Crystallization of polymer chains induced by graphene: Molecular dynamics study*

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The present work is devoted to a study of the molecular mechanisms of the crystallization of polymer chains induced by graphene by using molecular dynamics (MD) simulations. From the atomic configuration translation, the number distribution of the atoms, and the order parameter *S*, the crystallization process can be summarized in two steps, the adsorption and the orientation. By analyzing the diffusion properties of the polymer chains, we find that a graphene substrate has a great adsorption for the polymer molecules and the polymer molecules need more time to adjust their configurations. Therefore, the adsorption step and the orientation step are highly cooperative.

Keywords: polymer crystallization, molecular dynamics simulations, graphene, adsorption

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1. Introduction

Polymers reinforced with nanosize materials have been paid increasing attention both in industry and in academia.[1–7] Graphene is an atomically thick, two-dimensional (2D) sheet composed of sp^2 carbons arranged in a honeycomb structure.[1] Balandin *et al*. reported that single-layer graphene has a thermal conductivity of 5000 W/(m·K), which corresponds to the upper bound of the highest values reported for SWCNT bundles.[2] Single-layer graphene is the strongest material ever measured, with a Young's modulus of 1 TPa and an ultimate strength of 130 GPa.[3] Moreover, the single-layer graphene has a very high electrical conductivity up to 6000 S/cm, and unlike CNT, chirality is not a factor in the electrical conductivity.[4] Bunch *et al.* reported that a graphene sheet is impermeable for all gas molecules.[5] These properties indicate graphene's great potential for improving thermal, mechanical, electrical, and gas barrier properties of polymers.

Of the graphene-based nanofillers, polymer/graphene nanocomposites have been studied extensively in experiments.[8–11] Ramanathan *et al.* reported the creation of polymer nanocomposites with functionalized graphene sheets, which provide a superb polymer–particle interaction.[8] Rafiee *et al.* compared the mechanical properties of polymer nanocomposites with graphene platelets, single-walled carbon nanotubes, and multi-walled carbon nanotubes additives.[9] They found the superiority of graphene platelets over carbon nanotubes. Kalaitzidou *et al.* reported that the exfoliated graphite nanoplatelets may serve as a reinforcing agent to produce multifunctional polymer composites, and they found that the thermal conductivity of the polymer matrix is enhanced.[10]

If we want to design favorable microscopic and macroscopic structures of crystalline polymers, we need to know much more about the molecular mechanism of polymer crystallization.[11] The polymer crystallization controls the structural formation processes and the final properties of the graphene/polymer nanocomposites. The polymer crystallization is usually divided into two separate processes: primary nucleation and crystal growth. Most of the experiments have been interpreted with the Lauritzen–Hoffman (LH) theory,[12,13] but the polymer crystallization still has many controversies in view of the molecular level.[14–18] Thus, computer simulation is a powerful tool for investigating the process of polymer crystallization.

The experimental results show that the graphene has a strong ability to induce the crystallization of polymer.[19] In this study, we investigate the crystallization process of the polymer (PE) melt around a single-layer graphene with molecular dynamics (MD) simulations. MD simulations can provide a molecular level description for the interfacial interaction, which includes the distribution function, bond-orientational order parameter, and diffusion coefficient.

2. Model and simulation method

Polymer/graphene nanocomposites system in this study consists of 100 PE ($C_{30}H_{62}$) chains with a single-layer graphene (28.41 Å×54.12 Å). In the beginning, 100 PE chains are randomly distributed around the single-layer graphene.

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We perform MD simulations for 300 ps at high temperature ($T = 750$ K) to confirm that the PE chains have relaxed completely (see Fig. 1). Figure 1 shows the initial randomly distributed configuration of the PE chains around the single-layer graphene. In order to observe the spatial arrangement of the PE chains clearly, we have eliminated the hydrogen atoms in the image although they present in the calculations. Then we carry out 4000 ps MD simulations at the temperatures of 470 K and 500 K, which are the possible crystallization temperatures according to the previous literature.[20]

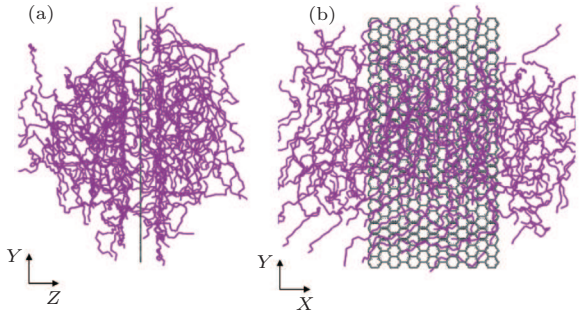


Fig. 1. (color online) Initial molecular model of polymer/graphene nanocomposites shown in (a) Y–Z plane and (b) Y–X plane.

The MD simulations are carried out with the Discover module in Materials Studio.[21] In our simulation, the time step is 1 fs and the cutoff distance is 9.5 Å. The *NVT* ensemble has been used during the simulations with undefined boundary conditions, which implies that the simulated volume is actually infinite. This method has been successfully used for the polymer composites systems.[20,22] The Anderson method is applied to control the temperature of the system.[23] The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) are used as the atomic force field.[24] The interatomic interactions are described using the second-generation COMPASS force field because it has a high accuracy in predicting the properties of polymeric materials.[25] Wu *et al*. validated that the properties of highly cross-linked polymer networks obtained with the COMPASS force field are in better agreement with experiments than the previous results with the DREIDING force field.[26] In addition, Tack *et al.* showed that the density prediction of thermosetting polymer using COMPASS is better than that using the cff91 force field.[27] The COMPASS force field potential is given as follows:[28]

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{nonbond}}, \qquad (1)$$

where E_{valence} is the valence energy, $E_{\text{cross-term}}$ is the cross-term interacting energy, and E_{nonbond} is the nonbond interacting energy.

3. Results and discussion

In order to investigate the crystallization process of polymer/graphene composites, we show in Fig. 2 the chain configurations at various time ($t = 1$ ns, 2 ns, 3 ns, 4 ns) for $T = 470$ K and 500 K. The single-layer graphene provides the nucleation sites for the PE chains, and the PE chains are continuously adsorbed to the growth surface. Because of the unique structural features of graphene, the first adsorption layer begins to align along the Y axis. Analyzing the crystallization process, we find that the first layer gives the orientation of crystallization for all other PE chains. Comparing the transition process of 470 K with that of 500 K, we can conclude that the PE chain is easier to overcome the energy barrier and adjust its configuration at a higher temperature. Figure 2 shows that the crystallization undergoes two stages. In the first stage, the PE chains adsorb on the graphene surface, and the configuration is a locally orientated ordered structure. In the second stage, the PE chains adjust their configurations and form an orientationally ordered structure. The results confirm that the graphene can act as a template nucleating agent for the polymer crystallization on its surface. Our simulations visually display the nucleation and growth mechanism of PE chains, the process is a molecular transformation from a random coil to a chain-folded crystalline.

Figure 3 shows the distribution function $\psi(Z)$ of carbon atoms along the Z axis for 470 K and 500 K at various time. The $\psi(Z)$ is the number of carbon atoms over the Z axis in a slab between Z and $Z + \Delta Z$. We set ΔZ to 1.0 Å in the present calculations. The figure reveals the following characteristics. (i) When $t = 1$ ps, only two peak appears at around 4.08 Å and -4.08 Å (see Fig. 3(b)), and no other obvious peak appears. This finding indicates that the PE chains are randomly distributed around the graphene surface. (ii) With the elapse of time, eight obvious peaks appear along the Z axis, which indicates that the CH_x groups are layered on the graphene surface. (iii) With the increase of time, the difference between peak and valley of $\psi(Z)$ keeps on increasing, which indicates that the PE chains adjust their configurations and form a highly orientationally ordered structure. Checking the figures carefully, we can find that the orientational ordering process of the PE chains has two stages. In the first stage, one layer of PE chains are adsorbed on the graphene surface in a short time because of the van der Waals (vdW) interaction between PE chains and graphene. Then, more PE chains adjust their configurations and form an ordered structure after longer time. Analyzing the ordering process of PE chains on the graphene surface (see Fig. 2), we can conclude that the geometric matching is the key factor for surface-induced polymer crystallization. Therefore, the polymer chains need more time to adjust their configurations. Figure 3(a) shows that the distances between the four crystallization layers and the graphene substrate are 4.08 Å, 8.45 Å, 12.66 Å, and 17.12 Å, respectively.

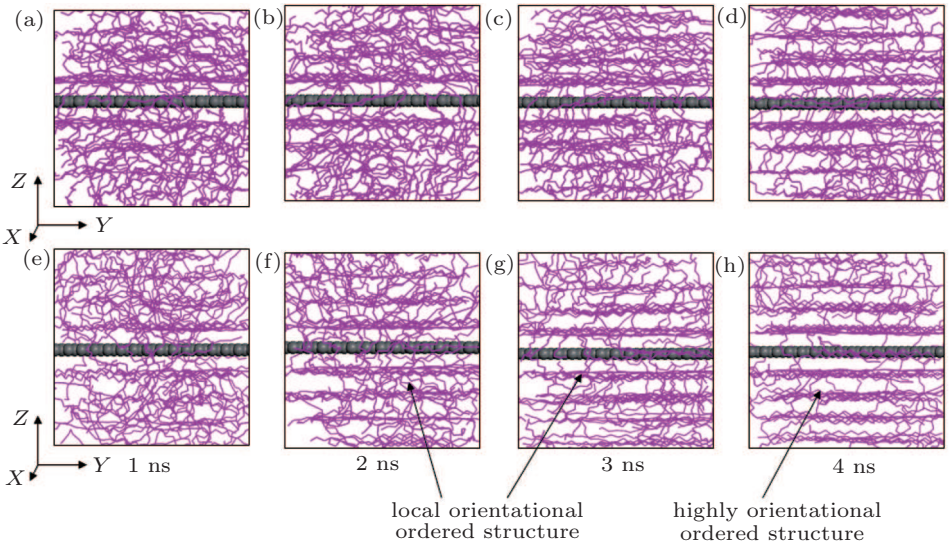


Fig. 2. (color online) The ordering processes of PE chains at [(a)–(d)] 470 K and [(e)–(h)] 500 K obtained from the MD simulations.

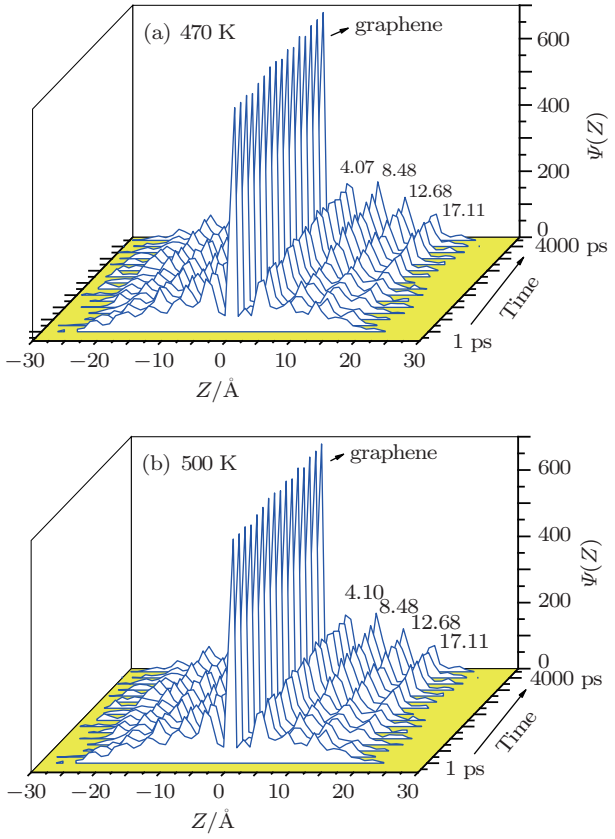


Fig. 3. (color online) Evolutions of the distribution function $\psi(Z)$ of carbon atoms along the Z axis at (a) 470 K and (b) 500 K. The time axis is non-linear.

To investigate the orientation order of the structure, we calculate the orientation order parameter S at various time, which measures the correlation between the orientation of a molecule backbone and the Y axis. The S is defined as

$$S = \left\langle \left\langle \frac{3\cos^2(\psi(Y)) - 1}{2} \right\rangle_{\text{bond}} \right\rangle, \tag{2}$$

where $\psi(Y)$ is the angle between the sub-bond vector $\boldsymbol{b}$ in a slab $[Y, Y + \mathrm{d}Y]$ and the Y axis, and $\langle \cdots \rangle_{\text{bond}}$ denotes the average over the sub-bonds in the slab between Y and $Y + \mathrm{d}Y$. Parameter S assumes the values of 1.0, 0.0, and -0.5 for the sub-bonds in slab $[Y, Y+\mathrm{d}Y]$ perfectly parallel, random, and perpendicular to the Y axis, respectively.[29] We set $\mathrm{d}Y$ to 1.0 Å in our calculations.

We show in Fig. 4 the bond-orientational order parameter S of the three layers close to the graphene surface versus time at 470 K and 500 K. This figure shows the following features. (i) At $t = 1$ ps, S is close to zero (0–0.2) independent of Y, indicating a random-coil structure. (ii) It is clear that S increases with the elapse of time. (iii) At $t = 4000$ ps, the orientationally order structure is formed, and there is a flat part between $Y = 20$ Å and 40 Å. The bond-orientational order parameter S in this flat region reaches 0.8 and 0.9 at 470 K and 500 K, respectively, which indicates that the sub-bonds in this region are almost parallel to the Y axis. (iv) Comparing the results of 450 K with those of 500 K, we can conclude that the high temperature leads to the high order parameter S. This is because the PE chains have more kinetic energy to overcome the energy barrier and adjust their configurations at 500 K. At the two end of the axis, S has a large fluctuation. This is because the PE chains are unconstrained at the end of the graphene.

Analyzing the orientationally ordered process of polymer chains obtained by our MD simulation in detail, we find that the stepwise addition of the crystalline stems onto the growth surface, just like Yamamoto pointed out in the literature.[30] Figure 5 shows the stem addition processes over a short time scale (0.25 ns interval) in detail viewed along the chain axis (Y axis). The interfacial interaction is very important in the polymer crystallization. Because the interfacial interaction of the polymer melt with the graphene substrate is extremely difficult to investigate by experiments, there has been no definitive information. To some extent, the surface nucleation and growth mechanisms of PE chains are revealed by our MD simulations.

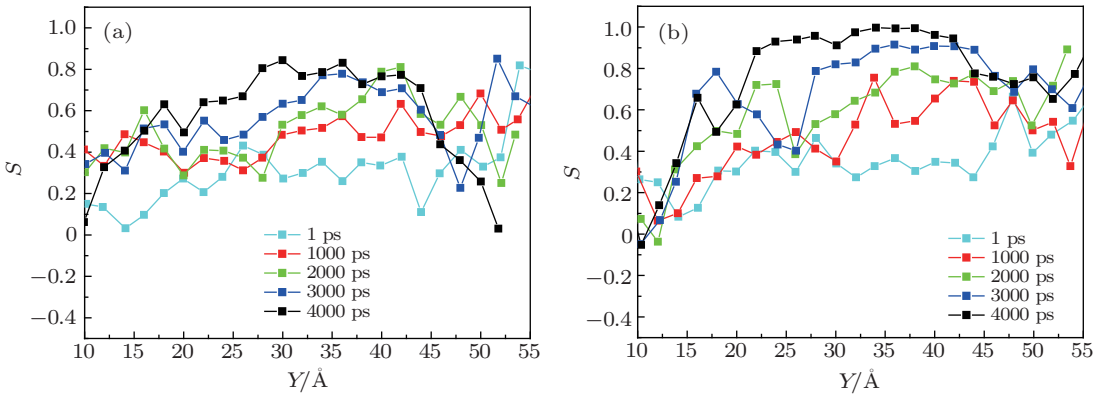


Fig. 4. (color online) Orientation order parameter S at various time at (a) 470 K and (b) 500 K.

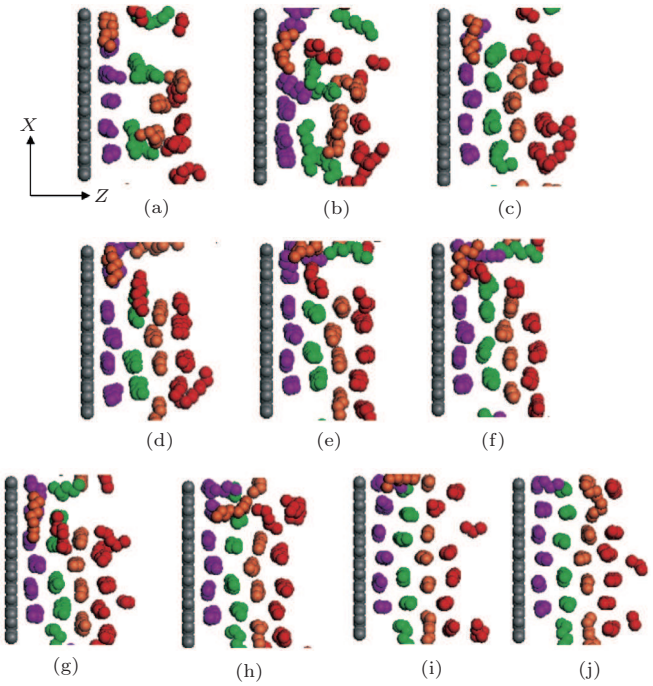


Fig. 5. (color online) Crystalline stems adsorption processes at 500 K, panels (a)–(j) show the configuration starting from 1.25 ns in every 0.25 ns.

The behavior of the PE chains around the graphene can be described through the mean-square displacement (MSD). Figure 6 shows the MSD of the PE chains as a function of time for 470 K and 500 K. However, the diffusion coefficient D of the PE chains is more direct to reflect the crystallization process. Coefficient D is related to the MSD function with the Einstein equation[31]

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \frac{1}{N}\sum_{i=1}^{N}[r(t+t_0)-r(t_0)]^2 \right\rangle, \qquad (3)$$

where $r(t_0)$ is the initial coordinate, and $r(t+t_0)$ is the position of the PE chains at time t. In order to avoid the statistical error at the two ends,[32] we use the MSD between 250 ps and 3500 ps to determine D. The values are 0.523×10^{-6} cm^2/s and 1.062×10^{-6} cm^2/s for 470 K and 500 K, respectively. We find the D at 500 K is more than twice of that at 470 K. which indicates that the high temperature leads to a fast structure formation. The previous works have shown that D is not a constant in all cases and that the time-dependent diffusion coefficient $D(t)$ is more proper to describe the properties.[33,34] Therefore, we calculate the time-dependent diffusion coefficient $D(t)$ of the PE chains with equation $D(t) = \partial\left\langle \Delta r^2 \right\rangle/\partial t$.[35] The results are presented in Fig. 7. Obviously, $D(t)$ has a sudden

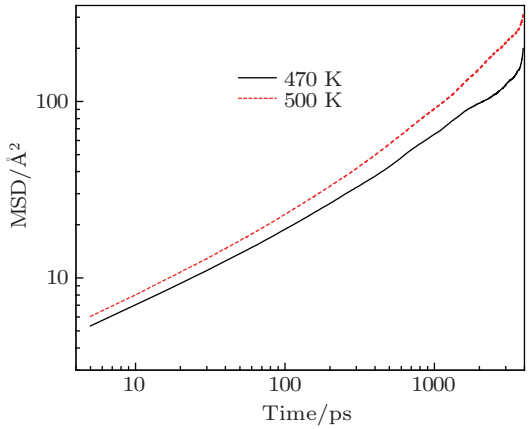


Fig. 6. (color online) The mean-square displacement of PE chains with different temperatures (T = 470 K, 500 K). MSD is defined as MSD $= \left\langle [r(t+t_0)-r(t_0)]^2 \right\rangle$. The diffusion coefficient D is the slop of the MSD versus time t.

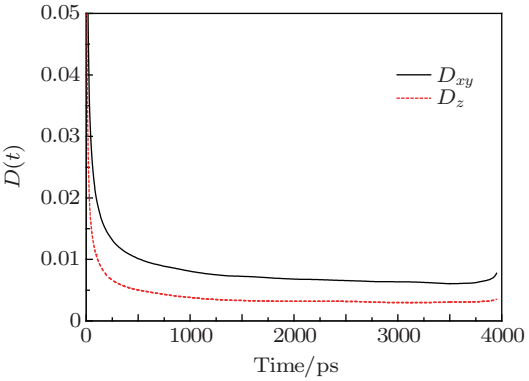


Fig. 7. (color online) The diffusion coefficient $D(t)$ as a function of crystallization time for the PE chain at 470 K.

drop in a very short period of time. At later time, $D(t)$ is found to reach a plateau value. The D_{xy} is larger than D_z, which indicates that the PE chains need more time to adjust their configurations and the graphene substrate has a great adsorption for the PE chains. Therefore, the adsorption step and the orientation step are highly cooperative.

4. Conclusions

In this work, we investigate the isothermal crystallization process of the PE chains around a single-layer graphene. Our simulations visually display that the crystallization behavior of the PE chains is significantly influenced by the surface of the graphene. The results confirm that the graphene provides the nucleation sites for the PE melt to become an orientational ordered structure. From the atomic configuration translation, the number distribution of the atoms, and the order parameter S, the crystallization process can be summarized in two steps, the adsorption and the orientation. By analyzing the diffusion properties of the polymer chains, we find that the graphene substrate has a great adsorption for the polymer molecules and the polymer molecules need more time to adjust their configurations. Therefore, the adsorption step and the orientation step are highly cooperative. The interfacial interaction of the polymer melt with the graphene substrate is difficult to investigate through experiments. The nucleation and growth mechanisms of PE chains on a graphene substrate are revealed by our MD simulations.

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