Effects of dispersion and orientation of nanorods on electrical networks of block copolymer nanocomposites

Shuaichao Zhang [a], Yangcong Feng [b], Nanying Ning [a], Liqun Zhang [a], Ming Tian [a,*], Jianguo Mi [a,*]

[a] State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
[b] Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510631, China

A B S T R A C T

In this article, the effects of nanorod–polymer interaction, aspect ratio of nanorods, block stiffness, and external tensile force on the microstructure and electrical properties of diblock copolymer nanocomposites have been investigated using molecular dynamics simulation. It is shown that, under suitable interactions of block-block and nanorod-block, a continuous localization of anisotropic nanorods in a continuous block with a slight uniaxial orientation can dramatically reduce the percolation threshold. Such effect is reinforced in the systems with high aspect ratio nanorods, but can be suppressed as block stiffness increases. Meanwhile, the external tensile strain breaks the continuity of the three-dimensional network but induces strong orientation along with the stretching direction, leading to a decrease of homogeneous probability and an increase of directional probability.

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1. Introduction

It is known that incorporation of conductive nanofillers into nonconductive polymer matrix can dramatically improve its electrical properties [1,2]. If the volume fraction of fillers reaches a critical value, which is called percolation threshold, a continuous network can be spread out over the polymer matrix, leading to an insulator-conductor transition. Such phenomenon is particularly intensive in block copolymers, wherein microscopic phases can be easily formulated between different blocks as well-defined spherical, cylindrical, bicontinuous, or lamellar domains at a size in the range of tens of nanometers [3–5]. It has been well addressed that selective incorporation of nanofillers in a continuous domain [6] or at the interface [7] is effective in reducing the electrical percolation threshold. Moreover, selective localization of anisotropic fillers such as carbon nanotubes may result in not only a huge improvement in electrical conductivity [8] but also in thermal conductivity [9] and mechanical [10] and photovoltaic properties [11].

The incorporation of anisotropic nanofillers in polymer matrix is anfractuous because of the additional orientational entropy [12–14], the restricted translational entropy [15,16], the depletion attraction induced by polymer conformational entropy [17,18], and the highly directed van der Waals interactions between fillers and polymer chains [19,20]. These entropic and enthalpic contributions show a synergistic effect on nanofiller localization and copolymer organization, and finally on the efficient conductive network [3]. Obviously, this behavior is not encountered for a similar copolymer system doped with spherical particles, emphasizing the role of particle dispersion under the interactions between doping particles and polymer blocks. Developing such a comprehensive understanding is uneasy due to the fact that the number of parameters controlling the behavior of the system is large; the final morphology will clearly depend on the size, shape, and concentration of nanofillers, the composition of binary copolymer, and the interaction energies between different species [21,22].

On the other hand, tensile forces are commonly involved in various processing methods, including extrusion, injection molding [23], spinning [24] or stretching [25]. These forces often play important roles in the filler morphology via the stress transfer between the matrix and the filler, and then in controlling the morphology of the conductive networks in polymer composites [25,26]. Under the stress–strain condition, the fillers will shift and rotate, resulting in the destruction and the reconstruction of conductive network [27–29].

In order to improve the conductive efficiency of polymer nanocomposites, it is critically important to make clear how the presence of the anisotropic nanofillers affects the self-assembly of block copolymers and in turn, how the microphase separation of polymer blocks affects the dispersion and orientation of the

* Corresponding authors.
E-mail addresses: tianm@mail.buct.edu.cn (M. Tian), mijg@mail.buct.edu.cn (J. Mi).

inclusions [30,31]. However, due to the complicated interactions, it is rather difficult to obtain a measurable conductivity in experiment to evaluate to which extent of individual contribution to adjust the microstructure and conductive network [32].

In this work, we employ the molecular dynamic simulation method to deal with the issue by selective localization of conductive nanorods in one phase or at interface of immiscible diblock copolymer. We focus on the morphologies of polymer nanocomposites, the dispersion and orientation of nanorods, and their conductive probabilities by exploring the major influence factors, including the aspect ratio of nanorods, the interaction strength of nanofiller-polymer, the rigidity of two blocks, and the external tensile force. Furthermore, we try to build up an open-and-shut structure-property relationship with diagrams. Thus, this study is expected to provide a theoretical guidance to obtain high conductive copolymer/nanorod composites over a wide range of block copolymer systems.

2. Models and simulation methods

For simplicity, the diblock copolymer is described by a bead-spring model [33]. Each polymer chain consists of 40 beads with diameter and mass equal to σ and m, respectively. The total number of simulated polymer beads is 24,000. The diameter of nanorod bead also equals to σ, and the number of beads per nanorod ranges from 5 to 13. The truncated and shifted Lennard-Jones potential is adopted to model non-bonded interactions, which is given by

$$U_{ij}(r) = \begin{cases} 4\varepsilon_{ij}\left[\left(\frac{\sigma}{r-R_{EV}}\right)^{12} - \left(\frac{\sigma}{r-R_{EV}}\right)^{6}\right] - U(r_{cutoff}), & 0 < r - R_{EV} < r_{cutoff} \\ 0, & r - R_{EV} \geqslant r_{cutoff} \end{cases}$$
(1)

where ε_{ij} denotes the interaction strength of different species, r_{cutoff} stands for the distance r at which the interaction is truncated and shifted to make the potential continuous, r_{cutoff} for A-block-B-block is $2^{1/6}\sigma$. For the purpose of selective location of the nanorods into the domain of B-block, r_{cutoff} for A-block-nanorod and B-block-nanorod are set to $2^{1/6}\sigma$ and $2 \times 2^{1/6}\sigma$, respectively. Thus, the A-block is the nanorod-poor phase, while the B-block is the nanorod-rich phase. All the interaction strengths are set to 1.0 except ε_{ij}, which stands for the interaction between nanorod and B-block in copolymer and varies to simulate different interfacial interaction strengths.

The interaction between the adjacent bonded beads, including both polymer chains and nanorods, is expressed by a harmonic function

$$U_{bond}(r) = k_r(r - r_0)^2$$
(2)

where k_r is set to be 10^3 and $10^4 \times \varepsilon/\sigma^2$ for polymer bonds and nanorod bonds. The bond length, r_0, is 1σ for polymer bonds and $3\sigma/4$ for nanorod bonds. To obtain straight nanorods, a bending potential is added with the form

$$U_{bend}(\theta) = k_\theta(\theta - \theta_0)^2$$
(3)

where $k_\theta = 200\varepsilon$ rad^{-2} and $\theta_0 = 180°$. For a diblock copolymer chain, the flexible segment and rigid one is connected with a free joint, and a cosine bending potential between three neighboring beads along the same polymer component can be given as follows

$$U_{bend}(\theta) = k_\theta(1 + \cos\theta)$$
(4)

where $k_\theta = 0$ for the flexible segment and $k_\theta = 10\varepsilon$ for the rigid one. In the following discussion, three different systems have been considered: flexible-flexible copolymer in which both A-block and B-block are flexible, flexible-rigid copolymer in which A-block is

flexible but B-block is rigid, and rigid-flexible system where A-block is rigid but B-block is flexible.

In NVT ensemble, the reduced density of polymer melt is fixed at $\rho* = 0.85$, which corresponds to a dense polymer. The temperature is fixed at $T* = 1.0$ through the Nose-Hoover thermostat. During the simulation, periodic boundary conditions are adopted in all three directions. The velocity–Verlet algorithm is applied to integrate the equations of motion with a time step $\delta t = 0.001$, where the time is reduced by the Lennard–Jones time (τ). It should be noted that we equilibrate all the structures over a long period of time so that each chain moved at least $2R_g$. Meanwhile, instantaneous values of the mean-square radius of gyration R_g^2 and the mean-square chain end-to-end distance R_e^2 are calculated to judge whether the system is at equilibrium. The structural and dynamical data are collected for ensemble average after equilibrium.

In order to investigate the effect of external tensile force, we divide our simulations into two parts. At first, we perform the simulation without deformation in a cubic box. Then we consider the deformation effect by setting the initial simulation box as rectangle with the same volume of the cubic one, and the cell parameters are determined based on the draw ratio. After tensile force, the rectangular box is stretched into the cubic type. As a result, the relative conductive probabilities are calculated in the boxes with the same shape.

To determine whether the conductive network is formed, one needs a criterion to judge whether any two nanorods are connected. According to the literature [34], there are three patterns of nanorod connection: (a) body-to-body; (b) end-to-end; (c) end-to-body. Tunnel conductivity theory and field launch theory [35,36] point out that any two nanorods can be connected if the shortest gap is less than the tunneling distance. The tunneling distance is not a fixed value. Here we choose 1.0σ from two aspects (one is in consideration of the sandwiched polymer chain; the other is that the ratio of the diameter of the nanotube to the maximum tunneling distance is nearly 1.0 [37]). We note that it merely affects the absolute probabilities but does not influence their regularities.

At the beginning of the computational implementation, each nanorod is assigned a site number and a cluster number. The site number is equal to the cluster number, ranging from 1 to N, where N is the total number of the nanorod. Then each nanorod is checked for connection with others. If two nanorods are connected, they will be assigned a common cluster number which is the smaller one of these two nanorods. Finally, all the nanorods with the same cluster number are in the same cluster. Therefore, different clusters are not connected. Once the network of nanorods spans one direction continuously from one side to the other, the system is conductive in this direction, whereas the polymer nanocomposite still acts as an insulator in other directions. In other words, the conduction is directional. If the nanorods network spans three-dimensional directions continuously, the system is homogeneously conductive.

At least 20 independent simulations are performed for each case to decrease the statistical error. After equilibration, more than 10,000 final configurations are dumped. The interval between any two adjacent frames is $l\tau$. The probability of conductive network formation is defined by the ratio of the number of the conductive frames to that of all frames. Finally, the number of the configuration, which is conductive in three-dimensional directions or in stretching direction, is counted, and the homogeneous probability or directional probability is determined to represent three-dimensional or one-dimensional conductivity.

3. Result and discussion

For the considered systems, it has proven that selective localization of conductive fillers in a continuous block of diblock copoly-