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## The effect of molecular weight of polymers grafted in two-dimensional filler on crystallization behaviors studied by dynamic Monte Carlo simulations



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#### ABSTRACT

The crystallization behaviors of polymers can be changed by grafting them onto the surface of fillers. In this work, the effect of molecular weight of polymers grafted in two-dimensional filler on the isothermal crystallization behaviors was studied by the dynamic Monte Carlo simulation. The result shows that the grafted polymer system can shorten the nucleation induction period compared with ungrafted polymer systems, but its ultimate crystallinity is reduced. With increasing molecular weight, the nucleation induction period becomes shorter and the final crystallinity becomes higher. The polymer system with low molecular weight shows the intermolecular nucleation, while it exhibits the intramolecular nucleation for the one with high molecular weight. In addition, at lower molecular weights, the crystalline bonds tend to perpendicular to the filler. As the molecular weight increases, the crystalline bonds progressively inclined to deviate from the *Z* direction and return to the direction parallel to the *Z* axis ultimately. These simulation results can illustrate the micro-mechanism of the effect of molecular weight on crystallization behaviors of polymer composites from a microscopic perspective, which can provide important theoretical basis for improving the properties of polymer composites.

#### 1. Introduction

The crystallization behavior of the polymer composites, such as the nucleation mechanism, orientation, morphology, crystallization kinetics can be changed by the addition of a small amount of nanoparticles (spheres, cylinders, plates) and it is of a significant research value [1–9]. The importance of the crystallization behavior of polymer nanocomposites is not only in the scientific sense, but also in the practical application, due to the crystal structure and morphology directly determine the macroscopic property of materials, such as mechanical strength [10]. Some reports suggest that nanoparticles serve as nucleating agents during the polymer crystallization process. The addition of nanoparticles can effectively induce heterogeneous nucleation on polymer surfaces, and decrease the nucleation free energy barrier and increase the nucleation rate, during the crystallization of polymers [11–13]. Wang et al. observed the crystal structure of polypropylene after adding attapulgite. The results suggest that the crystal form of polypropylene is not change, but attapulgite could act as the heterogeneous nucleation agent of polypropylene. At the same time, the strength and stiffness of the polymer materials are significantly improved [14]. Lincoln et al. found that the nucleation isothermal crystallization rate of Nylon-6 (PA6)/Montmorillonite nanocomposites are significantly faster than that of pure PA6 and the induction time was shortened [15]. In general, the addition of filler promotes the nucleation and crystallization processes to greatly enhance the performance of composite material.

However, some studies show that, due to weak interaction between polymer matrix and fillers, it also lead to the aggregation of nanoparticles and the poor mechanical properties of the nanocomposites. To avoid this phenomenon, researchers often grafted one end of the molecular chain to the surface of the filler so that it can be stably dispersed in the polymer matrix [16-21]. According to the related reports, the nucleation, growth and orientation of polymer crystals under confined conditions are obviously different from those under unconstrained conditions. Tang et al. grafted polypropylene (PP) onto silica nanoparticles and found that the addition of nanoparticles can accelerate the crystallization rate [22]. Intensive research works revealed that grafted polymer chains onto nanoparticles can improve their crystallization ability. Jana et al. grafted poly(ɛ-caprolactone) (PCL) onto carbon nanotubes (CNTs) and found that CNTs are contribute to nucleation for the crystallinity of PCL and decease the activation energy of crystallization. In addition, the nucleation ability of CNTs increases with the grafting degree [23]. However, some studies have the opposite conclusion. Kim et al. observed that the crystallization rate of multiwalled

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carbon nanotubes (MWNTs)-grafted Polyethylene (PE) was slower than that of pure PE during the non-isothermal crystallization [24]. Li et al. studied that the crystallization behavior of CNTs-grafted PA6 during the non-isothermal crystallization and found the similar phenomena [25]. In fact, there are many factors that directly affect the crystallization process of the grafted polymer system, for example, the molecular weight of the polymer [24], the grafting density [18], the polymer-filler interaction [26], the topological structure of the molecular chain [27], the filler content [24], and so on. The inconsistent conclusions resulted from the above experiments may be due to the competition effect among these factors. It has been found that the conformation of grafted polymer can be affected by molecular weight, which also significantly changes its crystallization behavior. Jana et al. investigated the isothermal crystallization process of PCL-grafted MWNTs and found that the crystallization temperature and crystallinity of the polymer system increase with the molecular weight of the grafted PCL [20]. Zhou et al. grafted PCL with different molecular weights onto the surface of carbon and observed the influence of molecular weight on the isothermal crystallization of grafted PCL. It was found that the molecular weight of PCL in MWNTs-g-PCL affects its movement ability and the chain conformation. With the growth of the molecular weight, the activation energy of crystallization is gradually reduced, making crystallization be easier [28]. Lai et al. grafted the four-arm poly(L-lactide) onto the silica surface and found that the crystallinity and crystallization rate depend primarily on the grafting length of the four-arm poly(L-lactide). The longer grafted chains serve as nucleation sites in the polymer matrix, which significantly improves the crystallization behavior of poly(Llactide) [29]. However, the detailed micro-mechanism of the effect of molecular weight on crystallization behavior of the grafted polymer is not completely revealed yet, due to the limitations of the experimental observation scale.

The computer simulation for the condensed matter system can detect the microscopic details of the changes in the phase state of the system and the process of the segmental dynamics, and then clarify the phase change mechanism [30,31]. Previously, our research group have investigated the effect of grafting density on the crystallization behavior of polymer systems grafted on the filler by dynamic Monte Carlo (MC) simulations, and found that as the increase of grafting density, the crystal rod first parallel to the surface of filler and then tilted to the surface, finally perpendicular to the surface. In addition, nucleation mode of the polymer molecular chains also change with the increase of grafting density [32]. In this work, we further research the effect of molecular weight near the two-dimensional filler on the crystallization behavior of the grafted polymers in order to prefect the crystallization mechanism of the polymer system.

#### 2. Simulation details

We study the crystallization behavior of grafted polymers with different molecular weight by dynamic MC simulations. Firstly, we established a simulation box of  $32^3$  cubic lattice (the simulation box is divided into 33 layers and each interval is one unit length) [32-42]. Then, a plane was placed in the bottom layer of the simulation box, which represents the filler (i.e. the red layer). Subsequently, 121 chains were regularly put into the simulation box along Z-axis directions and, all of the first segments of chains were grafted on the filler, as shown in Fig. 1. For the sake of simplicity, only six grafted chains were shown in Fig. 1. With a view to studying the effect of molecular weight on the crystallization behavior of the grafted polymer system, we simulated seven grafted polymer systems with 8, 10, 12, 14, 16, 20 and 30 chain segments of each chain, respectively. On the surface of filler, a molecular chain is grafted evenly at an interval of 3 unit length. Thus, there are total 121 grafted polymer chains in a simulation box. In the dynamic MC simulation process, there are two ways of movement for the polymer chain, one is that the chain segment jumps from the original position to the adjacent space, and the other is the chain segment



**Fig. 1.** The schematic diagram of molecular chains grafted onto the filler surface in a simulation box of  $32^3$  cubic lattice. The red plane represents the filler, the yellow spheres represent the grafted chain segments, and the blue spheres denote the chain segments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

moving along the chain length direction [43,44]. It should be noted that polymer chains in the process of movement cannot interrupt original bonds, and the bond which connected two chain segments can only be oriented along the lattice shaft or the diagonal. The chains cannot pass through the underlying filler in the process of movement as well. There are periodic boundary conditions in the *X* and *Y* direction and the periodic length 32 is enough according to the previous investigation [32].

As with previous work, in order to calculate the energy change in the crystallization process, two energy parameters are introduced in the simulation process:  $E_c$  and  $E_p$ , and the energy change of Metropolis sampling in simulation is

$$\Delta E = \Delta c \cdot E_c + \Delta p \cdot E_p \tag{1}$$

where  $E_c$  is the conformational energy parameters, representing the energy increment of non trans conformation,  $E_p$  is the interaction energy parameter between two adjacent bonds, representing an increase in energy caused by the non parallel arrangement of the two nearest neighbors [33,34],  $\Delta c$  and  $\Delta p$  is the change number of corresponding non trans conformation and non parallel arrangement of the two nearest neighbors before and after sampling in simulation. In this simulation calculation process,  $E_p/E_c$  was set to 1, which represents a flexible chain [6,43]. Herein, we mainly investigated the effect of molecular weight on the crystallization behavior of the polymer systems, without considering the interaction between the polymer chains and the filler.

Firstly, the original fully straightened molecular chains was relaxed for  $10^6$  MC cycles in the non-thermal state, and the molecular chains of the random coil state were obtained, as shown in Fig. 2. It can be seen that the space occupied by the grafting molecular chains in the system in the vicinity of the filler increases as the increase of molecular weight. Subsequently, the disordered molecular chains were quenched to a reduced temperature  $T^* = 2.2$  to observe the crystallization behavior of the grafted polymer systems. In order to compare the difference of crystallization process between grafted and ungrafted polymer systems, we also simulated seven polymer/filler blend systems, the number of molecular chain segments of each system were 10, 12, 14, 16, 18, 20 and 30, respectively. In those systems, the molecular chains which in a relaxed equilibrium state occupy the entire space of the simulation box. Download English Version:

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