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A probabilistic micromechanical modeling for electrical properties of nanocomposites with multi-walled carbon nanotube morphology

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ABSTRACT

The nanoscopic characteristics of the multi-walled carbon nanotubes (MWCNTs) used in composites are crucial for attempting to understand and design nanocomposites of a novel class. We investigate the correlations between the nanofiller properties and effective electrical properties of MWCNT-embedded polycarbonate composites by theoretical and experimental approaches. A probabilistic computational model is proposed to predict the influence of MWCNT morphology on the electrical behaviors of MWCNTs-embedded polymer composites. A parameter optimization method in accordance with a genetic algorithm is then applied to the model, resulting that the ideal sets of model constant for the simulation are computationally estimated. For the experimental validation purpose, a comparison between the present theoretical and experimental results is made to assess the capability of the proposed methods. In overall, good agreement between the predictions and experimental results can be observed and the electrical performance of the composites can be improved as the MWCNT length increases.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) have been utilized in a variety of composite applications as well as for reinforcements and nanofillers owing to their excellent mechanical, thermal, and electrical properties [1–3]. Specifically, the improved electrical characteristics of composites are expected to have a significant impact on numerous industrial applications [4], and therefore, the development of electric-related functionality has been actively researched in recent years [5,6]. However, the results of efforts to enhance the characteristics of composite materials can differ greatly depending on filler-matrix combinations and the fabrication methods used. Various studies which have attempted to optimize related variables have done thus far [5–9].

Polycarbonate (PC) has high toughness, exceptional impact resistance, and good dimensional stability as well as excellent optical clarity [7,8]. These outstanding properties of this PC resin make it a successful engineering thermoplastic which has been used in many engineering applications [8,9]. However, the utilization of PC-based polymers remains limited due to its insulating characteristics. Hence, electrical charge mitigation is a key factor which has been used to enhance the applicability of these polymers, offering protection from lightning and electromagnetic shielding. Although some studies [8,9] have addressed the electrical conductivity of PC composites filled with carbon nanotubes (CNTs), the relationship between the electrical conductivity and internal structure of the composites as analyzed based on non-destructive methods has not been clearly identified.

Hence, there has been a great interest in a theoretical method which can understand and analyzes electrical properties of nanoscale system. In general, atomistic modeling has been regarded as the most accurate approach [10,11]; however, the maximum simulation range being hundreds of nanometer made it challenging to generalize as a representative volume element of the nanocomposite [12]. Moreover, the atomistic modeling requires high levels of computational power, which makes it inaccessible without using a massive parallel supercomputer [13]. There was also a theoretical analysis of nanocomposites through classical microscopic method, but it was difficult to comprehend inherent characteristics in nanoscopic scale [14–16]. Hence, probabilistic modeling recently has grasped a keen interest as a new paramount research method to overcome these limitations. From this perspective, material properties that are difficult to obtain and generalize by experiments (e.g., interfacial resistivity, tunneling region, and filler waviness) would be determined probabilistically. A proper

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derivation of probabilistic material modeling not only makes it capable to explain through concepts when some test results cannot be answered, but also helps to predict a scientific phenomenon based on an initial condition of system.

The objective of this study is to develop a rigorous but effective probabilistic model to predict the electrical property of MWCNT-embedded polymer composites. Herein, the relationship between the MWCNT characteristics and the effective electrical properties of MWCNT-embedded PC matrix composites is investigated by theoretical and experimental approaches. A probabilistic micromechanics-based model taking into account interfacial resistivity, tunneling effects, and morphological waviness of MWCNTs is developed for predictions of the electrical behaviors with different material constituents [17]. The optimal combination of model constants for this simulation is estimated by the computational method based genetic algorithm [18]. In addition, two types (30–130 μm for short and 150–250 μm for long) of MWCNTs are considered as a nanofiller material to enhance the electrical properties of composites, and the effects of the internal morphology and the characteristics of the MWCNTs on the nanocomposites are analyzed.

2. Theoretical modeling

Based on the effective medium theory [19,20], the electrical conductivity of three-dimensional (3D) randomly oriented and distributed MWCNT-reinforced composites can be estimated as [19,20]

$$\phi_0[(\mathbf{L}_0-\mathbf{L}_e)^{-1}+\mathbf{S}_0\mathbf{L}_e^{-1}]^{-1}+\phi_1\left[(\mathbf{L}_1-\mathbf{L}_e)^{-1}+\mathbf{S}_1\mathbf{L}_e^{-1}\right]^{-1}=0 \quad (1)$$

with

$$(S_{11})_1=(S_{22})_1=\begin{cases}\frac{\alpha}{2(1-\alpha^2)^{1.5}}[\cos^{-1}\alpha-\alpha(1-\alpha^2)^{0.5}], & \alpha<1\\ \frac{\alpha}{2(\alpha^2-1)^{1.5}}[\alpha(\alpha^2-1)^{0.5}-\cosh^{-1}\alpha], & \alpha>1\end{cases} \quad (2)$$
$$(S_{33})_1=1-2(S_{11})_1$$

where ϕ denotes the volume fraction of the MWCNTs; $\mathbf{L}$ signifies the conductivity tensor; $\mathbf{S}$ is the aspect ratio (α) dependent depolarization tensor, which the subscripts 0, 1 and e represent the material phase of the polymer, MWCNTs, and effective nanocomposite, respectively. The components of $\mathbf{S}_1$, taking 33-direction as the symmetric axis of the MWCNTs, is given in Eq. (2), while $\mathbf{S}_0$ is mathematically converged to 1/3 [19].

By using the Cauchy's probabilistic model, the effective electrical conductivity of nanocomposites considering interfacial resistivity due to a tunneling effect can be expressed as [19,20]

$$\sigma_{ii}^c=\frac{r\alpha\sigma_{ii}}{r\alpha+S_{ii}\sigma_{ii}(1+2\alpha)\rho(\phi_1)} \quad (3)$$

in which

$$\rho(\phi_1)=\frac{\rho_0[1-F(\phi_1;\phi_1^*,\gamma)]}{[1-F(0;\phi_1^*,\gamma)]} \quad (4)$$

with

$$F(\phi_1;\phi_1^*,\gamma)=\frac{1}{\pi}\arctan\left(\frac{\phi_1-\phi_1^*}{\gamma}\right)+0.5 \quad (5)$$

and

$$\phi_1^*=\frac{9(S_{33})_1[1-(S_{33})_1]}{-9[(S_{33})_1]^2+15(S_{33})_1+2} \quad (6)$$

where σ_{ii}^c (i = 1 and 3) is the electrical conductivity of the MWCNTs in the i direction, the superscript c represents the thinly coated MWCNTs as surrounded by interface resistivity [19], and r is the outer radius of MWCNTs. ρ_0 is the interfacial resistivity between polymer and MWCNTs and γ is the scale parameter, which related with the probability density function [19].

In addition, the MWCNT shape within the polymer matrix is modeled as a 3D-variable helical spring (Fig. 1) to consider filler morphologies in the viscous PC matrix. The curviness of CNTs has generally been modeled as a sine function or given a bow-shaped appearance by many researchers [21–23]. These curvy shapes could be a good substitute for describing films and two-dimensional (2D) composites; however, in realistic 3D bulk cells, it is not possible to predict the influence of curves in another dimension. In order to develop a rigorous prediction to analyze the morphological effects of nanotubes, the helical aspect ratio (α) of an equivalent inclusion is approximated here as follows [24]:

$$\alpha=\frac{L}{D}=\frac{\varphi}{2\cos\theta} \quad (7)$$

In this equation, where L denotes the equivalent length, D is the spring diameter, φ signifies the polar angle and θ is the spiral angle. The descriptions of the symbols in Eq. (7) are illustrated in detail in Fig. 1.

From Eq. (7), α is fully agglomerated at φ = 0, while $\varphi\to\infty$ corresponds to a straight CNT. Given that the adopted effective medium theory [19] can consider only two-phase constituents (matrix and filler), the probability concept of the center of gravity (COG) of the polar angle is applied to set the representative value of φ, as follows:

$$\varphi_{cog}=\frac{\int_0^{2\pi}\varphi\cdot[CDF(\varphi_i)-CDF(\varphi_{i-1})]d\varphi}{\int_0^{2\pi}[CDF(\varphi_i)-CDF(\varphi_{i-1})]d\varphi} \quad (8)$$

In Eq. (8), the cumulative distribution function (CDF) can be simplified to a probability density function (PDF), as follows:

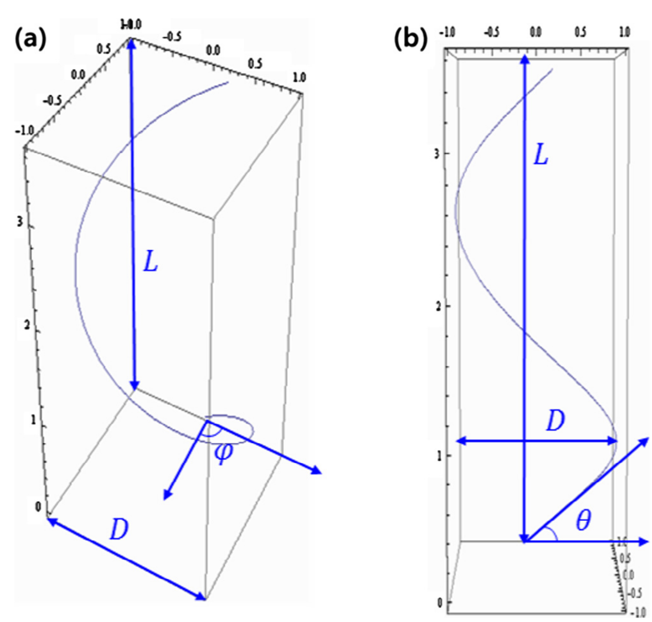

Fig. 1. Illustration in (a) 3D and (b) front view of the present curved MWCNTs: L and D denote the effective length and diameter of the curved MWCNT; φ and θ signify the polar and spiral angle, respectively. The representative value of φ is estimated by the center of gravity (COG) method with a cumulative distribution function, while the representative θ value is determined with the average method, as θ is not affected by φ when the nanotubes are randomly and uniformly distributed in the Cartesian coordinate system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)