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Electrical percolation of nanoparticle-polymer composites

Guotong Wang, Chengyuan Wang*, Faling Zhang, Xiaozhu Yu

Faculty of Civil Engineering and Mechanics, Jiangsu University, No. 301 Xuefu Road, Zhenjiang, Jiangsu 212013, China

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ABSTRACT

A highly conductive and stretchable gold nanoparticle (NP)-polymer composite is achieved where some NPs are self-assembled in slender chains. It suggests an NP-chain-polymer composite with even higher electrical conductivity at much lower NP content. This study is devoted to exploring the percolation process of this new design, measuring its excellent properties and revealing the underlying physics. The Monte Carlo simulations were performed, where the van der Waals interaction and the electron tunneling between NPs are considered. It was clearly shown that the slender chains of smaller NPs lead to largely decreased percolation threshold but significantly enhanced conductivity.

1. Introduction

Flexible conductors play an indispensable role in fabricating foldable LED displays [1], conformable biosensors [2], soft energy storage devices [3,4], organic transistors [5] and smart textiles [6]. Efforts were thus invested to develop highly flexible and conductive composites [7] via the percolation of conductive nanofillers in polymers [8].

Current research is mainly focused on the composites filled with carbon nanotubes (CNTs) [9,10] and silver nanowires (AgNWs) [11,12]. Experimental techniques [11,13–15], computer simulations [11,15–19] and theoretical models [20–22] were used to study the percolation of the composites filled with the nanofillers with very large length-to-diameter aspect ratio. Major issues discussed include the effects of inter-nanofiller van der Waals (vdW) interaction, the curviness and cross-sectional size of these slender nanofillers on the percolation threshold and electrical conductivity of the composites. In addition to these slender nanofillers, metal nanoparticles (NPs) with small aspect ratio around one were also used in the composites [23–25]. A typical example is the gold NP (AuNP)-polymer composite [25] which exhibits an electrical conductivity ($\sigma_{eff} > 10^4$ S/cm), orders of magnitude higher than those with slender nanofillers [7]. A large elongation up to 484% and substantial piezo-resistive effect are also obtained [25]. These excellent properties offer a new avenue to a conformable strain/stress sensor network able to detect the stress/strain distributions on curvilinear surfaces.

In particular, some NPs [25] are found to be self-assembled via the vdW interaction to form slender chains/nanofillers. This may offer a new design with largely decreased percolation threshold but further enhanced electrical conductivity. Motivated by the properties of the AuNP-polymer composites and the potential of this new design the present work aims to explore the distinctive percolation behavior and properties of the novel NP chain-polymer composites, reveal its electron transfer mechanisms and identify the key factors controlling the percolation process. The emphasis of the present study was placed on the key factors that determine the percolation threshold and the conductivity of the composite at different stages. These factors include the conductivity, shape and size of NPs, and the electron tunneling energy barrier of the matrix, which were not discussed in detail in previous studies. The present work thus has brought in new insights into the percolation behavior and the underlying physics for the conductive nanocomposite.

2. Methodology

2.1. Construction of the NP-matrix system

Here the goal was to construct a representative volume element (RVE) of the NP-based composites. Two different cases were considered, i.e., (1) NPs are chained to form slender nanofillers and (2) some NPs are self-assembled in chains while others are distributed randomly in the matrix. Attention was mainly focused on the first case. The second one was considered to reveal the shape effect of the nanofillers. To simplify the analysis, the NPs are treated as spheres of diameter D.

First, a hollow circular cylinder was created in an empty cubic. Its geometric center (x, y, z) was generated randomly in the cubic. To reproduce the structure of the composites synthesized by the layer by layer technique [25], the central line of the cylinder stays in a plane

* Corresponding author.
E-mail address: cywang@ujs.edu.cn (C. Wang).

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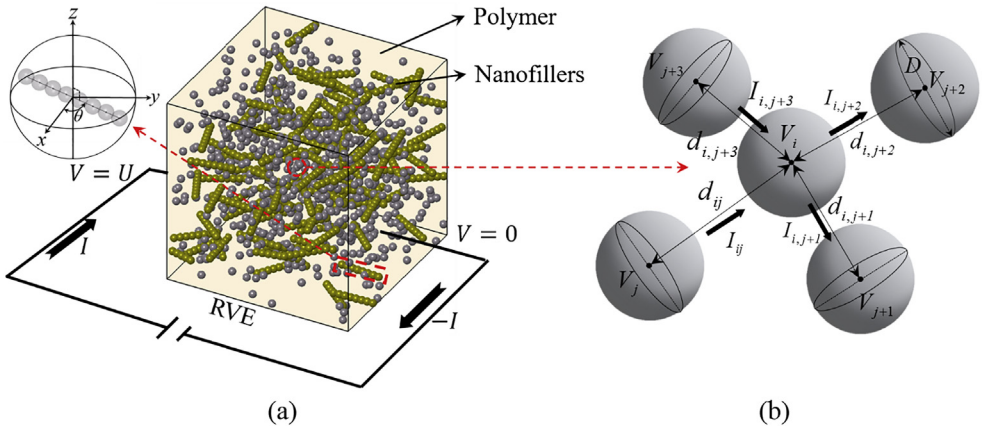

Fig. 1. Schematic of (a) a resistor model with some NPs chained in the slender nanofillers and (b) the electrical current between the *i-th* NP and its neighbors.

parallel with the **XY** plane. The orientation of the central line can then be specified by the angle θ between the central line and the **X** axis (Fig. 1). Here, θ is generated randomly between 0° and 360°. The diameter of the cylinder is equal to D and its length L is given by $L = ND + (N-1)d_{eq}$ where N is the number of NPs in the cylinder and d_{eq} is the distance between neighboring NPs. Here, $d_{eq} = 0.273$ nm is the equilibrium distance between NPs due to the vdW interaction. The value was obtained in our molecular dynamics simulations at $D = 5$ nm. Its dependence on the diameter and material of NPs is neglected. In this study, 12 NPs (i.e., $N = 12$) were placed in the cylinder with their geometric centers on the central line. Slender nanofiller were then achieved with diameter D, length L and aspect ratio $\frac{L}{D} = 12 + \frac{3}{D}$, which varies from 12.1 to 12.6 when D is in the range of [5 nm, 30 nm] and is close to the experimental observation [25]. Increasing the number of nanofillers we finally achieved a RVE with slender nanofillers and the desirable NP volume fraction (*VF*). Herein, the distance between the NP centers in different cylinders was kept larger than D to avoid the penetration of the nanofillers.

In addition, to distribute NPs outside the chains we randomly generated a point (x, y, z) and placed an NP at the point when its distance to the centers of the chained NPs was greater than D. Then we increase the number of NPs by repeating the procedure until the desired *VF* was achieved. In doing this, we assumed that the randomly distributed NPs are the 'soft-core' capped spheres and thus allowed to penetrate the adjacent ones. This will lead to some errors in predicting the percolation properties but their trend to change with the number of the chained NPs should be correct.

In generating the coordinates (x, y, z), we adopted the multiplicative congruential (MC) generator, the most common computer technique for producing random sequences. In the simulation, the MC generator can generate three random numbers x, y, and z ranging from 0 to 1, giving the coordinates of a randomly selected point [26,27].

2.2. Model of NP electrical contact

In Section 2.1 a RVE of the NP-based composite was achieved in Fig. 1a. Two electrodes were attached and an electrical voltage U was then applied to the RVE. When the NP content becomes sufficiently large the adjacent NPs will be in touch electrically (Fig. 1b). It is thus essential to define the conditions of NP electrical contacts.

Herein, NPs cannot be in physical contact due to the vdW interaction between them. Specifically, there exists an equilibrium distance d_{eq} between NPs associated with the minimum cohesive energy and zero vdW interaction. The distance d_{ij} between the *i-th* NP and *j-th* NP (i, $j = 1, 2, 3,\ldots$) is defined in Fig. 2 as the distance between their centers L_{ij} minus the diameter D. Two NPs were considered in electrical contact with zero contact electrical resistance, i.e., $R_{ij}^{o} = 0$, when $d_{ij} \leqslant d_{eq}$ (Fig. 2a). When the NPs become wider apart with $d_{ij} > d_{eq}$, they are

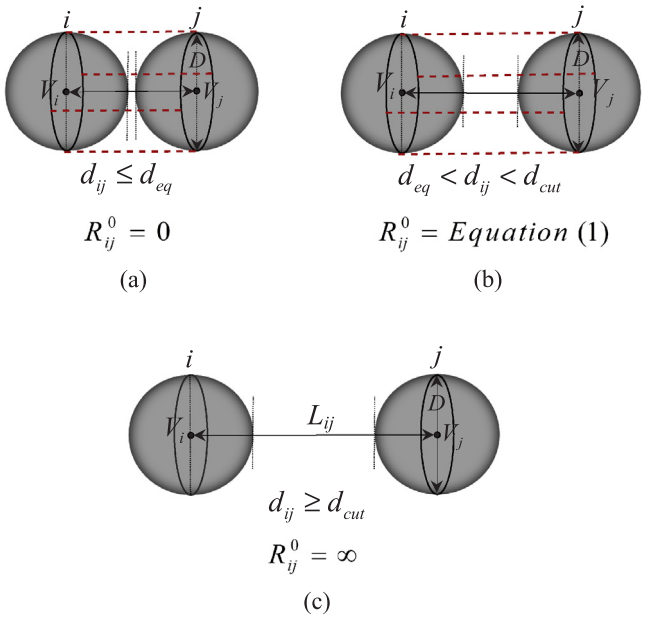

Fig. 2. Electrical connections between two NPs, i.e., (a) conductive contact, (b) electron tunneling junction and (c) no electrical current.

still in electric contact due to electron tunneling between them. In this case, the contact electrical resistance R_{ij}^{0} is given by (Fig. 2b)

$$R_{ij}^{0} = \frac{V_{ij}}{AJ} = \frac{h^2 d_{ij}}{Ae^2\sqrt{2m\lambda}}\exp\left(\frac{4\pi d_{ij}}{h}\sqrt{2m\lambda}\right) \quad (1)$$

where J is tunneling current density, V_{ij} is the electrical potential difference of the NPs, e is the single electron charge, m is the mass of electron, h is Planck's constant, λ is the height of the energy barrier, and A is the cross-sectional area of the tunnel, which is assumed to be the same as the cross-sectional area of NPs. When the distance d_{ij} further increases, and becomes greater than a cutoff distance d_{cut}, R_{ij}^{0} is considered as infinitely large and the two NPs are disconnected. In this work, d_{cut} is chosen as 1.5 nm as our study showed that further increasing the value does not significantly change the results. Herein, it is worth mentioning that d_{cut} may change with the size of the NPs. However, this radius-dependence is not considered for d_{cut} in previous studies [11,17,19]. In particular, good agreement has been achieved between the simplified model and experiments [11], which seems to suggest that such an effect of NP radius can be safely neglected. Thus, following the existing studies the simplified model was employed in the present study where d_{cut} is assumed to be independent of NP size. The total electrical resistance ($R_{ij} = R_{ij}^{0} + R_{NP}$) between the *i-th* NP and the *j-*