Effect of the polymer-substrate interactions on crystal nucleation of polymers grafted on a flat solid substrate as studied by molecular simulations

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ABSTRACT

The crystallization behaviors of three types of polymer systems grafted on a flat solid substrate with different grafting densities were investigated by dynamic Monte Carlo simulations. For both of the systems with low and medium grafting densities, nucleation induction period becomes shorter with the increasing polymer-substrate interactions. However, the nucleation mechanisms are different. For the systems with low grafting density, the increase of the attractive interactions results in the enhancement of heterogeneous nucleation process of grafted polymers. For the systems with medium grafting density, the attractive interactions can compensate for the conformational entropy loss induced by the restriction of the substrate, resulting in the increase of local segment density near substrate surface and the improvement of nucleation ability. Meanwhile, nucleation mode changes from intermolecular fringed-micelle nucleation to intramolecular chain-folding nucleation with the increasing interactions. For the systems with high grafting density, crystallization behaviors are almost not affected by polymer-substrate interactions. These findings are helpful to reveal the microscopic mechanism of crystallization behaviors of polymer nanocomposites and the corresponding reinforcement mechanism.

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1. Introduction

Crystallization behaviors of polymers, including crystal nucleation, crystallization kinetics, crystal orientation and crystalline morphology, can be changed significantly, when polymer chains are grafted onto substrate or filler surface. Recently, crystallization behaviors of some grafted polymer systems have been studied [1—8]. Some publications reported that the grafting of polymer chains results in the improvement of polymer crystallizability [9—12]. However, some different experimental results have also been reported [13,14]. For instance, Díez-Pascual et al. grafted aminated poly (phenylene sulphide) on carbon nanotubes (CNTs) and found that CNTs may play an inactive nucleating role [13]. As is well known, interfacial interaction is also an important factor that can directly influence polymer crystallization [13]. Ning et al. demonstrated that the presence of interfacial interactions can promote polymer crystallizability [15]. By adding a small amount of

CNTs into poly(ʟ-lactide) (PLLA), Li et al. found that crystalline induction time is shortened and final crystallinity is increased due to the strong interactions between polymer chains and CNT surface [6,16]. By grafting end-functionalized polypropylene (PP) onto graphene oxide (GO), Terano et al. found that both covalent grafting of PP and non-covalent interactions contribute to the improvements of polymer crystallizability and mechanical properties [17]. Apparently, interfacial interactions can affect chain conformations of grafted chains. The crowding of the grafted chains will induce the "standing" of these chains, while the presence of the interfacial attractions will cause the "lying" of the chains on the filler surface. These changes of chain conformations can further influence the crystallization process of the grafted chains. However, it is difficult to quantitatively measure the strength of the interfacial interactions in experiments. Thus, the microscopic mechanism of the effects of interfacial interactions on crystallization behaviors of grafted polymers has not been revealed completely.

Nowadays, molecular simulations have been used to directly explore micro-structural variations of polymer materials at molecular scale, which can make up for the deficiency of experimental measurements [18—29]. Some research groups have successfully

performed molecular dynamics (MD) or Monte Carlo (MC) simulations to study the effects of nanofillers on polymer crystallization [22,30−33]. However, to the best of our knowledge, simulation studies on crystallization behaviors of grafted polymers are lacking. Recently, we have investigated the microscopic process of crystallization behaviors of polymers grafted on a substrate by dynamic MC simulations of cubic lattice model [34]. Some experimental results were reproduced and the mechanism of the corresponding crystallization behaviors can be understood at molecular scale. However, the interfacial interactions were not taken into account. In the current paper, we further pay attention to the effects of polymer-substrate interactions on crystallization behaviors of grafted polymers. We found that the polymer-substrate interactions play different roles in the systems with different grafting densities.

2. Simulation details

Herein, dynamic MC simulations of cubic lattice model [19−21,34−36] were adopted to study the effects of interfacial interactions on the crystallization behaviors of three grafted polymer systems with various grafting densities at the specified temperatures. Firstly, a simulation box with 32^3 cubic lattices was constructed. Then, a plane with the thickness of 1 lattice site that represents a two-dimensional substrate was placed at the bottom of the box, as shown in Fig. 1a of the previous paper in this series [34]. Subsequently, the grafted chains were regularly put in the box, and each chain consists of 31 segments. All of the chain heads (i.e., the first segments) were grafted on the substrate. Initially, all of the chains were extended along the Z-axis direction, as shown in Fig. 1b of the previous article [34]. Simulations were carried out for three types of grafted polymer systems with low grafting density, medium grafting density and high grafting density, respectively. The distributions of the grafting segments for the three types of the systems are illustrated in Fig. 2 of the previous article [34]. In the current paper, only three types of the systems with the chain

number of 49 (low grafting density), 128 (medium grafting density) and 256 (high grafting density), respectively, were selected. Correspondingly, the grafting densities (the ratio of number of grafting segments to number of lattice sites of the substrate surface) of the three types of the grafted systems are 0.0479, 0.125 and 0.25, respectively. In the simulation box, one lattice site could only be occupied by one segment or one substrate site. Double occupations of one site by two segments or by one segment and one substrate site were not allowed. The bonds formed by two consecutive segments could be oriented along lattice axes or along diagonals. The grafted chains could move in the lattice box according to the micro-relaxation model [19,20]. A segment could jump in the box from an occupied site into a neighboring vacancy site, or slide along the chain. In addition, periodic boundary conditions were introduced only along X-axis and Y-axis directions, and the chains were not allowed to pass through the substrate.

The conventional Metropolis sampling algorithm was used for each attempt of segment motion. The corresponding change of the potential energy is

$$\Delta E = \Delta c \cdot E_c + \Delta p \cdot E_p + \Delta b \cdot E_b \qquad (1)$$

where E_c is the potential energy change due to non-collinear connection of consecutive bonds along the chain, which can be used to reflect chain flexibility, E_p is the potential energy change due to each pair of nonparallel packed bonds, reflecting molecular driving force for polymer crystallization, E_b is the mixing-interaction energy for one nearest-neighbor pair of segment and substrate site, reflecting polymer-substrate interactions [19], Δc is the net change of the number of non-collinear connection pairs of bonds, Δp is the net change of the number of pairs of nonparallel packed bonds, and Δb is the net change of the nearest-neighbor segment-substrate pairs. In the current simulations, the ratio of nonparallel-packed bonds potential to non-collinear potential, i.e., E_p/E_c, was set to 1 to achieve a proper flexibility of chains at crystallization temperatures, and kT/E_c (k is the Boltzmann's constant
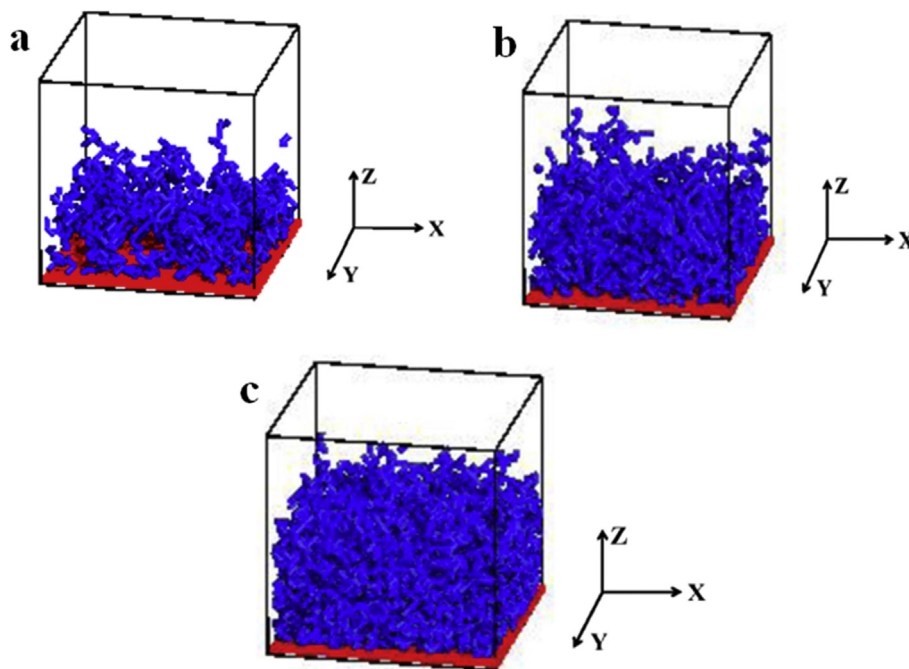

Fig. 1. Snapshots of relaxed polymer systems with the chain number of 49 (a), 128 (b) and 256 (c), in a box, respectively. The blue cylinders represent the chain segments, and the red plane denotes the two-dimensional substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)