Confinement Effects on Molecular Orientation in Multilayer Films of Low Molecular Weight Polypropylene

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ABSTRACT: Attributed to the confinement effect and unique properties, multilayer nanostructures have attracted extensive attention. Coarse-grained molecular dynamics simulations were carried out to understand the interfacial microstructure and mechanical properties of multilayer low molecular weight polypropylene (PP) films by comparison with those of the corresponding bulk material. The molecular order parameter, radius of gyration and end-to-end distance of the chains were calculated. Out of surprise, in the multilayer PP films, the confinement effects make the polymer chains at the interfaces keep being highly ordered, extended and perpendicular to the normal of the interfaces, and those in the layer keep unordered and shrunk, with little interlayer interpenetration. However, for their bulk material, all polymer chains are in the state of being highly extended, ordered, and crystallized. These results are distinct from those of general flexible linear polymers. We found that the dependence of the tensile strength of the multilayer PP film on the degree of interfacial integration between the layers is weak. The distinction of the microstructure between the multilayer films and its bulk material is a critical factor that influences the fracture behavior of material. These findings would give rise to better understandings about the mechanical properties and crystalline behaviors of the multilayer polymer films.

1. INTRODUCTION

Attributed to the confinement effect and distinct properties,[1,2] thin and ultrathin polymer films have attracted extensive attention recently. The distinction between the ultrathin films and their bulk states was found determined by the interfacial nature of film[3, 4] and film thickness[5-7]. Thomas[8] reported that the stability of the ultrathin film was affected by the nature of the interface. In addition, extremely small thicknesses in free-standing thin polymer films would slow down the acceleration of structural relaxation.[9] As particular duplicated forms of ultrathin polymer films, multilayer structures of polymer are widely used in various areas, such as optical films,[10, 11] electronic devices,[12] low-permeability films,[13, 14] and good mechanical materials.[15, 16] For multilayer structures, the interfaces between the layers provide parallel confinements for the polymers, which would lead to tremendous change of their microstructures, different from those in bulk.[17]

Nowadays one of the most efficient and convenient methods to produce multilayer nanostructures is micro-nano multilayer extrusion technology, which is able to be applied in industrial production.[10] It is an easy way not only to construct alternating layer structures with different polymer, but also to build
lamellar nanocomposites by adding functional components, such as nanoparticles,[18] nanotubes,[16] and graphene sheets.[15] High-performance optical materials could be produced by this way with multi-functional properties for thermal insulation and selective refraction of light.[10,19,20]

Researchers have made great efforts on improving the mechanical properties of polymeric materials. We have recently explored the behaviors of interfacial diffusion and bonding in the multilayer film of flexibility polyethylene (PE). The results show that multilayer structure produces a unique mechanical properties, distinct from its bulk material.[17] Attributed to the interfacial confinement effects, multilayer polymer films have structural heterogeneity with the chains near the interfaces orienting perpendicularly to the normal, while it is bulk-like in the central region of each layer, so the enhancement of mechanical properties of the multilayer nanostructure is due to the increase of the number of interfacial layers and the chain orientation.[17] Michler et al.[21] reported that the strength and strain of multilayer tapes of polystyrene/poly(methyl methacrylate) increase with decreasing the layer thickness. Li et al.[15] also found that layered structures of polymer films produced by lamination are able to provide in-plane oriented reinforcement for graphene sheets.

Although PP has similar linear structure with PE, PP chains are more rigid due to the presence of side methyl groups. Smirnova et al. [22] reported that the films based on rigid-chain copolyimide exhibit a lower tendency toward orientation under biaxial drawing, as compared with homopolyimide films. Zhang et al.[23] also reported that shear flow could induce isotactic PP orientation and crystallization in thin films. The interfacial confinement effects created by multilayer nanostructure may also give rise to unique properties and behaviors. At present, the microscopic details about the interfacial dynamics and interactions in the multilayer films of PP are still quite unclear, but they are critical to understand the interactions and confinement effect of interfacial layers in the film. In this work, we carried out molecular dynamics (MD) simulations to explore the confinement effects on the interfacial microstructure and mechanical properties of the multilayer film of PP.

2. MODEL AND SIMULATION DETAILS

2.1 MODEL

All simulations were performed with GROMACS 5.04, which is an open-source, highly efficient, massively parallel, load-balanced, and scalable molecular dynamics simulator.[24-28] The polymer was modeled with the Martini coarse-grained (CG) force field. The Martini CG force field has been developed
for the molecular dynamics simulations of lipids, proteins, sugars, polymers, and DNA, due to its high computational efficiency and simple operation. [23, 29-31]

In the previous work, we created the model of the multilayer PE, which was scaled down from hundreds nanometers in the lamination to a few nanometers for simulation (See Figure 1a). [17] Here we constructed a similar PP model to replace the full length chains, that is, a low molecular weight chain. The polymer chain is composed of 50 SC1 type CG beads with each bead representing 3 carbon atoms and 6 hydrogen atoms. The dimension of the whole simulation box is about 21×21×36 nm³, containing 3 nanolayers (See Figure 1b). Each layer consists of 1536 polymer chains with a layer thickness of 12 nm.

Harmonic potentials were used for bond stretching,

\[ E_{\text{bond}}(r) = \frac{1}{2} k_b (r - r_0)^2 \]  

(1)

where the force constant for bond stretching \( k_b = 48000 \text{ KJ/mol} \), and the equilibrium bond length \( r_0 = 0.298 \text{ nm} \). The bond-angle vibration between three adjacent polymer beads was described by a restricted bending potential,

\[ E_{\text{bend}}(\theta) = \frac{1}{2} k_\theta \left( \frac{\cos \theta - \cos \theta_0}{\sin^2 \theta} \right)^2 \]  

(2)

where the force constant for angle bending \( k_\theta = 78 \text{ KJ/mol} \), and the equilibrium angle \( \theta_0 = 119^\circ \). In this work, two potential functions were applied automatically to a single dihedral, that is, type 9 was used for dihedrals. The dihedral angle between four adjacent polymer beads was modeled as

\[ E_{\text{torsion}}(\phi) = k_\phi \left[ 1 + \cos \left( n\phi - \phi_0 \right) \right] \]  

(3)

where the force constants for the torsion interaction \( k_\phi = 3.1 \text{ KJ/mol} \) and \(-5.9 \text{ KJ/mol} \), the equilibrium dihedral angles \( \phi_0 = 100^\circ \) and \( 190^\circ \), and the multiplicity \( n = 1 \), respectively.

The truncated and shifted Lennard-Jones (LJ) potential was adopted for the non-bonded interactions,

\[ E_{\text{LJ}}(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6, & r \leq r_c \\
0, & r > r_c 
\end{cases} \]  

(4)

where the diameter of the CG polymer bead \( \sigma = 0.298 \text{ nm} \), the cutoff distance \( r_c = 1.2 \text{ nm} \), and the well depth \( \varepsilon = 3.5 \text{ KJ/mol} \).[17, 30]
2.2 SIMULATION DETAILS

The initial configuration for one layer was first generated following our previous work.[32, 33] A mass of “rigid” polymer chains were arranged in a “large” lattice box, which would be “pressed” to a target volume through a short time run of deformation dynamics simulation. We set the periodic boundary conditions in the x and y directions of simulation box for avoiding boundary effects. In order to eliminate the initial-configuration dependence, the polymers in the simulation box were relaxed for 30 ns at 1073 K and quenched to 500 K in 20 ns with a time step of 0.01 ps. After equilibration of 150 ns, monolayer was formed with the thickness of 12 nm along the z direction with a time step of 0.02 ps. Then we duplicated the equilibrated single layer to a three-layer polymer structure in the z direction with periodic boundary conditions for interfacial diffusion. The inter-layer diffusion sustained for 300 ns at 500 K with a time step of 0.02 ps. Considering the actual pressure of the melt in the laminator, we adopted the pressure of 30 bar and the temperature of 500 K throughout the simulation with a NPT ensemble. In the process of interlayer diffusion, the dimension of simulation box in z direction kept constant, and a series of intervening configurations at different diffusion time were extracted from the trajectory, and quenched to 298 K immediately. Finally, these configurations were stretched by the sudden tensile force along the x and y direction at a strain rate of $10^{10}$/s, and the time step was as short as 0.003 ps in a NPT ensemble. Temperature control was achieved using the Berendsen thermostat,[34] and pressure was maintained using the Berendsen barostat[35] throughout the work. The trajectory data were visualized and the corresponding snapshots were created by VMD 1.9.1.[36]

3. RESULTS AND DISCUSSION
3.1 INTERFACIAL MICROSTRUCTURE

In order to get better understanding of the interfacial confinement effects, the microstructure of polymers in the multilayer PP film were investigated. First, we calculated the end-to-end distance and the radius of gyration. Figure 2a shows the profile of the z-component of the end-to-end distance. It reveals that the two ends of the polymer chain at the interface are much closer to each other in the z direction than those in the layers for the whole process of interfacial diffusion. The end-to-end distance for the multilayer and bulk samples is shown in Figure 2b. We could find that the end-to-end distance of polymer chains for multilayer PP structure is continuously unchanged with diffusion time, and the end-to-end distance at the interface is greater than that in the layer, while the end-to-end distance of polymer chains for the bulk material is continuously in a large level.

![Figure 2](image_url)

**Figure 2.** (a) Profile of z-component of the molecular end-to-end distance along the normal of the interface for multilayer samples at different diffusion time and for a bulk sample. (b) Profile of the molecular end-to-end distance along the normal of the interface for multilayer samples at different diffusion time and for a bulk sample.

Figure 3a shows the profile of 2D radius of gyration of the polymer about the z-axis along the normal of the interface for multilayer samples at different diffusion time and for a bulk sample. The obtained data reveal that the 2D radius of gyration at the interface is much longer than that in the layers, and the difference between them changes little with diffusion time. Figure 3b shows the radius of gyration of the
polymer chain long the normal of the interface for the multilayer samples at different diffusion time and for a bulk sample. The figure shows that the radius of gyration at the interface is much longer than that in the layers and it changes little with diffusion time, while the radius of gyration of polymer chains for the bulk material is extremely longer than that for the multilayer PP film. The findings above illustrate that the polymer chains near the interfaces in the multilayer structure are in the state of being extended in the planes parallel to the interfaces and compressed in the direction perpendicular to the interfaces, while the polymer chains in the layer are in the state of being shrunk due to the interfacial confinement effects. With interlayer diffusion, this state is continuously retained. But the polymer chains for the bulk material are in the state of being highly extended in the planes parallel to the interface. The difference between them illustrates the confinement effects of interface weakens the extension of the polymer chain and hinders the orientation and crystallization of the polymer chain in the layer instead.

![Figure 3](image_url)

**Figure 3.** (a) Profile of 2D around-z-axis radius of gyration of the polymer along the normal of the interface for multilayer samples at different diffusion time and for a bulk sample. (b) Profile of radius of gyration of the polymer chain long the normal of the interface for multilayer samples at different diffusion time and for a bulk sample.

In addition, we also calculated the molecular order parameter of the PP chains. Here we adopted the same approach for the calculation of the molecular order parameter in our previous work.[17] The molecular order parameter of the polymer chains is defined as
where \( \theta_z \) is the angle between the orientation vector of the whole polymer chain and normal the interface, i.e. the z direction in this work. The molecular order parameters can vary from -0.5 to 0 to 1, which represent full order perpendicular to the normal, the case of isotropic orientation of the polymer chain, and full order along the interface normal, respectively. [17]

\[
s_z = \frac{3}{2} \langle \cos^2 \theta_z \rangle - \frac{1}{2}
\]

\( (5) \)

Figure 4. (a) Profiles of molecular order parameter along the z direction for the multilayer PP structure at different diffusion time, and those for the multilayer PE film at the diffusion time of 200ns and for the bulk material are still shown for comparison. (b) Average of molecular order parameter at the interfaces of the multilayer PE and PP structure as a function of diffusion time. (c) Orientational distribution of the polymer chain for the multilayer PP structure at different diffusion time, and those for the multilayer PE film at the
diffusion time of 200ns and the bulk material are also shown for comparison. $\theta$ is the angle between the orientation of the polymer chain and the z-axis.

Figure 4a shows the profiles of molecular order parameter along the z direction for the multilayer PP structure at different diffusion time, the multilayer PE structure at the diffusion time of 200ns and the bulk material. For the multilayer PP structure, the molecular order parameters for the polymers near the interfaces basically don’t change with the diffusion time, and the values are closed to -0.5, which indicates that the orientation direction of chains is perpendicular to the normal of the interface. However, the polymer chains inside the layer are oriented slightly perpendicular to the normal of the interfaces at the beginning of diffusion time, and they would finally converge to isotropic orientation with the increasing of the diffusion time. For bulk material, the molecular order parameters along the z direction vary between -0.4 and -0.5, which illustrates the polymer chains are basically oriented perpendicular to the normal of the interfaces. For the multilayer PE structure at the diffusion time of 200ns, the polymer chains would finally converge to isotropic orientation in the whole space of the structure. Figure 4b shows the molecular order parameter at the interfaces of the multilayer PE and PP structure as a function of diffusion time. It is revealed that for the multilayer PE structure, the orientation of the polymers at the interfaces changes rapidly from being perpendicular to the normal of the interfaces to being isotropic after inter-layer diffusion for about 90 ns. However, for the multilayer PP structure, the orientation of the polymers at the interfaces changes little with the diffusion time, and the polymer chains are in the state of being highly ordered in the plane parallel to the interface. Figure 4c shows the orientational distribution of the polymer chain for the multilayer PP structure at different diffusion time, the multilayer PE structure at the diffusion time of 200ns and the bulk material, where $\theta$ is the angle between the orientation of the polymer chain and the z-axis. We could find that the orientational distributions of the polymer chain for the multilayer PP structure vary little with diffusion time. However, a large number of the polymer chains have orientational angles closed to 90 degrees with the normal of interfaces for the bulk material. And the polymer chains become uniformly distributed over the full range with the proceeding of diffusion for the multilayer PE structure.

For the multilayer PP structure, although the polymers near the interfaces are highly ordered and the molecular order parameters change little with the diffusion time, the polymer chains of bulk material are always in the state of being highly extended and ordered in the planes parallel to the interface without the
interfacial confinement effects. We could also find that the polymer chains at the interface do not penetrate into each other with continuously increasing diffusion time because of the chain rigidity and the interfacial confinement effects. The confinement effects result in highly ordered polymer chains at the interface and hinder the orientation and crystallization of the polymer chains in the layer. However, for the multilayer PE film, these molecules at the interface are ordered with chains perpendicular to the normal of the interface at the start of diffusion, and they would finally converge to isotropic orientation in the whole space of the structure with increasing the diffusion time.

3.2 STRESS-STRAIN RESPONSE OF MULTILAYER PP FILMS

We also calculated the mechanical properties and the interfacial bonding of the multilayer PP structure. [37, 38] Here the tensile stress-strain curves along x-axis and y-axis direction were calculated for the multilayer PP structure at room temperature, which is shown in Figure 5. To note that the material for tensile deformation was in solid state at 298 K. The stress commonly increases with strain rate.[39] In this work we adopt a strain rate of $10^{10}$/s, which represented a sudden tensile loading.

![Tensile stress-strain curves](image_url)

**Figure 5.** (a) Tensile stress-strain curves of the multilayer polymer film at different diffusion time and of the bulk material along x axis. (b) Tensile stress-strain curves of the multilayer polymer film at different diffusion time and of the bulk material along y axis. The strain rate is $10^{10}$/s.

Figures 5a and 5b show the tensile stress-strain curves along x axis and y axis, respectively. We could find that there is no obvious yielding point for multilayer films and the bulk material, and it directly and rapidly transits from elastic deformation to hardening stage to break. But the elastic modulus of bulk
material is slightly higher than that of multilayer structure, which illustrates that the bulk material is much harder because most of the polymer chains are ordered and crystalline without confinement effects. Figure 5a shows that the fracture strength of bulk material along x axis is very close to that of multilayer structure, as high as about 218 MPa. Figure 5b shows that the fracture strength of bulk material along y axis is higher than that of multilayer structure. And stress-strain curves of multilayer structure vary little with diffusion time. These findings illustrate that the majority of the polymer chains of bulk material is ordered in the plane parallel to interface.

![Figure 5a](image1.png)

**Figure 5.** (a) Profiles of degree of interfacial integration along the z direction for the multilayer structure at different diffusion time and for the bulk material. (b) Average degree of interfacial integration at the interfaces of the multilayer film as a function of diffusion time.

In the previous work, we calculated the tensile stress-strain curves at room temperature along the normal of the interfaces for the multilayer PE structure after different diffusion time. The results revealed that the bonding between the layers in the multilayer PE structure is critical for the mechanical strength of the material.[17] Although PP is similar with PE in property because of linear structure, the molecular chain of PP is harder due to the presence of side methyl groups. In order to get an insight into the dependence of tensile properties on the degree of interfacial integration (DII) of the PP film, we use the same definition method with PE films in previous jobs, which is defined as

![Figure 6](image2.png)

**Figure 6.** (a) Profiles of degree of interfacial integration along the z direction for the multilayer structure at different diffusion time and for the bulk material. (b) Average degree of interfacial integration at the interfaces of the multilayer film as a function of diffusion time.
where \( L \) and \( S \) represent the length of chain across the interface and the density of chain-crossing in the interface, respectively.\([17]\) The brackets \(< \cdots >\) represent the ensemble average over all polymer chains across the interface. DII was also called as interfacial adhesion,\([37]\) phase continuity,\([40]\) inter-laminar continuity,\([41]\) and degree of continuity\([42]\) in other work.

Figure 6a shows the profile of DII along the \( z \) direction for the multilayer structure at different diffusion time and for the bulk material. We could find that at the beginning of diffusion, DII is closed to zero at the interfaces in the multilayer structure, but has a relatively high value in the layers, which is also higher than that of the bulk material. With the proceeding of diffusion, DII of the multilayer structure at different positions has a small floating growth. It indicates that the confinement effects make polymer chains at the interface to being highly ordered, which leads to rigid PP chains are difficult to move and further hinders the interface integration. Figure 6b shows DII at the interfaces of the multilayer film as a function of the diffusion time. The figure reveals that DII at the interfaces increases nonlinearily with the diffusion time, and tends to equilibrium state after interfacial diffusion for about 20 ns. The increasing rate of DII is much faster at the beginning of diffusion, but the DII value is not much increased. This may result in stress-strain curves of the multilayer polymer film have little change with the diffusion time. These findings illustrate that the dependence of tensile property of the multilayer polymer film on DII is evidently small. The distinction of the microstructure between the multilayer films and bulk material is critical factors that influence the fracture strength.

4. CONCLUSIONS

In this work, we studied the interfacial microstructure and mechanical property for the multilayer PP films and corresponding bulk material using CG MD simulations. The DII was also calculated to get better understanding about these differences.

For multilayer PP films, the confinement effects make polymer chains at the interface to being highly ordered and extended perpendicular to the normal of the interface, which leads to rigid PP chains are difficult to move and further hinders the interface integration, and polymer chains in the layer are in the state of isotropic orientation. However, for bulk material, the polymer chains are in the state of high degree of being extended and ordered in the planes parallel to the interface without the confinement effects. So the
elastic modulus and the fracture strength along y axis of bulk material are higher than that of multilayer structure. And we found that the dependence of tensile property of the multilayer PP film on DII is evidently small. The distinction of the microstructure between the multilayer films and bulk material is critical factors that influence the fracture strength. These findings illustrate that the interface confinement effects of multilayer structure are not conducive to the molecular orientation of rigid chains.

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**Note**

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