

Brush가 달린 두 층 간에 한정된 고분자 용융체의 거동에 미치는 전단 효과:
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The Effect of Shear on the Behavior of Polymer Melt Confined between Two
Brushed Layers: A Molecular Dynamics Simulation Study

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1. Introduction

The nature of the confined fluids has been shown to be dramatically different from that of the bulk fluids in the local relaxation(Bitsanis *et al.*, 1993), the mobility(Manias, 1995) and rheological properties(Manias *et al.*, 1996). For monomeric systems many simulation studies provide a clear information on the dynamics of confined films of small spherical molecules(Somer *et al.*, 1992, Schoen *et al.*, 1994). On the other hand, for confined polymers less works has been done, toward the understanding of the dynamics of nanoscopic confined polymer melt. Particularly, the dynamics of polymer confined between the brushed layers has attracted much attention lately in relation with polymer/clay nanocomposite. In the present work, we use molecular dynamics simulation to investigate the rheological behavior of polymer melt confined between two brushed layers under shear.

2. Simulation Model and Method

The model system under consideration consists of polymers and brush layers confined between two parallel surfaces as depicted in Fig. 1. Polymer chains and brush chains are both represented by anharmonic bead-spring chains, using the model of Kremer and Grest(Kremer and Grest, 1990). For the model system, the chain dynamics is described by the Langevin dynamics:

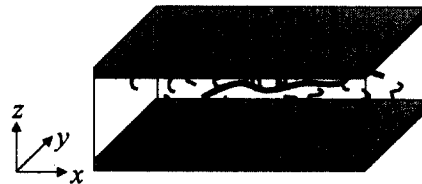


Fig. 1. The simulation box consists of polymers, brush layers and surfaces. Brushes are grafted to the surfaces, and polymer is located between the brush layers.

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla U_i - m \xi \frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i \quad (1)$$

where ξ is the friction coefficient and \mathbf{W}_i is the Gaussian random force. The potential U_i composed of two terms: $U_i = U_{\text{nonbond}} + U_{\text{bond}}$.

U_{nonbond} for describing nonbonded interaction is given by a Lennard-Jones(LJ) potential:

$$U_{\text{nonbond}}(\mathbf{r}) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right], & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (2)$$

By a proper truncation of Eq. (2) with different cutoff radius, the interactions between polymer and surface, and the interactions between polymer and brush are set to be attractive ($r_c = 2.2\sigma$), while other pairwise interactions are set to be purely repulsive ($r_c = 2^{1/6}\sigma$).

The potential between two successive bonded beads, U_{bond} is given by the finite extendable nonlinear elastic(FENE) potential (Bird, Armstrong and Hassager, 1987)

$$U_{\text{bond}}(\mathbf{r}) = \begin{cases} -0.5kR_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], & r \leq R_0 \\ \infty, & r > R_0 \end{cases} \quad (3)$$

with $k=30 \varepsilon_p / \sigma^2$ and $R_0=1.5\sigma$.

The system constants used in this study are summarized in Table 1 where all the dimensional quantities are reduced by the quantities of polymer species. The surfaces are modeled as face-centered-cubic(fcc) cluster surfaces with (111)planes of fcc packing parallel to the xy plane. The grafting sites of brush chains are located randomly at the interstitial sites of the fcc lattice. An end bead of each brush chain

Table 1. The system constants in this system. All the dimensional quantities are reduced by the quantities of polymer species. The x and y dimensions of simulation box are $21\sigma_p$ and $8\sigma_p$, respectively.

	bead diameter	bead mass	chain length	number of chains
polymer	σ_p	m_p	12	20
brush	$0.6\sigma_p$	$0.216m_p$	9	92
surface	$0.6\sigma_p$	$50m_p$	—	—

is rigidly fixed at a grafting site.

The equations of motion are integrated using a velocity-Verlet's method (Allen *et al.*, 1989) with a time step $\Delta t = 0.0001 \sigma_p (m_p / \varepsilon_p)^{1/2}$. Periodic boundary conditions are applied in the x and y directions.

In order to equilibrate the system with respect to surface separation, we performed molecular dynamics at constant temperature ($kT=1.0 \epsilon_p$) and pressure ($5.2 \epsilon_p \sigma_p^{-3}$). Though the equilibration, the surface separation (h) is determined ($h=3.23 \sigma_p$). The determined surface separation is enough smaller than the contour length of a polymer. To endow the upper surface with steady shear, the upper surface was moved with constant velocity (v_1) at constant temperature and volume. The rheological properties as normal stress is calculated and averaged over 10 independent runs.

3. Simulation Results and Discussion

Fig. 2 present the normal stress acting on the upper surface as a function of apparent shear rate ($\dot{\gamma}_{app} = v_1/h$). At relatively low shear rates, as expected, Fig. 2 shows that the normal stress increases as the shear rate increases until it reaches a maximum value. However, at the shear rates higher than a critical rate ($0.62 (\epsilon_p/m_p \sigma_p)^{1/2}$), the normal stress decreases with increasing shear rate, suggesting that the propagation of the shear force from upper surface to the confined polymer is somehow suppressed as the shear rate increases. This behavior is closely related to the arrangement and orientation of brush and polymer chains.

Fig. 3 shows the tilt of the each brush on the upper and lower surface plotted against apparent shear rate, where θ is the angle of inclination of brush from the surface. At $\dot{\gamma}_{app} < \dot{\gamma}_{app,c}$, the values of $\langle \cos \theta \rangle$ for brush layers at both surfaces increases with $\dot{\gamma}_{app}$, indicating that the mean orientation of brush become tilted to the shear direction from its initial value. At $\dot{\gamma}_{app} > \dot{\gamma}_{app,c}$, the tilt for the brush grafted at lower surface decreases as the shear rate increases. From Fig. 2 and Fig. 3, it is indirectly suggested that as the applied shear force become strong so as to exceed $\dot{\gamma}_{app} > \dot{\gamma}_{app,c}$, the brush chains grafted at upper surface are stretched and lies down and

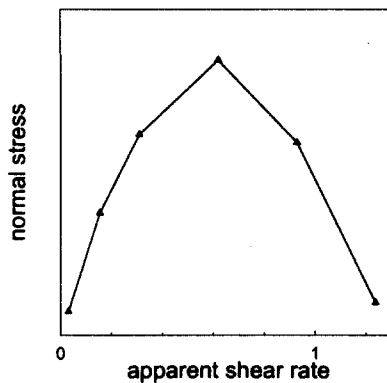


Fig. 2. Normal force on the upper layer is shown as a function of the apparent shear rate.

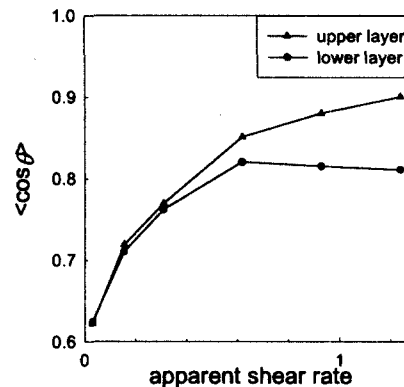


Fig. 3. The tilt of brush chains, $\langle \cos \theta \rangle$, versus apparent shear rate.

the polymer chains are squeezed out of brush layer. Therefore, a slip may occur at the boundary brush layer grafted at upper surface and polymer confined.

Such interlayer slip can be quantified by measuring the ratio of shear rate of the polymer to the apparent shear rate ($\omega = \dot{\gamma} / \dot{\gamma}_{app}$) as presented in Fig. 4. When the slip is small, $\omega \doteq 1$, whereas $\omega \ll 1$ for a large slip (Subbotin *et al*, 1995). Fig. 4 shows that at relatively high shear rates, the slip characterized by the shear rate ratio ω become large, i.e. $\omega \ll 1$. This might be interpreted by the fact that polymers in the vicinity of brush layer are squeezed out due to tilt of brush chains.

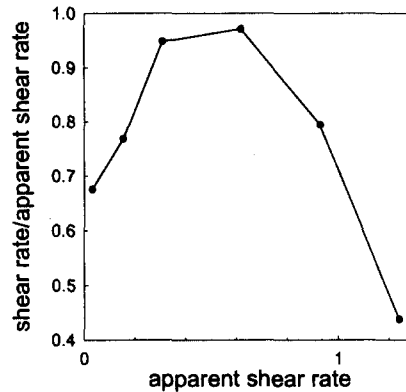


Fig. 4. The ratio of shear rate of the polymer to apparent shear rate is shown as a function of the apparent shear rate.

4. References

- Allen, M. P. and Tildesley, D. J., 1989, Computer simulations of liquids, *Oxford University Press*, Oxford.
- Bird, R. B., Armstrong, R. C. and Hassager, O., 1997, Dynamics of polymer liquids, *Wiley*, New York.
- Bitsanis, I. A. and Pan, C., 1993, The origin of "glassy" dynamics at solid-oligomer interfaces, *J. Chem. Phys.*, **99**, 5520.
- Kremer, K. and Grest, G. S., 1990, Dynamics of entangled linear polymer melts: A molecular-dynamics simulation, *J. Chem. Phys.*, **92**, 5057.
- Manias E., 1995, Nanorheology of strongly confined molecular fluids: A computer simulation study, *Ph. D. thesis*, University of Groningen, Groningen.
- Manias, E., Hadziioannou, G. and ten Brinke, G., 1996, Inhomogenities in sheared ultrathin lubricating films, *Langmuir*, **12**, 4587.
- Scheon, M., Diestler, D. J. and Cushman J. H., 1994, Fluids in micropores.IV. The behavior of molecularly thin confined in the ground isostress ensemble, *J. Chem. Phys.* **100**, 7707.
- Somers S. and Davis T. H., 1992, Microscopic dynamics of fluids confined between smooth and atomically structured solid surfaces, *J. Chem. Phys.* **96**, 5389