Composites Science and Technology 155 (2018) 252–260

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

A simple model for electrical conductivity of polymer carbon nanotubes nanocomposites assuming the filler properties, interphase dimension, network level, interfacial tension and tunneling distance

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ARTICLE INFO

Article history:
Received 8 July 2017
Received in revised form
6 October 2017
Accepted 9 October 2017
Available online 10 October 2017

Keywords:
Polymers
Nano composites
Carbon nanotubes
Electrical properties
Interphase
Interface

ABSTRACT

This manuscript proposes a simple model for electrical conductivity of polymer carbon nanotubes (CNT) nanocomposites including the crucial parameters such as the volume fraction, effective volume fraction, percolation threshold, dimensions, waviness and conduction of CNT, interphase thickness, network fraction, interfacial tension between polymer and nanoparticles and tunneling distance between adjacent CNT. The proposed model is verified by the experimental data from various samples. Furthermore, the dependence of predicted conductivity on the model parameters is determined and discussed to approve the proposed model. The calculations of the proposed model successfully agree with the experimental conductivity data in the reported samples. In addition, the model parameters demonstrate acceptable effects on the conductivity. Some parameters such as filler volume fraction, tunneling distance, network fraction and interfacial tension meaningfully affect the conductivity of nanocomposites. On the contrary, the dimensions, conduction and percolation threshold of CNT insignificantly change the conductivity.

1. Introduction

Carbon nanotubes (CNT) with exceptional stiffness and strength, high thermal and electrical conductivities in addition to large aspect ratio (length/diameter) and low density have generated substantial interest in production of multifunctional and high-performance nanocomposites [1–6]. Such conductive nanocomposites are ideal materials for many applications and extensive researches have focused on their optimization in recent years. The dispersing of CNT into polymer matrices can form electrically conductive nanocomposites with many applications in electronics, sensors, aerospace and shielding [7–9].

The conductivity of nanocomposites mostly improves at a critical filler concentration as percolation threshold creating the conductive networks for charge transferring [10,11]. The percolation threshold depends on several factors such as aspect ratio, orientation, distribution and agglomeration of fillers [12,13]. The effective parameters on the percolation threshold of nanoparticles undoubtedly affect the electrical conductivity of polymer nanocomposites. The morphological control of conductive networks during the preparation of nanocomposites has critical impact on the electrical properties [14]. Several techniques have been proposed to control the network and the electrical properties of nanocomposites such as application of shear, polymer blends, thermal annealing, mixed filler, latex particle. The roles of these parameters in the conductivity can be studied by modeling techniques. The electrical conductivity of conventional polymer composites was studied by several methods like image processing, numerical simulation and micromechanical modeling [15]. However, few models can estimate the electrical conductivity in a full range of filler concentrations. In addition, some models include some complex parameters such as orientation angle, which is not easy to characterize. Generally, the available models are suitable for conventional composites and cannot predict the conductivity of nanocomposites.

Some models were developed or suggested for conductivity of polymer nanocomposites. The simplest ones include the micromechanics models that easily calculate the conductivity by the properties of nanofiller and filler network. Some authors have developed the micromechanics models for nanocomposites by the

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https://doi.org/10.1016/j.compscitech.2017.10.007
0266-3538/

roles of filler arrangement, tunneling distance, filler agglomeration and CNT waviness [16–18], but some complex and unclear equations and parameters limit their applications in practice. Moreover, the main weakness of available models is disregarding of interphase regions in polymer nanocomposites. The interphase regions between polymer matrix and nanoparticles play the reinforcing and percolating roles in polymer nanocomposites [19–21]. The reinforcing roles of interphase in the mechanical properties of polymer nanocomposites were argued in the previous articles [22,23]. Moreover, the percolating role of interphase regions, which can produce the conductive networks at low filler fractions was reported in some studies [24–26]. However, a model is required that can assume the roles of effective parameters such as interphase, waviness, interfacial tension and tunneling distance in the electrical conductivity of nanocomposites. In this paper, a simple model is suggested which proposes the electrical conductivity of polymer CNT nanocomposites by the effective parameters such as filler fraction, filler size, filler waviness, filler conduction, interphase thickness, network fraction, interfacial tension, tunneling distance and percolation threshold. The experimental results of various samples are applied to examine the suggested model. Furthermore, the influences of all parameters on the predicted conductivity are discussed to confirm the suggested model.

2. Suggestion of model

Deng and Zheng [17] proposed a simple model for electrical conductivity of polymer nanocomposites reinforced with random distribution of CNT as:

$$\sigma = \sigma_0 + \frac{f\varphi_f\sigma_f}{3} \tag{1}$$

where "σ_0" and "σ_f" are the conductions of polymer and nanoparticles, respectively, "f" is the percentages of nanotubes belonging to network phase after percolation and "φ_f" is volume fraction of nanofiller. The poor level of "σ_0" as about 10^{-15} S/m can be disregarded from this model. In addition, this model was developed by Takeda et al. [16] to consider the tunneling distance between nanotubes. Although the original model considers the roles of filler fraction, filler conductivity and percolated network in the conductivity of nanocomposites, it generally disregards some effective parameters such as interphase regions, interfacial tension between polymer matrix and nanoparticles as well as tunneling distance. Here, we try to develop this model and suggest a new simple model for conductivity of nanocomposites assuming the mentioned parameters. The validity of the suggested model is evaluated by the experimental results and the analysis of its parameters.

The interfacial tension between polymer matrix and nanoparticles governs the distribution and agglomeration of nanofiller in polymer nanocomposites [27]. Since a low wettability and poor distribution of nanoparticles are required for contacts among nanoparticles and formation of network structure, the role of interfacial tension in the conductivity of nanocomposites is unavoidable [15]. The interfacial tension between polymer and filler is approximated by:

$$\gamma_{pf} = \gamma_f + \gamma_p - 2\left(\gamma_f\gamma_p\right)^{1/2} \tag{2}$$

where "γ_p" and "γ_f" are the surface energies of polymer and filler, respectively.

Furthermore, Ryvkina et al. [28] indicated that the electrical conductivity of polymer CNT nanocomposites is dominated by electron tunneling, where electrons are moved by tunneling effect between adjacent nanotubes. So, the tunneling distance between nanotubes (d) is an important parameter which controls the nanocomposites conductivity. Some authors have studied on the tunneling distance in polymer CNT nanocomposites [28,29]. These studies reported that the tunneling distance is correlated to $\varphi_f^{-1/3}$. Since the nanocomposites conductivity shows a linear correlation with "φ_f", it can be suggested that the conductivity can be inversely correlated to d^3.

Based on these descriptions, the conductivity of nanocomposites directly and inversely relates to the interfacial tension and tunneling distance. Accordingly, a new model is suggested for electrical conductivity of polymer nanocomposites as:

$$\sigma = \frac{0.1\gamma_{pf} f\varphi_f\sigma_f}{\left(\frac{d}{z}\right)^3} \tag{3}$$

where "z" is tunneling parameter (z = 1 nm). This equation considers the roles of filler concentration, filler conduction, network fraction, interfacial tension and tunneling distance in the conductivity of polymer nanocomposites. However, "f" parameter should be defined based on the concentration and percolation of filler. Also, the roles of waviness and interphase regions in the conductivity of nanocomposites should be considered.

Long nanotubes are commonly waved in polymer nanocomposites and their effective length decreases [18]. An equivalent/effective length (l_{eq}) is considered for curved nanotubes as the smallest distance between two ends of nanotube. Similarly, a relation between the length of straight CNT (l) and "l_{eq}" can be defined as:

$$u = \frac{l}{l_{eq}} \tag{4}$$

where a higher level of "u" shows more waviness (less straightness).

Besides, the electrical conduction of CNT decreases by waviness and an inverse link was suggested between "σ_f" and "u" [18] as:

$$\sigma_{fw} = \frac{\sigma_f}{u} \tag{5}$$

The interphase areas around nanoparticles grow the effectiveness of nanoparticles on the general performances of nanocomposites. The effective volume fraction of CNT [30] assuming the waviness and interphase thickness (t) can be defined by:

$$\varphi_{eff} = \frac{(R+t)^2(l/u+2t)}{R^2 l/u}\varphi_f \tag{6}$$

where "R" is CNT radius.

Moreover, percolation threshold in nanocomposites containing random distribution of cylindrical CNT was suggested by volume (V) and excluded volume (V_{ex}) of nanoparticles [31] as:

$$\varphi_p = \frac{V}{V_{ex}} \tag{7}$$

$$V = \pi R^2 l \tag{8}$$

$$V_{ex} = \frac{32}{3}\pi R^3\left[1 + \frac{3}{4}\left(\frac{l}{R}\right) + \frac{3}{32}\left(\frac{l}{R}\right)^2\right] \tag{9}$$

where excluded volume consists of the space around a particle into