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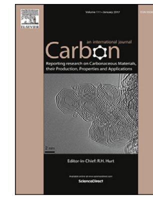

A frequency-dependent theory of electrical conductivity and dielectric permittivity for graphene-polymer nanocomposites

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ABSTRACT

Many experiments have shown that electrical conductivity and dielectric permittivity of graphene-polymer nanocomposites are strongly dependent on the loading frequency, but at present no theory seems to be able to address the continuous influence of frequency. In this work we present a new effective-medium theory that is derived from the underlying physical processes including the effects of filler loading, aspect ratio, percolation threshold, interfacial tunneling, Maxwell-Wagner-Sillars polarization, and the extra frequency-affected electron hopping and Debye dielectric relaxation, to determine the loading-frequency dependence of these two fundamental properties. The theory is formulated in the context of complex conductivity under harmonic loading. We highlight this new theory with an application to PVDF/xGnP nanocomposites, and demonstrate that the calculated conductivity and permittivity are in close agreement with the reported experimental data over the frequency range from 10^2 to 10^7 Hz. We also show that the electrical conductivity tends to increase with frequency but the dielectric permittivity tends to decrease. We find that, at low frequency, the properties are dominated by filler loading but at high frequency the loading frequency is the dominant factor. The theory also reveals that the percolation phenomenon is clearly defined at low frequency but becomes blurred at high frequency.

1. Introduction

In recent years the issue of dielectric materials with high permittivity (high-k materials) has received considerable attention due to the urgent need in electronic industry [1–4]. High-k materials can greatly improve the efficiency of electronic devices owing to their capacity to store large amount of electric energy [5–7]. In this connection carbon-based nanocomposites have become the top choice because of their outstanding dielectric permittivity [3,8,9] and superb electrical conductivity [10,11]. Typical examples of carbon nanofillers include carbon blacks (CBs), carbon nanotubes (CNTs), and graphene [12]. Graphene is an one-atom-thick two-dimensional layer of sp^2-bonded carbon with extraordinary electronic transport properties on the basal plane [13]. Flexibility and lightweight are also desired in various applications of high-k materials such as high-charge storage capacitors, active vibration control, and aerospace devices [14,15]. However, single-composition materials are hard to attain high permittivity while maintaining flexibility and lightweight [16]. Consequently graphene-polymer nanocomposites have been adopted to meet all these requirements. In such materials a small amount of graphene fillers is added to the polymer matrix to achieve high electrical conductivity and dielectric permittivity while preserving the flexible and lightweight nature of the polymer.

For many electronic components the most common form of external loading is AC field. Under such loading the advantages of utilizing graphene-based nanocomposites as high-k materials have also been known for some time. Comprehensive reviews can be found, for instance, in Dang et al. [6] and Li and Zhong [17]. At present most research efforts are focusing on the experimental investigation and phenomenological modeling [4,16,18,19]. Very few microstructure-based theories that could bring the underlying features of the nanocomposite up to the macroscopic level to directly connect the AC frequency to the effective electrical conductivity and dielectric permittivity of the nanocomposites have been proposed. These microstructure features include the amount of filler loading, aspect ratio, percolation threshold, interfacial tunneling, Maxwell-Wagner-Sillars polarization, and the extra frequency-affected electron hopping and Debye dielectric

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relaxation; they are directly responsible for the remarkable properties of the nanocomposites. It is with this objective that the present study was undertaken.

To develop such a theory, two major issues must be confronted. The first one is the homogenization method to determine the effective electrical conductivity and dielectric permittivity of the graphene-based nanocomposites. This is a high aspect ratio and high property contrast problem. For a composite with a perfect interface, the Ponte Castaneda-Wills (PCW) model [20], Mori-Tanaka (MT) approach [21], and the Bruggeman's effective medium approximation (EMA) [22] are among the most widely used ones. As extensively discussed in Nan et al. [23], percolation is a very fundamental phenomenon for such high aspect ratio and high property contrast problems, especially for the electrical conductivity and dielectric permittivity of graphene (or carbon nanotube) composites. For an isotropic composite containing 3-D randomly oriented ellipsoidal inclusions, the PCW approach does possess a percolation threshold, but the calculated effective properties beyond percolation can easily go out of the Hashin-Shtrikman (HS) bounds [24–26]. Conversely, the MT approach has the merit that the calculated effective properties always lie on or within the HS bounds but it cannot capture the feature of percolation threshold [27]. Among the three, only EMA has the virtues that the predicted results possess a percolation threshold and are always on or inside the HS bounds [27]. As such, EMA appears to be the most suitable one for the present problem and will be adopted as the starting point in the theoretical development. The EMA - also known as the coherent potential approximation - is a special form of self-consistent methods that treats both constituent phases on equal geometrical footing. It has also been used by Landauer [28] to calculate the electrical conductivity under DC loading and by Lagarkov et al. [29,30] to calculate the electrical conductivity and dielectric permittivity under AC loading. In both cases the inclusions are taken to be spherical and perfectly bonded to the polymer matrix.

The second issue is the interface conditions. This is a far more complex one. First of all the interface between graphene and polymer matrix usually is not perfect. A common way to treat an imperfect interface is to introduce a weak, diminishingly thin interphase layer to form a thinly coated inclusion. This approach has been adopted by Dunn and Taya [31], Nan et al. [32], and Duan and Karihaloo [33]. For electrical conductivity one must also consider the additional contribution of electron tunneling [34–37] and, for dielectric permittivity, the effect of Maxwell-Wagner-Sillars (MWS) polarization [38–40]. In addition, the extra frequency-assisted electron tunneling [41] and Debye dielectric relaxation [42] must also be added to fully address the issue of interface effects under AC loading. These have not been done in the past.

In this article a new effective-medium theory with all these interface effects will be developed. It will be shown that the theory can provide the continuous frequency dependence of electrical conductivity and dielectric permittivity at various graphene loadings.

2. The theory

The theoretical development will consist of five parts: (i) the setting of complex conductivity under AC loading, (ii) the effective-medium theory with a perfect interface, (iii) the percolation threshold at low frequency, (iv) the static interface effects, and (v) the additional frequency-affected interface effects. The static effects will include an imperfect interface, tunneling-assisted interfacial conductivity, and formation of MWS nanocapacitors, while the frequency-affected effects will further include the frequency-assisted electron tunneling and Debye dielectric relaxation.

2.1. The complex conductivity under AC electrical loading

A typical morphology of graphene-polymer nanocomposite is schematically shown in Fig. 1(a), where the inter-connected blue regions with various orientations constitute the graphene as the inclusions, and the yellow region represents the polymer matrix. The red connected segments illustrate a percolation path. If the composite is subjected to a cyclic (say harmonic) electrical loading at the infinity, the long-term response of the material is also harmonic [43]. In particular, we suppose the graphene-based nanocomposite to be subjected to an electric potential on its boundary that gives rise to the cyclic overall electric field, $\bar{\mathbf{E}}$, as

$$\bar{\mathbf{E}} = \tilde{\mathbf{E}} e^{i\omega t}, \tag{1}$$

where $\tilde{\mathbf{E}}$ is the amplitude of the electric field, i is the imaginary unit, $\omega = 2\pi f$ is the circular frequency (in *rad/s*) of the electric field, and f is the AC frequency (in *Hz*). Similarly the overall cyclic current density will take the form

$$\bar{\mathbf{J}} = \tilde{\mathbf{J}} e^{i\omega t}, \tag{2}$$

where $\tilde{\mathbf{J}}$ is the amplitude. The over bar in $\bar{\mathbf{E}}$ and $\bar{\mathbf{J}}$ signifies that the quantities refer to the overall composite.

Following the idea of complex moduli in viscoelastic composites (see, for instance [44]), a parallel capacitor-resistor circuit model as depicted in the inlet of Fig. 1(a) will be employed here to simulate the response of the nanocomposites [45]. The amplitudes of the electric field $\tilde{\mathbf{E}}$ and the current density $\tilde{\mathbf{J}}$ are connected to each other through

$$\tilde{\mathbf{J}} = \boldsymbol{\sigma}^* \tilde{\mathbf{E}}, \tag{3}$$

where $\boldsymbol{\sigma}^*$ is the complex conductivity tensor, defined by

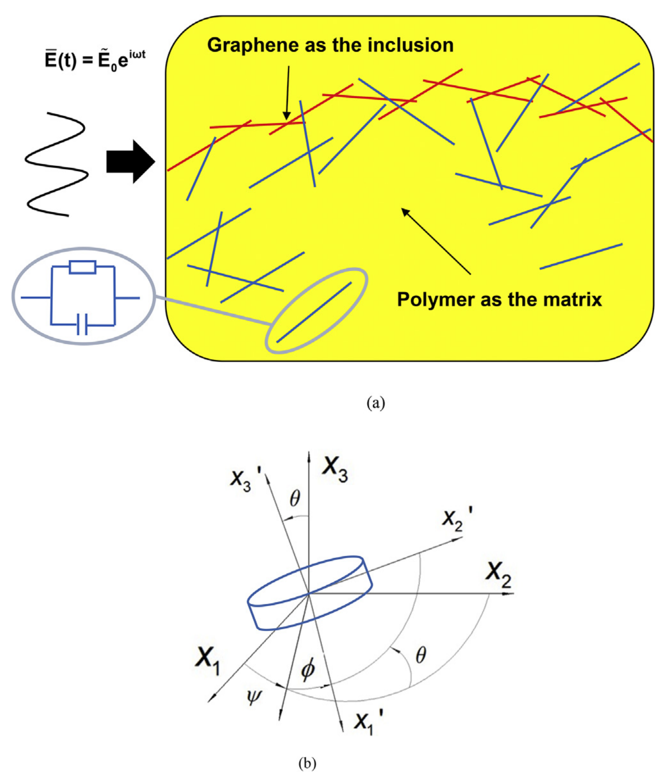

Fig. 1. (a) Schematic of the graphene-polymer nanocomposites subjected to AC electrical loading, (b) schematic of Euler angles describing the orientation of graphene filler with respect to the Cartesian coordinate. (A colour version of this figure can be viewed online.)