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A theoretical study on the piezoresistive response of carbon nanotubes embedded in polymer nanocomposites in an elastic region

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ABSTRACT

Herein, we report a theoretical study of polymeric nanocomposites to provide physical insight into complex material systems in elastic regions. A self-consistent scheme is adopted to predict piezoresistive characteristics, and the effects of the interface and of tunneling on the effective piezoresistive and electrical properties of the nanocomposites are simulated. The overall piezoresistive sensitivity is predicted to be reduced when the lower interfacial resistivity of multi-walled carbon nanotubes (MWCNTs) and the higher effective stiffness of nanocomposites are considered. In addition, thin film nanocomposites with various MWCNT weight percentages are manufactured and their electrical performance capabilities are measured to verify the predictive capability of the present simulation. From experimental tests, the nanocomposites show clear piezoresistive behaviors, exhibiting a percolation threshold at less than 0.5 wt% of the MWCNTs. Three sets of comparisons between the experimental data and the present predictions are conducted within an elastic range, and the resulting good correlations between them demonstrate the predictive capability of the present model.

1. Introduction

Over the past decade, functional composites consisting of nano-scale materials and polymers have attracted extensive attention due to their significant impact on industrial applications [1]. In particular, the carbon nanotube (CNT) filler in the polymer matrix can enhance both the mechanical and electrical characteristics, resulting in composites with better properties compared to those of the pure polymer [2]. The enhanced characteristics can provide functional properties of CNT-reinforced nanocomposites (*e.g.*, piezoresistive response), and they are mostly originated from the CNT filler [3,4]. However, the changes and complexity in the polymer characteristics with the addition of CNTs are poorly understood, which restricts precise predictions of the multi-physical behavior of nanocomposites [5]. Hence, understanding the nature of multi-physical responses from functional nanomaterials is critical to design and utilize the nanomaterial in actual applications [6–8].

To date, various attempts have been made to model the physicochemical effects of nanoscale fillers on the electro-mechanical and/or piezoresistive behaviors of nanocomposite materials. However, most of the studies in the theoretical fields have focused on separate predictions for each phenomenon. Wang et al. [9] proposed a continuum model based on an effective medium theory that describes the electrical conduction process in CNT-reinforced nanocomposites [9]. Furthermore, the model was recently extended by Ref. [10] in order to simulate the electrical properties of graphene nanocomposites [10]. Although the above-mentioned studies demonstrated that the newly developed models successfully captured the quantitative behavior of nanocomposites, such as elastic modulus, electrical conductivity, and percolation threshold, the consideration of the relation between electrical-mechanical behaviors was not included. Generally, two kinds of methods are often utilized to simulate the piezoresistive responses of polymer-

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based composites. The first one can be referred to as numerical network model that is based on a combined three-dimensional statistical method and fiber reorientation technique [11,12]. The numerical network model has an advantage that can consider piezoresistive response under both tensile and compressive loading; however, the numerical network model does not reflect the hardness of materials, which limits the application of the current composite system. The second method is the analytical microscale formulation [13,14], which can be implemented into the finite element (FE) -based system to analyze engineering problems [15,16]. Nevertheless, these approaches also remain limited due to their inherent characteristic that may describe a simple uniaxial tensile loading and difficult to predict the inherent nanoscopic characteristics.

In addition, researchers have developed various piezoresistive materials based on polymeric matrices with the incorporation of conductive fillers, such as carbon fibers [17], carbon black [18], graphite [19], and CNTs [20–24]. Among all these conductive fillers, CNTs have attracted the most attention to be used in piezoresistive composites due to their dramatic change of electrical conductivity under external load [25] and thus, polymer nanocomposites containing CNTs have been widely employed for their great piezoresistive, mechanical, and electrical properties [25,26].

For instance, the incorporation of 8 wt% of multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) in the polyurethane matrix resulted in 5–50% of electrical resistance change under 35–40% of applied tensile strain, respectively [27]. In another study, the piezoresistive characteristics of MWCNTs within thermoplastic polyurethane (TPU) were studied under cyclic compression strains up to 90% [28]. In another research work [29], showed that 0.05 wt% of SWCNTs in polyimide (PI) matrix resulted in 2% electrical resistance change under 16 MPa of applied tensile stress, while the electrical resistance of a 10 wt% MWCNT/PI system altered up to 0.35% under similar loading conditions [29]. Moreover [30], studied the piezoresistive characteristics of epoxy-based nanocomposites using MWCNTs as conductive nano-fillers under applied tensile load. In accordance with their results, as the MWCNT loading was increased from 0.1 to 0.5 wt%, the electrical resistance change rate increased from 7 to 12% [30]. In another work, the piezoresistive response of MWCNTs/polysulfone (PSF) nanocomposite film was obtained. The 0.5 wt% of MWCNTs filled in PSF showed the electrical resistance change of 18% under applied tensile fracture strain of 3.5% [21].

However, most of the polymers used for the fabrication of piezoresistive composites were mechanically and thermally weak to be used in applications in harsh environments with high temperatures. Aromatic PIs are high-performance polymers with a number of outstanding properties, such as a low dielectric constant, high thermal stability, and favorable chemical and mechanical properties [31,32]. In previous studies, it was shown that the addition of CNTs could effectively enhance the thermal properties of the CNT/PI nanocomposites [33,34]. For instance, in Ref. [31], the TGA results support the fact that the CNT/PI nanocomposites are highly thermally stable. This suggests the idea that the CNT/PI piezoresistive sensors can be used in harsh environments with high temperatures.

In the present study, the piezoresistive response predictions were carried out based on the self-consistent effective medium theory that accounts for the interface and tunneling effects. With the derived formulation, the effects of the MWCNT weight percentages, lengths, and tunneling effects on the piezoresistivity of the nanocomposites were discussed in detail. The novelty of the present model is in the flexibility and simplicity of the derivation to represent the piezoresistive response with a limited number of model parameters. In addition, it is straightforward to extend the proposed model for use as a user-defined material (UMAT) with implementation into the finite element method (FEM) to predict a more complex structural system. The capability of the present model to predict the overall electrical behaviors of nanocomposites is demonstrated through a number of parametric investigations. Furthermore, MWCNT/PI films with various weight percentages of MWCNTs were fabricated for validation purposes. A doctor-blade method was used to fabricate piezoresistive specimens, and their electrical and mechanical properties were correspondingly evaluated by a four-point probe method and by uniaxial tensile testing. Comparisons between the experimental data and the predictions based on the present theoretical study were then carried out for a further demonstration of the capability of the proposed model.

2. Theory

2.1. Piezoresistive response of nanocomposites considering interface and tunneling effects

A self-consistent effective medium theory is introduced here to predict the effective piezoresistive behavior of nanocomposites. The effective medium theory [9,10] is adopted to model electrical conductivity of nanocomposites containing MWCNTs with imperfect interfaces, and the tunneling model is modified in this study to represent piezoresistivity characteristics. Key features of the present study and comparisons with senior author's papers are addressed below.

The piezoresistive response of nanocomposites has been modeled by a filler orientation-based method in previous papers [5,10–13]. However, the methods published literature may not be suitable for the stiffer polymer- and/or ceramic-based composites (*e.g.*, polyimide and cement) since the displacement levels of those materials are very small (less than 2–3 mm). Despite the low level of filler and external deformation, piezoresistivity can be confirmed by various experimental results [28,35], and the insoluble phenomena is attributed by the tunneling effect [22]. In this study, therefore, the sensitivity of piezoresistivity of nanocomposites is assumed to be simulated by choosing an appropriate scale parameter of tunneling, denoted by γ.

First, let us consider the two-phase composite composed of the matrix (phase 0) with the electrical conductivity σ_0, and 3D randomly oriented ellipsoidal CNTs (phase 1) with the electrical conductivity σ_1. In order to understand and predict the piezoresistive behavior on the MWCNT/PI films, we conducted the effective medium theory-based simulation. In the present study, the fillers are assumed to be non-interacting and embedded firmly in the matrix [36,37]. Then, the medium representative volume element (RVE) of two-phase composites containing arbitrary non-aligned fillers can be represented by Refs. [9,10,59].

$$\phi_0\left[\left(\sigma_0-\sigma^*\right)^{-1}+\mathbf{S}_0\left(\sigma^*\right)^{-1}\right]^{-1}+\phi_1\left[\left(\sigma_1-\sigma^*\right)^{-1}+\mathbf{S}_1\left(\sigma^*\right)^{-1}\right]^{-1}=0 \tag{1}$$

where ϕ_r denotes the volume fraction of the r-phase ($r=0,1$) and σ^* is the effective electrical conductivity (electrical conductivity of composites). $\mathbf{S}$ is the shape-dependent depolarization tensors of associated phases [10]. Since the matrix shape is envisioned to be spherically symmetric, the components of $\mathbf{S}_0$ are defined as 1/3 in all direction [9]; while $\mathbf{S}_1$ for ellipsoidal CNT fillers with a symmetric axis 3 are explicitly given as [38]