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Controlling the conductive network formation of polymer nanocomposites filled with nanorods through the electric field

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ABSTRACT

Facilitating the electric field to fabricate high performance polymer nanocomposites (PNCs) is always a great and promising strategy. In this work, the effect of the electric field on the conductive property of the PNCs is investigated by adopting coarse-grained molecular dynamics simulation. The translational and rotational diffusion of the nanorod gradually decreases with the increase of the nanorod aspect ratio; however, it is nearly independent of the nanorod volume fraction. Under the electric field, it exhibits a limited decrease, but more anisotropy of the translational diffusion of the nanorod. Meanwhile, the nanorods can not experience the random rotation, which is attributed to the electrostatic force. In addition, on one hand, the electrostatic force exerting on the nanorods induces the nanorod orientation, leading to the decrease of the homogeneous conductive probability; however, the electrostatic interaction induces the connection of the nanorod, resulting in the increase of the homogeneous conductive probability. Additionally, the directional conductive probability parallel to the electric field direction increases; however, the directional conductive probability perpendicular to the electric field direction shows a continuous decrease. Considering these two effects, the decrease or the increase of the homogeneous conductivity probability depends on the competition between the electrostatic force and the electrostatic interaction. The relationship among the anisotropy of the conductive probability, the nanorod volume fraction, the electrostatic force and the electrostatic interaction can be described quantitatively by an empirical formula. Another empirical formula is adopted to quantitatively describe the relationship among the percolation threshold, the electrostatic force and the electrostatic interaction. Meanwhile, the evolution process of the conductivity network structure is studied with or without the electric field. In summary, this work quantitatively describes the effect of the electric field on the conductive property of the PNCs, which can provide some useful guidances to design and fabricate PNCs with excellent conductivity properties by taking advantage of the external electric field.

1. Introduction

Conductive polymer nanocomposites (PNCs) consisting of an insulating polymer matrix and a conductive filler, such as carbon black, carbon nanotubes (CNTs) and carbon fibers, have attracted extensive attention [1–6]. As the nanofiller volume fraction reaches a critical value, a continuous path of the nanofiller network is formed in the matrix, leading to a transition from non-conductivity to conductivity. Meanwhile, the CNTs can form the connected conductive network more easily than the spherical carbon black, because of high CNT aspect ratio [7–9]. From the application viewpoint, percolation achieved at low nanofiller content can improve the electrical conductivity and reduce cost for manufacturing materials.

When the nanofillers align along one direction in the matrix, the

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obtained materials show excellent electrical conductivity along this direction. Many approaches have been investigated for the nanofiller alignment in the polymer matrix [10–16]. Among these methods, utilizing the electric field to induce the nanofiller alignment seems more practical from the industrial view. The electric field can induce the CNTs to be electrically polarized [17], which makes CNTs orientate along the electric field direction. For example, the alignment of the CNT network in an epoxy matrix is observed under the electric field [18]. Moreover, the CNT alignment induces the strong anisotropy of the electrical conductivity which is improved by four orders of magnitude along the electric field direction [19]. Namely, the formation of CNT conductive network along the electric field direction is much easier than that perpendicular to the electric field direction [20]. Meanwhile, high nanofiller volume fraction reduces the anisotropy of the composite's electrical conductivity [21]. In addition, the electric field-induced CNT alignment causes the decrease in the activation energy of the conductive pathway formation. The CNT alignment in the polycarbonate melt results in the transition from a conductor to an insulator as the electric field changes from 500 to 1 V/cm [22]. However, the activation energy of the continuous carbon black path formation keeps unchanged with carbon black alignment in the polyethylene matrix [23]. Furthermore, 1D tubular morphology endows conducting CNTs mechanical sensitivity along the electric field direction [24]. By considering structural distortion of CNT walls at crossed junctions, a new CNT percolation network model is developed [25]. The anisotropy of the electrical property of aligned CNT/polymer composites is mainly affected by the average conductive pathway density, which depends heavily on CNT alignment structure. The highest conductivity of the CNT filled poly(methyl methacrylate) composites occurs for slightly aligned, rather than isotropic dispersion of CNT [26]. At present, some works have summarized the experimental and theoretical work on the electrical percolation in the CNT/polymer composites [27–29]. However, experimental techniques are unable to intuitively analyze the variation of the conductive network and electrical properties.

Computer simulation provides another good choice to study the electrical conductivity behavior. By employing a 3-dimensional Monte Carlo study, the dependence of the percolation threshold of the three-dimensional sticks systems on the aspect ratio is reported by using randomly oriented objects [30]. Furthermore, Taya et al. [31] studies the electrical conductivity of straight short fibers in 3D systems. As the increase of the fiber flexibility, the electrical conductivity decreases significantly [32]. A partial agglomerate structure rather than the uniform structure of nanofillers can benefit the high electrical conductivity [33,34]. The shear field can induce the CNT alignment in the flow direction, which leads to the anisotropy of the electrical conductivity [33]. This behavior depends on the CNT aspect ratio and the shear rate. The electrical conductivity can be enhanced by facilitating the formation of the conductive aggregates under the shear flow, which further increases with higher curvature and aspect ratio of CNTs [35]. In addition, the increase or the decrease of the conductive property of PNCs depend on the initial nanorod dispersion state under the shear field [36].

Based on the presented research, in this work we aim to systematically investigate the effect of the electric field on the conductive behavior of the nanorod filled polymer nanocomposites via molecular dynamics simulation, which has not been investigated to our knowledge. Three kinds of conductive probabilities are considered in this work, namely homogeneous conductive probabilityΛ, directional conductive probability$\Lambda_{||}$ parallel to the electric field direction, and directional conductive probability$\Lambda_{\perp}$ perpendicular to the electric field direction. First, we characterize the microstructure and the kinetics of the nanorod in the matrix. Then, the dependence of the conductive probability on the electric field intensity (E) is analyzed. Meanwhile, an empirical formula is used to describe the change of the anisotropy of the conductive probability with the nanorod volume fraction, the electrostatic force and the electrostatic interaction. Then, we adopt another empirical formula to describe the relationship among the percolation threshold, the electrostatic force and the electrostatic interaction. At last, the evolution of the conductivity network structure is studied with or without the electric field.

2. Model and simulation methods

Here, a coarse-grained model of the PNCs is adopted. The classic bead-spring model [37] is used to simulate polymer chains consisting of thirty beads. The total number of polymer beads is fixed at 18000. Each nanorod contains five beads (M = 5). The diameter and mass of each bead are equal to σ and m respectively. Although these chains are rather short compared to real polymer chains, they are already able to display the static and dynamic characteristic behavior of long chains. Each bond in this model corresponds to three to six covalent bonds along the backbone of a real chemical chain when mapping the coarse-grained model to a real polymer.

The truncated and shifted Lenard-Jones (TSLJ) potential is used to compute the non-bonded interactions between all beads:

$$U(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - U\left(\mathrm{r_{cutoff}}\right) & r < r_{cutoff} \\ 0 & r \geq r_{cutoff} \end{cases} \quad (1)$$

In this equation, the constant term U(r_{cutoff}) refers to the standard 6–12 LJ potential energy at the cutoff distance r_{cutoff}. It can satisfy the condition that the potential is continuous everywhere. r is the distance between two interaction sites. The polymer-polymer interaction parameter and its cutoff distance are $\varepsilon_{pp} = 1.0$ and $r_{cutoff} = 2^{*}2^{1/6}$. And the nanorod-nanorod interaction parameter and its cutoff distance are $\varepsilon_{nn} = 1.0$ and$r_{cutoff} = 1.12$. The polymer-nanorod interaction parameter ε_{np} is 1.0 with its cutoff distance $r_{cutoff} = 2.5\sigma$, which stands for weak attractive interaction. Since it is not our aim to study any specific polymers, the mass m and the diameter σ of each bead is set to be unit. Thus, all calculated quantities are dimensionless.

Additionally, the bonded interaction between the adjacent beads including both polymer chains and nanorods is represented by a stiff finite extensible nonlinear elastic (FENE) potential:

$$V_{FENE} = -0.5kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] \quad (2)$$

where $k = 30\varepsilon/\sigma^2$ and $R_0 = 1.5\sigma$, guaranteeing a certain stiffness of the bonds while avoiding high-frequency modes and chain crossing.

The rod-like character of the nanorod is enforced by a bending potential, given by

$$U_{angle} = K(\theta - \theta_0)^2 \quad (3)$$

where θ is the bending angle formed by three consecutive rod beads, K is equal to 1000 and θ_0 is set to be 180.

First, we put all the polymer chains and nanorods into a large box. Then the NPT ensemble is adopted to compress the system, where the temperature and pressure are fixed at $T^{*} = 1.0$ and $P^{*} = 0.0$ respectively by using the Nose-Hoover temperature thermostat and pressure barostat. Periodic boundary condition is employed in all three directions. The velocity-Verlet algorithm is applied to integrate the equations of motion with a timestep of