IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

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To cite this article: N Kerdkaen *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **773** 012025

IOP Conf. Series: Materials Science and Engineering **773** (2020) 012025 doi:10.1088/1757-899X/773/1/012025

Monte Carlo simulations of nano-rod filler in stretched polymer nanocomposites

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Abstract Conductive polymer nanocomposites material (PNCs) is one type of alternative polymeric materials to replace high-cost intrinsically conductive polymers (ICPs). PNC is a composite of electrical insulative polymer matrix and electrically conductive filler in which it is made by less complicated synthesis protocols but has similar quantitative conductive properties to existing conducting polymers. Therefore, PNC is a candidate for many applications, such as, light-emitting diodes, flexible electrodes, batteries and strain sensors [1]. In this study, an in-house Monte-Carlo simulation was used to investigate the percolation paths of the 3D model of nanorod filler network in the polymer lattice and estimate the nanorod concentration at percolation threshold [2]. The model also includes the nanorod filler orientation angles. We then focused on the effects of stretching lattice on the percolation threshold. The dimension of lattice length was varied with constant volume for each simulation system (incompressible material). Results of simulations showed that the percolation thresholds decreased when increasing the lattice stretching and the nanorod orientation angles have been confined by finite lattice dimension which shows there is the effect of orientations angle on the percolation threshold. Our finding will be a useful guideline for designing polymer nanocomposite as a switching sensor.

1. Introduction

Intrinsically conductive polymers (ICPs) are a class of polymers whose conductivity is an intrinsic property based on their chemical nature [3]. ICPs can be used in many applications but they also are expensive and have complex chemical synthesis routes. Polymer nanocomposites (PNCs) are alternative polymeric materials to replace high-cost ICPs. A PNC is a mixture of two materials, where

IOP Conf. Series: Materials Science and Engineering **773** (2020) 012025 doi:10.1088/1757-899X/773/1/012025

the matrix is a polymer and the filler consists of nanoparticles [4]. PNCs possesses a lower-cost and least-complex synthesis route than ICPs. The quantitative conductive property of PNCs can be adjusted to the level similar to the existing ICPs. In insulator PNCs with conductive nanorod filler, the percolation path has been established within nanorod network. As the concentration of filler is increased, nanorods interact with its neighbors and form the conductive network for transporting electrons across the material. Therefore, PNCs can transit between insulator and conductor and the concentration that transition occurred is known as the percolation threshold [5]. In this study, we used Monte Carlo simulation [6] to investigate the percolation path of the 3D model of nanorod filler network in the polymer lattice and to estimate the nanorod concentration at percolation threshold. We then investigated the effect of lattice dimension on the percolation threshold. A lattice system was set up by generating a "nanorod" model by a 3D rigid spherocylinder-shaped model, represented the conductive nanofillers. The position and orientation of nanorods were filled with uniform-random function. The electrical percolation path in a lattice was determined. The percolation probability was also evaluated by the ratio of the number of percolated lattice and the number of simulations.

2. Methodology

2.1. Model and Intersection of Nanorod

Computer simulation techniques have been used in many fields of research as a "virtual experiment" to observe behavior of systems and reduce the cost from real experiment. However, large time consuming is required for computer simulation techniques. The models are needed to be simplified to reduce system complexity and computational time [2]. In this study, polymer nanocomposites consist of insulating polymer matrix and conductive nanorod filler. Insulating polymer matrix was represented by a fixed volume with closed cuboid lattice. Conductive nanorod fillers were represented by 3D spherocylinder-shaped particles [7]. Each rod consists of an impenetrable inner hard-core to represent the nanorod material and the penetrable outer soft-shell to represent the effective range of electron tunneling effect [7]. If the soft-shell of a rod is overlapped with the hard-core of another rod, the rods are considered to be electrical contact.

2.2. Percolation Path Search

Percolation theory has been successful and widely accepted for describing the conductive transition of polymer nanocomposite. The PNCs exhibit a transition from "insulator" to "conductor" when the filler concentration exceeds the critical value, so-called percolation threshold [8]. We used Monte Carlo method to solve the percolation threshold. Our in-house program starts with filling a closed cuboid lattice with randomly-positioned 3D spherocylinder-shaped particles and observe the orientations angle of each nanorod filler. After that, the percolation paths of nanorod filler network in the lattice are investigated. The simulations were performed 3000 lattices in each simulation parameter to calculate the probability of having percolation path in the lattice with Monte Carlo method. The percolation probability will be related to overall conductive property of PNCs.

2.3. Simulation Setup

Our simulation program requires several control parameters. In this study, hard-core part of a nanorod filler is 20 arbitrary unit (AU) in length and 2 AU in diameter. Soft-shell thickness (t) of a nanorod filler is 0.8 AU. Filler concentration was varied from 0 to 12 % by volume with 0.4 intervals to find the percolation threshold. The lattice was defined by a cuboid shape. The width was kept fixed at 100 AU. The height was varied by 100, 80, 60, 40 and 20 AU, corresponding to the lengths of 100, 125, 167, 250 and 500 AU, respectively (shown in Figure1). Therefore, the volume of lattice is constant (incompressible material).

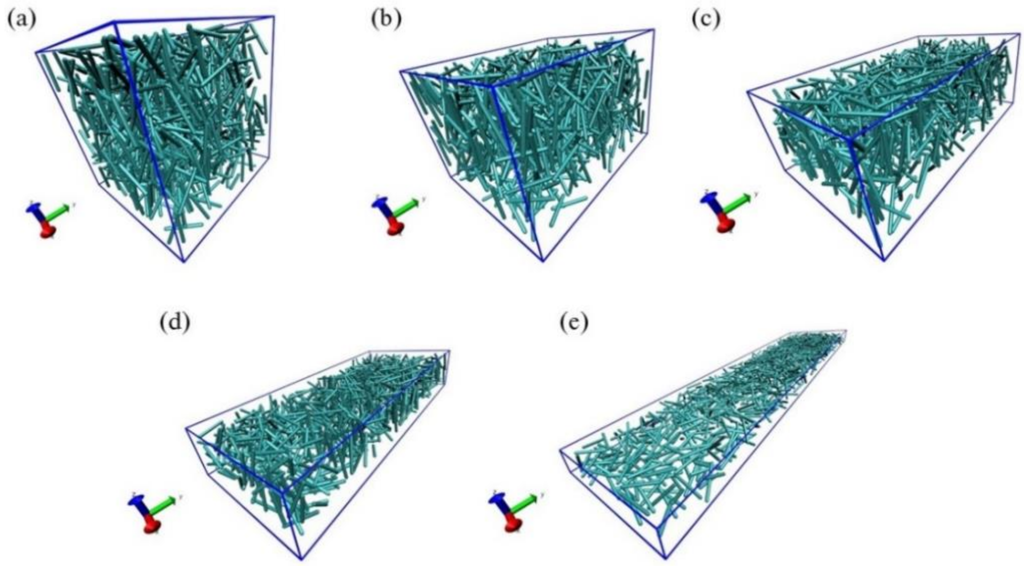

Figure 1. The lattice filling with nanorod filler at the lattice height of (a) 100 AU, (b) 80 AU, (c) 60 AU, (d) 40 AU and (e) 20 AU. Visualizations were done by Visual Molecular Dynamics(VMD)[9]

3. Result and discussion

3.1. Percolation Probability

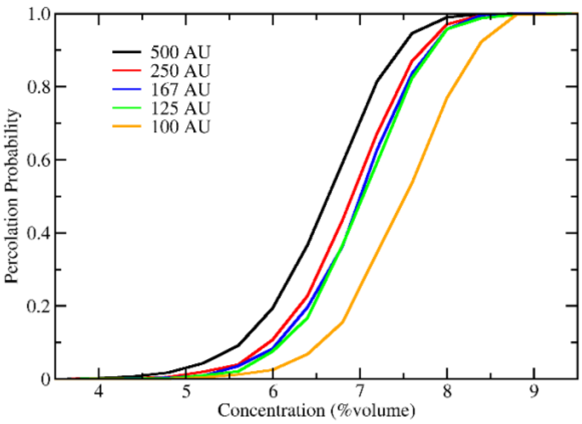

Figure 2. Percolation probability as a function of nanorod filler concentration

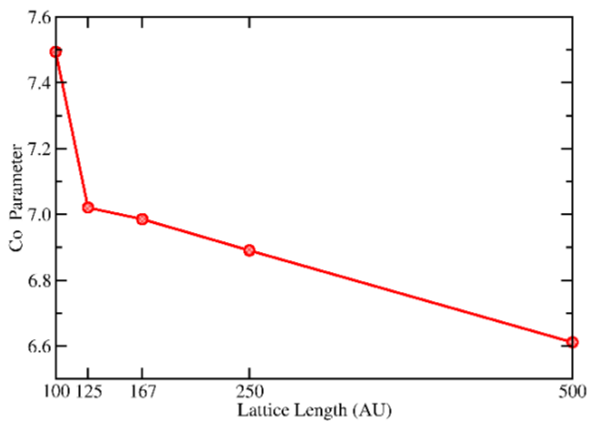

Figure 3. Percolation thresholds for different lattice lengths

The percolation probabilities with various lattice dimensions and constant lattice volume are shown in Figure 2. Percolation probability is dependent on nanorod filler concentration. The curves are S-shape and agreed well with logistic function. The curve of the lattice with long length was begun to rises up at lower concentration than the one with short lattice length. We fitted the percolation probability curves with a logistic curve and obtained the percolation threshold (C_o) parameter for the concentration value of the curve midpoint. Therefore, the percolation threshold, C_o was found approximately 7.4 %volume in the cube lattice of 100 AU and it is decreasing to 6.6 %volume when the lattice length increased to 500 AU. Percolation thresholds in this work are larger than in the previous works [5, 6] of approximately 3 - 7 %volume. Note that: the previous models were considered very thinned lattice [5] and large aspect ratio of nanorod [6].

3.2. Nanorod Orientation Angle

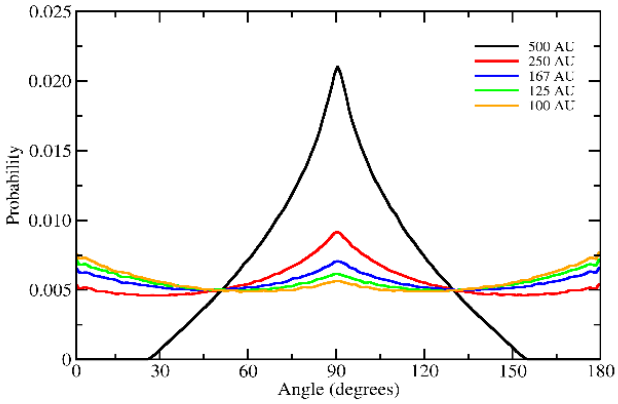

Figure 4. Distribution of nanorod filler orientations in the different lattice length at filler concentration equal to 7.2 %volume.

Orientation angles were defined by the angles between the nanorod vector and the Z-axis (parallel to lattice height). Finite size effect on the orientation of nanorod was observed in our simulation. The nanorods were confined within the long lattice length (the thinned lattice). Figure 4 shows that the probability of orientation at 90 degrees (perpendicular to the Z-axis) is higher than other angles and further increased as the increase of lattice length. At the lattice length 500 AU (with lattice height 20 AU, equal to the length of a rod), the probability of orientation at 90 degrees became significantly higher than other lattice lengths and two times higher than probability at 40 AU as seen Figure 2. The results showed that nanorod fillers are oriented perpendicular to the Z-axis when lattice was thinned in which indicated the more probability of nanorod connect to each other, the easier percolation paths in lattice form.

4. Conclusions
Monte Carlo simulations of the 3D rigid spherocylinder-shape filler model in closed cuboid lattice of polymer were used to estimate nanorod concentration at the percolation threshold. Our simulation results can show the relationship between percolation threshold and lattice length. The percolation threshold was predicted. Moreover, the percolation probability is increased as the increase of lattice length. The simulation results in this study help to understand the stretched conditions of the polymer nanocomposite with conductive nanorod filler.

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