Results in Physics 10 (2018) 81–90

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.elsevier.com/locate/rinp

Estimating and understanding the efficiency of nanoparticles in enhancing the conductivity of carbon nanotube/polymer composites

A. Mora, F. Han, G. Lubineau*

King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Keywords:
Carbon nanotube
Composites
Electrical conductivity
Representative volume element
Geometric modeling

ABSTRACT

Carbon nanotubes (CNTs) have been widely used to improve the electrical conductivity of polymers. However, not all CNTs actively participate in the conduction of electricity since they have to be close to each other to form a conductive network. The amount of active CNTs is rarely discussed as it is not captured by percolation theory. However, this amount is a very important information that could be used in a definition of loading efficiency for CNTs (and, in general, for any nanofiller). Thus, we develop a computational tool to quantify the amount of CNTs that actively participates in the conductive network. We then use this quantity to propose a definition of loading efficiency. We compare our results with an expression presented in the literature for the fraction of percolated CNTs (although not presented as a definition of efficiency). We found that this expression underestimates the fraction of percolated CNTs. We thus propose an improved estimation. We also study how efficiency changes with CNT loading and the CNT aspect ratio. We use this concept to study the size of the representative volume element (RVE) for polymers loaded with CNTs, which has received little attention in the past. Here, we find the size of RVE based on both loading efficiency and electrical conductivity such that the scales of "morphological" and "functional" RVEs can be compared. Additionally, we study the relations between particle and network properties (such as efficiency, CNT conductivity and junction resistance) and the conductivity of CNT/polymer composites. We present a series of recommendations to improve the conductivity of a composite based on our simulation results.

1. Introduction

Carbon nanotubes (CNTs) are ideal nanofillers either to improve the electrical conductivity of polymers [47,49] or to tailor their piezoresistive behavior, making them suitable as strain sensors and for structural health monitoring applications [1,33,55]. CNT-filled polymers are also useful for applications that are constrained by electrical charge mitigation [41]. Increasing the electrical conductivity of the polymer by the addition of CNTs reduces the polymer's dielectric properties. This, in turn, reduces the accumulation of electrical charge, preventing damage to electronic equipment due to electric discharge [19].

The addition of CNTs to a polymer matrix modifies its electrical properties through a percolation process [43]. An important quantity is the percolation threshold, which describes the minimum concentration that ensures the development of one or multiple percolated network(s) from one side to the other side of the sample. For such conductive networks to form, the conductive nanofillers need to be close to each other because conduction between particles is impossible when the nanofillers are separated by more than a few nanometers [24,44]. Due to this limitation, nanofillers that are not close enough to the network will not be part of it. The amount of CNTs that actively participates in the conduction of electricity is unknown and has been largely ignored in the literature. In this work, we quantify the amount of CNTs that actively participates in the conduction of electricity. We use this quantity to provide a definition of loading efficiency that has not been yet offered in the literature. To achieve this, we develop a computational tool that generates geometric representations of CNT networks. We use this tool to study the loading efficiency of polymers filled with CNTs at different volume fractions and aspect ratios. This tool is based on our previous work and has been shown to reproduce realistic CNT networks [15]. An empirical expression to approximate the fraction of percolated CNTs was proposed by Deng and Zheng [10]. However, this expression was not presented as a definition of loading efficiency nor were its limitations studied. Considering that this expression continues to be used [14,28,52], we highlight the importance of studying the validity and limitations of this expression. Thus, we compare our efficiency results with those obtained by the expression presented by Deng

* Corresponding author.
E-mail address: gilles.lubineau@kaust.edu.sa (G. Lubineau).

https://doi.org/10.1016/j.rinp.2018.05.019
Received 16 April 2018; Accepted 8 May 2018
Available online 22 May 2018

and Zheng [10] and present an improved estimation for the fraction of percolated CNTs.

For simulations and measurements to be reliable, they need to be performed on a sample that is at least the size of the representative volume element (RVE). The RVE is the minimum volume at which a property becomes size-independent. The concept of RVE for CNT/polymer nanocomposites has been rarely investigated in the literature and is commonly defined as the simulated volume [33,51]. In other studies, the RVE has been defined as having enough fillers without providing an exact geometry [12]. Periodic unit cells have been defined as RVEs [39]. However, periodicity is not representative of an actual CNT/polymer composite, especially when percolation has to be accurately described. Song et al. [42] obtained the RVE size for a single CNT geometry and used that same RVE size to perform simulations of CNTs with different geometries. However, they did not investigate the dependence of the RVE size on CNT loading or CNT geometry. Lubineau et al. [27] also obtained the RVE size for CNT/polymer composites and considered its dependency on CNT loading, aspect ratio and tortuosity. Here, we build on the results obtained by Lubineau et al. [27] and use electrical conductivity (providing a "functional" definition) and loading efficiency (providing a "morphological" definition) to better understand how to define the RVE size of CNT/polymer composites.

This paper is organized as follows. In Section 2, we present the methodology to generate computational representations of CNT networks and the procedure to determine the backbone and the electrical conductivity of those networks. In this section, we introduce a definition of loading efficiency based on the backbone of the CNT network. In Section 3, we determine the RVE size based on efficiency and electrical conductivity. We compare our results on efficiency with the fraction of percolated CNTs proposed by Deng and Zheng [10] to propose an improved estimation. Additionally, we perform a sensitivity analysis of our model on the electrical conductivity of CNTs and junction resistance. We present recommendations to improve the efficiency and electrical conductivity of CNT/polymer composites based on these results. Finally, we offer conclusions in Section 4.

2. Numerical modeling for RVE determination

2.1. Geometric representation of a CNT network

The algorithm presented by Lubineau et al. [27] is utilized to generate computational representations of CNT networks in cubic samples of size $[a \times a \times a]$. This algorithm is briefly summarized here. For further details, we refer the reader to the original study [27].

In a global Cartesian coordinate system defined by $(\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z})$, a CNT comprises n interconnected cylinders with length l and radius r, as shown in Fig. 1. The axis of the $(i + 1)$-th cylinder, for $0 \leqslant i \leqslant n-1$, is a segment from point s_i to point s_{i+1}. The starting point of a CNT, s_0, is generated randomly following a uniform distribution in the cube. A local Cartesian coordinate system $(\boldsymbol{x}_i, \boldsymbol{y}_i, \boldsymbol{z}_i)$ with origin at s_i is defined

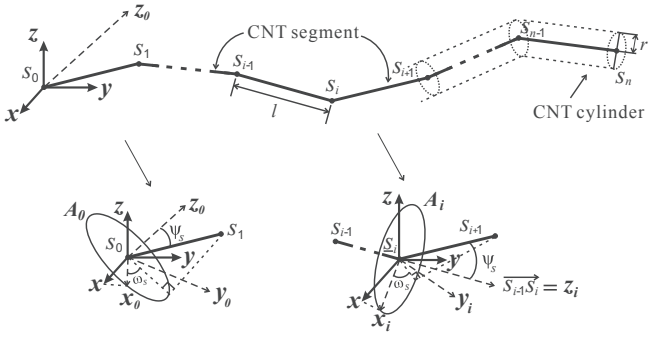

Fig. 1. Geometrical representation of a CNT.

to generate the point s_{i+1} $(0 \leqslant i \leqslant n-1)$. In this local coordinate system, $\boldsymbol{x}_i$ is the projection of $\boldsymbol{x}$ on A_i, where A_i is the plane containing the point s_i with normal vector $\boldsymbol{z}_i$. Here, for $i = 0$, the direction vector $\boldsymbol{z}_0$ is calculated differently from [27]. First, three numbers, v_x, v_y and v_z, are generated randomly following a uniform distribution in the interval $[-1, 1]$. These three numbers define the components of a vector $\boldsymbol{v} = [v_x, v_y, v_z]^T$. Then, we set $\boldsymbol{z}_0 = \boldsymbol{v}/(\boldsymbol{v}\cdot\boldsymbol{v})$. For $1 \leqslant i \leqslant n-1$, $\boldsymbol{z}_i$ has the same direction as $\overrightarrow{s_{i-1}s_i}$. Then, the point s_{i+1} has spherical coordinates (l, ω_s, ψ_s) in the local coordinate system $(\boldsymbol{x}_i, \boldsymbol{y}_i, \boldsymbol{z}_i)$.

Different specifications for the ranges and probability functions for ω_s and ψ_s result in networks with different microstructures such as random or aligned CNTs [15]. Finally, the interpenetration of CNTs during the generation process is avoided to reproduce more realistic CNT networks. Details on how to avoid the interpenetration of CNTs are presented in [27].

2.2. Loading efficiency

Electrical conductivity is possible through a percolated network formed by the CNTs inside the polymer. However, not all CNTs form part of the percolated network nor all CNTs in the percolated network contribute to electrical conductivity. An illustration of this is the 2D network shown in Fig. 2(a). In this network, the CNTs can be separated into an electrically percolated network and some isolated particles, or clusters of particles, that do not participate in the electrical conduction (Fig. 2(b)). The percolated network can be further separated into: 1) the backbone, which is the current carrying member of the percolated network, 2) some zero-current branches that do not bear any current despite their connection to the percolated network, and 3) some balanced branches that form closed loops that do not bear any current either.

Since it is only the backbone network that actually carries electricity, extracting the backbone from a percolated network becomes an important task. In previous work, we described a methodology to extract the backbone from a CNT network [27], which we briefly summarize here.

We start by finding and grouping all CNTs in electrical contact into clusters, by using the Hoshen-Kopelman algorithm [2,17]. We consider two CNTs to be in electrical contact when they are separated by less than the maximum distance that allows transfer of electrons due to tunneling or hopping of electrons [31]. Here, we use a commonly used cutoff distance of $d_t = 1.8$ nm [24].

We then find the percolated clusters, i.e., those clusters that span from one boundary to the opposite one in a cubic sample. The backbone network is extracted from each percolated cluster by applying the direct electrifying algorithm (DEA) [21,22]. This algorithm turns the CNT network into a network of electrical resistors. Then, using the current-carrying definition of the backbone, zero-current paths are found. This network consists of two types of resistors: junction resistors and CNT resistors. When two CNTs are in electrical contact, a junction resistor is added. On the other hand, a CNT resistor comes from the intrinsic electrical resistance of a CNT. Thus, every CNT is initially represented as a resistor. However, when a junction resistor is added between two CNTs, each CNT is divided into two CNT resistors, as shown in Fig. 3.

Next, a voltage is applied to the network of resistors. Then, the system of equations that determines the voltage distribution over the resistor network is solved. Once the voltage at each resistor is known, the current passing through each resistor is calculated. Only those resistors that possess a non-zero current belong to the backbone. For numerical stability and solely to extract the backbone, all resistors are set to 1 Ω. Because of the large differences in magnitude between CNT resistors and junction resistors (e.g., around 1.2×10^5 Ω [27] and 10^{18} Ω [9,24], respectively), having these values in the same matrix causes it to be ill-conditioned. Then, the conditioning number of the matrix is improved by using resistors that have the same magnitude. In addition,