



Dynamic Monte Carlo simulations of effects of nanoparticle on polymer crystallization in polymer solutions



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ABSTRACT

The presence of different nanoparticles can result in different polymer crystallization behaviors. Dynamic Monte Carlo simulations were used to study the effects of filler dimension and size on polymer crystallization. One-dimensional nanoparticle has the strongest ability to induce polymer crystallization, and can induce the formation of crystals with uniform orientation. The system filled with two-dimensional nanoparticle has the stronger crystallizability than that filled with zero-dimensional nanoparticle. Two factors, i.e., surface area and segmental orientation in interfacial regions, contribute to the different crystallizability. Further simulations revealed that more surface area can result in more interfacial oriented segments. In addition, it was found that the decrease of the length of one-dimensional filler causes the decrease of polymer crystallization rate and number of crystal lamellae. The decrease of the length of one-dimensional filler also leads to the drop of the degree of segmental orientation in interfacial regions, and thus crystal orientation was disrupted. These findings indicate that polymer crystallization behaviors could be effectively controlled by the addition of different nanofillers.

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1. Introduction

To design new polymer materials with excellent physical properties, researchers are focused on the investigation of polymer nanocomposites with tailored structures [1,2]. Physical properties, such as mechanical, electrical or thermal properties, can be dramatically improved by the addition of a small amount of nanofillers [3–5]. Then, reinforcement mechanism and structure control of polymer nanocomposites become one of the research hotspots in the field of polymer science and engineering. For semicrystalline polymers, the improvements in physical properties are mainly derived from the changes of polymer crystallization behaviors due to the addition of nanoparticles [6–8]. Nie et al. reported that the addition of nanoclay can effectively improve the resistance to crack growth in natural rubber due to the enhancement of ability of strain-induced crystallization [9].

On the one hand, nanoparticles can supply effective heterogeneous nucleation sites for polymer chains and induce the reduction of free-energy barriers for crystal nucleation [10], leading to the acceleration of polymer crystallization kinetics [6,10–12]. For instance, Li et al. observed that the presence of carbon nanotubes (CNTs) can significantly shorten crystalline induction time and

increase final crystallinity of poly(L-lactide) (PLLA) [13,14]. Müller et al. even found that CNTs can produce supernucleation effects on crystallization of polyethylene (PE) and poly(ε-caprolactone) (PCL) [15–17]. On the other hand, the inclusion of nanoparticles may result in the changes of polymer crystalline morphology. Li et al. observed that CNTs can induce the formation a novel nanohybrid shish-kebab (NHSK) structure in polymer solutions, in which CNTs act as shish and induce crystallization of polymer chains on filler surface to form crystals with orientation along the long axis of the fillers (kebabs) [18]. These changes of crystalline morphology can directly influence final properties of crystalline polymers. Fu et al. found that the tensile strength and modulus of polymer nanocomposites were dramatically improved due to the appearance of the NHSK structure [6,8].

However, it should be noted that there are some factors influencing polymer crystallization behaviors. For instance, polymer crystallization behaviors are closely dependent on filler dimension. Nowadays, two kinds of nanoparticles with different dimensions, i.e., one-dimensional CNTs and two-dimensional graphene nanosheets, have attracted considerable attentions due to their great potential for the improvement of physical properties of polymer materials. The two different nanoparticles exert different effects on polymer crystallization. Xu et al. observed that CNT has a stronger ability to induce polymer crystallization compared with graphene [19]. Subsequently, Yang et al. applied molecular

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dynamics (MD) simulations to investigate the crystallization of alkane melts induced by CNTs and graphene, and their findings provide a support at molecular level for the corresponding experimental observations [20].

Filler dimension can also influence polymer crystalline morphology. The NHSK structure formed on the surface of CNTs exhibits uniform crystal orientation. However, crystal lamellae nucleated on the surface of graphene nanosheets always show random orientation [19–21]. Since polymer crystalline morphology determines macroscopic properties of polymer materials, it is very meaningful for researchers to achieve precise tailoring of polymer crystalline morphology. Prior to the realization of precise tailoring of crystalline structure, the microscopic mechanism of polymer crystallization induced by nanoparticles with different dimensions should be first understood. Nowadays, molecular simulation is considered as another powerful research tool that can be used to reveal microscopic mechanism of experimental results [22–27]. Up to now, most of simulation works are focused on polymer crystallization induced by anisotropic nanofillers (one-dimensional or two-dimensional fillers) rather than isotropic ones (zero-dimensional fillers) [20,28–32]. For zero-dimensional nanoparticles, all the three dimensions are in nanoscale. For instance, fullerenes are considered as the zero-dimensional nanoparticles. Using MD simulations, Yang et al. found the presence of two stages (adsorption and orientation) in isothermal crystallization process of single PE chain on single CNT [29]. Jerónimo et al. observed that the detailed organization process of single PE chain on the surface of CNTs at the early stage of crystallization is closely dependent on chain topology [28]. Previously, we performed dynamic Monte Carlo (MC) simulations to study the nucleation process of NHSK structures in polymer solutions [33,34], the crystallization behaviors of polymer chains grafted on filler surface [35–37] and the co-effects of chain orientation and one-dimensional nanofillers on polymer crystallization [38].

In the present paper, we further used dynamic MC simulations to comparatively study polymer crystallization induced by nanofillers with different dimensions (zero-, one- and two-dimensions, respectively) or sizes in polymer solutions. It was found that both the changes of filler dimension and size can induce the variations of polymer crystallization rate and crystal orientation. These current simulation findings can provide some new ideas to control polymer crystallization behaviors or crystalline morphology by the addition of nanofillers with different dimensions or sizes. Then, “engineered, designed and tailored” polymer nanocomposites could be prepared based on the relationships between microscopic structures and macroscopic physical properties.

2. Simulation details

In dynamic on-lattice Monte Carlo simulations, polymers can move on lattice space according to a micro-relaxation model. Chains can either jump in local regions or slide along local chain sections [39]. On the one hand, the occurrence of such sliding moves greatly increases the rate at which the polymers can sample configuration space. On the other hand, this motion mode mimics the real dynamics of polymers. For this reason, this micro-relaxation model allows us to gain some insights into the dynamics by which an initial nonequilibrium state of the polymer system relaxes.

Firstly, a lattice box with the size of 64^3 cubic cells was established. Then, 256 lattice chains, each with the length of 128 monomers, were regularly put into the simulation box. In this condition, the occupation density of polymer chains was 0.125 to mimic a dilute polymer solution. The coordination number of each lattice site was 26, containing 6 neighbors along lattice axes, 8 long body

diagonals and 12 along face diagonals. In order to reveal the effect of filler dimension on polymer crystallization, one nanoparticle with different dimensions, i.e., the zero-dimensional nanoparticle with the size of $8 \times 8 \times 8$ (XYZ) lattice sites, the one-dimensional nanoparticle with the size of $57 \times 3 \times 3$ (XYZ) lattice sites and the two-dimensional nanoparticle with the size of $16 \times 16 \times 2$ (XYZ) lattice sites, was placed at the middle of the simulation box, respectively, as shown in Fig. S1 in supporting information. The surface details of these nanoparticles were ignored. The long axis of the one-dimensional nanoparticle was parallel to the X-axis of the simulation box. The normal direction of the surface (XY plane) of the two-dimensional nanoparticle was along the Z-axis of the simulation box. The zero-, one- and two-dimensional nanoparticles occupied 512, 513 and 512 lattice sites, respectively, and thus the volume fraction of the fillers for the three systems was almost the same (about 0.002). The calculated surface area of the three kinds of nanoparticles was listed in Table 1. The vacancy sites that were not occupied by polymer or filler played the role of solvent. The interaction between polymer and solvent was ignored. It should be noted that one lattice site could be only occupied by one monomer or one filler site, and double occupation would be rejected. Chain motion in the simulation box could be achieved using a micro-relaxation model [39], during which a monomer jumped from an occupied site to a neighboring vacancy site, or slide in a local section along the chain. In order to eliminate confinement effect of the lattice box, periodic boundary conditions were introduced along X-axis, Y-axis and Z-axis directions.

The conventional Metropolis sampling algorithm was used to judge each trial move with the potential energy penalty

$$E = cE_c + pE_p + bB + \sum_i f_i E_f \quad (1)$$

where E_c denotes the potential energy change due to one non-collinear connection of consecutive bonds along the chain, reflecting the chain flexibility, E_p is the potential energy change caused by one pair of nonparallel packed bonds, reflecting the molecular driving force for polymer crystallization [40], B is the potential energy change for one monomer-filler pair, representing the strength of polymer-filler interaction, E_f represents a frictional barrier for one pair of parallel-packed bonds hindering chain sliding diffusion in crystals [41], c is the net change of non-collinear connection pairs of consecutive bonds along the chain, p is the net change of nonparallel packed pairs of neighboring bonds, b is the net change of pair contacts between monomers and filler, and $\sum_i f_i$ is the number of parallel neighbors of the i th bond along the path of local sliding diffusion. Herein, the value of E_p/E_c was fixed at 1 to ensure a proper chain flexibility, the value of E_f/E_c was set to 0.02 for a high mobility of chain sliding in crystals, the value of B/E_c was chosen as -1 (the minus means that there is attractive interaction between polymer and filler), and the reduced system temperature kT/E_c (k is the Boltzmann's constant and T is the temperature) was set to 2.7 for polymer crystallization.

The initially regularly arranged chains were relaxed to obtain a random-coil state for 10^6 MC cycles under athermal condition, as seen in Fig. 1 (one MC cycle represents the step when each monomer has one chance to move on average. The athermal condition

Table 1
The volume and the surface area of one nanoparticle with different dimensions.

	Zero-dimensional filler	One-dimensional filler	Two-dimensional filler
Volume (lattice sites)	512	513	512
Surface area (lattice sites)	384	702	640

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