Rheology of Confined Polymer Melts under Shear Flow: Weak Adsorption Limit

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ABSTRACT: The dynamics of a confined polymer melt between weakly adsorbing surfaces is considered theoretically. The finite chain extensibility is taken into account explicitly, and the tangential stress and the first and the second normal-stress differences are calculated as functions of shear rate $\dot{\gamma}$. For small shear velocities ($u < u^{**}$) the surface slip is large, and the apparent viscosity, η_{app}, is proportional to the layer thickness h and is independent of the shear rate. For very high shear rates, the surface slip is small and the tangential stress increases with velocity to the power $^1/_3$. Alternatively, the apparent viscosity η decreases as a function of $\dot{\gamma}$ with a characteristic $-^2/_3$ power law.
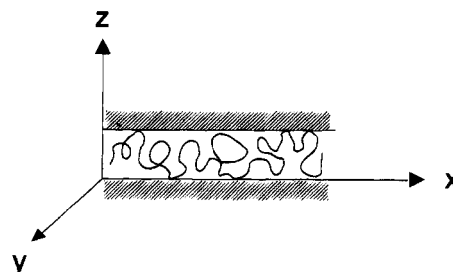
1. Introduction

Polymer–surface interaction becomes an important parameter for polymer flow in a confined state when the characteristic size of the system is of the order of the polymer coil size. This fact is confirmed by a number of experiments devoted to the dynamics of thin polymer films.[1-5] In a number of cases, where the adsorption between polymer and surface is weak enough, surface slip is observed.[6-8] Obviously, this surface slip depends on the mobility of the polymer segments near the wall and is in general determined by the strength of the polymer–surface interaction.

In the present study we investigate theoretically the rheological behavior of a thin polymer melt film confined between two weakly adsorbing surfaces and subjected to a shear due to a constant imposed velocity. The opposite case of strong adsorbing surfaces has been completed recently.[9] Most of the methodology is already presented in the previous paper on nonlinear rheology in the bulk state.[10]

As before, we assume the chains to consist of N statistical segments of length a and excluded volume v. The thickness of the confined film, h, is assumed to be smaller or equal to the size of the coils ($h \leq aN^{1/2}$). The area of contact per segment is v/a, and an adsorbed chain has on average Na/h contacts with the surfaces. The polymer chains in a melt polymer layer locally obey Gaussian statistics.[11] The global effect of the solid walls on the chain statistics can be accounted for by the mirror-image principle.[12]

2. Nanorheology in the Confined State: Weak Adsorption Limit

In our previous paper[10] bulk systems were considered, i.e. systems for which the distance h between the walls greatly exceeds the size of the polymer coil, $h > aN^{1/2}$. Now we consider the opposite case of a confined polymer melt with $h < aN^{1/2}$. The polymer–surface interaction will have a strong influence on the dynamics of the chains in this case. The mobility of polymer segments on the surfaces and far away from it will be different.

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Figure 1. Characteristic conformation of the chain in the confined state.

In the middle part of the confined film the mobility of the chain segments is determined by a friction coefficient ζ_0, which in principle can be much larger than the bulk value ζ. The motion of adsorbed chain segments on the other hand is governed by a friction coefficient ζ_1 different from ζ_0, due to the surface potential with a typical scale $\sim a$. If the polymer–surface interaction is attractive, ζ_1 is expected to be greater than the friction coefficient $\zeta_0/\zeta_0 > 1$. Here it is assumed that this condition is satisfied.

It is convenient to consider a polymer chain as a sequence of blobs of size h, each blob consisting of $g_0 \sim h^2/a^2$ segments. A finite fraction of the blobs (e.g. $\sim^1/_2$) must form bridges between the surfaces (a blob is called a "bridge" if it has contacts with both walls[11]); each bridge implies on the order of $g_0^{1/2} \sim h/a$ contacts with the surfaces. Other blods constitute loops (a loop has $\sim h/a$ contacts with one of the surfaces) (Figure 1).

When a velocity u is imposed, the fraction force impacts both on the loops and on the bridges. In order to calculate this force let us assume that the surface slip velocity is u_s, and therefore the shear rate inside the layer is given by

$$\dot{\gamma} = (u - 2u_s)/h \tag{1}$$

We furthermore assume that the coil conformation can still be described by the equilibrium statistics. Then, the characteristic friction force acting on a loop is

$$f_1 \sim \zeta_0 \dot{\gamma} h g_0 \tag{2}$$

Obviously, this force, by means of the chain elasticity, causes a slip velocity u_s near the surface corresponding to the surface friction force
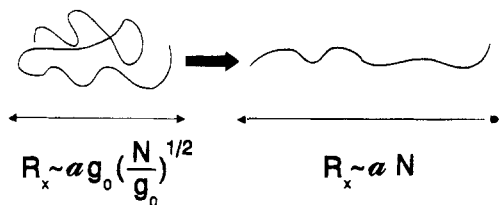
$$f_1' \sim \zeta_1 u_s g_0^{1/2} \tag{3}$$

Figure 2. Characteristic conformation of a chain before and after the transition point.

From the condition $f_1 = f'_1$ the slip velocity is found to be

$$u_s = u/(2 + \mu) \qquad \mu = (\zeta_1 a)/(\zeta_0 h) \qquad (4)$$

In this regime, the slip is large, if the parameter $\mu \ll 1$. From here on, this condition is supposed to be valid. The opposite case $\mu \gg 1$ was investigated in ref 9. For $\mu \ll 1$ the shear rate $\dot\gamma$ inside the film can be expressed in terms of the apparent shear rate $\dot\gamma_{app} = u/h$ by

$$\dot\gamma = \dot\gamma_{app}\mu/2 \qquad (5)$$

The total elongation force acting on a bridge is given by[9]

$$f_2 \sim u\zeta_1 g_0^{1/2} \qquad (6)$$

For strong surface slip $f_2 \sim f_1$. Thus each g_0 blob is elongated by a characteristic force $\sim f_1$.

Let us introduce the two-dimensional position $\mathbf{r}_n$ in the plane (x, y) for the center of mass of the nth blob (n increasing along the chain). The dynamical equation of the chain on the plane is given by

$$\zeta^*\frac{\partial \mathbf{r}_n}{\partial t} = \kappa^*\frac{\partial^2 \mathbf{r}_n}{\partial n^2} + f_n \mathbf{e}_x \qquad (7)$$

where the random force f_n impacts on the nth blob and has the following characteristics

$$\langle f_n \rangle \sim f_1 \qquad \langle f_n f_m \rangle - \langle f_n \rangle \langle f_m \rangle \sim f_1^2 \delta_{nm}$$

the boundary conditions are

$$\frac{\partial \mathbf{r}_n}{\partial n} = 0 \qquad n = 1, N/g_0 \qquad (8)$$

where $\zeta^* \sim \zeta_1 g_0^{1/2}$, $\kappa^* \sim 1/a^2 g_0$, and $\mathbf{e}_x$ is the unit vector directed along the x-axis. The chain moves along the x-axis with average velocity

$$v \sim f_1/\zeta^* \sim u/2 \qquad (9)$$

From eq 7 we can conclude that the conformation of the chain on the (x, y) plane is Gaussian (Figure 2). Note however that the chain is anisotropic: it is more extended in the x direction since the blobs are stretched along the flow. The typical chain sizes are (we assume that $f_1 > 1/h$):

$$R_x \sim f_1 a^2 g_0 (N/g_0)^{1/2} \qquad R_y \sim aN^{1/2} \ll R_x \qquad (10)$$

The above results are valid as long as the condition $f_1 < 1/a$ is satisfied. This corresponds to an imposed velocity $u < u^*$, where
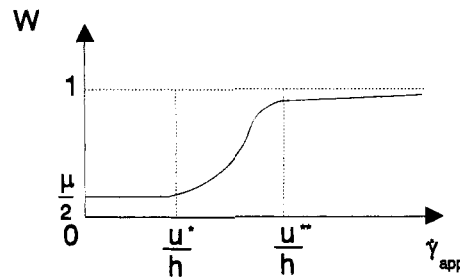
Figure 3. Dependence of the ratio $w = \dot\gamma/\dot\gamma_{app}$ on $\dot\gamma_{app} = u/h$.

$$u^* = \frac{a}{\tau_0\mu}\left(\frac{a}{h}\right)^2 \qquad (11)$$

If the shear velocity u exceeds u^*, the force $f_1 > 1/a$ exceeds the thermal force. Due to the finite extensibility of the chain, reflected in a nonlinear force–extension relation,[10] this force induces a strong compression force in the normal direction. As a result, the characteristic normal size of the g_0 blob ξ becomes smaller, i.e. $\xi < ag_0^{1/2}$. In this case a chain might be separated from both surfaces, and its conformation becomes strongly elongated (Figure 2). The transition from a Gaussian conformation to an extended one takes place at a critical velocity which is proportional to u^*. At this point the chain changes its size along the x-axis from $R_x \sim ag_0(N/g_0)^{1/2}$ to $R_x \sim aN$.

Beyond this transition point, the surface slip velocity will obviously be modified. Let us consider a chain adsorbed to the surface. This chain has $\sim (N/g)g^{1/2} \sim N(\dot\gamma\tau)^{1/3}$ contacts with the surface, where $g \sim (\dot\gamma\tau)^{-2/3}$; see ref 10. If the slip velocity is u_s, the surface friction force acting on the chain is given by

$$f \sim Nu_s\zeta_1(\dot\gamma\tau)^{1/3} \qquad (12)$$

This force must be counterbalanced by the flow force f' given by

$$f' \sim N\dot\gamma\zeta_0\xi \qquad (13)$$

As a result, using the equality $f = f'$, the following equation for the ratio $w = \dot\gamma/\dot\gamma_{app}$ is obtained

$$\frac{\mu}{2}\left(\frac{h}{a}\right)^2(\dot\gamma_{app}\tau_0)^{2/3}(1 - w) = w^{1/3} \qquad (14)$$

This equation has the following asymptotical solutions

$$w \sim u^2\mu/(8u^{*2}) \qquad u^* < u < u^{**} = u^*\mu^{-1/2} \qquad (15a)$$

$$w \sim 1 - 2\mu^{-1/3}(u^*/u)^{2/3} \qquad u > u^{**} \qquad (15b)$$

The dependence of the ratio w on the imposed velocity u is shown in Figure 3. When the velocity $u \to \infty$, the ratio $w \to 1$, and the surface slip becomes small.

The stresses in the confined system can be calculated by the same method as used in the bulk.[10] When the imposed velocity is high ($u > u^*$), the dependence of the shear stress and normal stresses on the shear rate $\dot\gamma$ are described by the same equations as for the bulk (ref 10, eqs 17, 18, and 21). The only difference being that τ has to be replaced by $\tau_0 \sim a^2\zeta_0$

$$\sigma_{xz} \sim (\dot\gamma\tau_0)^{1/3}/v \qquad (16a)$$

$$N_1 \sim N(\dot\gamma\tau_0)^{2/3}/v \qquad (16b)$$

$$N_2 = 0 \qquad (16c)$$

In order to calculate the stresses for small velocities $u < u^*$, let us consider g_0 blobs. These blobs can be
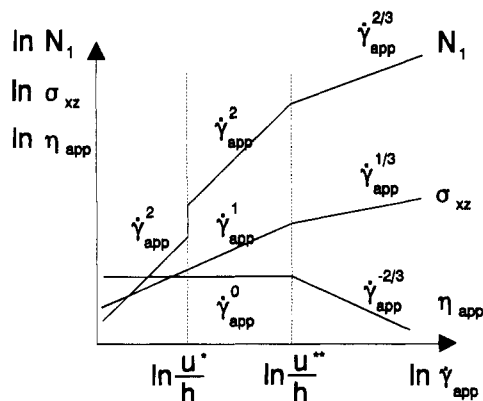
Figure 4. Plot of tangential (σ_{xz}) and normal (N_1) stresses and the apparent viscosity (η_{app}) as a function of shear rate $\dot\gamma_{app}$.

considered as being independent from each other because there are no long-range correlations along the chain. Therefore, the tangential and normal stresses for this case must be the same as in the bulk of chains containing g_0 segments. Hence, the final results can be obtained from the corresponding results in the bulk (ref 10, eqs 4 and 14) by substituting g_0 for N and τ_0 for τ

$$\sigma_{xz} \sim (\dot\gamma\tau_0)g_0/v \tag{17a}$$

$$N \sim (\dot\gamma\tau_0)^2 g_0{}^3/v \tag{17b}$$

$$N_2 = 0 \tag{17c}$$

The apparent viscosity, η_{app}, can be defined as

$$\eta_{app} = \sigma_{xz}h/u \tag{18}$$

Equations 17 and 18 imply that

$$\eta_{app} \sim (\tau_0/v)(\zeta_1/\zeta_0)(h/a) \qquad u \ll u^{**} \tag{19a}$$

$$\eta_{app} \sim \dot\gamma^{-2/3}\tau_0{}^{1/3}/v \qquad u > u^{**} \tag{19b}$$

where

$$u^{**} \sim (a/\tau_0)(\zeta_0/\zeta_1)^{3/2}(a/h)^{1/2}$$

Note that $u^{**} \gg u^*$ and that in the region $u > u^{**}$ the slip is small (see eq 15b).

The qualitative dependence of σ_{xz}, N_1, η_{app} as a function of shear rate is shown in Figure 4. The first

normal-stress difference N_1 has a jump in the point $u \sim u^*$, or $\dot\gamma \sim 1/(\tau_0 g_0{}^{3/2})$, because the chain changes its conformation at this point from Gaussian to elongated.

3. Discussion and Conclusions

In this paper we present a theory for nonentanglement polymer melts confined between two weakly adsorbing surfaces. Our calculations show that the chain nonlinearity has profound influence on the surface slip behavior. The slip is large for small enough shear rates only, when the chains are still close to Gaussian. For high shear rates, the chains become strongly elongated along the flow direction and, due to the nonlinearity, compressed in the normal direction. This fact leads to a decreasing surface slip.

The principal difference between bulk and confined melt consists of the scale of the relaxation times. Although, a consistent description of relaxation processes in the confined melt does not exist yet, experiments do show[1-5] that the relaxation processes are strongly suppressed in the confined state. As a result nonlinear behavior for confined polymer melts occurs at much smaller shear rates, as manifested by the inverse proportionality of the critical shear velocity u^* to the segmental relaxation time τ_0.

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