MOLECULAR DYNAMICS SIMULATIONS FOR VISCOSITY GROWTH AND CONFORMATIONS OF UNENTANGLED POLYMERS UNDER SHEAR FLOW

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ABSTRACT

Melts and solutions unentangled polymers exhibit shear thinning under fast shear. Colby et al[1] reported that the shear thinning behavior is universal and the flow curve of the steady state viscosity can be fitted to the Carreau model. Recently, Costanzo et al[2] conducted rheological measurements including very high shear rate regions, and reported that dilute unentangled solutions exhibit the shear thickening behavior followed by the shear thinning behavior. Matsumiya et al[3] combined the rheology and dielectric measurements and studied the dynamics of polymer chains under fast shear. These experimental data suggest that an effective friction for segments is modulated under fast shear. In this work, to study the dynamics of unentangled polymers under fast shear in detail, we perform molecular dynamics (MD) simulations. We show that the shear thinning behavior depends on the method to apply the shear flow. We discuss the molecular level mechanism which gives the different shear thinning behaviors.

MODEL

We use the Kremer-Grest model[4], in which a polymer is modeled by connecting repulsive beads by bonds. The repulsive interaction between beads is expressed by the truncated Lennard-Jones potential (the Weeks-Chandler-Andersen potential), and the bond is expressed by the finitely extensible non-linear (FENE) potential.

In the original Kremer-Grest model, the Langevin equation is employed as the dynamic equation for beads. To apply shear flow to the system, we should change the dynamics model. The most widely used method to apply shear is the SLLOD (strictly speaking, the atomic SLLOD) model. In the atomic SLLOD model, the following dynamic equations are utilized:

$$\frac{d\boldsymbol{r}_{i,k}(t)}{dt} = \frac{\boldsymbol{p}_{i,k}(t)}{m} + \boldsymbol{\kappa} \cdot \boldsymbol{r}_{i,k}(t), \tag{1}$$

$$\frac{d\boldsymbol{p}_{i,k}(t)}{dt} = -\frac{\partial \mathcal{U}(\{\boldsymbol{r}_{i,k}(t)\})}{\partial \boldsymbol{r}_{i,k}(t)} - \boldsymbol{\kappa} \cdot \boldsymbol{p}_{i,k}(t) - \alpha(t)\boldsymbol{p}_{i,k}(t). \tag{2}$$

Here, $\boldsymbol{r}_{i,k}$ and $\boldsymbol{p}_{i,k}$ are the position and peculiar momentum of the k-th bead in the i-th chain. m is the mass of a bead, $\boldsymbol{\kappa}$ is the velocity gradient tensor, and $\mathcal{U}(\{\boldsymbol{r}_{i,k}\})$ is the total interaction potential energy. $\alpha(t)$ is the coefficient of the Nosé-Hoover thermostat. The SLLOD dynamic equations (1) and (2) assume the homogeneous shear flow for all beads. Although the atomic SLLOD works well for low shear rates, it is reported that it shows some artificial behaviors for high shear rates[5].

In actual rheology experiments, shear flow is generated by moving fixtures (such as the parallel plates and cone-plate). Also, the temperature of polymers are not directly controlled but indirectly controlled by the heat conduction from fixtures. To mimic such a situation, we introduce walls and control the shear flow and temperature by using walls. We employ the canonical equations as the dynamic equations for beads in polymer chains:

$$\frac{d\boldsymbol{r}_{i,k}(t)}{dt} = \frac{\boldsymbol{p}_{i,k}(t)}{m}, \quad \frac{d\boldsymbol{p}_{i,k}(t)}{dt} = -\frac{\partial \mathcal{U}(\{\boldsymbol{r}_{i,k}(t)\})}{\partial \boldsymbol{r}_{i,k}(t)}. \tag{3}$$

The walls consist of fixed wall particles and graft chains attached to wall particles. The wall particles are moved with a constant velocity to generate a shear flow. The Langevin thermostat is used for the graft chains, and the temperature of the graft chains are controlled. The flow and temperature of polymer chains are controlled only via the interaction potential (in Eq. (3)) between polymer chains and walls (wall particles and graft chains).

In what follows, we use the dimensionless units by setting the Lennard-Jones parameters as $\sigma = 1$ and $\epsilon = 1$, and the mass as $m = 1$. We set the degree of polymerization (number of beads per one chain) as $N = 25$, which is below the entanglement polymerization degree. The thermostat temperature is set to $k_B T = 1$ and the density of beads is $\rho = 0.83$. The viscoelastic Rouse relaxation time determined from the linear viscoelasticity (LVE) data is $\tau_R = 2.4 \times 10^2$. The (apparent) shear rate $\dot{\gamma}$ is changed in the range from 0.0001 to 0.1. (The range of the Weissenberg number $\mathrm{Wi} = \tau_R \dot{\gamma}$ is from 0.024 to 24.) The shear rate for a wall-driven system is determined from the gradient of the velocity field at the steady state.

RESULTS

Fig. 1(a) shows the viscosity growth functions for SLLOD and wall-driven systems with several different shear rates. Both the SLLOD and wall-driven systems show similar viscosity growth curves. If the Weissenberg number is sufficiently low ($\mathrm{Wi} = 0.24$), the viscosity growth functions at the long-time region almost coincide to the LVE envelope. As the Weissenberg number increases ($\mathrm{Wi} = 2.4$), we observe that the viscosity decreases (the shear thinning behavior) in both systems. If the Weissenberg number becomes sufficiently large ($\mathrm{Wi} = 24$), we observe that two systems exhibit qualitatively similar but quantitatively different viscosity growth functions. **Fig. 1**(b) shows the steady state viscosity data for the SLLOD and wall-driven systems. At the low Weissenberg number region, two systems show almost the same viscosity. However, if the Weissenberg number becomes large ($\mathrm{Wi} \gtrsim 10$), the viscosity of the wall-driven system becomes clearly higher than that of the SLLOD system.

We consider that there are several origins which cause the difference in the shear viscosities in the high shear region. One is the viscous heating effect. In the wall-driven system, the temperature is controlled only at the wall region. By applying the shear flow, polymers are heated by the viscous dissipation and the temperature will be inhomogeneous. In fact, we can observe that the temperature of the wall-driven system is clearly inhomogeneous in the high shear region. Such a change of the temperature affects the viscosity. We expect that the viscous heating may not be negligible in some experimental systems.
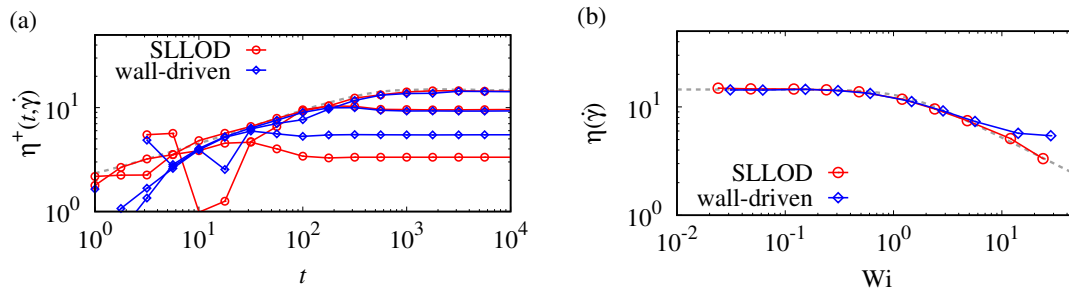
Figure 1: (a) The viscosity growth curves of SLLOD and wall-driven systems for $\mathrm{Wi} = 0.24, 2.4$, and 24 (from top to bottom). The dashed gray curve is the LVE envelope. (b) The steady state viscosities. For comparison, fitting to the Carreau model[1] is also shown as the dashed gray curve.

Another is the artifact of the atomic SLLOD model and the thermostat[5]. In the SLLOD model, all beads effectively feel the forces generated by a homogeneous shear field. Also, beads feel the forces exerted by the Nosè-Hoover thermostat. These forces may become artificially strong when the shear rate is high. Then polymers will be driven too strongly and the viscosity will be underestimated. The rotational motion of a polymer chain can be also affected by the artifact in a similar way. In both systems, $\eta(\dot{\gamma})$ can be well correlated to the gyration tensor: $\eta(\dot{\gamma}) \propto S_{yy}^{1.4}$ (S_{yy} is the yy-component of the average gyration tensor at the steady state). S_{yy} can be related to the angular momentum, and thus this result implies that the viscosity is strongly related to the angular momentum and also to the rotational behavior. Careful examination of the SLLOD equations and thermostats will be required to clarify the dynamics of polymer chains under fast shear.

ACKNOWLEDGMENTS

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