Composites Part B 156 (2019) 64–71

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Simplification and development of McLachlan model for electrical conductivity of polymer carbon nanotubes nanocomposites assuming the networking of interphase regions

Yasser Zare, Kyong Yop Rhee*

Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin, 446-701, Republic of Korea

ARTICLE INFO

Keywords:
Polymer carbon nanotubes nanocomposites
Conductivity
Interphase
Tunneling distance
Modeling

ABSTRACT

This paper simplifies and develops the conventional model suggested by McLachlan for electrical conductivity of polymer CNT nanocomposites. The original model expresses the conductivity as a function of filler concentration, filler conductivity, filler percolation threshold and an exponent. However, this model is developed by considering the roles of interfacial tension between polymer matrix and nanoparticles, tunneling distance between adjacent nanotubes, interphase regions around nanoparticles and waviness of CNT. The experimental results of conductivity for some samples and the analysis of the effects of various parameters on the conductivity evaluate the developed model. The predictions demonstrate fine agreement with the experimental results and the parameters show acceptable roles in the conductivity of nanocomposites. A large tunneling distance significantly decreases the conductivity to zero. Likewise, the higher and slighter surface energies of the polymer matrix and filler, respectively cause an improved conductivity. A thin interphase produces very low conductivity, while a thick interphase and a low waviness improve the conductivity.

1. Introduction

Conductive nanocomposites suggest new applications in electronics, sensors, fuel cells, and energy storage devices [1–3]. To produce the conductive nanocomposites, carbon nanotubes (CNT) are preferred among the conductive fillers, because of higher mechanical, physical and thermal properties [4–9]. CNT can induce high conductivity in the polymer nanocomposites even at very small concentration due to their superior properties. CNT normally form a continuous network in nanocomposites after a critical concentration as percolation threshold [10]. The percolation level depends on the aspect ratio of CNT (ratio of length to diameter) and the dispersion level of nanoparticles [11,12]. The CNT dispersion in the matrix is the crucial factor that affects the percolation threshold and thus the dispersion method influences the morphology of the produced nanocomposites. The percolation threshold can be determined by the electrical conductivity of nanocomposites, because the conductivity of nanocomposite significantly improves when percolation occurs.

Many parameters can affect the electrical conductivity of polymer nanocomposites. The concentration, size, conductivity, orientation, waviness and surface energy of nanoparticles were reported to be effective in the electrical conductivity of polymer nanocomposites [13–15]. Also, it was explained that the main mechanism for electrical conductivity of polymer CNT nanocomposites is electron tunneling, where charges are conveyed between nanotubes by tunneling effect, even when nanotubes are not physically joined [16]. Hence, the conductivity of CNT nanocomposites also depends on the distance between adjacent nanotubes to promote the electrical percolation.

The effects of different parameters on the conductivity can be studied by modeling methodologies as it offers low-cost and effective techniques to study the behavior of nanocomposites. Many methods such as statistical simulation, image handling, analytical and micromechanical modeling were applied for modeling of electrical conductivity in polymer composites [17]. However, the simplest and clearest method includes the estimation of conductivity by micromechanics models. The simplest model is a power-law form based on conventional percolation theory which correlates the conductivity to filler concentration, percolation threshold and an exponent [11]. This model also well agrees with the electrical conductivity of polymer nanocomposites [18–20], but it does not consider the excellent physical properties of nanoparticles such as nano-size and big surface area. Some researchers also developed the micromechanics models for conductivity of PCNT assuming other effective parameters such as the waviness of CNT, interfacial tension and tunneling effect [21,22]. However, these

* Corresponding author.
E-mail address: rheeky@khu.ac.kr (K.Y. Rhee).

https://doi.org/10.1016/j.compositesb.2018.08.056
Received 7 August 2018; Accepted 19 August 2018
Available online 20 August 2018

models commonly include vague and complex parameters, which limit their applications. Actually, there is not a simple model, which accurately shows the effects of main parameters on the conductivity of polymer nanocomposites.

The available models commonly cannot show the influence of interphase regions between polymer matrix and nanoparticles, which can change the percolation level and network extents. The formation of interphase regions has been reported in many polymer nanocomposites, due to the excellent surface area of the nanofiller [23,24]. The interphase regions also have positive effects on the percolating of nanoparticles in polymer nanocomposites. They produce a continuous network throughout the nanocomposites, which causes the percolation threshold before the real connection of nanoparticles. Although the impact of interphase percolation on the mechanical properties of nanocomposites has been studied, the roles of interphase zones in the electrical percolation and conductivity of polymer nanocomposites have not been clearly understood.

In this study, the conventional model suggested by McLachlan [25] based on general effective media theory is simplified and developed for electrical conductivity of polymer CNT nanocomposites. The simplified model shows the conductivity as a function of filler concentration, filler conductivity, filler percolation and an exponent. This model is developed in the current paper by the roles of interfacial tension between polymer matrix and nanoparticles, tunneling distance between adjacent nanotubes, interphase region around nanoparticles and waviness of CNT. In other words, the developed model assuming the roles of effective parameters can calculate the conductivity of nanocomposites. The developed model is evaluated by the experimental results of conductivity in some polymer CNT nanocomposites and by the analysis of the effects of main effective parameters on the nanocomposites conductivity.

2. Development of conventional model

McLachlan et al. [25] improved the statistical model based on a general effective media equation for any system containing a high-conductive-material embedded in a poorly conducting matrix. This model takes into account the conductivities of constituent materials and for composites containing polymer matrix and conductive fillers is expressed as:

$$\frac{\varphi_f(\sigma_f^{1/h}-\sigma^{1/h})}{\sigma_f^{1/h}+A\sigma^{1/h}}+\frac{(1-\varphi_f)(\sigma_0^{1/h}-\sigma^{1/h})}{\sigma_0^{1/h}+A\sigma^{1/h}}=0 \tag{1}$$

$$A=\frac{1-\varphi_p}{\varphi_p} \tag{2}$$

where "σ_0", "σ_f" and "σ" denote the electrical conductivities of matrix, filler and composite, respectively, "φ_f" is filler volume fraction and "φ_p" is volume fraction of filler at percolation threshold. Also, "h" is a constant parameter. McLachlan [25] showed that "h" exponent depends on the demagnetization or depolarization coefficients of matrix and filler.

In this study, this conventional model is simplified and developed to predict the electrical conductivity of polymer nanocomposites, particularly those reinforced with CNT.

The polymers commonly show very poor conductivity as about 10^{-15} S/m which cannot change the conductivity of polymer nanocomposites. So, "σ_0" can be removed from Eq. (1). However, it should be noted that some polymers such as polyaniline, polypyrrole and polythiophene have good conductivity and thus "σ_0" cannot be removed for them. Additionally, the volume fraction of CNT in nanocomposites is very low. As a result, the term (1- φ_f) can be regarded as 1, which simplifies Eq. (1) to:

$$\frac{\varphi_f(\sigma_f^{1/h}-\sigma^{1/h})}{\sigma_f^{1/h}+A\sigma^{1/h}}+\frac{-1}{A}=0 \tag{3}$$

When the latter equation is restructured and simplified, the following equation is obtained:

$$\sigma^{1/h}=\frac{\varphi_f\sigma_f^{1/h}-\frac{\sigma_f^{1/h}}{A}}{1+\varphi_f}\cong\varphi_f\sigma_f^{1/h}-\frac{\sigma_f^{1/h}}{A} \tag{4}$$

which expresses the conductivity of polymer nanocomposites by:

$$\sigma=\left(\varphi_f\sigma_f^{1/h}-\frac{\sigma_f^{1/h}}{A}\right)^h \tag{5}$$

By substituting of "A" from Eq. (2) into above equation, the electrical conductivity of nanocomposites as a function of percolation threshold is given by:

$$\sigma=\left(\varphi_f\sigma_f^{1/h}-\frac{\varphi_p\sigma_f^{1/h}}{1-\varphi_p}\right)^h \tag{6}$$

However, "h" parameter should be defined by the effective parameters on the electrical conductivity of polymer nanocomposites.

The surface energies of polymer and nanoparticles affect the wettability of nanofiller by polymer chains which can control the filler distribution and agglomeration [17]. The morphology of nanoparticles in nanocomposites changes the networking level of nanofiller, which influences the conductivity. Taherian [17] expressed a simple equation for wettability as:

$$\cos\theta=\frac{\gamma_f-\gamma_{fp}}{\gamma_p} \tag{7}$$

where "γ_p", "γ_f" and "γ_{fp}" are the surface energies of polymer, filler and filler/polymer interface, respectively and "θ" is the wetting angle. As known, "γ_{fp}" can be estimated by the surface energies of polymer and filler [17] as:

$$\gamma_{fp}=\gamma_f+\gamma_p-2(\gamma_f\gamma_p)^{1/2} \tag{8}$$

Moreover, some authors have indicated that the main mechanism of conductivity in polymer CNT nanocomposites is electron tunneling, in which electrons are transferred between neighboring nanotubes by tunneling mechanism [26,27]. The distance between neighboring CNT (d) is more important which determines the level of tunneling effect and the conductivity of nanocomposites. Therefore, another important parameter, which manages the conductivity of polymer CNT nanocomposites is "d" parameter. Also, other effective parameters on the conductivity such as the concentration, percolation threshold and electrical conduction of CNT were considered by Eq. (6).

The "h" parameter can be defined by wettability and tunneling distance between nanotubes as:

$$h=\left(\frac{d}{z}\right)\cos\theta=\left(\frac{d}{z}\right)\left(\frac{\gamma_f-\gamma_{fp}}{\gamma_p}\right) \tag{9}$$

where "z" is a tunneling parameter (z = 1 nm) and "d" is expressed by nm unit.

By substituting of the latter equation into Eq. (6), the electrical conductivity of nanocomposites can be calculated by a developed model.

Additionally, the roles of interphase regions and waviness of CNT should be considered in the conductivity. They affect the conductivity of nanocomposites by manipulating the percolation threshold and the effective volume fraction of nanoparticles.

The percolation threshold of randomly dispersed nanoparticles in polymer CNT nanocomposites was suggested [28] as:

$$\varphi_p=\frac{V}{V_{ex}} \tag{10}$$

where "V" and "V_{ex}" are volume and excluded volume of filler,