A morphological investigation of conductive networks in polymers loaded with carbon nanotubes

G. Lubineau [a,*], A. Mora [a], F. Han [a], I.N. Odeh [b], R. Yaldiz [c]

[a] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia
[b] Saudi Basic Industries Corporation, 1600 Industrial Blvd., Sugar Land, TX 77478, USA
[c] Saudi Basic Industries Corporation, P.O. Box 319, 6160 AH Geleen, The Netherlands

ABSTRACT

Loading polymers with conductive nanoparticles, such as carbon nanotubes, is a popular approach toward improving their electrical properties. Resultant materials are typically described by the weight or volume fractions of their nanoparticles. Because these conductive particles are only capable of charge transfer over a very short range, most do not interact with the percolated paths nor do they participate to the electrical transfer. Understanding how these particles are arranged is necessary to increase their efficiency. It is of special interest to understand how these particles participate in creating percolated clusters, either in a specific or in all directions, and non-percolated clusters. For this, we present a computational modeling strategy based on a full morphological analysis of a network to systematically analyse conductive networks and show how particles are arranged. This study provides useful information for designing these types of materials and examples suitable for characterizing important features, such as representative volume element, the role of nanotube tortuosity and the role of tunneling cutoff distance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Over the past two decades, research efforts have focused on adding highly conductive nanoparticles to polymeric materials to impart increased electrical conductivity [49] or on tailoring piezoresistive behaviors [35,43] to composites. These materials are necessary for applications that are constrained by electrical charge mitigation. For example, recent works have aimed to increase the electrical conductivity of polycarbonate-based thermoplastic parts for interior aircraft applications [49] and to improve the electrical properties of classical polymers for solar cells and flexible electronics. Conductive polymeric materials are a promising technology for creating transparent electrodes [19,20,33]. Tailoring of not only the electrical conductivity, but also the electro-mechanical properties (piezoresistive effect in particular [1]) of polymeric materials, makes them suitable to use as strain sensors and paves the way for the design of smart materials and structures [22,45,48].

Multifunctional materials are usually achieved by loading the pristine polymer with a cloud of highly conductive nanoparticles, which can be as diverse as carbon-based particles (e.g. carbon nanotubes (CNTs) [49] or carbon black [9]) or metallic nanoparticles [33]. The content of the particles is quantified by the weight and/or the volume fraction of the particles in the final compound (probably because this is the raw data directly related to the process). Nanoparticles are incorporated by various techniques (we refer to [31] for a review of processing techniques) with the objective of optimizing their exfoliation and dispersion; however, small-scale nanoparticle-nanoparticle electrostatic interactions of nanodoped polymers cause them to aggregate into clusters [17,18]. Thus, it is generally difficult to achieve a high-quality dispersion and may require the use of both mechanical and chemical techniques.

In most studies, macroscopic electrical behavior is also studied as function of the nanoparticle volume/weight fraction. It is well known that for low weight/volume fractions, nanoparticles remain isolated (far enough apart that no conduction can take place between them) and improvement to electrical properties is moderate; however, even at a minimum value (the percolation threshold), a network of connected particles is established. This threshold is detected by a rapid increase in the macroscopic electrical conductivity and is strongly dependent on the geometry of the particles. Special efforts have since been made to explain how the geometrical factors (especially the aspect ratio) of the particle influence the percolation threshold [3,39].

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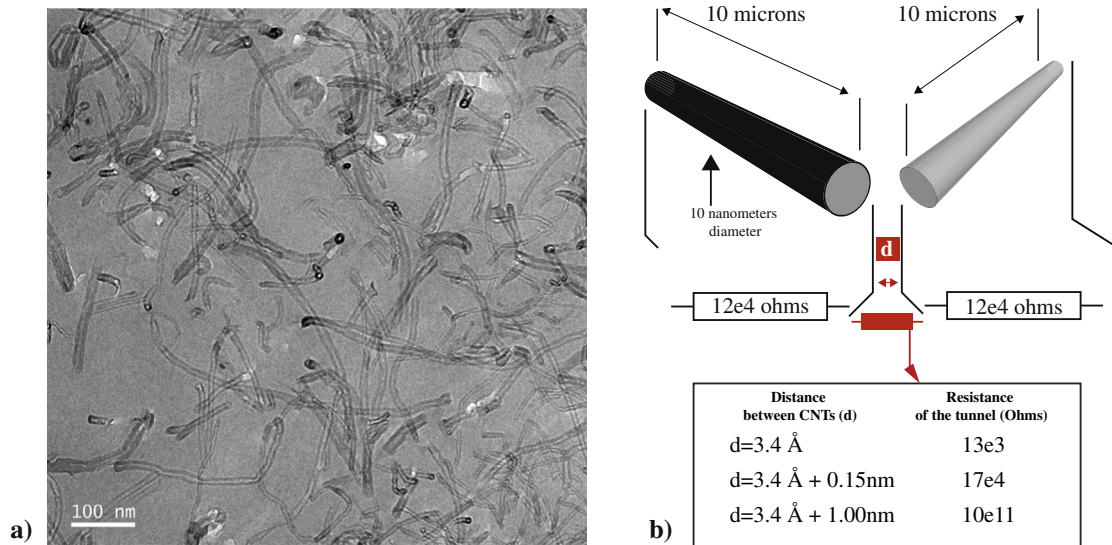   E-mail address: gilles.lubineau@kaust.edu.sa (G. Lubineau).

Fig. 1. (a) A TEM image of a multi-walled carbon nanotube (MWCNT)/epoxy composite (from [17]) and (b) a rapid estimation of the competition between the resistance of the fillers and the resistance of the junctions in a nanoparticle network while varying the distance between particles.
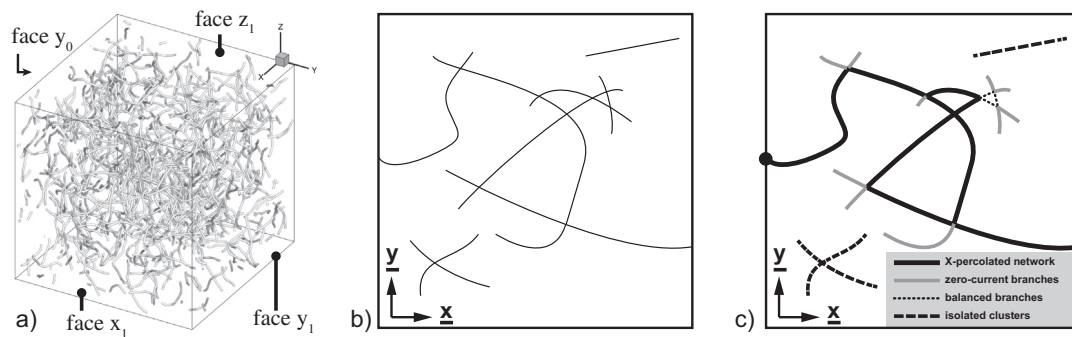

Fig. 2. The morphology of a network of CNTs: (a) in a complex 3D network and (b) in a simple 2D network. (c) The classification of CNTs in a simple 2D network

Although it is used in many studies, the weight and/or the volume fraction alone is a very global quantity, making it a very poor evaluator of a doping configuration. First, when comparing similar volume fractions, the spatial arrangement of the nanoparticles largely influences the macroscopic conductivity. Improvements to conductivity have been attempted by targeting specific microstructures, such as aligned arrays of CNTs [12,44]. Second, regardless of the spatial distribution of the nanoparticles (randomly dispersed or aligned), only a fraction of these nanoparticles are expected to actively contribute towards conductivity. Here, we provide insights into the efficiency of introduced nanoparticles. If we know which particles in the fraction actually participate in conduction and how they are organized (e.g., geometrical parameters and fraction of nanoparticles in the compound), we can optimize the doping strategy. More conductive materials could be designed using fewer nanoparticles, reducing production cost and their environmental footprint.

A nanoparticle joins a percolated network only if an efficient conduction path connects them. Due to the high insulatory behavior of the bulk polymer, inter-nanoparticle conduction has to take place through a tunneling mechanism: electrons can tunnel from one nanoparticle to another provided they are in close proximity. The tunnel effect has been studied in detail [13,40], and a maximum distance (typically a few nanometers) is expected above which tunneling is unlikely [23,40]. Thus, most particles actually remain isolated or form clusters that percolate only on a small

scale. Some pioneering works have targeted the extraction of the electrically conducting backbone (from the complete cloud of nanoparticles) [27,28]. We wish to extend these works by classifying isolated and clustered nanoparticles of different sizes and directions of percolation. With this information we revisit the concept of a representative volume element (RVE) for these materials, which defines the minimum volume for which this classification becomes scale independent.

In Section 2, we review some basic concepts about inter-nanoparticle conduction mechanisms and percolation, which is necessary to introduce characteristic length scales. We propose a classification system for nanoparticles that is meaningful for electrical conductivity (mainly isolated or clustered). In Section 3, we detail our algorithm, describing the generation of simulated microstructures and the classification algorithm used to organize the nanoparticles according to the categories chosen in Section 2. And in Section 4, the morphology of various configurations (with varying geometry of the nanoparticles, interparticle distance, volume fractions) is investigated and the efficiency of nanodoping is discussed. We also perform a detailed investigation of how an RVE is formed from small to large scale.

2. Morphological description of the arrangement of the fillers

Here, we briefly review the key relevant features regarding the transfer of electrical charges in polymers loaded with CNTs. We