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Modeling of electrical conductive graphene filled epoxy coatings

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ABSTRACT

Electrical conductive coatings were prepared by incorporating various fractions of graphene nanoplatelets (GNPs) into epoxy resin, i.e. 0–2.5 wt.%. High stability of GNPs as dispersed form in chloroform and their uniform distribution in epoxy matrix were proved by UV–vis spectroscopy, turbidimetry and optical microscopy techniques. SEM images were also used to check the GNPs state in each step of fabrication. All epoxy coatings underwent electrical conductivity measurement, the conductivity of epoxy coating increased 13 orders of magnitude by addition of 2.5 wt.% GNP. Through this experiment, GNP fraction as low as 0.5 wt.% was defined as percolation threshold. Four types of conductivity models were analyzed (i.e. Kirkpatrick and Zellen, GEM, updated Mamunya and additive model) to select the most precise one for predicting epoxy/GNP coating conductivity behavior. It was finally demonstrated that the additive model presented the best correlation with the experimental data. We also revised the additive model parameters to further promote its accuracy. Finally, mechanical properties of coatings studied by DMTA demonstrated relative increase of about 100% in storage modulus of coating at percolation threshold with respect to neat coating, approving the desired conductivity and mechanical attributes for graphene containing epoxy coating.

1. Introduction

Being one of the most astounding materials in the world, graphene with extraordinary electron mobility (500,000 cm^2V^{-1} s^{-1} [1], excellent thermal conductivity (5000 W m^{-1} K^{-1} [2] and mechanical stiffness (Young's modulus value of 1.1 TPa) [1] rivals the superior materials in each category. This incredibility arises from a two-dimensional monolayer sp^2 -bonded carbon atoms [3]. One promising approach to harness these properties is incorporating graphene nanoplatelets (GNPs) into various polymeric matrices to achieve multicomponent coatings or nanocomposites. Graphene will provide the polymeric matrix with new characteristics at a critical volume fraction known as "percolation threshold" [4,5].

The statistical theory of percolation in mathematics and physics was first introduced in 1957 and since then has been widely applied to various phenomena [6]. The capability of percolation theory in describing physical properties of multicomponent heterogeneous materials made it a feasible tool in this research field. Since, all these materials experience continuum percolation (geometric transition) while the particles of minor phase start to form a continuous network through the matrix at the volume fraction of percolation threshold, φ_c. Dramatic change of physical properties such as electrical and thermal conductivity in composite materials is the result of approaching φ_c [7]. Graphene based polymeric coatings are regarded as such materials in which an insulating behavior is transitioned into a conducting one thanks to electrical percolation. The most prominent characteristic which stands out as advantage of these types of materials is that their electrical percolation is obtained at a very low graphene volume fraction. This results primarily from the graphene high aspect ratio which eases the direct physical contact of GNPs, leading to expeditious formation of a lattice-like structure. Moreover, the propensity of electrons for hopping across a thin layer of insulating polymer matrix to reach neighboring unconnected GNPs promotes the graphene electron transport. Accordingly, the conducting mechanism of graphene based polymeric materials takes place by electron movement through two main pathways described above, i.e. direct contact and hopping [8].

Percolation threshold in graphene based polymeric materials is governed by various factors, the importance of which must be considered to obtain the desired properties at the lowest possible percolation threshold. These factors include intrinsic conductivity of graphene and polymeric matrix [9–11], physical characteristics of graphene e.g. shape, size and surface area [11–14], GNPs distribution and orientation in matrix since uniform distribution is desired [9,14–17], fabrication method which determines media viscosity and

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the type of tension exerted to prevent GNPs agglomeration [12,18–23], graphene interaction with polymeric matrix [14,24] which is affected by their surface properties [25] and matrix viscosity [26]. Choosing proper materials and methods improves the quality of final product as the result of favored interaction between its components. Any factor that may assist the electron movement through its pathways will facilitate approaching the percolation threshold.

Designing and developing graphene based polymeric materials with new desired performance requires quantitative prediction of electrical behavior trend with increasing graphene content, in order to minimize the experimental efforts. Different models have been proposed to find this trend in carbon-filled composites [27], a few of which concern graphene based polymeric nanocomposites specifically [28,29]. Despite the complexity of generating a comprehensive correlation between various microscopic factors, aforementioned previously, and macroscopic properties of a graphene based material, some of developed models can govern this correlation to a great extent [28,29]. Considering more factors in a proper function results in more precise prediction.

Although thick molded nanocomposites have been employed in modelling studies to a great extent, thin polymeric coatings especially graphene filled ones have not been investigated in this field, to the best of our knowledge. This paper intended to develop an electrical conductive graphene based epoxy coating and correlate its experimental conductivity data with structural parameters through some current practical models. Initially, it was targeted to find the best fitted model among various types, in order to study whether the facts governing thick nanocomposites are working with thin coatings or not. Subsequently, the focus was placed on modifying the best fitted model to achieve the highest possible accuracy. Epoxy resin as one of the most common materials in coating industry, can be utilized in more extended application areas by incorporating GNPs. Electrical conductive graphene based epoxy coatings can be considered as a material of choice in electronic devices, semiconductors, electrostatic dissipation (EDS), electromagnetic and radio frequency interference shielding (EMI/RFI) [30].

2. Theoretical background

The models predicting the electrical conductivity of a composite material (composed of insulate polymer as matrix and conductive filler as minor phase) are of diverse basis. Physical characteristics of filler, its distribution in matrix, interaction between filler and matrix and fabrication process have been determined as the most noteworthy parameters affecting the percolation threshold. Models based on these parameters are categorized into four main types i.e. statistical, thermodynamic, geometric and structure oriented [31].

The majority of associated literature is devoted to the statistical models, the base of which is probability of filler particles contacts within the matrix. The power-law equation of Kirkpatrick and Zallen model in early 1970s (Eq. (1)) was pioneer of many statistical models [31]. In Kirkpatrick and Zallen model, a lattice built up of sites and bonds are considered (typically simple cubic, face centered or body centered lattice), the fraction of existing sites and bonds in a percolating system is determined by means of statistical laws and computer simulation. The correlation between percolation threshold and electrical properties at concentrations higher than percolation threshold resulted in Eq. (1).

$$\sigma = \sigma_f(\varphi - \varphi_c)^s \tag{1}$$

Where σ is electrical conductivity of mixture, σ_f is conductivity of filler; φ, volume fraction of filler; φ_c, percolation threshold and s is critical exponent. None of 4 main parameters affecting the percolation threshold are recognized in this equation and the specified values of φ_c and s only depend on lattice dimensions. Thus, for various composite systems s value might deviate from the universal value determined in literatures [31–33]. In evaluating Eq. (1) along with real electrical behavior of a system has manifested the key role of filler shape in determining critical exponent, since the closest distance between two filler particles is highly controlled by this factor. Closest distance between two filler particles directly influences tunneling mechanism in such systems, which literatures have not taken it into account while determining universal value for s. Hence, the existence of tunneling mechanism is considered as another reason for probable non-universality of s value [7,34].

General effective media (GEM) equation has emerged by combining theories of percolation and effective media [35]. Effective media theory describes properties of a multicomponent material as a whole, using property of each constituent and its relative fraction in mixture. Eq. (2) represents GEM equation where ρ, ρ_m, ρ_f are resistivity of mixture, matrix and filler, respectively. Similar to previous model, φ is volume fraction of filler; φ_c, percolation threshold and t is the critical exponent. According to GEM approach, φ_c and critical exponent help to characterize filler shape, fillers distribution in matrix and their interconnectivity.

$$\frac{(1-\varphi)(\rho^{1/t}-{\rho_m}^{1/t})}{\rho^{1/t}+(\frac{1-\varphi_c}{\varphi_c}){\rho_m}^{1/t}}+\frac{\varphi(\rho^{1/t}-{\rho_f}^{1/t})}{\rho^{1/t}+(\frac{1-\varphi_c}{\varphi_c}){\rho_f}^{1/t}}=0 \tag{2}$$

Discrepancy between statistical models prediction and experimental values of percolation threshold led to evolution of thermodynamic models to incorporate more vital factors affecting percolation [31]. Updated Mamunya model could be considered as a comprehensive one of this type due to variety of included parameters. The original model of Mamunya was developed based on polymer/carbon black composites and in spite of its success for such systems, it was rather unsatisfactory for systems containing other fillers [36]. In updated version of Mamunya model, the constant values have been derived by taking into account various types of composites (polymers and fillers), in order to expand generality of the model [37]. The updated Mamunya model uses Eq. (3) to predict electrical conductivity of a composite material at filler volume fractions higher than percolation threshold. At fractions lower than percolation threshold, the conductivity is approximated as the matrix's. In Eq. (3), σ, σ_f, φ, φ_c are electrical conductivity of mixture, electrical conductivity of filler, volume fraction of filler and percolation threshold, respectively. σ_{max} represents electrical conductivity of mixture at maximum filler volume fraction, F. Maximum filler fraction in media depends on its shape and aspect ratio, thus these two geometric parameters are employed in model implicitly. The value of exponent k is not constant for different multicomponent materials and is calculated through Eq. (4). The parameter K in Eq. (4) is a function of interfacial tension (Eq. (5)). Interfacial tension between filler and matrix (γ_{mf}) is obtained via a modified form of Fowkes equation (Eq. (6)) [25]. The closer the surface energy values of filler and matrix get, the better dispersion is achieved due to higher compatibility. In Eq. (6), m and f subscripts stand for matrix and filler, respectively.

$$\log\sigma = \log\sigma_m + (\log\sigma_{max} - \log\sigma_m)(\frac{\varphi-\varphi_c}{F-\varphi_c})^k \tag{3}$$

$$k = \frac{K\varphi_c}{(\varphi-\varphi_c)^{0.7}} \tag{4}$$

$$K = 0.11 + 0.03\,\gamma_{mf} \tag{5}$$

$$\gamma_{mf} = \gamma_m + \gamma_f - 2\,(\gamma_m\gamma_f)^{0.5} \tag{6}$$

Geometric models originally were aimed to be applied for dry premixed and sintered mixture of conductive and insulating powders. Diameter of constituents and the arrangement of components near each other were the main included parameters in such models. Unfortunately, these models were not precise enough in prediction [31,36].

Structure-oriented models originate from the idea that reproducible percolation threshold is reached only by employing compression