Comparative Study on Electrical Properties of Orientated Carbon Nanotubes/Epoxy Composites

Jianfeng Dai,[1,2] Junhong Wang,[2] Xiaowen Mu,[2] Xiaoting Chen[2]

[1]*State Key Lab. of Gansu Advanced Non-ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, China*
[2]*School of Science, Lanzhou University of Technology, Lanzhou 730050, China*

Received 26 March 2011; accepted 29 May 2011
DOI 10.1002/app.35025
Published online 5 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The percolation threshold of carbon nanotubes (CNTs)/epoxy resin composites was simulated in the Bruggeman' Effective-Medium Theory based on experiment. Both distinct percolation effect and low percolation threshold in the aligned CNTs/epoxy composites were predicted. With the CNTs loading larger than the percolation threshold, the critical exponent of CNTs/epoxy composites rises rapidly with the increase of aspect ratio of CNTs. It is shown that the electrical conductivity of composites presents distinct aeolotropism, the percolation threshold is sensitive relative to the tiny change of the orientation factor, the aspect ratio, and the structure of CNTs in the composites matrix. The simulated results are consistent with the experimental results basically, and the discrepancy between simulated results and experimental results has been interpreted reasonably. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 647–653, 2012

Key words: single-walled carbon nanotube; composites; percolation threshold; electrical conductivity; Effective-Medium Theory

INTRODUCTION

There has been intense interest in the use of composites made of an insulating matrix and conductive fillers which electromagnetically shield and prevent electrostatic charging of electronic devices.[1–4] In addition, epoxy resin is well established as advanced composites, displaying a series of interesting characteristics, which can be adjusted within broad boundaries. It is widely used in applications ranging from microelectronics to aerospace. Recent experimental studies show that the addition of a small amount of carbon nanotubes (CNTs) in a polymer-based composite could result in a substantially large enhancement of the electrical conductivity.[5–13] Moreover, the nonlinear dependence of the electrical conductivity on CNT volume fraction was experimentally found,[6–13] whereas the conventional theoretical predictions fail to explain the experimental results.

However, to develop CNTs/polymer composites with high performance, main problems and challenging tasks rest with creating a good dispersion, well alignment, and strong interface between bonding of CNTs and the polymer matrix, forming a structural frame and an electrical conducting path, and increasing the electrical conductivity.[14,15] In this research, effective medium theory (EMT) was generalized to investigate the percolation threshold of the CNTs/epoxy composites.

PERCOLATION SIMULATION FOR CNTS/EPOXY COMPOSITES

The effective medium approximations (EMAs) are analytical models that describe the macroscopic properties of a medium based on the properties and the relative fractions of its components, and it is derived to investigate the effective linear and nonlinear responses of two-component composites. As we know, the derivations of both approximations of the Maxwell-Garnett's approximation and the Bruggeman's EMA were based on the assumption that the granular inclusions are spherical and ellipsoidal in shape, which is not suitable for the CNTs/epoxy composites. To eliminate this deficiency, a new modeling approach has been presented based on EMA. In this modeling, for simplicity, we assume that epoxy resin with volume fraction $1 - f$ is spherical in shape, while the CNTs with volume fraction f are

Correspondence to: J. Dai (daijf@lut.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50873047.
Contract grant sponsor: Natural Science Foundation of Gansu Province, China; contract grant number: 3ZS061-A25-039.
Contract grant sponsor: Foundation of the Education Department of Gansu Province, China; contract grant number: 0603-02.

Journal of Applied Polymer Science, Vol. 124, 647–653 (2012)

orientated homogeneously in the matrix. Second, the CNTs, modeled by ellipsoids with a large eccentricity, can be regard as orientated bars with large aspect ratio approximately.

To construct the EMA, it could be assumed that the embeddings of both component 1 and component 2 in the composite matrix are replaced by a fictitious homogeneous one with conductivity equal to the effective conductivity σ. The polarization factor (P_1,P_2) produced in the granular inclusions made of component 1 and component 2 with σ_1 and σ_2 can be written as[16]

$$P_1 = \frac{\sigma_1 - \sigma}{3} \sum_{j=x,y,z} \frac{1}{\mathrm{d}_j\sigma_1 + (1 - d_j)\sigma}, \quad (1)$$

$$P_2 = \frac{\sigma_2 - \sigma}{2} \sum_{j=x,y,z} \frac{1}{\mathrm{d}_j\sigma_1 + (1 - d_j)\sigma}, \quad (2)$$

where d_j is the depolarization factor of the granular inclusions made of component 1 and component 2 along three-symmetric axes and can be used to describe the shape of the granular inclusions. Note that the sum rule $d_x + d_y + d_z = 1$ must be satisfied.

The effective linear conductivity σ can then be determined by imposing the consistency requirement that the arithmetic average of the polarization over different types of granular inclusions must vanish, i.e.

$$fP_1 + (1 - f)P_2 = 0. \quad (3)$$

In the CNTs/epoxy composites, when granular inclusions made of the CNTs are randomly orientated bars with large aspect ratio ($d_x = d_y = 1 - d_z/2$) and epoxy resin is perfectly spherical in shape (i.e., $d_x = d_y = d_z = 1/3$), eq. (3) reduces to

$$f\frac{\sigma_1 - \sigma}{\sigma + \mathrm{d}_z(\sigma_1 - \sigma)} + 3(1 - f)\frac{\sigma_2 - \sigma}{\sigma_2 + 2\sigma} = 0. \quad (4)$$

which is an effective medium approximation with dipole–dipole interaction (EMADD).

Conductivity of composites enhanced in the orientated direction along with the orientation of CNTs improved. According to effective aspect ratio η varied in the orientated direction along with the different orientation of CNTs, η was defined as $\eta = l{\cdot}\cos\theta/r$. The depolarization factor was written as follows:

$$d_z = \frac{1}{(l\cdot\cos\theta/r)^2 - 1}\left[\frac{l\cdot\cos\theta/r}{\sqrt{(l\cdot\cos\theta/r)^2 - 1}}\cdot \times \ln\left(l\cdot\cos\theta/r + \sqrt{(l\cdot\cos\theta/r)^2 - 1}\right) - 1\right] \quad (5)$$

where θ is the angle of the CNTs with orientated direction, l and r are length and radius respectively.

Based on the above calculation, it is obvious that there exists distinct relationship between the conductivity and the CNTs content of CNTs/epoxy composites, as well as the relationship of the percolation threshold with the aspect ratio and the orientation factor of CNTs. In addition, the critical exponent of CNTs/epoxy composites appears naturally during simulation.

EXPERIMENTAL DETAILS FOR THE ELECTRICAL CONDUCTIVITY MEASUREMENT

As shown in Figure 1, the purified quasi-straight CNTs with average diameter of 1.2–1.5 nm and lengths about 600–2000 nm used in this research were produced by an anode arc-discharge method in our laboratory. The CNTs/epoxy resin composite was prepared using solution casting method. The nitric acid treated CNTs were dispersed in ethanol and sonicated for 30 min first. The composites were prepared by mixing CNTs/ethanol solutions with different CNTs weight fractions into bisphenol-A type epoxy resin (E-51). The mixtures were then sonicated for 2 h to remove air bubbles and allow evaporation of the superfluous solvent. Hardener *N*,*N*-dimethylbenzylamine (BDMA) was added into the nanotube/epoxy mixtures in two steps by a total specified resin-hardener weight ratio of 1 : 0.23. The half BDMA was added into the nanotube/epoxy mixtures before stretching to prevent the mixture being too sticky or too fragile. The mixture was sonicated and stirred at 1500 rpm simultaneously again for 1 h to produce uniformly distributed nanotube composites. Another half BDMA was added after repeated stretching process.[11]

The fabricated semidried CNTs/epoxy as described above was stretched along one direction at a draw-ratio of 50 every time before it was dried, and then folded it along the same direction and stretched repeatedly for 100 times at ambient atmosphere manually to achieve a good alignment and dispersion. The stretching speed was about 0.05 m/s and the full stretching process last about 30 min.

All samples were remained in the vacuum at a room temperature for 7 days before the electrical testing. The specimens we adopt were about 50 mm length, 10 mm width, and 2 mm thickness, and the end of the cross-section areas were painted with conductive silver to provide good contact with the specimen. The electrical measurement results were obtained from measurements of DC resistance between two terminals using a multimeter with a range of resistance from 20 Ω to 20 MΩ.

To investigate the alignment degree, the Herman factor of CNTs in electrospun fibers was calculated

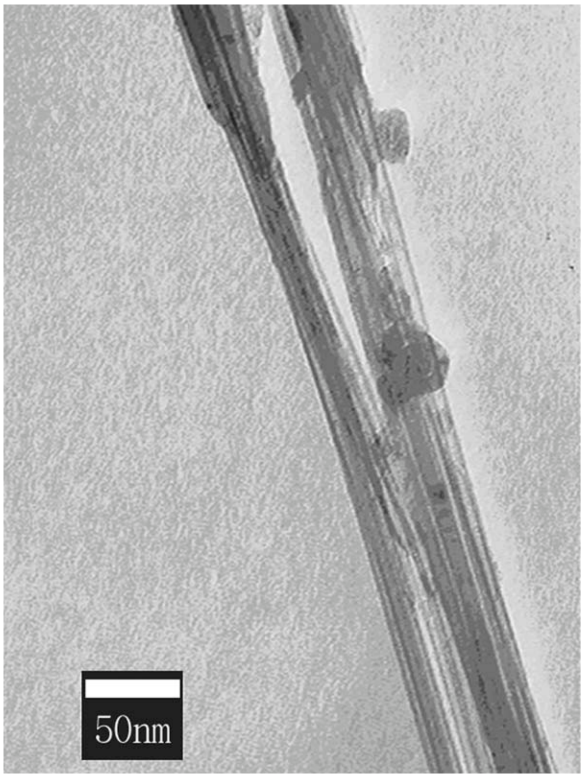

Figure 1 A TEM image of the purified quasi-straight CNTs.

based on the polarized Raman spectra with the specimen stage at 0°, 30°,60°, and 90° with respect to the excitation polarization direction. As shown in Figure 2(a), the Raman peaks at 192 cm^{-1}, 1350 cm^{-1} and 1593 cm^{-1} associated with the radial breathing mode (RBM), D-band, and G-band, respectively. A large decrease in the intensity of the peaks can be observed when the specimen stage is rotated from parallel ($\psi = 0°$) to perpendicular ($\psi = 90°$) to the polarization direction which suggests an obvious predominant orientation of CNTs along the fiber axis.

The intensity of the G-band (1593 cm^{-1}) as a function of angle was used to quantify the degree of nanotube alignment, based on the theoretical curve for perfectly aligned single-wall carbon nanotube (SWNT) and fiber bundle, where intensity is proportional to cos 4ψ. Due to the electrostatic charge accumulation on composite fibers, the partially disorder arrangement can be found in surface of fibers layer to some extent, which can influence the intensity of the polarized Raman spectra peaks and the calculation of orientation degree of CNTs in base. According to hypothesis that the CNTs orientation follows the Lorentzian distribution, the intensity of a Raman peak at a given angle, ψ, between specimen stage the and polarization axes, can be represented by

$$I = \int_{\theta_1-\frac{\pi}{2}}^{\theta_1+\frac{\pi}{2}} \int_{\psi-\frac{\pi}{2}}^{\psi+\frac{\pi}{2}} C \frac{\Delta_1/2\pi}{(\theta_1-\psi)^2+(\Delta_1/2)^2} \cdot \frac{\Delta_2/2\pi}{(\theta_2-\theta_1)^2+(\Delta_2/2)^2} \cos^4\theta_2 d\psi d\theta$$

where θ_1 is the angle between the fiber axis and the incident excitation polarization. θ_2 is the angle between the CNTs and fiber axis. C is a parameter that gives the maximum intensity when $\theta_1 = 0$ and $\theta_2 = 0$. Δ_1, Δ_2 are the full width at half maximum (FWHM) of the distribution of CNTs. As shown in Figure 2(b), performing a least of squares fit of equation above to the experimental data yields a best fit value of $\Delta_2 = 12°$, which mean the Herman's factor

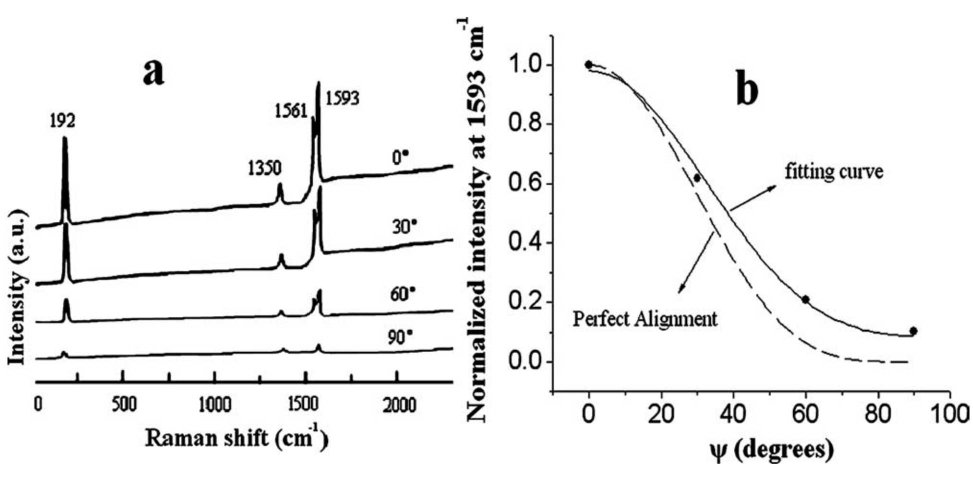

Figure 2 (a) Raman spectra of an quasi-aligned CNTs/epoxy with the specimen stage at 0°, 30°, 60°, and 90° with respect to the excitation polarization direction. (b) The effect of fiber angle, ψ, on the normalized Raman intensity at 1593 cm^{-1} (G-band) for CNTs/epoxy. The lower dashed line represents the relationship between relative intensity and fiber angle for perfect or unidirectional alignment of both CNTs and composite.

TABLE I
Parameters of the Simulations

Aspect ratio	Volume fraction	Critical exponent	Orientation factor		
500	0.005%	1.5	1	0.89	0.3
	0.05%	2	1	0.89	0.3
	0.1%	2.5	1	0.89	0.3
1000	0.005%	1.5	1	0.89	0.3
	0.05%	2	1	0.89	0.3
	0.1%	2.5	1	0.89	0.3
1500	0.005%	1.5	1	0.89	0.3
	0.05%	2	1	0.89	0.3
	0.1%	2.5	1	0.89	0.3

of CNTs in composites equals 0.89, as well as an excellent orientation uniformity of CNTs along the fiber axis.

RESULTS AND DISCUSSION

Percolation threshold for electrical conductivity

The transition from an insulating to a conducting composite as a function of filler concentration is known as percolation and the critical concentration at which this drop occurs is called percolation threshold.[4,17–19] According to this theory, the mechanism of electrical conduction of CNTs/epoxy composites is the formation of the conductive network which is made up of conductive inclusions in the direct contact. In this research, the CNTs network provides the three-dimensional conductive paths in CNTs/epoxy composites.

The volume conductivity data were fitted to a power law in terms of volume fraction of CNTs. The conductivity is linear with $f - f_c$ in a logarithmic scale and the relationship is described by the equations below

$$\sigma = A(f - f_c)^t, \quad (6)$$

$$\log \sigma = \log A + t \log(f - f_c). \quad (7)$$

where σ is the conductivity of the composites, f is the volume fraction of the CNTs in the composites, f_c is the critical volume fraction, A and t are fitted constants.

We can simulate the relationship between the conductivity and the orientation factor by substituting the eq. (5) into eq. (4), and the cosine of the angle of the CNTs with orientated direction was used as the orientation factor. Table I contains the parameters of the simulations. According to the calculated results of Raman spectra (Fig. 2), the orientation factor which used in simulations was 0.89. The simulated result shown in Figure 3 reveals that a low CNTs volume fraction can lead to a dramatic increase in the electrical conductivity of CNTs/epoxy composites in the CNT aligning direction, but the electrical conductivity of CNTs/epoxy composites in the transverse direction is scarcely reinforced. The inset figure demonstrates a distinct percolation effect.

The DC volume conductivity of CNTs/epoxy composites as a function of CNTs concentration was plotted in Figure 4. Both the experimental and simulated results indicate the intensive anisotropy in the aligned CNTs/epoxy composites as shown in Figures 3 and 4.

To determine the percolation threshold of the composites, the first derivative of the logarithmic electrical conductivity plots ($\frac{1}{\sigma \ln 10}\frac{\partial \sigma}{\partial f}$) along the CNTs aligning direction was calculated, and the result is plotted as a function of CNTs content in Figure 5.[11] The CNTs contents corresponding to the highest absolute derivative was taken as the percolation threshold.[19] The experimental percolation thresholds for CNTs/epoxy composite in the CNTs aligning direction is 0.05 vol %. Moreover, the same technique was adopted to calculate the percolation threshold in simulation process, as shown in Figure 6. The theoretic percolation threshold of CNTs/epoxy composite is 0.035 vol % when the aspect ratio of CNTs is 500. We used the minimum

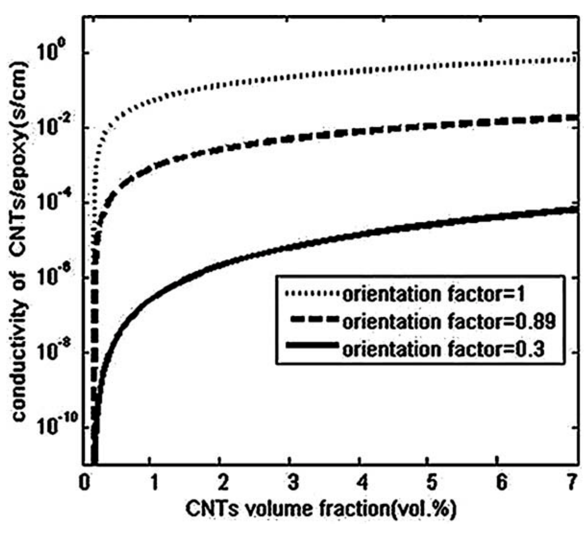

Figure 3 Simulated curve of conductivity of CNTs/epoxy with different orientation factors vs. the volume.

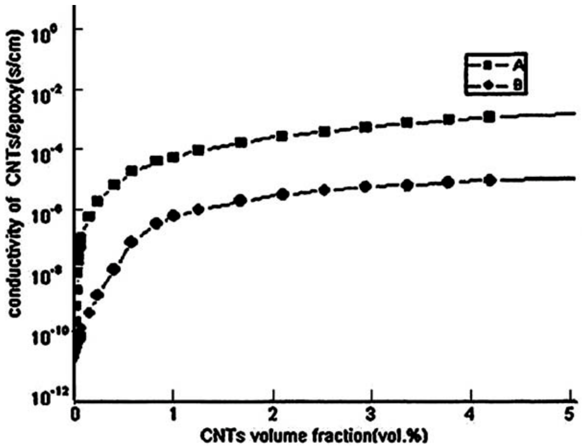

Figure 4 Experiment curve of DC volume conductivity vs. CNTs content of CNTs/Epoxy composites. A: Along the stretching direction, (B): perpendicular to.

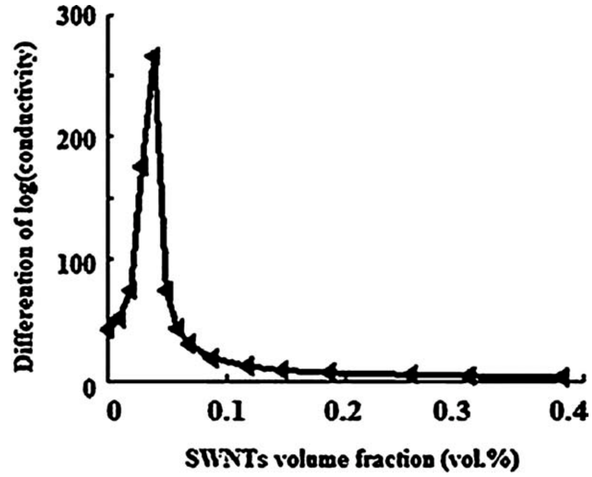

Figure 6 Simulated curve of DC volume conductivity increased ratio vs. the volume fraction of CNTs with aspect ratio of 500 and orientation factor of 1.

numerical value for the length of the CNT was shortened with stirred, stretched and other process. The minimum length of CNT was about 600 nm, so the 500 aspect ratio was adopted.

Theoretical predictions and experimental values of the critical exponent, ranging from 1.3 to 3.1 have been reported.[20] To determine the percolation threshold, the curve of critical exponent with various orientation factors versus the aspect ratio of CNTs was achieved by fitting the simulative data using eq. (7), as shown in Figure 7.

The most basic description of the orientation factor, a critical parameter in the application of polymer composites, is the probability distribution function which will give us a measure of the state of CNTs orientation at that location.[21] Thus one can define $\phi(\theta,\varphi)\sin\varphi d\varphi d\theta$ which describes the probability of a CNTs being orientated between the specific angles θ and $\theta + d\theta$, and angles φ and $\varphi + d\varphi$. Here, $\sin \varphi d\varphi d\theta$ is the increment in area on the surface of the unit sphere. In this article, we define the corresponding orientation factor as the average of the second Legendre polynomial of orientation of embedded rods,

$$Q = \int_{0}^{2\pi}\int_{0}^{\pi}\left[\frac{3}{2}\cos^{2}\phi - \frac{1}{2}\right]\phi(\varphi)\sin\phi\, d\theta\, d\varphi \qquad (8)$$

The isotropic case can be given by orientation factor = 0, and the orientated alignment can be given by orientation factor = 1. The critical exponent deduced from EMT is in reasonable agreement with both experimental results and other theoretical predictions. It revealed distinctly a strong dependence of the critical exponent on the aspect ratio of CNTs

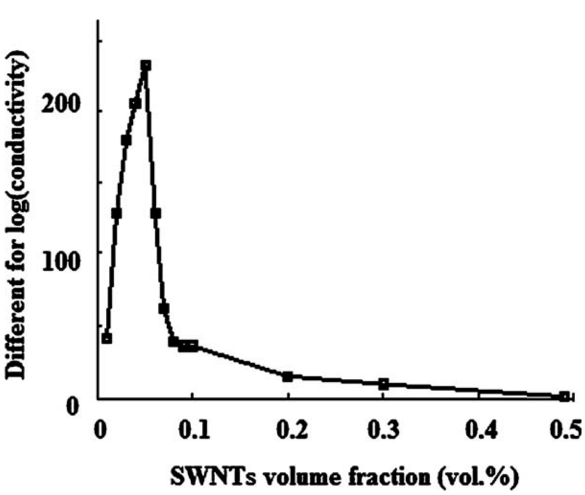

Figure 5 Experimental curve of DC volume conductivity increased ratio vs. the volume fraction of CNTs.

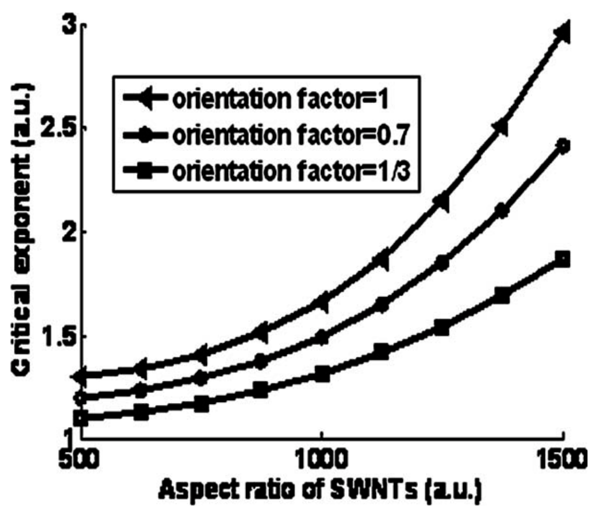

Figure 7 Curve of critical exponent with different orientation factor vs. the aspect ratio of CNTs.

with the CNTs loading larger than the percolation threshold.

The influence of the aspect ratio and the orientation factor on percolation threshold

In terms of the present model, the percolation threshold with the aspect ratio of 1000, 1500, and 2000, respectively, were plotted as a function of the orientation factor in Figure 8. It is obvious that the percolation threshold is more sensitive to the orientation factor of CNTs at the smaller aspect ratio and is less sensitive to the aspect ratio of CNTs with larger orientation factor. The reason is that the probability of the intersection between CNTs becomes lower for high anisotropy so as to affect the percolation threshold in composite systems.

The dependence of percolation threshold with different orientation factors on the aspect ratio of CNTs was well predicted in Figure 9. It reveals distinctly that the percolation threshold depends on the aspect ratio of CNTs strongly and falls rapidly with the increase of aspect ratio of CNTs. Furthermore, it can be found that with the CNTs larger aspect ratio, the percolation threshold of composites tends to become less dependent on the orientation factor, which can be used to interpret a great deal of discrete results about the low threshold of composites containing CNTs discovered so far.

The simulated predictions were in agreement with the experimental results; however the noticeable discrepancy between them exists. The electrical conductivity of orientated CNTs/epoxy composites given by our model exceeds the experimental value along the aligning direction of CNTs. In the experimentation, the percolation threshold is much higher than the value given by our simulation. This discrepancy may be attributed to the following factors. One reason is definitely that our model did not include the real state of the dispersion and the orientated alignment of CNTs along the aligning direction, e.g., the magnitude of CNTs agglomerates and the disorder degree of CNTs alignment were not taken into account. Furthermore, the electrical conductivity and the aspect ratio of CNTs should be discrete; however fixed values of the electrical conductivity and the aspect ratio of CNTs were adopted in the simulation.

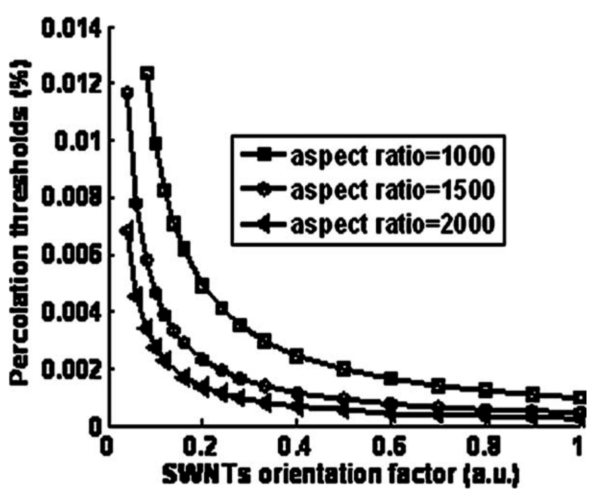

Figure 8 Variation of percolation threshold with aspect ratio for different orientation factor.

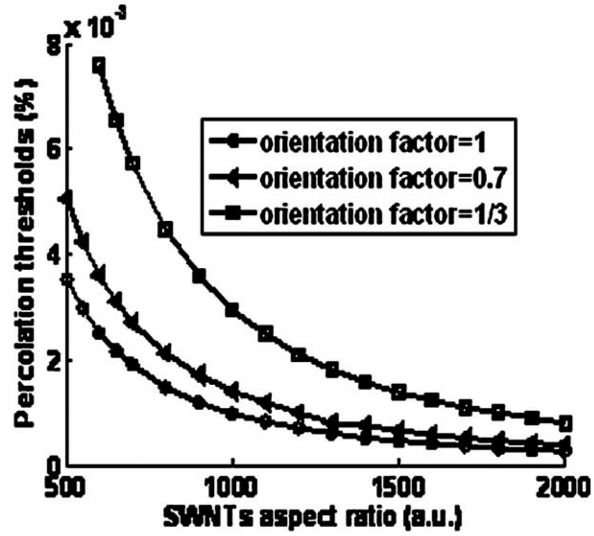

Figure 9 Variation of percolation threshold with orientation factor for different aspect ratio.

CONCLUSIONS

The results demonstrate distinct percolation effect and very low percolation threshold in the CNTs/epoxy composites. The percolation threshold is relative to the orientation factor and the aspect ratio of CNTs in the composite matrix strongly. The simulated percolation threshold of the orientated CNTs/epoxy composites is 0.035 vol % when the aspect ratio of CNTs is 500. The critical exponent of CNTs/epoxy composites rises rapidly with the increase of aspect ratio of CNTs with the CNTs loading larger than the percolation threshold. Although the simulated results are not consistent with the experimental results absolutely, a same tendency is represented in both over plots.

References

1. Du, F.; Fischer, J. E.; Winey, K. I. J Polym Sci Part B: Polym Phys 2004, 41, 3333.
2. Dai, J. F.; Wang, Q.; Li, W. X.; Wei, Z. Q.; Xu, G.J. Mater Lett 2007, 61, 27.
3. Valentini, L.; Puglia, D.; Frulloni, E.; Armentano, I.; Kenny, J. M.; Santucci, S. Compos Sci Technol 2004, 64, 23.
4. Ounaies, Z.; Park, C.; Wise, K. E.; Siochi, E. J.; Harrison, J. S. Compos Sci Technol 2003, 63, 1637.

5. Kovacs, J. Z.; Velagala, B. S.; Schulte, K.; Bauhofer, W. Compos Sci Technol 2007, 67, 922.
6. Moisala, A.; Li, Q.; Kinloch, I. A.; Windle, A. H. Compos Sci Technol 2006, 66, 1285.
7. Zhu, B. K.; Xie, S. H.; Xu, Z. K.; Xu, Y. Y. Compos Sci Technol 2006, 66, 548.
8. Zhang, Q. H.; Rastogi, S.; Chen, D. J.; Lippits, D.; Lemstra, P. J. Carbon 2006, 44, 778.
9. Fugetsu, B.; Sano, E.; Sunada, M.; Sambongi, Y.; Shibuya, T.; Wang, X.; Hiraki, T. Carbon 2008, 46, 1256.
10. Singh, I.; Bhatnagar, P. K.; Mathur, P. C.; Kaur, I.; Bharadwaj, L. M.; Pandey, R. Carbon 2008, 46, 1141.
11. Wang, Q.; Dai, J. F.; Li, W. X.; Wei, Z. Q.; Jiang, J. L. Compos Sci Technol 2008, 68, 1644.
12. Huang, Y.; Li, N.; Ma, Y. F.; Du, F.; Li, F. F.; He, X. B.; Lin, X.; Gao, H. J.; Chen, Y. S. Carbon 2007, 45, 1614.
13. Lee, S. H.; Cho, E.; Jeon, S. H.; Youn, J. R. Carbon 2007, 45, 2810.
14. Breuer, O.; Sundararaj, U. Polym Compos 2004, 25, 630.
15. Xie, X. L.; Mai, Y. W.; Zhou, X. P. Mater Sci Eng R 2005, 49, 89.
16. Gao, L.; Li, Z. Y. J Phys Condens Matter 2003, 15, 4397.
17. Ogasawara, T.; Ishida, Y.; Ishikawa, T.; Yokota, R. Compos A 2004, 35, 67.
18. Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. Polymer 2003, 44, 5893.
19. Li, J.; Vaisman, L.; Marom, G.; Kim, J. K. Carbon 2007, 45, 744.
20. Weber, M.; Kamal, M. R. Polym Compos 1997, 18, 711.
21. Fan, Z. H.; Advani, S. G. Polymer 2005, 46, 5232.