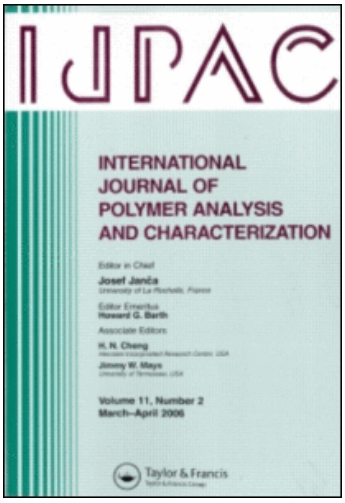

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A Brownian Dynamics Simulation of a Polymer/Wall Interface Under Shear

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A Brownian Dynamics Simulation of a Polymer / Wall Interface Under Shear

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In this paper the polymer/wall interface is simulated under simple shear by using the method of Brownian dynamics. The polymer system is considered as a network of polymer strands whose dynamics are described by a Hookean dumbbell model. The dumbbells break off the wall due to the excessive tension imposed by the bulk fluid motion and, as a result, slip occurs at the interface. The convection equation arising in kinetic theories of polymeric liquids is solved to calculate the time evolution of the configurational distribution function $\Psi(Q, t)$ by using a direct stochastic interpretation method [12]. The stress tensor and the slip velocity are calculated by averaging the proper relations over a large number of Hookean dumbbells. Because the model probabilisitically evolves in time, dynamic slip velocity calculations become possible for the first time. Finally, the results are compared with experimental slip velocity data.

KEY WORDS Dynamic slip, Brownian dynamics, polyethylene, interface failure

INTRODUCTION

In the processing of polymer plastics, the polymer melts are subject to such large and rapid deformations that the shear stress at a solid wall can reach very high levels and, as a result, the no-slip boundary condition ceases to be valid [1–3]. To simulate such processes realistically, it is necessary to have available slip velocity models, which can adequately describe both the dynamic and steady-state behavior of the slip phenomenon.

Several slip velocity models have been proposed in the literature [1–8] which are capable of describing only steady-state slip velocity data (static slip velocity models). However, their use in the numerical simulation of polymer processes is limited, due to the fact that slip exhibits characteristics of a relaxation process.

Hatzikiriakos and Dealy [3] carried out steady and dynamic shear experiments (exponential and large amplitude oscillatory shear) in a sliding plate rheometer to study the slip behavior of a high-density polyethylene (Sclair 56B). They found that the steady-state slip velocity data determined from steady shear experiments could not explain the shear stress response obtained from dynamic experiments. A finite time (slip relaxation time) is required for slip to attain its steady-state value. In addition, in very rapid deformations slip may not occur even if the shear stress

exceeds the critical value provided that the strain is relatively small [9]. These observations of dynamic slip cannot be explained by a static slip velocity model.

A dynamic slip velocity model was recently developed by Hatzikiriakos and Kalogerakis [10]. The behavior of a polymer/metal interface was simulated by using a network kinetic theory. The polymer segments were modeled as Hookean springs which are deformed affinely. In this paper, the dynamics of the polymer segments are described by Hookean dumbbells which do not only feel the affine deformation but also a retractive force and Brownian motion. The resulting diffusion equation (Fokker-Planck) is solved numerically by using a method developed by Petruccione and Biller [11, 12] in order to calculate the shear stress and slip velocity as functions of time in steady and dynamic shear flows.

POLYMER NETWORK MODELS

A rubber is considered to be composed of strands which are permanently cross-linked at junctions. To allow for a liquid-like behavior these permanent entanglements are considered to be only temporary in the case of polymer melts. Thus an idealized polymer network model consists of segments temporarily cross-linked at junctions which break up and reform continuously. Each polymer segment can be represented by a vector, Q, which defines its size and orientation.

The vectors Q follow the configurational distribution function Ψ whose time evolution is governed by a PDE which is known as the convection equation in kinetic theory for polymer solutions and melts [13]. This equation, for an ensemble of Hookean dumbbells, which not only feel the affine deformation but also a retractive frictional force and a Brownian random motion, takes the following form [14].

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial Q} \cdot \left(\kappa Q \Psi - \frac{2}{\zeta} F \Psi - \frac{2kT}{\zeta} \frac{\partial}{\partial Q} \Psi \right) = h(Q)(\Psi_0 - \Psi) \qquad (1)$$

where κ^T is the velocity gradient tensor, Ψ is the configurational distribution function of the vectors Q, $h(Q)$ is the proportionality constant of the rates of creation and loss of dumbbells, and F is the Hookean spring force ($F = HQ$). Note that the rate of loss is assumed to be proportional to the configuration distribution function Ψ, and the rate of creation is assumed to be proportional to the equilibrium distribution function Ψ_0 [11, 12].

The equilibrium distribution, Ψ_0, is assumed to be a trivariate Gaussian distribution which reduces to

$$\Psi_0(Q) = \frac{n_0}{(2\pi\sigma^2)^{3/2}} \exp\left[-\frac{Q^2}{2\sigma^2} \right] \qquad (2)$$

where σ^2 is one-third of the mean-square equilibrium length of the dumbbells, and n_0 is the equilibrium number density of the segments of the network (number of polymer segments per unit volume).

The stress tensor can be evaluated by averaging the tension of all Hookean dumbbells,

$$\tau = H\langle QQ\rangle \tag{3}$$

where H is the Hookean constant of the spring defined as $H = n_0 kT/\sigma^2$, k is the Boltzman's constant and T is the absolute temperature.

To solve Equation (1), one has to specify $h(Q)$ and the type of flow, that is, the tensor κ. In this paper the slip velocity is studied for simple shear flow occurring in the space between two parallel plates by means of a sliding plate rheometer. Namely, the polymer is placed in the space between two parallel plates and at time, $t = 0$, the upper plate starts moving with velocity V. The nominal shear rate in this case is defined as the ratio of the velocity of the upper plate to the gap spacing between the two plates d, this is $\dot{\gamma}_n \equiv V/d$. For zero slip velocity the nominal $\dot{\gamma}_n$ and actual shear rates $\dot{\gamma}$ are the same. However, under slip conditions one may easily show that,

$$\dot{\gamma}_n \equiv V/d = \dot{\gamma} + \frac{2u_s}{d} \tag{4}$$

For simple shear the tensor κ is

$$\kappa = \dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{5}$$

The dynamics of the vectors Q satisfy the following Langevin equation,

$$\dot{Q} = \kappa Q - \frac{2}{\zeta}F(Q)) + \eta(t) \tag{6}$$

where η is Gaussian white noise with zero mean and the two time correlations

$$\langle \eta_i(t)\eta_j(t')\rangle = \frac{4kT}{\zeta}\delta_{ij}\delta(t - t') \tag{7}$$

More details one may find in references 14–17.

To quantify the net rate of creation of the dumbbells,the following functional form of $h(Q)$ proposed by Petruccione and Biller [11, 12] is considered,

$$h(Q) = \frac{1}{\lambda_0}\left[1 + \log\left(1 + \varepsilon\frac{Q^2}{\sigma^2}\right)\right] \tag{8}$$

where λ_0 is a time constant and ε is a dimensionless parameter. Equation (8) has been found to give reasonable rheological predictions in simple flows [11, 12]. This equation should be modified before applied to dumbbells at the polymer/wall interface. This is done in the next section.

POLYMER / WALL INTERFACE

Consider that the polymer is attached to a rigid wall through Hookean dumbbells. For each dumbbell at the interface, two types of links are considered. A link of type A between segments (temporary cross-links) and a link of type B between the solid wall and the dumbbell. Dumbbells are lost more frequently due to destruction of links of type A than due to the destruction of links of type B. This should be taken into account in modifying the loss rate function at the polymer/wall interface.

We assume that the number of active sites per unit area of solid wall at equilibrium is n'_0. The surface density, n'_0 should be related to the number density, n_0, through a length scale comparable to the absolute average length of polymer segments in the direction normal to the solid boundary, that is σ. These numbers have the same value but different units. n'_0 is the number of segments per unit area and n_0 is the number of segments per unit volume.

As a proper function for the constant of the dumbbell loss rate at the polymer/wall interface due to the destruction of their B-links, we modify Equation (8) as follows,

$$h'(Q, Q^*) = \frac{1}{\lambda_0}\left[1 + \log\left(1 + \varepsilon\frac{(\|Q\| - Q^*)^2}{\sigma^2}\right)\right] \tag{9}$$

where Q^* is a critical length above which the tension of the strand is capable of overcoming the work of adhesion [10]. Equation (8) determines the number of segments to be removed from the ensemble. However to calculate how many of the lost segments are destructed due to the destruction of their B-link, Equation (9) is used. These segments contribute to the slip velocity calculation.

To calculate the slip velocity, the following expression is proposed:

$$u_s = n'_0\sigma^2\left\langle n(\kappa\dot{Q})t_h\right\rangle \tag{10}$$

where n is a unit vector parallel to the direction of flow, and t_h is the hovering time of each broken dumbbell (time elapsed between the breakage and reformation of the adhesive link).

After breaking off the wall, the dumbbells start relaxing before they become candidates for entering the ensemble again. For simplicity the hovering time is assumed to be the same for all members of the ensemble. Note that in the slip velocity calculations if a dumbbell is lost due to the breakage of its A-link, it is not taken into account in the slip velocity calculations. Only loss of dumbbells due to the destruction of their B-link contributes to slip calculations.

SIMULATION

Before the simulation, the equations are nondimensionalized by using the energy scale kT, the length scale σ, and time scale λ_0. Equation (1) is solved by using a

numerical method developed by Petruccione and Biller [11, 12]. According to this method, the diffusion equation (Eq. 1) is translated into a stochastic Langevin equation (Eq. 7). In step form this is:

S1. Generate a Gaussian distribution consisting of N_0 dumbbells at time 0. Due to the fact that polymer segments at the interface have a preferred direction, the method of "reflecting wall" is used to correct their y-component (normal to the solid wall) which should always be positive. Such a distribution is also used later in the simulation for reformation of the broken dumbbells.

S2. For each dumbbell in the actual ensemble calculate the new configuration after a small time step Δt: $Q(t + dt) = Q(t) + \Delta t[(\kappa(\gamma, t)Q(t) - 0.5Q(t)] + \sqrt{\Delta t}\, f(t)$, where $f(t)$ is a normally distributed random numbe [14]. Note that the Euler stochastic integration scheme is used to discretize Equation (7) (Ito stochastic interpretation). Note also that Equation (5) should be used to calculate the true shear rate.

S3. For each dumbbell calculate the probability that is lost due to destruction of its A-link at the time interval Δt, that is $p = 1 - \exp\{-h\,\Delta t\}$. Also for each dumbbell with a length greater or equal to Q^* calculate the probability that breaks off the wall at the time interval Δt, that is $p' = 1 - \exp\{h'\,\Delta t\}$. Note that p is much less than p' and most of the dumbbells are lost due to the desstruction of their A-link. Keep record of those that break off the wall for the slip calculations.

S4. Calculate the mean wall shear stress and the mean slip velocity by averaging over all the ensemble. Note again that destruction of type-B links does not contribute to the slip calculations.

S5. Calculate the probabilities that some of the destructed dumbbells reform and include them into the ensemble.

S6. If desired time has been reached end the simulation, otherwise repeat steps 2–6.

S7. Finally repeat the calculations for several time steps (here we have used $\Delta t/\lambda_0 = 0.02, 0.05, 0.08$) because the results are time-step dependent. Use linear extrapolation to time step zero in order to obtain the final results [18].

VISCOSITY

In the subsequent sections, we discuss the simulation results and compare them with available experimental data for a high density polyethylene (HDPE, resin Sclair 56B) reported in reference 3. Some of the results are presented in dimensionless form.

First we calculated the viscosity. This is necessary in order to fit some of the model parameters. Viscosity calculations were perfomed with ensembles of 50,000 dumbbells which were found to give good statistics. The simulations were run for three time steps ($\Delta t/\lambda_0 = 0.02, 0.05, 0.08$) and the results were linearly extrapolated to time step of zero. A small correction was resulted from this procedure.

Figure 1 compares the viscosity of a HDPE (Sclair 56B), with that calculated from the simulations. Excellent agreement is obtained for $\lambda_0 = 0.4$ s, $n_0 kT = 1.15 \times 10^5$ Pa and $\varepsilon = 0.1$. Once the viscosity has been fitted, thus adjusting some of the parameters, slip calculations are performed next.

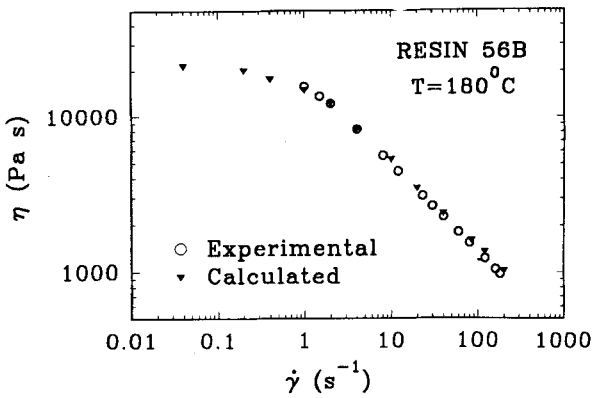

FIGURE 1 The experimental and calculated viscosity of resin Sclair 56B at 180°C. The viscosity was fitted using $n_0kT = 1.15 \times 10^5$ Pa, $\lambda_0 = 0.4$ s, and $\varepsilon = 0.1$.

SLIP IN STEADY SHEAR

Resin Sclair 56B slips over metal surfaces for wall shear stresses greater than the critical value of 0.09 Mpa [3]. Using this value, one may estimate the value of Q^* that predicts a flow curve which deviates from the no-slip flow curve at the critical value of 0.09 MPa. It was found that a value of dimensionless Q^* of 100 estimates the critical wall shear stress for the onset of slip to be about 0.09 MPa.

As was noted above, the results depend on the chosen time step and therefore the simulations should be run for at least three different time steps ($\Delta t/\lambda_0 = 0.02$, 0.05 and 0.08 were used here). Consequently, linear interpolation to time step zero is used to determine the final results. Figures 2 and 3 illustrate this for the slip velocity and shear stress calculations. It can be seen that the slip velocity is clearly time-step dependent and a large correction results by using linear interpolation. However, for the shear stress the resulting correction is much smaller as can be seen in Figure 3.

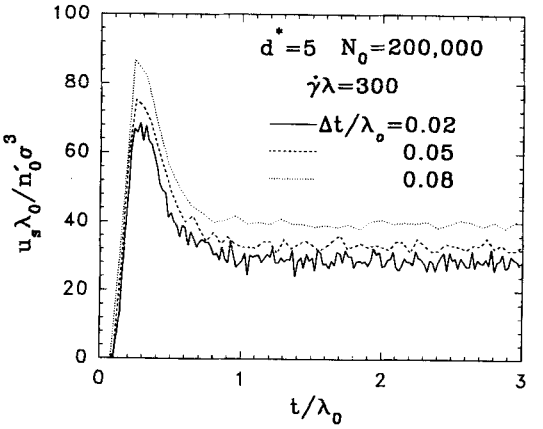

FIGURE 2 Dimensionless slip velocity vs time curves in a steady shear numerical experiment for three time steps ($\Delta t/\lambda_0 = 0.02, 0.05, 0.08$). Note that the obtained curves are time-step dependent and a linear interpolation is required to obtain the final results which correspond to time-step zero.

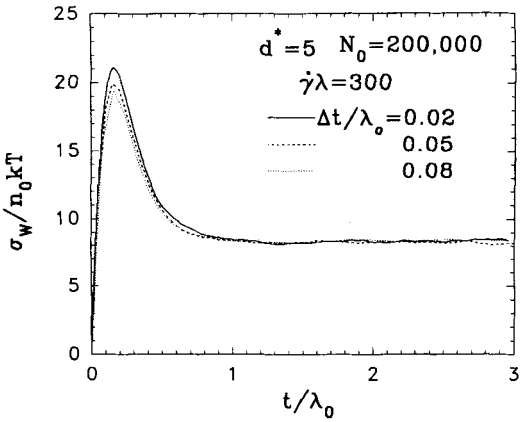

FIGURE 3 The corresponding to Figure 2 dimensionless shear stress vs time curves.

Figure 4 shows dimensionless slip velocity curves for several values of the nominal shear rate. It can be observed that at the dimensionless nominal shear rate of 100 the no-slip boundary condition ceases to be valid and a small but finite slip velocity is calculated. In can also be seen that the steady state value of the slip velocity increases with nominal shear rate and thus with wall shear stress. Note that the slip velocity curves do not start from the origin. This is due to the fact that for slip to occur, the wall shear stress should be higher than a critical value. In addition, slip is a relaxation process and a finite time is required before it attains its full effect. This will be clear in the next section, where the dynamics of slip are discussed.

Figure 5 is the corresponding shear stress curves to Figure 4. It can be seen that the shear stress increases with time and after overshooting it relaxes to its steady-state value. Also the steady-state value of the wall shear stress increases with dimensionless nominal shear rate as expected. Comparing Figures 4 and 5, it can be observed that the shear stress curves are much smoother (better statistics)

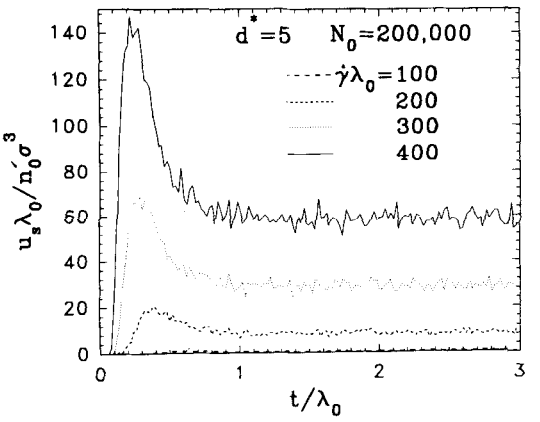

FIGURE 4 Dimensionless slip velocity curves in steady shear experiments for several nominal shear rates.

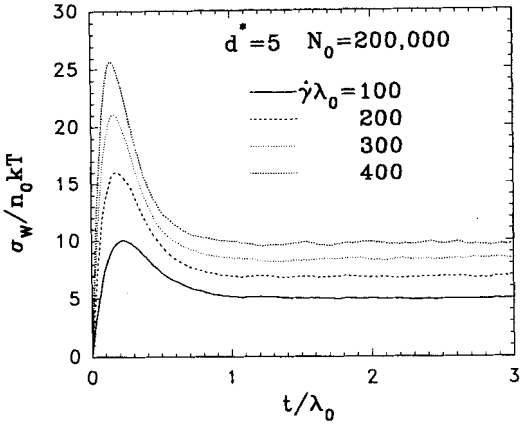

FIGURE 5 The corresponding shear stress curves of Figure 4 for several nominal shear rates.

than those of the slip velocity. This is due to the fact that the number of polymer dumbbells considered in the shear stress calculations is significantly larger than that which contributes to the slip velocity calculations (dumbbells which break off the wall).

In the slip simulations, the gap spacing between the two parallel plates should be defined as opposed to the viscosity calculations (no-slip). In the latter case the calculations are independent of the geometric dimensions. We define a dimensionless gap, $d^* \equiv d\lambda_0/n'_0\sigma^3 t_h$ whose form can be obtained from Equation (4). Slip velocities were calculated for several values of the dimensionless gap d^* (namely, 3, 5, and 10), in order to ensure the consistency of calculations. As may be seen from Figure 6, the u_s–σ_w relationship is independent of d^*.

Figure 6 also compares the slip velocity data of Sclair 56B at four temperatures as a function of the wall shear stress reported in reference 3 with the model predictions. Note that all the data have been reduced to 180°C by using the shift factor, a_T, of the time–temperature superposition method. The calculated slip

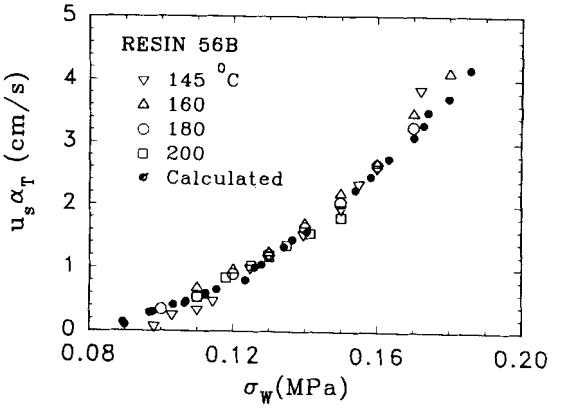

FIGURE 6 Experimental and calculated slip velocities of resin Sclair 56B for several temperatures and gap spacings. The experimental data have been reduced to 180°C by using the time–temperature superposition method.

velocity depends on the temperature through the relaxation time, λ_0, which, according to the network kinetic theory of polymer melts, is assumed to be proportional to the shift factor a_T [13]. The data were fitted by using $n_0 kT = 1.15 \times 10^5$ Pa (determined in fitting the viscosity) and $n_0' \sigma^3 t_h / \lambda_0^2 = 0.012$ cm/s; the agreement seems to be satisfactory.

SLIP IN TRANSIENT SHEAR

Exponential Shear

Exponential shear is a strong flow and it has been discussed in detail in reference 19. In this flow the nominal strain varies with time as follows

$$\gamma_n = A(e^{\alpha t} - 1) \tag{11}$$

where A is the strain scale factor and α is the exponential rate constant. Note that under no-slip conditions the nominal strain is equal to the true strain γ imposed to the polymer melt.

Using a sliding plate rheometer, Hatzikiriakos and Dealy [3] carried out exponential shear experiments for resin Sclair 56B. They found that in rapid unsteady deformations, a relaxation time is required to explain the observed slip. Based on their findings, they proposed a phenomenological dynamic slip velocity model which explained qualitatively some of the experimental findings.

Figure 7 plots the steady-state experimental slip velocity together with dynamic experimental slip velocity for two different deformation histories. The dynamic slip velocity data have been obtained from reference 20. The corresponding closed symbols are calculated slip velocities. First it can be seen from Figure 7 that the dynamic slip velocity is smaller than the calculated one. In addition, it can be seen that the deviation of the dynamic slip velocity curve depends on the rapidity of the deformation history. In the exponential shear, a measure of the deformation

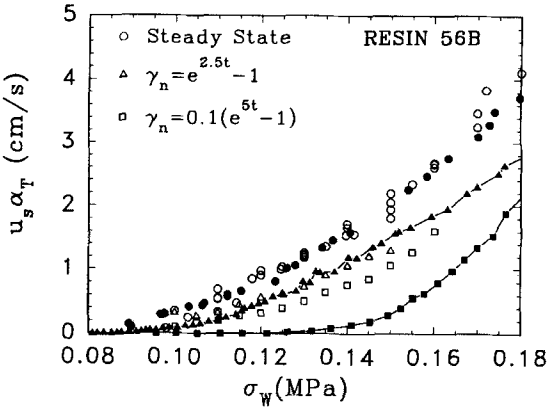

FIGURE 7 Experimental and calculated steady-state slip velocities (also plotted in Figure 6) and experimental and calculated dynamic slip velocities for two exponential shear deformation histories.

rapidity is the exponential rate constant. Note that the model agrees qualitatively with this observation. However, as may be seen from Figure 7, the quantitative agreement is poor. It is our belief that this is due to the fact that in transient situations multiple relaxation times should be used to obtain a reasonable quantitative agreement. In view of this, the recent work of Herman and Petruccione [21] is very useful.

CONCLUSIONS

A stochastic slip velocity model was developed to simulate the behavior of the polymer wall interface at high values of the wall shear stress where polymers has been observed to slip. This model is based on the network kinetic theory of polymer melts. The polymer system is considered as a network of polymer strands whose dynamics are described by the Hookean dumbbell model. The convection equation arising in this kinetic theory was solved to calculate the time evolution of the configuration distribution function $\Psi(Q,t)$ of the dumbbells. Based on this function, the wall shear stress and slip velocity were calculated by averaging the proper relations over a large number of polymer segments.

The steady-state model predictions have been shown to be in good quantitative agreement with steady-state experimental results. In transient situations, it was found that a finite time is required before the onset of slip. Thus, while steady-state slip velocity data shows that the onset of slip occurs at a critical value of the wall shear stress, dynamic slip may first occur at considerably higher values of the wall shear stress. This was found to depend on the rapidity of the deformation. Finally, the model predictions were found to be in qualitative agreement with dynamic experimental observations.

Acknowledgments

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Nomenclature

$f(t)$	Normally distributed random number
$F(Q)$	spring force
$h(Q)$	proportionality constant of rates of creation and loss of dumbbells
$h'(Q)$	constant of rate of loss of dumbbells due to destruction of their B-link
H	Hookean spring constant
k	Boltzman's constant
n	unit vector normal to the polymer/wall interface
n_0	number density of dumbbells
n'_0	surface number density of dumbbells
Q	vector defining the size and orientation of a dumbbell

Q^* critical length of a dumbbell beyond which the tension may overcome the work of adhesion
t time
t_h hovering time of broken dumbbells
T absolute temperature

Greek Letters

γ_n nominal strain
γ strain
$\dot{\gamma}_n$ nominal shear rate
$\dot{\gamma}$ shear rate
ε dimensionless constant in the expressions of $h(Q), g(Q)$
ζ friction coefficient
η viscosity
$\eta(t)$ White noise
κ^T velocity gradient tensor
λ_0 time constant
σ standard deviation of vectors Q at equilibrium
σ_w wall shear stress
σ_c critical shear stress for the onset of slip
τ stress tensor
Ψ_0 equilibrium configuration distribution function of Q
Ψ configuration distribution function of Q

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