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Monte Carlo simulations of nanorod filler in composite polymer material

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Abstract Conductive polymer (CP) is a special class of polymeric materials with conductive property which possesses high potential for the fabrication of future advanced electronic devices. To design a higher conductivity polymer, composite polymer material with conductive nanorod filler is one of alternative ideas to replace the high-cost intrinsically conductive polymeric materials. In this study, our in-house Monte-Carlo simulation was performed to generate a number of randomly-positioned nanorods within a 3D confined-space box and to assess percolation paths formed by nanorods that connected two electrodes for each configuration. The results showed that the probability of finding connection path was related to the concentrations of nanorod filler in 3D confined-space box. The increasing probability to find connection paths when adding more filler concentrations was found to be a logistic growth, in which growth rate and threshold concentration depended on soft-shell filler radius. Our finding will be beneficial for designing composite conductive polymer for switching sensor.

1. Introduction

Conductive polymer (CP) is a special class of polymeric materials with electronic and ionic conductivity [1] that can be used in many applications such as sensors and rechargeable battery. Moreover, their organic properties can be used to control drug delivery system. However, CPs are expensive and poorer mechanical properties than other classes of polymeric materials [1]. One of the solutions to develop the properties of conductive polymer is to design the composite polymeric materials with conductive nanoparticles filler. The conductive polymers nanocomposites [2] can be used as an alternative for CPs. In order to obtain the design for nanocomposites with desired mechanical properties, computer simulations have been used as a virtual experiment to observe behavior of system that greatly reduce time consuming and cost from trial and error processes in the laboratories. However, the complex system, such as nanocomposites, still consume remarkably large amount of computing resources. Therefore, the system must be simplified to reduce computational time. In this study, a polymer composite system with nanowire fillers was represented by a closed cubic box filled with uniformly sized spherocylinder. The electrical percolation behaviors at different concentrations, electronic interaction ranges and sizes of the confined-space box were investigated, as the composite became conductive when the filler concentration reached the percolation threshold [3]. The effects of spherocylinder filler concentrations on the conductivity were determined from the probability of percolated path formation in a large number of nanorod configurations.

2. Methodology

2.1. Hard-core with Soft-shell Spherocylinder Model for Nanorod Fillers

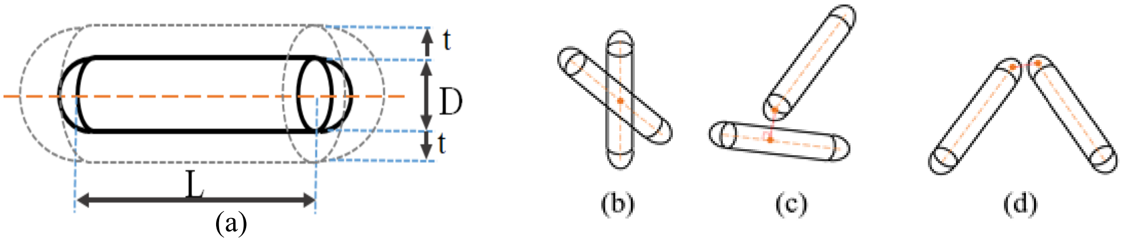


Figure 1. (a) A filler particle model consisting a spherocylinder hard-core made of two hemispheres of diameter (*D*) connected by a cylinder of length (*L*) with similar diameter and the outer of thickness (*t*). Three possible contacts patterns for nanorod electrical consist of (b) side-to-side, (c) side-to-end and (d) end-to-end.

In this study, the rod-like filler particles were represented by 3D spherocylinder-shaped particles [4]. Each of them consists of a rigid and impenetrable inner hard-core to represent the nanorod material and the penetrable outer soft-shell to represent the effective range of electron tunneling effect and the interactions between the matrix and filler (see figure 1a). If the soft-shell of a rod penetrate to touch the hard-core of another rod (The minimum distance between filler was less than sum of a soft-shell filler thickness and twice a hard-core filler radius.), they are considered to be in electrical contact Figure 1(b-d) display three possible types of electrical connections in the model [4].

2.2. Software Methods and Simulation Setup

Our in-house python program was developed to generate a number of randomly-positioned individual spherocylinder filler units in a confine-spaced box (Nanorods were only allowed to be within the box.) and to determine the probability to find a percolated path that represent the conduction of the composite. The program consisted of three main parts. In the first part, the program randomize the position and orientation for each filler unit within the confine-spaced box and avoid overlapping between the hard-cores of all fillers. Then, in the second part, the program determined the list of connected filler units as defined in section 2.1 and searched for percolated path. The last part of the program considered whether existence of a percolated path. A continuous network of nanorod filler units formed between two opposite sides of the confined-space box in the system is defined as 'conductivity' (see figure 2). The processes were repeated many times in order to calculate the probability of conductivity for each system condition.

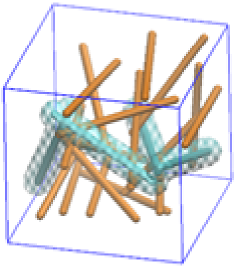


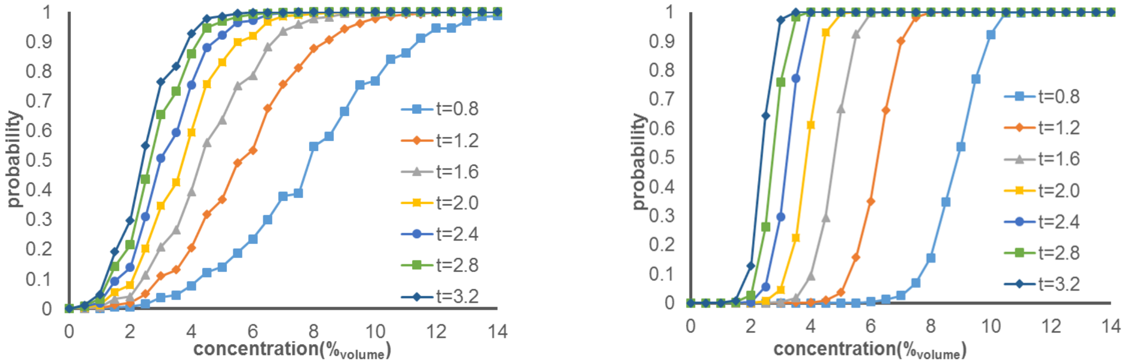
Figure 2. Example of confine-spaced box. The percolated or 'conductive' path is shown in cyan.

In this study, dimensions of the nanorods and the confined-space box, nanorod concentrations and electronic interaction ranges were varied to see their effects on conductivity. Hard-core part of a spherocylinder filler length is 20 Arbitrary Unit (AU) and diameter is 2 AU. Filler concentration was varied from 0 to 15 % by volume with 0.5 intervals. Confined-space box was a cube of length dimension 30, 50, 70 and 100 AU. Soft-shell thickness (*t*) was varied from 0.8 to 3.2 AU with 0.4 interval to observed the impact of the electronic interaction ranges on the electrical conductivity.

3. Results and discussions

3.1. Probability of Electrical Conductivity

In this study, our in-house python program be used to simulation confined-space box matrix with uniformly sized spherocylinder filler model to analyze the probability of electrical conductivity(*P*) as a function of confined-space box sizes, filler's concentrations(*C*) and filler soft-shell thicknesses. The results for several conditions that varied filler's concentrations and soft-shell thicknesses (constant confined-space box size) are shown in figure 3.



(a) (b)

Figure 3. Percolation probability of nanorod filler confined within the confine-spaced cube of dimensions (a) 30 AU and (b) 100 AU. 3000 samples were calculated as function of nanorod filler concentration at different soft-shell inner thickness (*t*). The nanorod filler length (*L*) was set at 20 AU.

As figure 3 shown, the conductivity probability increases slowly from zero when filler's concentration rise up, and the increasing positions from zero depend on soft-shell thickness. When concentration rise up, the filler's concentration at the half of maximum probability is called "critical filler's concentration". Critical filler's concentration depends on soft-shell thickness and confined-space box size. At high filler's concentration, probability of electrical conductivity at any soft-shell thickness rise up to maximum probability. Each curve line in figure 3 is concordant to basic shape of the curve of a logistic function. Therefore, relationship of the systems can be described by logistic function.

3.2 Logistic Function

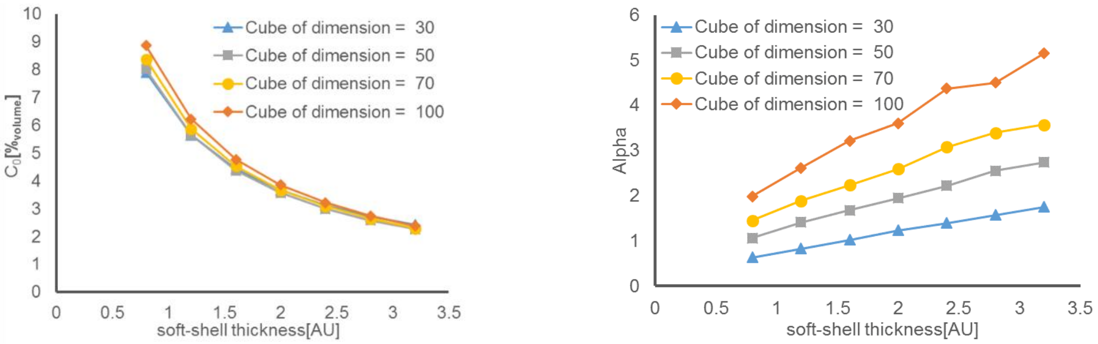
Logistic function is a common “S” shape curve with equation (1):

$$\mathrm{f}(x) = \frac{L}{1+\mathrm{e}^{-K(X-X_0)}}. \tag{1}$$

Where X_0 is the x-value of curve’s midpoint, L is the curve's maximum value, and K is the steepness of the curve. Variable in equation (1) can be compared to variable of logistic function. Critical filler’s concentration (C_0), maximum probability and growing rate of probability (α) are standed for X_0, L and K respectively. Therefore, the applicable function for this study is shown in equation (2),

$$P(C) = \frac{1}{1+\mathrm{e}^{-\alpha(c-c_0)}} \tag{2}$$

Logistic function variable that fitting curve to the result be found as shown in figure 4. The fitting parameters α and C_0 are shown in figure 4 (a) and 4 (b), respectively. Both figures show that α and C_0 depended on soft-shell filler thickness in any confined-space box size but the ratio are different. The results suggested that probability of electrical conductivity not only depends on filler’s concentration but also on soft-shell filler thickness.



(a) (b)

Figure 4. (a) critical filler concentrations (L_0) as function of soft-shell thickness (t) at different box dimension and (b) probability growth rate (α) as function of soft-shell thickness (t) at different box dimension

4. Conclusions

The in-house python program is capable of generating a number spherocylinder filler in a confined-space box and adjusting several parameters such as filler concentrations and soft-shell radii in order to calculated probability of electrical conductivity on the basis of Monte Carlo simulations. The results show that probability of electrical conductivity is related to logistic function of filler concentration. The critical filler concentrations (C_0) and probability growth rate (α) are depended on soft shell thickness (t). This program can be used as an aid in studying and fabrication conductive composite polymer in switching stress sensor.

5. References

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