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Development of a conventional model to predict the electrical conductivity of polymer/carbon nanotubes nanocomposites by interphase, waviness and contact effects

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ABSTRACT

A model for electrical resistivity of composites based on contacts between fibers is developed in this paper for electrical conductivity of polymer/CNT nanocomposites. The developed model considers the influences of interphase regions and CNT waviness on percolation threshold, effective CNT concentration and network dimension. Many experimental results are applied to assess the developed model. Also, the developed model is used to study the influences of all parameters on the conductivity of nanocomposite. It is shown that thin interphase and small diameter of contact area result in poor conductivity. In addition, a desirable conductivity is obtained by the high fraction of percolated CNT in the conductive network as well as the large number of contacts between nanotubes in the nanocomposite.

1. Introduction

Polymer nanocomposites containing carbon nanotubes (PCNT) are appealing much attention, due to their extraordinary mechanical, thermal and electrical properties which develop potential applications in electronics, shielding, conductive products, etc. [1–6]. The high aspect ratio of CNT causes the enhancement of properties by a little amount of CNT compared to conventional particles such as carbon black and clays. There are various nanotube types including single wall nanotubes (SWCNT), double wall nanotubes (DWCNT) and multi wall nanotubes (MWCNT) which can produce a high level of specific surface area (area per weight). Also, their surfaces can be functionalized with some functional groups to improve their interaction with polymer matrices [7,8].

The electrical conductivity of PCNT is based on the percolated paths of conductive CNT. A three-dimensional (3D) network of CNT usually forms in polymer matrix above a determinate concentration as percolation threshold which strongly depends on the aspect ratio of CNT and their dispersal level in polymer matrix [9–11]. Interestingly, the large aspect ratio of CNT in a range of 500–1000 can create a conductive network by very low loading of CNT. The percolation level can be experimentally assessed by measurement of electrical conductivity. However, the main mechanism for conductivity of PCNT is electron tunneling, where electrons are transferred between nanotubes by hopping [12]. In this method, the nanotubes are not bodily coupled and neighboring CNT transfers the charges by electron jumping.

The interphase regions are commonly formed in polymer nanocomposites, due to the outstanding surface area of nanoparticles and strong interfacial adhesion between matrix and filler phases [13–16]. The mechanical properties of polymer nanocomposites such as tensile modulus and strength effectively depend on the interphase properties [17–19]. So, the interphase regions play a remarkable reinforcing effect in nanocomposites. Besides, the positive role of interphase regions in the percolating structure of nanoparticles was reported, because the interphase regions can create a continuous network before the physical connection of nanoparticles [20,21]. Therefore, a lower percolation threshold is observed in nanocomposites containing interphase which displays the significance of interphase in the conductivity. However, the contributions of interphase regions to the electrical conductivity of nanocomposites have not been considered.

The electrical conductivity of polymer nanocomposites particularly PCNT has been analyzed by several models. The widely used methodology is a conventional power-law model based on percolation theory of composites which expresses the conductivity by

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filler concentration, percolation threshold and an exponent [22]. This model demonstrates a good fitting with the electrical conductivity of PCNT [23–25]; however, it cannot reflect the excellent physical aspects of CNT such as nano-size and surface area. Some researchers also developed the micromechanics models for conductivity of PCNT assuming different parameters such as arrangement and waviness of CNT, interphase and tunneling distance [26–28], but they generally expressed some intricate equations which are not appropriate in practice.

Feng and Jiang [27] assumed the electron tunneling in PCNT by an interphase layer around CNT. Their results suggested that both electron tunneling and conductive networks contribute to the conductivity of nanocomposites, but the conductive networks are dominant at high CNT fractions. It was also indicated that the size of CNT have significant effect on the conductivity of nanocomposites. Moreover, Takeda et al. [28] considered the tunneling distance in PCNT by extending the CNT and suggested a model for conductivity of nanocomposites. Also, they formulated the tunneling distance as a function of filler volume fraction. However, some complex and unclear equations in these studies limit their application for PCNT. In fact, there is not a simple and accurate model for electrical conductivity of PCNT.

Kim et al. [29] also suggested an analytical homogenization approach to predict percolation threshold effect, tunneling role and effective electrical conductivity of polymer nanocomposites. They showed a good agreement between experimental results and calculations. Also, the thermal conductivity of polymer nanocomposites containing CNT, graphene or both of them (synergetic effect) were theoretically studied assuming the geometries of nanoparticles [29–33]. However, the available models cannot properly present the influences of interphase and waviness on the percolation threshold and conductivity.

Weber and Kamal [34] suggested a model for resistivity of polymer fiber composites which assumes the contacts between fibers and the dimensions of fiber and network. This study aims to develop this model for PCNT by the influences of interphase and CNT waviness on percolation threshold, effective CNT concentration and network level. Thus, this model is adjusted for polymer nanocomposites and proper equations for the mentioned terms are suggested. Actually, the developed methodology simply presents the percolation threshold, the volume fraction of networked CNT and conductivity of nanocomposites by filler size, waviness, interphase thickness, network fraction and contact number, while the previous models did not assume these terms for conductivity. The developed model is examined by experimental results. Moreover, the relations between the conductivity of PCNT and different parameters are explained to show the predictability of the developed model. We hope that the presented model can be applied in future studies on PCNT, because the available models cannot properly calculate the conductivity of PCNT.

2. Developed model

Most models in literature do not assume the particle-particle contacts in composites. In addition, the contacts between fibers are probably body-to-body rather than end-to-end and end-to-body [34]. As a result, the contact area is much lesser than that of end-to-end arrangement which affects the conductivity.

Weber and Kamal [34] suggested the longitudinal and transverse resistivity of polymer fiber composites assuming fiber-fiber contacts as:

$$\rho_{long} = \frac{\pi R^2 \rho_N X}{\phi_N d_c l \cos^2\theta} \tag{1}$$

where "R" is fiber radius, "ρ_N" is resistivity of fiber, "ϕ_N" is the volume fraction of networked fibers, "d_c" is diameter of contact circle, "l" is fiber length and "θ" is angle of fiber orientation. "X" is also related to the average number of contacts between CNT in the nanocomposite (m) as:

$$X = \frac{1}{0.59 + 0.15m} \tag{2}$$

where the maximum "m" was indicated as 15.

This model can be developed for PCNT containing random distribution of CNT assuming the percolation threshold, interphase and waviness of CNT. In the case of random distribution of CNT in the nanocomposite, it can be approximated that $\cos(\theta) = 1/3$ [35]. Also, the resistance of CNT and nanocomposites are inversely related to their conductivities restructuring the latter equation to:

$$\sigma = \frac{\phi_N d_c l \sigma_N}{3\pi R^2 X} \tag{3}$$

where "σ_N" is conductivity of CNT. The formation of interphase and CNT waviness commonly affects the general properties of PCNT. The influences of these terms in percolation threshold, effective fraction of CNT and the percentages of networked CNT are given in the following.

The percolation threshold in PCNT containing random orientation of nanoparticles can be proposed [36] as:

$$\phi_p = \frac{V}{V_{ex}} \tag{4}$$

where "V" and "V_{ex}" are the volume and excluded volume of CNT, respectively. The excluded volume comprises the capacity neighboring a nanotube into which the center of a similar particle cannot enter.

"V" and "V_{ex}" for soft-core rigid sphero-cylinders randomly oriented in three dimensions were suggested [36] as:

$$V = \pi R^2 l + (4/3)\pi R^3 \tag{5}$$

$$V_{ex} = \frac{32}{3}\pi R^3 \left[1 + \frac{3}{4}\left(\frac{l}{R}\right) + \frac{3}{32}\left(\frac{l}{R}\right)^2\right] \tag{6}$$

The interphase regions around CNT frequently shift the development of a conductive network to lower filler fractions which should be considered in percolation effect. The interphase layer decreases the excluded volume [37] as:

$$V_{ex} = \frac{32}{3}\pi (R+t)^3 \left[1 + \frac{3}{4}\left(\frac{l}{R+t}\right) + \frac{3}{32}\left(\frac{l}{R+t}\right)^2\right] \tag{7}$$

where "t" is interphase thickness. The interphase forms around the nanoparticles in polymer nanocomposite. The interphase thickness is assumed as the thickness of interphase regions surrounding CNT from the CNT surface to polymer matrix. So, the interphase is an intermediate phase between CNT and polymer matrix, which shows different properties than matrix and nanoparticles [38].

Furthermore, the high aspect ratio of CNT (length to diameter) causes waviness which declines the effectiveness of nanotubes in nanocomposites. An equivalent nanotube with effective length of "l_{eq}" can be assumed for a curved nanotube according to Fig. 1a which defines a waviness parameter as:

$$u = \frac{l}{l_{eq}} \tag{8}$$

where u = 1 shows an straight nanotube (no waviness), while the higher levels of "u" exhibit more waviness and less effective length.