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Epitaxial polymer crystal growth influenced by partial melting of the fiber in the single-polymer composites

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Abstract

We report dynamic Monte Carlo simulations of polymer melt crystallization induced by the same species of the fiber. We found that partial melting on the lateral surface of the fiber postpones the epitaxial crystal growth of the matrix, while the crystal growth rate has been little affected. The delay can be attributed to the recrystallization on the lateral surface of the fiber due to the prior melting. In addition, we observed the highly stretched status of those polymers melted from the fiber, which is responsible for an instant initiation of the recrystallization at a low temperature. The relevance of our results to the experimental observations of isotactic polypropylene has been discussed.
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1. Introduction

One of the main strategies in the production of reinforced polymer composites is an introduction of strong polymer fibers into the bulk polymer matrix [1]. In favor of recyclability, polymers in the fibers are often of the same species as in the matrix, from which the system is named as self-reinforced single-polymer composites, such as for polyethylene [2], for polypropylene [3,4], and for poly(ethylene terephthalate) [5]. The fibers formed by the same species of polymers will induce the epitaxial crystal growth of the bulk polymer matrix, as the well-known homoepitaxy, giving rise to the self-seeded trans-crystalline growth [6]. Such a behavior in the composite could enhance the adhesion between the fiber and the matrix [7].

Recently, the interfacial morphology of the fiber in the self-reinforced composites of isotactic polypropylene has been observed by the microscopy [8,9]. It reveals that, a thermal treatment making a partial melting of the fiber leads the transcrystalline phase to select the beta-form rather than the alpha-form in the temperature window from 100 °C to 140 °C, while without any prior melting the alpha-form has always been selected as a result of epitaxial crystal growth induced by the alpha-form fiber [8,9]. The observation was explained on the basis of a scenario showing the highly oriented status of molten polymers on the surfaces of the fiber [9]. However, up to now, the microscopic mechanism for the influence of partial melting of the fiber on the homoepitaxial crystal growth has not been studied yet.

Molecular simulations of polymers have been developed into a powerful tool in the study of the microscopic origins of polymer crystallization behaviors. Many valuable efforts have been devoted to the molecular dynamics simulations [10—22], which keep the atomistic details of structural information well, albeit with the expense of computational efficiency. Upon coarse-graining, Brownian dynamics simulations of off-lattice models earn much computational efficiency with a good balance between the efficiency and the molecular details [23—26]. Monte Carlo simulations of lattice models bear the significant advantage of fast computation for a relatively large system at various levels of sacrifice in the

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structural details [27–53]. In the simplest lattice model, polymer crystal growth has been reproduced in the unit of blocks without a rigorous consideration of chain connections [27–29]. Some lattice models forbid any micro-relaxation or reorganization of polymer conformation upon crystal growth [30–33]. The others allow the chain perform micro-relaxation in the lattice space for a spontaneous crystallization behavior [34–43]. In the last case, the crystalline order of polymers can be assigned to the parallel packing of neighboring bonds in the lattice [35–43]. Here, we will make use of the last approach to address the above issues raised by the experiments for such a large system like the single-polymer composite.

In this report, by means of dynamic Monte Carlo simulations of lattice polymers, we study polymer melt crystallization induced by a preset single fiber that is formed by the extended chains with the same species as in the matrix. The result will show that at low temperatures partial melting of the fiber postpones the induced homoepitaxial crystal growth of the matrix, while the growth rate of the latter appears little changed. In addition, the highly stretched status of polymers melted from the fiber is observed. This result provides evidence to the microscopic scenario in the explanation of the above-mentioned experimental observations.

The rest of the paper is organized as follows. After an introduction to the simulation details and sample preparation, the results on the study of the melting behavior of the fiber will be reported. Then, the crystallization behaviors of polymer matrix induced by the fibers with various periods of a prior partial melting are compared. After that, the paper ends up with a summary of our conclusions.

2. Simulation details and sample preparation

The lattice model of bulk polymers assumes that polymer chains consecutively occupy the lattice sites and perform micro-relaxation in a cubic lattice with periodic boundary conditions [44]. The micro-relaxation is realized by the monomer jumping into a neighboring vacancy site, with partial sliding diffusion along the chain if necessary. Meanwhile, double occupations and bond crossings are avoided to mimic the excluded-volume interactions between polymers. The unit of time evolution is defined as the Monte Carlo (MC) cycle that is the average amount of trial moves summed over all the monomers in the sample system.

The employed micro-relaxation model was developed from the well-known single-site bond-fluctuation model, in which the bonds were allowed to stay in the diagonals of the lattice [45]. Partial sliding diffusion has been introduced into the model [44]. The model brings new bond orientations into the middle of the polymer chain, and hence provides a high efficiency of sampling to collect more conformation of the polymers. It has been proved that with the employed micro-relaxation model, the conformation of polymers follows the Gaussian-chain statistics, and the motion of short chains reproduces the Rouse-chain dynamics [35]. Even the transition of polymer dynamics from the Rouse chain to the reptation chain

with the increase of the chain lengths has been studied by the bond-fluctuation model [46].

To construct a fiber-reinforced composite in our simulations, we first set a fiber with the size of $8 \times 8 \times 128$ (*XYZ*) at the center of a cubic lattice box (size $64 \times 64 \times 128$). Sixty-four extended chains, each containing 128 monomers, formed the fiber; and the chain ends distributed randomly along *Z*-direction with periodic boundary conditions. The amount of extended chains was chosen as a representative of the fiber at the microscopic scale, although in reality the thickness of the fiber could be much larger and the impact of the fiber to the matrix crystallization would be much stronger. Then, the other space of the box was filled with random coils of 3776 other chains in the same chain lengths to form a bulk matrix with the overall occupation density 0.9375. Some vacancy sites are necessary for the micro-relaxation of polymers, playing the role of the phantom free volume in the bulk amorphous polymer phase. The random coils were prepared by relaxing the preset fully ordered chains in the space of matrix for a long period (1.5×10^6 MC cycles) under the athermal conditions; meanwhile, those polymers in the fiber were not allowed to relax together with the matrix. Thus, the composite sample containing a (single) fiber surrounded with bulk amorphous polymers was ready to go further simulations, as demonstrated in Fig. 1. For the purpose of comparison, we also prepared the bulk amorphous polymers with the occupation density 0.9375 and no fiber in the same size of cubic lattice.

The conventional Metropolis sampling was employed in each step of micro-relaxation according to the potential energy change $\Delta E = (pE_p + cE_c)/(kT) = (pE_p/E_c + c)E_c/(kT)$, where p and c were net numbers for non-parallel pairs of neighboring
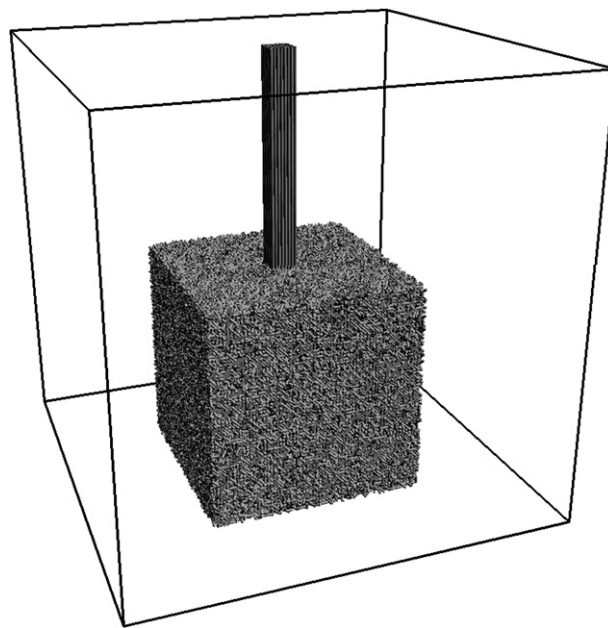

Fig. 1. Snapshot of the composite sample with $8 \times 8 \times 128$ fiber formed by the extended chains at the center of $64 \times 64 \times 128$ cubic lattice box. For clarity, only the lower half of the amorphous matrix is shown. All the polymer bonds are drawn in cylinders.

bonds and for non-collinear connections of consecutive bonds along the chain, respectively; E_p and E_c were the corresponding potential energies deviated from the fully ordered ground state; as usual, k was the Boltzmann constant, and T the temperature. In practice, we chose $E_p/E_c = 1$ that reflects the semi-flexibility of polymer chains, and set E_c/kT variable as the system temperatures. To monitor the crystallization and melting process, we defined the crystallinity to be the fraction of the bonds containing more than five parallel neighbors. The parallel neighbors of a bond were searched through 26 coordinates (lattice axes 6, face diagonals 12, body diagonals 8), and the collinear connections along the chain were not taken into account as parallel neighbors. Therefore, the criterion of five is a proper demarcation between crystalline and non-crystalline states of the bond. Furthermore, in the estimation of crystallinities, we distinguished those polymers preset in the fiber from those preset in the amorphous matrix.

In the following, we first observed the melting behavior of the fiber at high temperatures in order to make a proper thermal treatment to the fiber, and then we observed the fiber-induced polymer crystallization at low temperatures.

3. Results and discussion

3.1. Melting behavior of the fiber

We first quenched the composite sample at several selected high temperatures and allowed the polymers in the fiber to relax together with those in the matrix. In previous simulations with the same techniques [35], the equilibrium melting point of polymers with the chain length 128 has been estimated to be 5.0 E_c/k. The selected melting temperatures are thus higher than the equilibrium melting point. The time evolution of crystallinities for the polymers belonging to the original fiber reveals the melting behaviors of the fiber at high temperatures, as shown in Fig. 2.

From Fig. 2, one can see that the higher the temperature is, the faster the fiber melts. The melting process of the fiber appears as in two stages separated with different melting rates. The snapshots of the residual crystalline phase of the fiber demonstrate the differences in the melting surfaces between these two stages, as shown in Fig. 3. According to Fig. 3, the first stage can be assigned to the melting on the lateral surface of the fiber. The constant melting rate implies the interfacial-controlled mechanism of the melting. Along with the further melting on the lateral surfaces, the fiber will eventually be broken up. Thus, the extremely fast melting at the second stage includes the additional melting on the broken ends of the fiber. In other words, the second stage exhibits

Fig. 3. Snapshots of the fiber on the isothermal melting at the temperature 5.8 E_c/k for (a) 2.6×10^5 MC cycles (at the first stage) and (b) 3.5×10^5 MC cycles (at the second stage). For clarity, only the bonds having more than five parallel neighbors are drawn in cylinders.
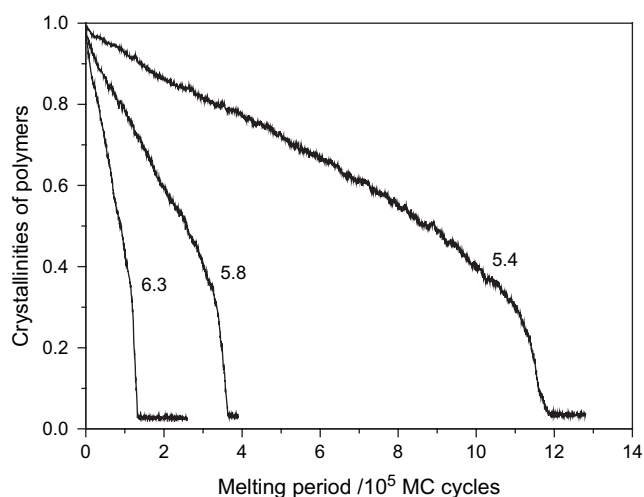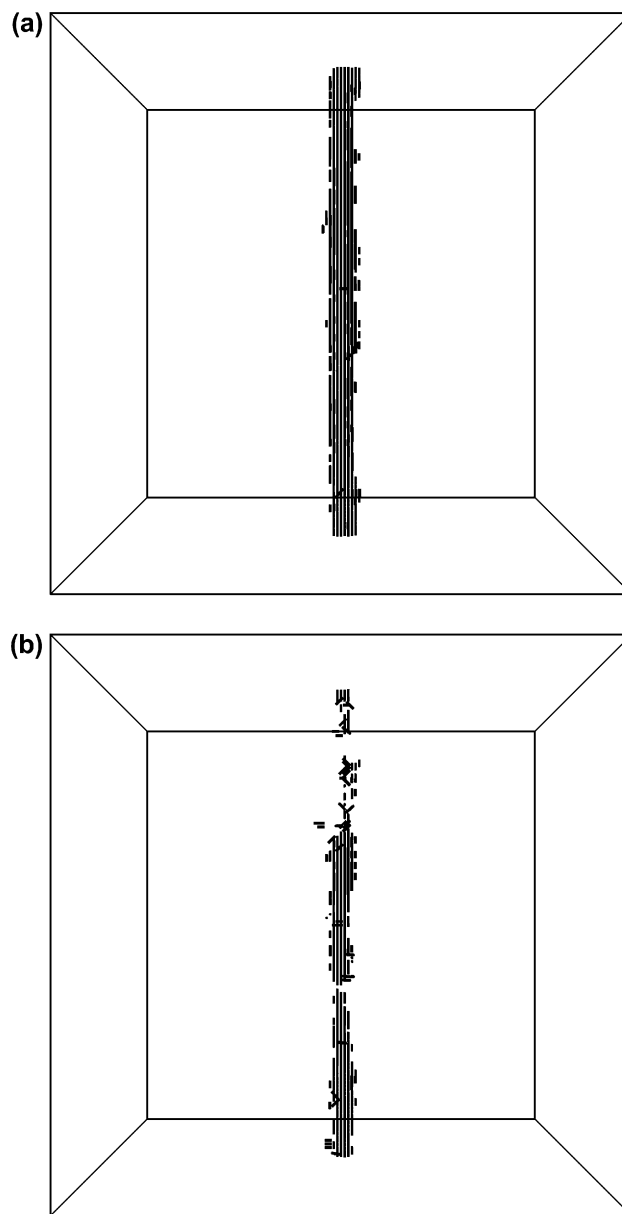

Fig. 2. Time-evolution curves of the crystallinities of polymers derived in the fiber at variable melting temperatures as denoted nearby in the unit of E_c/k. The data were collected in every 500 MC cycles. Only the segments connecting the data points were drawn for clarity.

the melting on both the lateral and the sectional surfaces of the fiber.

3.2. Fiber-induced polymer crystallization

To demonstrate the inducing effect of the fiber on polymer crystallization, we first cooled both the composite sample and the bulk amorphous polymer sample from high temperatures, and traced the crystallinities of the polymers in the matrix. In the composite sample, to avoid the fusion of the fiber at high temperatures, the polymers in the fiber were not allowed to relax together with those in the matrix. The results are shown in Fig. 4, where the cooling curves of crystallinities show the significantly advanced crystallization of the composite sample due to the presence of the fiber. The onset temperature of crystallization in the composite sample is about 4.3 E_c/k, and that in the purely amorphous polymers is about 3.8 E_c/k, so their difference is 0.5 E_c/k and the relative difference around 4.0 E_c/k is 0.5/4.0 = 0.125. Assuming in reality the crystallization temperature to be around 400 K, the fiber-induced crystallization can thus provide an advance of 50 K to the onset temperature on cooling.

The enhancement of polymer crystallization can be attributed to the epitaxial crystal growth induced by the lateral surface of the fiber [6]. In principle, the registration of the lattice in the induced crystalline order follows that on the substrate [47]. Therefore, for isotactic polypropylene, the alpha-form crystalline phase is expected as the common result of homoepitaxy on the lateral surface of the alpha-form fiber.

We then picked up several composite samples from various periods of thermal treatment at a high temperature, e.g. 5.8 E_c/k. We quenched these samples into the low temperature 4.3 E_c/k and compared the time-evolution behaviors of their crystallinities in the matrix. In this case, polymers in the fiber are allowed to relax together with those in the matrix. The time-evolution curves of the crystallinities in the matrix are shown in Fig. 5.

From Fig. 5, one can see that the longer the melting treatment, the later the initiation of the induced crystallization in the matrix. When the fiber has been completely melted for the time period 3.75×10^5 MC cycles at the high temperature, no crystallization of the matrix could be induced at the low temperature within the time window of our observations.

With a partial melting of the fiber, the induced crystallization of the matrix at the low temperature is simply postponed. The growth rates of the induced crystals (the up-going slopes of the crystallinity curves in Fig. 5) are little affected by the prior partial melting on the fiber. This implies that the partial melting of the fiber only takes a delaying effect at the initiation stage of the induced crystallization in the matrix.

To understand the microscopic mechanism of the delaying effect, we made visual inspections on the detailed morphologies of crystallites at the very early stage of crystallization. The snapshots for the induced crystallites and the fibers in the composites with and without a prior thermal treatment are shown in Fig. 6.

In a comparison between Fig. 6a and b, one can see that the recrystallization of the polymers melted from the fiber happens first, followed with the induced crystallization of the matrix on the lateral surface of the fiber; thus, within the same time periods, less crystallites of the matrix have been induced by the fiber due to a prior partial melting. The delaying effect can simply be attributed to the additional time period required for the prior recrystallization of those polymers melted from the fiber.

Fig. 6 also demonstrates the shish-kebab crystallites, which are the morphology typically observed in real polymers under shear/extensional flow [48—54]. Dating back to 1955, Keller has already observed the flow-induced row structure of polymer crystallites where the lamellar crystallites were found to
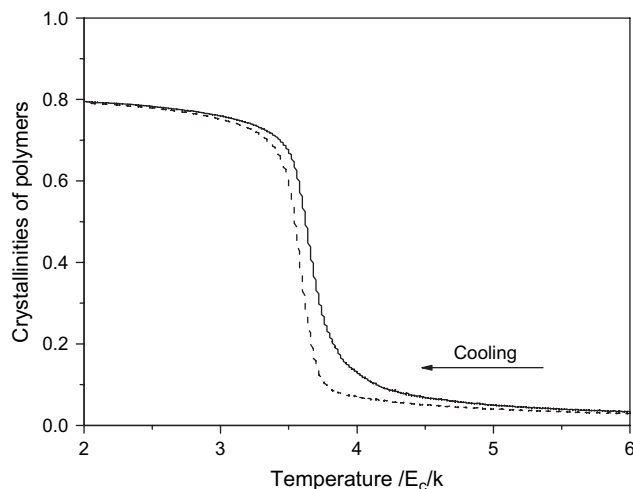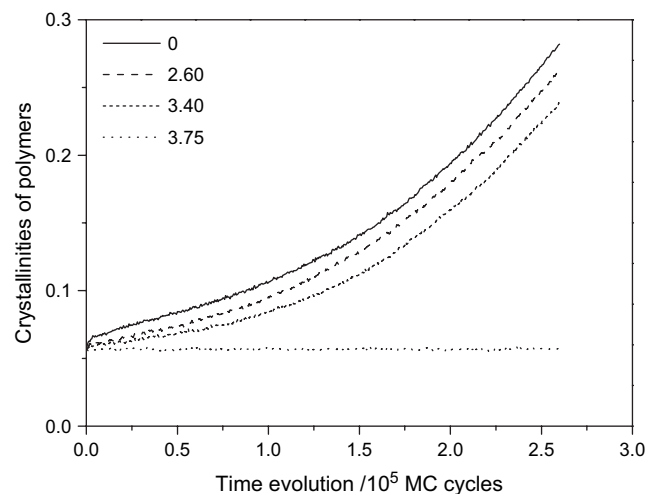

Fig. 4. Cooling curves of the crystallinities for polymers in the matrix of the composite sample (solid curve) and the bulk amorphous sample (dashed curve). The cooling program is a stepwise decrease of the temperature from 6.0 to 2.0 with the step length 0.02 and the step period 2500 MC cycles. Only the segments connecting the data points are drawn for clarity.

Fig. 5. Time-evolution curves of crystallinities for polymers in the matrix at the temperature 4.3 E_c/k, with the fiber melted at the high temperature 5.8 E_c/k for various periods as denoted in the unit of 10^5 MC cycles. The data were collected in every 500 MC cycles. Only the segments connecting the data points are drawn for clarity.

stack in parallel and the shish appeared too thin to be visible [55]. Later on, Pennings proposed the microscopic mechanism of the shish-kebab crystallites similar to the fiber-induced epitaxial crystal growth for the folded-chain lamellar crystals [56]. Recent years, this mechanism in polymer melt crystallization has become observable under the atomic force microscopy [57]. The shish-kebab crystallites play an essential role in the fiber formation upon melt spinning of polymers [58]. Even without any flow, the shish-kebab-like bundle lamellae have

been observed at the early stage of crystal growth for spherulite crystallites [59].

Upon quenching the composite with the partially melted fiber at the low temperature, there exists a competition between the recrystallization of polymers melted previously from the fiber and the induced crystallization of polymers in the matrix. In consistence with the morphological observation, Fig. 7 further demonstrates that at the very early stage of crystallization, polymers melted from the fiber have the priority to come back to the fiber if the fiber has not been completely melted. This is most probably because of their spatial occupation in the vicinity of the fiber, regarding to the fact that the polymers have no time to diffuse away from the fiber right after the melting. The initiation of the induced crystallization of the matrix appears rather gradual even when the recrystallization becomes saturated after 2×10^4 MC cycles. In contrast, the initiation of recrystallization of those polymers derived from the fiber occurs without any delay.

The instant initiation of recrystallization can be related with the fact that polymer chains right after melted from the fiber
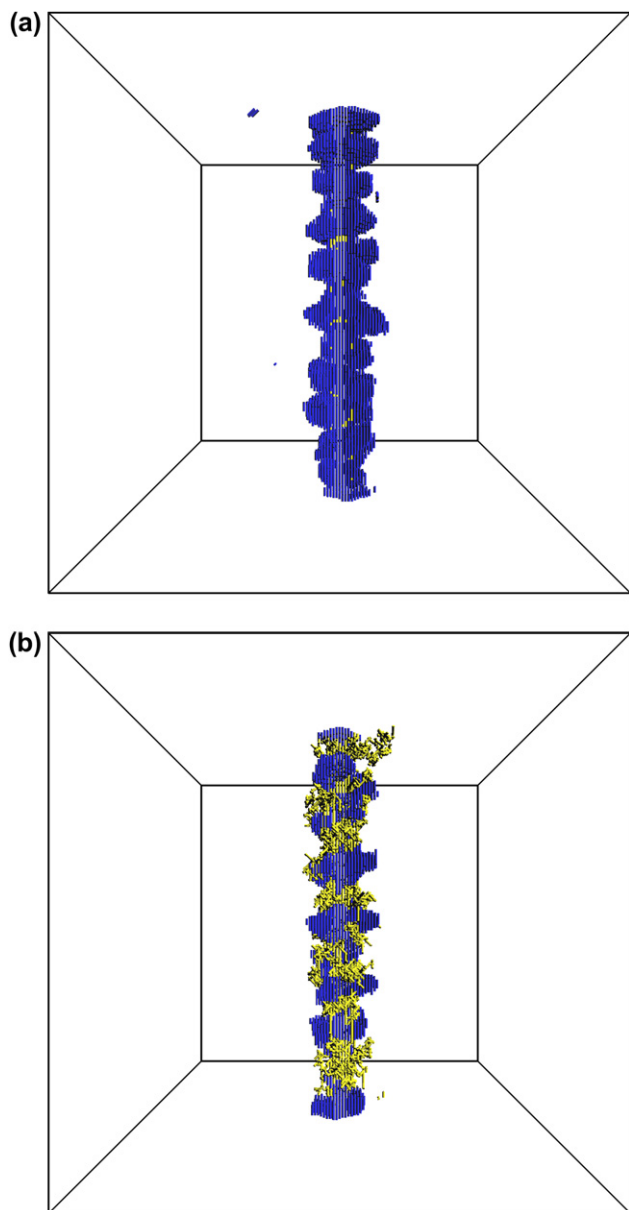

Fig. 6. Snapshots of the samples showing polymers derived from the fiber (drawn in yellow) and crystallites induced in the matrix (drawn in blue) obtained from isothermal crystallization at the temperature 4.3 E_c/k and at a period of 1.0×10^5 MC cycles. (a) The case in which the fiber has no prior melting; (b) the case in which the fiber has the prior melting at the temperature 5.8 E_c/k for a period of 2.6×10^5 MC cycles. All polymer bonds are drawn in cylinders. For crystallites induced in the matrix, only the bonds having more than 15 parallel neighbors are drawn. The white transparent stripes in the middle of the picture are due to the lattice spacing.
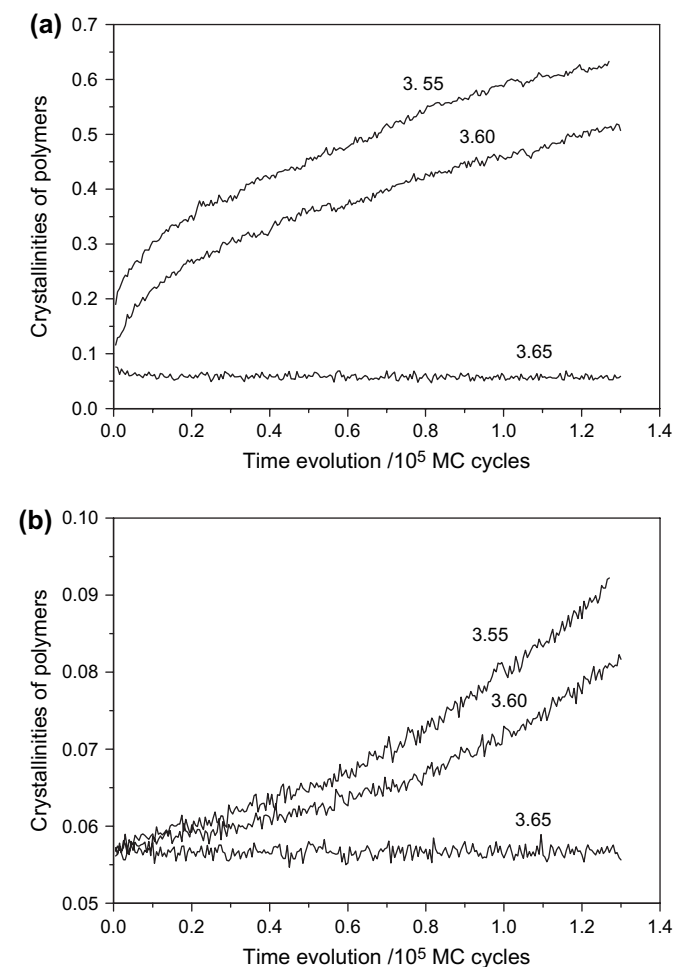

Fig. 7. Time-evolution curves of crystallinities for polymers derived from (a) the fiber and (b) the matrix at the early stage of isothermal crystallization under the temperature 4.3 E_c/k. The composite samples were thermally treated at the high temperature 5.8 E_c/k for various periods as denoted in the figure with the unit of 10^5 MC cycles.

still hold their orientational order of the fiber (more or less, even though they may lose their positional order). Under thermodynamic considerations, the oriented polymer chains have a less penalty of the entropy change in the crystallization, and thus enhance the secondary nucleation of polymer crystallization on the fiber surface. Since we have all the coordinate information of the monomers in the sample system, this advantage allows us to make estimations to the mean square radius of gyration according to the monomer distances to the coil center. If each non-crystalline bond is the bond surrounded with less than five parallel neighbors, and the polymers melted from the fiber contain more than 80% of bonds in non-crystalline, their mean square radius of gyration can be estimated as 257.0, the value much larger than that of polymers in the amorphous matrix (34.9). The large coil sizes imply a highly stretched status of polymers. In the previous simulations [37], Wang et al. have observed that the orientational relaxation of extended long-chain polymers usually requires for a long time, in comparison with that of short-chain polymers. The incompletely relaxed status of long-chain polymers offers a priority of their crystallization in the mixture with the relaxed short-chain polymers, and hence induces the epitaxial crystal growth of the latter [37]. Therefore, one can say that the highly stretched status of polymers surrounding the fiber is responsible for the instant initiation of the recrystallization.

In the experiments of polypropylene samples, it has been found that a pulling of the inset fiber could induce more beta-form transcrystalline phase in the matrix [60,61]. The pulling of the fiber will enhance the orientational order of polymers surrounding the fiber. In thermodynamic principle, the stretching of polymers will decrease their entropy of fusion and hence increases the equilibrium melting point [62]. For isotactic polypropylene, the selection of the crystalline phases depends pretty much upon the competition of the crystal growth rates between two crystalline phases [63]. With the decrease of the temperature, there exists a crossover of the crystal growth rates, below which the beta-form crystals grow faster than the alpha-form crystals and hence dominates the crystallization [63]. The shifting-up of the equilibrium melting point due to the stretching of polymers will enhance both crystal growth rates of two phases and thus moves their crossover to a higher temperature. This implies that at some specific temperatures, the preference of the crystalline phase may switch from the alpha-form to the beta-form with the increase of the orientational order of polymers due to the shift-up of the crossover temperature.

The similar situation on the orientational order of polymers surrounding the fiber can be made by the partial melting of the fiber in the composites, as observed in the above simulations. Although the lattice model employed here could not bear the atomic details of the structural information for variable crystalline forms, it is anticipatable for isotactic polypropylene in the same scenario that, at the specific temperature, the high stretching of polymers melted from the fiber may shift-up the crossover temperature to prefer the metastable beta-form upon the instant recrystallization. Following the recrystallization, the beta-form transcrystalline phase is thus induced from the matrix. At a higher temperature above the crossover, the alpha-form still dominates the recrystallization of polymers melted from the fiber as well as the epitaxial crystal growth of the matrix, as has already been observed in the experiments [8].

4. Summary

By means of molecular simulations, we have observed the polymer crystallization induced by the inset fiber with and without a prior partial melting. As the results of parallel comparisons, the delaying effect of partial melting of the fiber on the induced crystallization from the matrix has been found, although the crystal growth rate is not affected. Visual inspections on the snapshots of microscopic crystalline morphologies and the analysis on the crystallinities demonstrated that the delaying effect could be attributed to the recrystallization due to the prior partial melting on the fiber. Moreover, the highly stretched status of polymers melted from the fiber has been observed, which explains the instant initiation of recrystallization. The observation of the stretched status provides microscopic evidence to the scenario proposed to explain the beta-form transcrystalline structure in the self-reinforced composites of isotactic polypropylene.

Acknowledgements

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