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Short communication

Tuning the electrical percolation threshold of polymer nanocomposites with rod-like nanofillers

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In this communication, a stochastic approach based upon Komori and Makishima's work has been used for predicting the electrical percolation threshold of cylindrical nanofillers with three-dimensional (3D) spatial orientations in a typical nanocomposite system. Specifically, the proposed model was able to predict the volume fraction based percolation threshold of nanofillers with a wide range of aspect ratios (10–1000), which was substantiated with a variety of experimental data sets obtained from the literature. The anisotropic behavior of 3D aligned nanofillers was successfully introduced via in-plane and out-of-plane orientation distributions. The percolation threshold values of nanofillers were also found to be comparable with those obtained from the stochastic model that has incorporated the excluded volume effect.

1. Introduction

Nanoscale conductive particles, such as carbon nanotubes, carbon nanofibers, metallic nanowires, graphene flakes, etc. have gained considerable attention in the field of nanocomposites due to their excellent electrical properties. Such characteristics are the gateway to replace monolithic metals in numerous emerging applications including flexible microelectronics, e-paper, organic light emitting diodes, sensors, antistatic coatings and touch screens [1–5]. These targeted applications can be practically achievable when maximum electrical conductivity of nanocomposites is attained with the lowest possible filler concentration, which inevitably reduces the cost. Enhancing the electrical conductivity of the nanocomposites in a cost-effective manner is triggered by means of percolation threshold that describes the minimum loading of conducting nanorods in a polymeric/colloidal medium, which are capable of forming a connected network through rod-rod contacts. The transition in the electrical conductivity at the percolation threshold level has been observed to be several orders of magnitude [6]. Alternatively, the concentration of nanorods at which the material exhibits an abrupt transition from insulator to a conductor is characterized by the percolation threshold. In conducting nanocomposites containing nanofillers, the percolation threshold is dependent upon the filler attributes including aspect ratio, electrical properties, and dispersity in filler properties [7–9].

Percolation phenomena in polymer nanocomposites have been critically investigated through numerical [10–18], analytical [19–21] and semi-empirical modeling [22–25] techniques. Some of these modeling techniques were compared and subsequently, combined together to predict the percolation threshold of nanocomposites. For instance, the excluded volume model is a universally accepted continuum analytical model that has been applied in combination with Monte Carlo simulations for predicting the percolation threshold of a wide variety of fillers in nanocomposites [10,13,16,18,19]. However, the classical excluded volume model has been primarily developed for fillers with large aspect ratios, which can be computationally intensive for numerical modeling techniques [10]. Furthermore, the nanofillers with modest aspect ratios (<100) either grown inherently or as a result of sonication, are present in nanocomposites [7,18,26]. In addition, the excluded volume model considers the random distribution of fillers but in reality, these fillers can align in preferred in-plane or out-of-plane directions as a result of polymer processing techniques (extrusion, molding, drawing, fiber spinning) [27] or due to the application of electrical or magnetic fields [28]. Therefore, it is of paramount importance that the 3D orientation distribution of fillers should be considered for predicting the percolation threshold. In the present work, the analytical model to predict the

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percolation threshold of 3D aligned nanofillers covering a wide range of aspect ratios based upon stochastic approach has been proposed. The stochastic approach is essentially based upon Komori and Makishima's geometrical probability approach [29] which has been successfully applied in the past for predicting various properties of different types of fibrous systems [30–33]. The theoretical results have been compared with the other stochastic approach that accounted for the excluded volume effect [34]. The analytical model has been validated with a variety of experimental data sets, obtained from the literature.

2. Theoretical analysis

For a disordered system such as nanocomposites to be percolative, the fundamental criterion is the continuity to transport electrons should be maintained, which can be modulated through rod-rod contacts, as shown in Fig. 1. Although, the thin layer of the polymer matrix in the range of few nanometers between the nanofillers can still allow the passage of electrons via quantum mechanical tunneling mechanism [35]. Neglecting the tunneling effect in this analysis due to the fact that the electrical conductivity of the network primarily results from rod-rod contacts [36]. Therefore, the rod-rod contacts of nanofillers which are responsible for (dis)continuity in the electron path should be critically analyzed. Considering the orientation of each cylindrical rod defined by a pair of orientation angles (θ,φ) in a spherical coordinate system, where θ and φ are polar and azimuthal angles, respectively. The probability density function or the orientation distribution function, $\Omega(\theta,\varphi)$ is the probability of a rod lying in an infinitesimal range of angles θ and $\theta+d\theta$, and φ and $\varphi+d\varphi$ is given by $\Omega(\theta,\varphi)\sin\theta d\theta d\varphi$, which satisfies the following normalization condition.

$$\int_0^\pi d\varphi \int_0^\pi \sin\theta\,\Omega(\theta,\varphi)d\theta = 1 \tag{1}$$

Komori and Makishima [29] described a stochastic approach by assuming the rods to be straight cylindrical entities with constant length and diameter and the rod-rod contact condition would only occur if the center of mass of rod A of defined orientation (θ,φ) enters into the neighbourhood region of rod B with orientation (γ,ζ), as shown in Fig. 1. Based on defined number of contacts in a volume (V) along with the probability of formation of a contact, the mean distance between the rod-rod contacts ($\overline{b}_{KM}$) is given by [29],

$$\overline{b}_{KM} = \frac{V}{2DLI} \tag{2}$$

where $I = \int_0^\pi d\theta \int_0^\pi J(\theta,\varphi)\sin\theta\,\Omega(\theta,\varphi)d\varphi$; $J(\theta,\varphi) = \int_0^\pi d\zeta \int_0^\pi \sin\chi(\theta,\varphi,\gamma,\zeta)\Omega(\gamma,\zeta)\sin\gamma d\gamma$ and $\sin\chi = [1-\{\cos\theta\cos\gamma+\cos(\varphi-\zeta)\sin\theta\sin\gamma\}^2]^{1/2}$where D is the nanofiller diameter, L is the total length of the nanofiller defined in volume V, I is an orientation parameter defining the orientation characteristics of nanofillers in the assembly, χ is the angle between the two axes of nanofillers having defined types of orientation distributions, $\Omega(\theta,\varphi)$ and $\Omega(\gamma,\zeta)$.

Also, the volume fraction of rods (μ) can be calculated through the following equation.

$$\mu = \frac{\pi D^2 L}{4V} \tag{3}$$

Combining Equations (2) and (3),

$$\overline{b}_{KM} = \frac{\pi D}{8I\mu} \tag{4}$$

It is worth mentioning that Komori and Makishima [29] have not accounted for the changes in the probability of a contact with the successive contacts, i.e. excluded volume effect has been neglected [34]. In other words, an existing contact reduces the effective contact length of a rod, which diminishes the probability of formation of new contacts. On the other hand, the existing rod-rod contact also tends to reduce the free volume of the nanofiller assembly that results in enhancing the chances of making new contacts [37]. Therefore, the excluded volume effect is a trade-off between the reductions in effective contact length and that of free volume [38]. In reality, this effect may not significantly alter the number of rod-rod contacts as the critical volume fractions for attaining desired percolation thresholds are often realized at significantly lower levels. Nevertheless, we also calculated the mean distance between the contacts based upon Pan's approach [34] that considered the excluded volume effect by modifying and extending Komori and Makishima's model [29], as shown below.

$$\overline{b}_{Pan} = \frac{(\pi+4\mu\psi)D}{8\mu I} \tag{5}$$

where $\psi = \int_0^\pi d\theta \int_0^\pi d\varphi J(\theta,\varphi)K(\theta,\varphi)\Omega(\theta,\varphi)\sin\theta$; $K(\theta,\varphi) = \int_0^\pi d\gamma \int_0^\pi d\zeta \frac{\Omega(\gamma,\zeta)\sin\gamma}{\sin\chi(\theta,\varphi,\gamma,\zeta)}$

Next, it is pertinent to note that each rod should make atleast

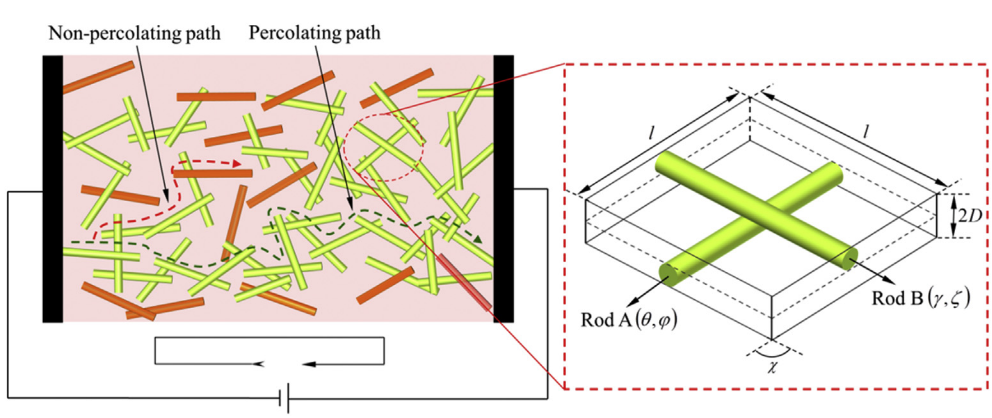

Fig. 1. A cartoon depicting percolating and non-percolating network of electrically conductive nanofillers. Here, each nanofiller is displayed as a cylindrical rod. The magnified image illustrates rod A defined by a pair of orientation angles (θ,φ) in contact with rod B which is aligned with a pair of orientation angles (γ,ζ).