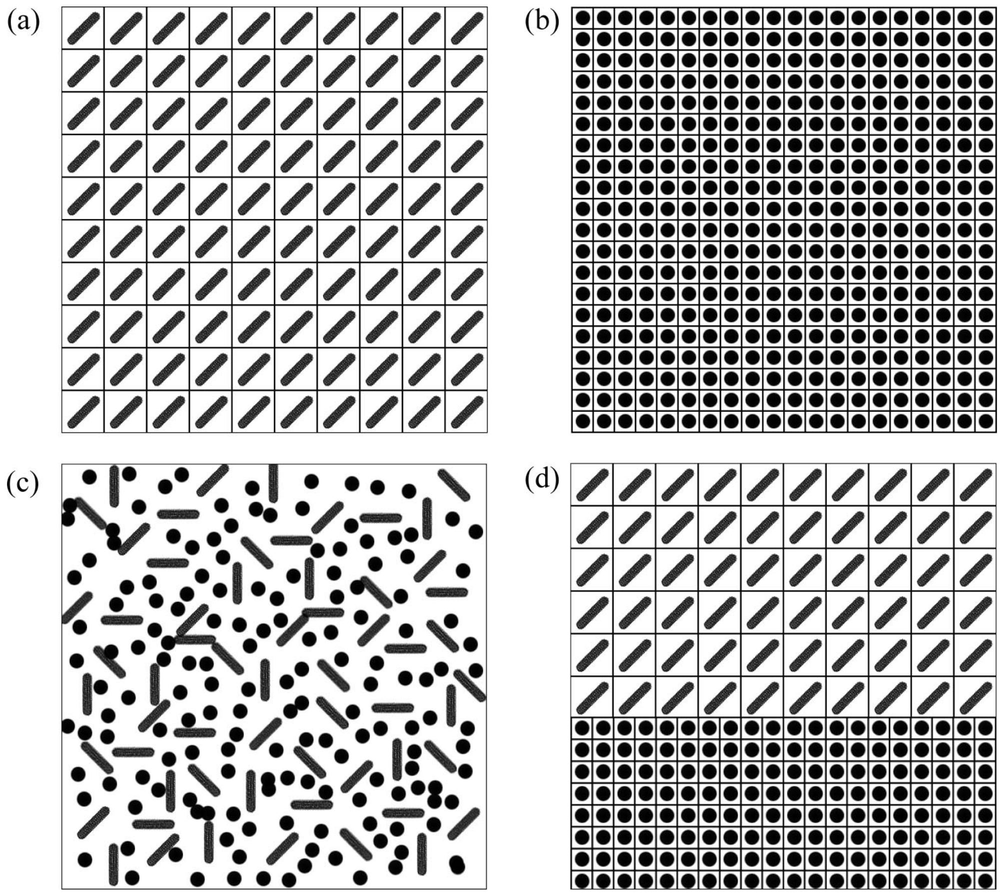

Figure 3. Schematic illustrations of the excluded volume for single filler system (a) CNT and (b) CB as well as two-filler (CNT and CB) systems in (c) the real state and (d) an extreme state.

$$\frac{V_{\mathrm{CNT}}}{\phi_{c,\mathrm{CNT}}}+\frac{V_{\mathrm{CB}}}{\phi_{c,\mathrm{CB}}}=1 \qquad (8)$$

For systems containing two different types of conductive fillers A and B, eq 8 can be generalized as

$$\frac{V_{\mathrm{A}}}{\phi_{c,\mathrm{A}}}+\frac{V_{\mathrm{B}}}{\phi_{c,\mathrm{B}}}=1 \qquad (9)$$

That means when $V_{\mathrm{A}}/\varphi_{c,\mathrm{A}} + V_B/\varphi_{c,\mathrm{B}} = 1$, the conductive fillers begin to percolate in the polymer matrix; when $V_{\mathrm{A}}/\varphi_{c,\mathrm{A}} + V_{\mathrm{B}}/\varphi_{c,\mathrm{B}} > 1$, the conductive fillers connect to each other, and the material is conductive; when $V_{\mathrm{A}}/\varphi_{c,\mathrm{A}} + V_{\mathrm{B}}/\varphi_{c,\mathrm{B}} < 1$, the conductive fillers separately disperse in the polymer matrix, and the electrical resistivity is high.

A better understanding of eq 9 can be gained from Figure 3d, an extreme situation where the unit volume is divided into two regions, one of which is occupied by type A filler and the other by type B filler. When two types of fillers A and B occupy and get percolated, $V_A/\varphi_{c,A}$ percent and $V_B/\varphi_{c,B}$ percent of the unit volume, respectively, and the sum of the two percentages is 100, percolation occurs.

It should be noted that the condition of using eq 9 is that the dispersion of one type filler is not affected by the presence of the other because in the building up of the model, the excluded volumes of the two types of objects are kept constant in single-filler-filled and mixed-filler-filled systems.

Previous studies on single-filler-filled systems have shown that deviation occurs when the filler is considered to be a specific shape because the filler has a wide range of dispersion.[25] In eq 9, the dispersion state of the fillers A and B are reflected in $\varphi_{c,\mathrm{A}}$ and $\varphi_{c,\mathrm{B}}$ because the percolation concentration is usually closely related to the dispersion state of the filler.[25,31,32] Therefore, the advantage of eq 9 is that on the one hand, one does not need to calculate the excluded volumes of each type of the fillers, but on the other hand, it can be used as long as the processing parameters are consistent.

Eq 9 is simple to use. It can provide guidance for predicting the electrical properties of two-filler-filled polymers, providing that the percolation concentrations for the corresponding single-filler-filled systems, $\varphi_{c,\mathrm{A}}$ and $\varphi_{c,\mathrm{B}}$, are known. Furthermore, the volume fraction used in eq 9 can be generalized as the weight fraction for the convenience of practical use and the avoidance of the uncertainty of the fillers' density.[33,34] Therefore, eq 9 can be written as follows for practical use

$$\frac{m_{\mathrm{A}}}{P_{c,\mathrm{A}}}+\frac{m_{\mathrm{B}}}{P_{c,\mathrm{B}}}=1 \qquad (10)$$

where m_{A} and m_{B} are the weight fractions of fillers A and B, respectively, and $P_{c,\mathrm{A}}$ and $P_{c,\mathrm{B}}$ are the corresponding percolation concentrations when A and B are used alone.

Examination of Equation 10 with Experimental Data. Equation 10 is examined with the experimental data shown in Figure 1. In Figure 1a, $P_{c,\mathrm{A}}$=1.78 wt % and $P_{c,\mathrm{B}}$ = 3.71 wt %, as calculated from the power law. When 1 wt % of MWCNTs and 2 wt % of CB are used as mixed fillers, that is, $m_{\mathrm{A}} = 1$, $m_{\mathrm{B}} = 2$, $m_{\mathrm{A}}/P_{c,\mathrm{A}} + m_B/P_{c,\mathrm{B}} = 1/1.78 + 2/3.71 = 1.10 > 1$, the resistivity of the composites is low ($\sim 10^4$ $\Omega\cdot$cm) and the composite material is conductive. When 1 wt % of MWCNTs and 1 wt % of CB are used, that is, $m_{\mathrm{A}} = 1$, $m_{\mathrm{B}} = 1$, $m_{\mathrm{A}}/P_{c,\mathrm{A}} + m_{\mathrm{B}}/P_{c,\mathrm{B}} = 1/1.78 + 1/3.71 = 0.83 < 1$, then the electrical resistivity of the composite is very high ($\sim 10^{16}$ $\Omega\cdot$cm).

According to eq 10, the mass fraction required for CB is 1.63 wt % to get the composite percolated. Because MWCNT content is 1 wt %, the total mass fraction of the conductive filler is 2.63 wt %. All data shown in Figure 1a fit eq 10 well.

In Figure 1b, the percolation concentration of G ($P_{c,\mathrm{B}}$) cannot be calculated from the power law because of the lack of experimental data. However, the percolation range of mixed fillers can still be estimated. From eq 10, at percolation

$$m_\mathrm{B} = \left(1 - \frac{m_\mathrm{A}}{P_{c,\mathrm{A}}}\right) P_{c,\mathrm{B}} \quad (11)$$

Then

$$m_\mathrm{A} + m_\mathrm{B} = m_\mathrm{A} + \left(1 - \frac{m_\mathrm{A}}{P_{c,\mathrm{A}}}\right) P_{c,\mathrm{B}} \quad (12)$$

Because m_A = 1 wt %, $P_{c,\mathrm{A}}$ = 1.78 wt %,and 20 wt % < $P_{c,\mathrm{B}}$ < 30 wt % (shown in Figure 1b), the calculated results are 9.7 wt % < $m_\mathrm{A} + m_B$ < 14.1 wt %; this estimated percolation threshold range is basically in line with the actual experimental data (9−13 wt %).

Similarly, in Figure 1c, m_A = 0.5 wt %, $P_{c,\mathrm{A}}$ = 0.89 wt %, and 15 wt % < $P_{c,\mathrm{B}}$ < 20 wt %, the estimated percolation threshold range of mixed fillers from eq 12 is 7.6−9.8 wt %, whereas the actual experimental percolation range is 7−13 wt %. The two percolation range values are similar. Furthermore, deviation could have occurred because POM can be degraded to some degree during processing.

Conclusions

A model describing the electrical percolation of mixed carbon fillers MWCNTs and CB (or G) is proposed on the basis of the excluded volume theory. The equation that was developed from the model fits the experimental results well and is useful for predicting the percolation threshold of mixed fillers and the electrical properties of polymer-based composites. Therefore, it provides a general guidance for the design of conductive polymer composite materials.

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