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Roles of filler dimensions, interphase thickness, waviness, network fraction, and tunneling distance in tunneling conductivity of polymer CNT nanocomposites

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HIGHLIGHTS

- A simple model for tunneling conductivity of polymer-CNT nanocomposites is suggested.
- Interphase thickness, fraction of networked CNTs, and tunneling distance are assumed.
- The model expresses the percolation threshold and the fraction of networked CNTs.
- The model is tested using experimental results from the literature and parametric analyses.
- The predictions show good agreement with the experimental results in all samples.

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ABSTRACT

We present a simple model to express the tunneling conductivity of polymer CNT nanocomposites as a function of the filler dimensions, filler conductivity, interphase thickness, waviness, fraction of networked CNTs, and tunneling distance. This model expresses the percolation threshold and the fraction of networked CNTs in terms of filler dimensions, waviness, and interphase thickness. The model was tested using experimental results from the literature. The predictions show good agreement with the experimental results in all samples, demonstrating the model's robustness for estimating tunneling conductivity. Moreover, the tunneling distance decreases as the filler concentration increases in all samples. The model parameters have a reasonable effect on the tunneling conductivity. The waviness and tunneling distance inversely affect the tunneling conductivity. Further, the waviness weakens the effective length of the nanotubes, and large tunneling distances cannot effectively transfer electrons between two adjacent nanotubes. The interphase thickness directly controls the tunneling conductivity, because a thick interphase reduces the percolation threshold. Poor percolation also creates large and dense conductive networks in nanocomposites, which is desirable for conductivity.

1. Introduction

The unique physical and mechanical properties of carbon nanotubes (CNTs) have garnered substantial interest in their use as nanoscale fillers for polymer matrices to produce multi-functional and high-performance nanocomposites [1–5]. These unique properties include considerable modulus and strength, high thermal and electrical conductivities, a large aspect ratio (length to diameter), and a low density. The percolation threshold, defined as the critical concentration of nanoparticles required to form a conductive network in a polymer CNT nanocomposite, strongly depends on the aspect ratio of CNTs, the extent of filler dispersion, the mixing method, and the phase structure [6,7]. The percolation threshold can be established from electrical conductivity measurements at various filler concentrations. Electron tunneling has been suggested as the mechanism for electrical conductivity of polymer CNT nanocomposites, in which electrons are transported via tunneling effects [8,9]. Although the nanotubes are not linked, neighboring CNTs can demonstrate conductivity via electron jumping. Thus, the tunneling effect mostly depends on the distance

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between adjacent nanotubes or the tunneling distance. The tunneling resistance grows with increasing temperature, so, the tunneling effect is temperature-dependent [10].

Electrical conductivity in polymer composites has been estimated using several techniques, including numerical simulations, image processing, and analytical models [11,12]. However, very few models can predict the electrical conductivity over a full range of filler concentrations on both sides of the percolation threshold. Additionally, some models contain complex parameters, such as orientation angle, which cannot be easily measured. Most available models are applicable for micro-particles, but do not reflect the low filler concentration percolation threshold of nanoparticles in polymer nanocomposites. The most widely-used model for conductivity in polymer nanocomposites is a power-law model based on conventional percolation theory, which agrees with the measurements of electrical conductivity [13,14]. Additionally, some micromechanics models have been developed that account for the tunneling effect, interfacial energy between polymer and nanoparticles, agglomeration, and waviness of CNTs [15–17], but some unclear and complex parameters make these models not applicable. Recently, Hu et al. [14] developed a power-law equation and suggested a model for the conductivity of CNT nanocomposites assuming the aspect ratio, aggregation, and curvature of CNTs. They reported that a high concentration of aggregates, curved CNT, and a low CNT aspect ratio lead to a higher percolation threshold and lower electrical conductivity in polymer nanocomposites. Moreover, Bao et al. [18] developed an improved three-dimensional (3D) percolation model to investigate the effect of CNT alignment on the conductivity assuming both intrinsic and contact resistances in the connective paths. Also, Fang et al. [13] developed a model to express the CNT networks and the conductivity contributed by the continued CNT network across the boundary of adjacent representative volume elements. However, the available models for the conductivity of nanocomposites do not take into account the interphase regions around nanoparticles. Also, two latter studies did not present simple equations for prediction of conductivity. Interphase zones commonly form in polymer nanocomposites due to the significant interfacial area and interaction between the polymer matrix and filler [19–23]. In fact, the interphase is different from both the polymer matrix and the nanoparticles, possessing intermediate properties, i.e., its properties lie somewhere between those of the polymer matrix and nanoparticles. The thickness of the interphase is assumed to be the distance between the surface of nanoparticles and the bulk polymer matrix.

The role of interphase properties in the mechanical performance of polymer nanocomposites has been widely discussed [24–26]. Moreover, interphase regions can create continuous networks that lower the percolation threshold and create bigger conductive networks in nanocomposites [27,28]. Thus, interphase regions effectively improve the conductivity of nanocomposites, although the role of the interphase in the conductivity has not been reported in detail. In summary, there is not a simple model for the conductivity of polymer nanocomposites that uses the properties of conductive nanoparticles and the interphase regions. In fact, the models for the conductivity of CNT nanocomposites available in the literature cannot simply and comprehensively study the roles of important parameters such as the interphase thickness, tunneling distance, percentage of networked CNTs, and waviness at the same time.

In this paper, a simple and applicable model is developed to reflect the tunneling conductivity of polymer nanocomposites as a function of filler dimensions, filler conductivity, interphase thickness, waviness, networked fraction, and tunneling distance. This model is based on the correlation between tunneling distance and filler concentration, and expresses the percolation threshold and fraction of networked CNTs in terms of filler dimensions, waviness and interphase thickness. Experimental results from the literature are applied to evaluate the developed model and calculate the interphase thickness and tunneling distance. The accuracy of the developed model is discussed, considering the influences of the model parameters on the predicted conductivity. Compared to previous models in this area, the present model easily predicts the roles of interphase thickness, tunneling effect, percentage of networked CNTs, and waviness in the conductivity of nanocomposites by simple equations. Additionally, the present work provides simple equations for percolation threshold, effective filler concentration and the fraction of networked CNT by filler dimensions, waviness, and interphase thickness. In particular, strain sensors made from polymer CNT nanocomposites have attracted much interest in the recent years [29–31]. They perform based on the variation of network properties and electrical conductivity in nanocomposites, so the present model can be developed to analyze the sensing behavior.

2. Development of model and equations

Deng and Zheng [32] suggest the following simple model for the electrical conductivity of polymer CNT nanocomposites above the percolation threshold:

$$\sigma = \sigma_0 + \frac{f\phi_f\sigma_N}{3} \tag{1}$$

where σ_0 and σ_N are the conductivities of the polymer matrix and the nanoparticles, ϕ_f is the volume fraction of the nanofiller, and f is the fraction of nanoparticles belonging to networks above the percolation threshold. Small values of σ_0 may be neglected in this equation. However, this model does not assume the tunneling conductivity of nanocomposites.

The tunneling distance between nanotubes was reported as a function of CNT concentration in some studies [7,8], given as:

$$d \propto \frac{1}{\phi_f^{1/3}} \tag{2}$$

Which expresses that the tunneling distance is inversely related to the filler concentration.

Takeda et al. [17] suggested the following equation for tunneling distance by assuming the tunneling effect:

$$d = \frac{0.12}{\phi_f^{0.43}} \tag{3}$$

However, its dependence on filler concentration is different from other studies. The latter equation can be used to derive the following:

$$d = \frac{0.12}{\phi_f^{1/3}} \tag{4}$$

This result can be used to deduce the following equation for ϕ_f:

$$\phi_f \cong \frac{0.002}{d^3} \tag{5}$$

This expression for "ϕ_f" can be plugged into Eq. (1), thus defining the role of the tunneling effect in the conductivity of nanocomposites as:

$$\sigma = \frac{0.002f\sigma_N}{3d^3} \tag{6}$$