

Friction Dependence on α -Relaxations in a Tethered Polymer Monolayer

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ABSTRACT

Functionalized low-molecular-weight polyisobutylene is commonly used as a lubricant additive to control low-velocity friction in clutches. The friction of tethered monolayers as a function of temperature and velocity was examined using lateral force microscopy. The friction force was found to obey time–temperature superposition, which indicates that the friction originates from a single relaxation mode. The scaling factors are identical to those obtained from neutron spin echo experiments of α -relaxations, linking the friction directly to segmental motion.

Considerable experimentation and computer simulation over the past decade has shown that fluids behave increasingly glasslike when confined to molecular dimensions.^{1–5} Measurements of elastic and loss moduli have demonstrated a plateau behavior at low frequencies in confinement, in contrast with the inverse frequency dependence in bulk rheology.⁵ Further, apparent viscosities become higher than that for bulk fluids at low shear rates. The concept of a “time-thickness superposition” has been advanced to universally describe shear behavior in terms of a reduced set of moduli and frequency variables. The scaling with frequency results from a dramatic decrease in molecular mobility with increasing confinement. Given the smoothly changing relaxation times extracted from ratios of elastic and loss moduli, it has become clear that neither a first-order phase transition nor surface crystallization is necessary to explain the results.^{4,6}

Most of the experimental data has been obtained from the surface forces apparatus, which confines the fluid between atomically flat surfaces under modest pressures and controllable thicknesses, but can be employed only near room temperature. We sought to determine whether these results can be reproduced using more typical tribological conditions in which normal forces are 2–3 orders of magnitude higher and compression and release occur in fractions of a second. Here we use the atomic force microscope to mimic a single asperity contact to measure the load, temperature, and velocity dependence of a model tethered poly(isobutylene) (PIB) molecule. The inclusion of temperature as a variable allows us to relate the friction response to the dynamic motion of the polymer, to monitor the occurrence of glass transitions, and to demonstrate the effect of applied normal forces on the “shear-thinning” behavior.

Piranha-solution-cleaned silicon wafers were chosen as a substrate and were soaked in a 1% solution of 2000 Da aminated poly(isobutylene) (Infineum Corp.) in toluene for 1 h. The solvent was evaporated and the film subsequently rinsed with pure toluene. Again, solvent was evaporated by heating the samples to 80 °C for 1 h, yielding a film thickness of 7 ± 0.5 nm as measured via optical reflectance. Assuming the film possesses the same density as bulk PIB, the graft density is approximately 20%. Because the distance between grafts is larger than the radius of gyration of a single molecule, the polymer is not in a “brushlike” state.⁷ All experiments were performed at temperatures well in excess of the glass transition (200 K).

Low-energy ion spectroscopy (LEIS) was used to confirm the molecular orientation as one in which the surface atoms are predominantly carbon, with few nitrogen atoms. The nanotribological behavior was characterized using a single Si_3N_4 rectangular cantilever with a spring constant of 40 Nm^{-1} in a nitrogen protecting atmosphere. As is typical in friction force microscopy, the friction was obtained by taking the difference of the two lateral force signals in the forward and backward scan direction, and then dividing by two. During these measurements, the resolution was usually 256 lines by 256 pixels each and scan areas of $1 \times 1 \mu\text{m}^2$. The poly(isobutylene) was strongly adsorbed. Subsequent to obtaining all high-load (to 1412 nN) and high-temperature data (to 80 °C), friction and topographic data were obtained under room temperature and low load conditions to ensure that there were no changes in surface character.

The friction of bare silicon was found to be temperature and velocity independent, in agreement with literature.⁸ Thus, all friction variations are attributable to the PIB film. Figure 1 demonstrates the power-law dependence of friction on tip velocity. In AFM experiments, a tip velocity can be

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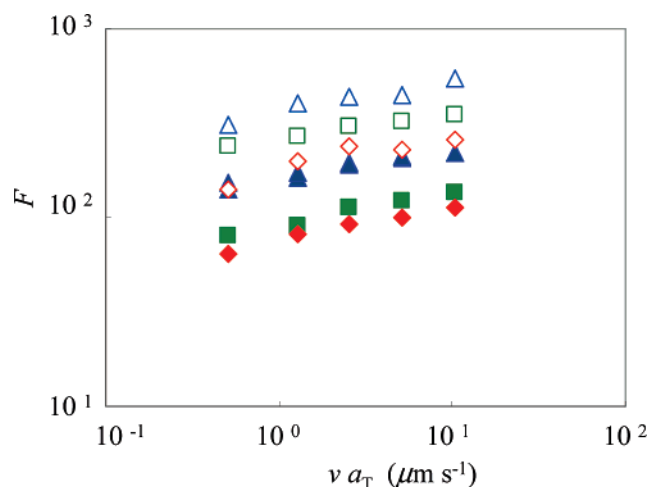


Figure 1. Plot of friction force (arbitrary units) vs scaled tip velocity for the two lowest applied loads. Filled and open diamonds 80 °C, 178 and 420 nN, respectively. Squares are at 60 °C and triangles are room temperature.

considered equivalent to a deformation frequency. The frequency in AFM experiments is given by the scanning velocity divided by the contact diameter. This concept has been successfully applied to thin polymer films to correlate AFM friction results to bulk rheological behavior. Hammer-schmidt et al.⁹ correlated peaks in AFM friction as a function of velocity to maxima in loss moduli as a function of frequency for poly(ethylene terephthalate), polystyrene, and poly(methylmethacrylate). This indicated that the dominant contribution to friction was viscoelastic mechanical loss.

Applying velocity shift factors based on the WLF time–temperature superposition (TTS) formalism yields master curves.¹⁰ For the friction data, shift factors a_T are obtained at each temperature by rescaling both the friction and the shear rate by a constant a_T ($F \rightarrow F/\nu a_T$ and $\nu \rightarrow \nu a_T$) such that the tribological data superpose. This scaling is analogous to that used to extend the frequency range of rheological testing by heating and cooling the sample. For bulk rheological samples of poly(isobutylene), the shift factor as a function of temperature has been measured and is expressed as the WLF correlation $\ln a_T = -20.91(T - 298.2)(209 + T - 298.2)^{-1}$.¹⁰ In Figure 3, shift factors have been obtained by a rescaling that superposes the friction force divided by tip velocity data (equivalent to a scaled “viscosity”) as a function of tip velocity. A key result is that these shift factors are in complete agreement with those derived from bulk moduli measurements of poly(isobutylene) (Figure 2). This is surprising considering the widely different physical constraints and deformation conditions between bulk flow and tribological flow. It is also counterintuitive considering the large body of literature illustrating the differences between bulk and confined flow. A discussion follows.

In rheological measurements of entangled polymer networks, TTS is based on equivalence between increasing temperature and decreasing dynamic shear frequency. It generally applies in situations where the range of frequencies probes a single relaxation mode or in situations where

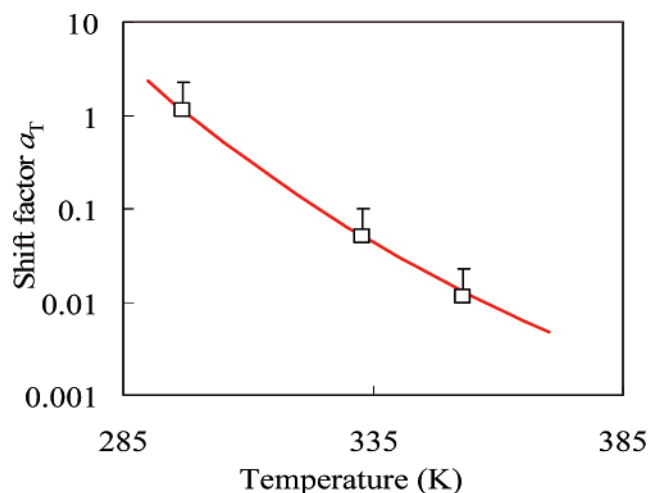


Figure 2. Plot of shift factors as a function of temperature. The WLF equation $\ln a_T = -20.91(T - 353.2)(209 + T - 353.2)^{-1}$ is shown as the straight line. An Arrhenius equation where $E_a = 0.72$ eV superposes the WLF equation.

multiple relaxation modes have the same temperature dependence. In macroscopic tribological experiments, a number of surfactant-coated surfaces have shown friction TTS. However, for confined polymer melts, the dynamics of the chain–surface interactions would be expected to play a role in friction, but a lesser role in bulk rheological flow where no interfacial slip occurs.⁴ Significantly different relaxation times would be expected. For the moment, we will assume this effect is insignificant, but will return to this later in the discussion.

Appealing naively to Rouse dynamics, rough calculations of molecular dimensions aid in evaluating the appropriate relaxation processes. Twice the radius of gyration of bulk 2000 Da PIB is approximately 9 nm, which is thicker than the film and slightly larger than the diameter of a compact molecule (8.5 nm) at a height of 6 nm. Thus, some degree of molecular overlap is predicted, but not significantly enough to be considered entangled. If this is the case, why does the friction data scaling factors agree with those of bulk rheology where entanglement relaxation predominates? The answer lies in analyses of the temperature dependence of segmental relaxations. Neutron spin–echo (NSE) experiments on PIB have been used to measure decay times of the density autocorrelation function (the structure factor) as a function of wave vector. In q -ranges at and above the structure factor peak, these decays were found to obey time–temperature superposition using scaling factors identical to those used in bulk rheological experiments. This supports the concept that PIB is thermorheologically simple: multiple relaxation modes possess the same temperature dependence.¹¹ In addition, dielectric spectroscopy measurements likewise show that α relaxations can be scaled using rheological data. Further NSE experiments at lower wave numbers, reflective of intrachain β processes, indicate structures that relax with a smaller temperature dependence.¹² These NSE data explain why, in the absence of entanglements, the temperature dependence of friction follows that of rheological data. Specifically, the friction is tied to α relaxations of the polymer.

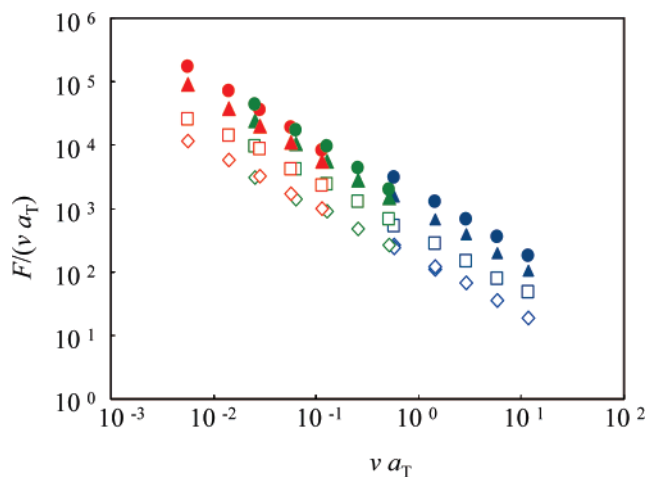


Figure 3. Scaled “viscosity” vs scaled tip velocity as a function of all four applied loads. From bottom to top: 178, 420, 921, 1412 nN.

Table 1. Values of Log–Log Fit of the Data Shown in Figure 3 for Each Load^a

applied load	exponent n	prefactor A	correlation
178 nN	0.834	0.42	0.9993
419 nN	0.850	0.46	0.9980
921 nN	0.875	0.56	0.9993
1412 nN	0.884	0.65	0.9943

^a The exponent n and prefactor A are from the function $F(va_T)^{-1} = A(va_T)^{-n}$.

Turning attention to the velocity dependence of friction, the friction data is divided by the scaled velocity as shown in Figure 3. Collectively considering all data obtained *under the same applied load*, the tip speed is proportional to shear rate, and the friction divided by this scaled tip velocity is proportional to viscosity. Note that comparisons across different applied loads cannot be made because the contact area and film thickness change with load, changing the proportionality between tip velocity and shear rate. Therefore, data reduction is performed on sets of data obtained under identical loading conditions. Because friction at each load can be considered equivalent to a shear stress, Figure 3 can be compared to plots of viscosity versus shear rate. Numerous SFA experiments have shown an extreme power-law “shear thinning” of confined fluids.^{13–15} These PIB results are no exception. Values of the exponent n obtained when the friction is fit to the power-law equation $F(va_T)^{-1} = A(va_T)^{-n}$ at each load are tabulated below (Table 1). These exponents are quantitatively consistent with those obtained on the SFA for a wide variety of fluids and indicate that this behavior is surprisingly independent of the specifics of the contact geometry and shear conditions. (The term *shear thinning* may be a misnomer because of the likelihood that the fluids do not undergo simple shear flow in a continuum sense.) The similarity between SFA and AFM results is unexpected because the PIB is tethered to the surface, whereas the SFA data is obtained on “free-moving” fluids. AFM experiments are expected to have a slip plane (at the tip surface), whereas the SFA may or may not have a slip plane at the mica surface

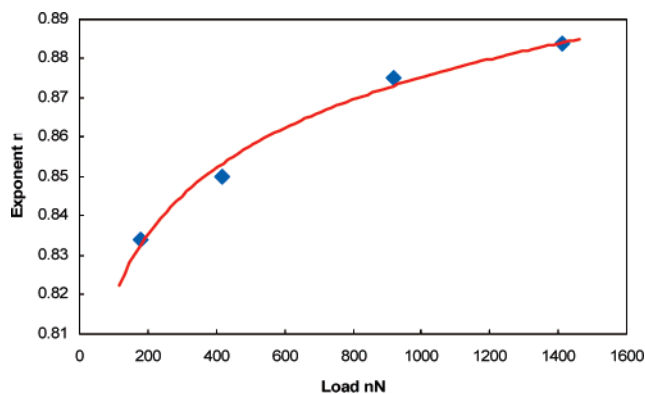


Figure 4. Plot of exponent n as a function of applied load according to Table 1. The line has been added to guide the eye.

depending on whether polymer is bound to the surfaces. It has been suggested that the repulsive forces observed in SFA experiments on polymer melts are similar to those obtained on polymer brushes where one surface is tethered. This would imply that polymer molecules may be pinned to one or both mica surfaces under confinement.^{4,14} Slip may not be a significant issue, however. Simulations have suggested that the power-law exponent is independent of the details of the nature of the strain, whether uniformly applied across the film or localized at the wall–fluid interface.¹⁶ These simulations, as well as the equivalence between SFA and AFM results, may help explain the insensitivity of the friction to details of the relaxations at the interface.

One principal difference between AFM and SFA experiments is the range of compressive forces applied to the films. The higher AFM pressures substantially increase relaxation times even in unconfined polymers. For PIB, NSE KLL α -relaxation times of bulk PIB were lengthened by 2 orders of magnitude at 300 MPa to 10 ns and are independent of molecular weight for $M > 1000$ Da.¹⁷ At lower molecular weights, greater scattering contributions originate from the faster relaxations of the polymer ends. We estimate the AFM contact time to be approximately 1000 Hz at the fastest speeds, which is far too slow to see the effects of segmental relaxations, even under extreme pressure. This is consistent with the constant friction power-law behavior: the scaled shear velocities do not overlap with any relaxation mode. Still, we expected to see the influence of pressure on the temperature dependence of the friction. In bulk fluids, particularly branched molecules, higher pressures increase the viscosity activation energy. Current experimentation on linear and branched isomers is elucidating this. However, the power-law exponents show a definite monotonic increase with compression. As pressure is increased (or PIB film is decreased), n increases (Figure 4).

These values are much higher than those predicted and measured in fluids undergoing a glass transition, where $n = 2/3$. Nonetheless, the increase in n with pressure qualitatively agrees with simulations.¹⁶

The AFM friction data presented here on a PIB monolayer clearly show the role of segmental relaxations. In the case of PIB, the similarity in scaling factor between friction data and bulk rheological data is likely attributable to its thermo-

rheological simplicity. For nonthermorheologically simple fluids, correlations between segmental relaxations (rather than reptation) and friction might be expected. That the rheology- and tribology-derived temperature dependence is the same is surprising, but can perhaps indicate strain- and/or surface independent response. Clearly, the ability to predict aspects of friction behavior on the basis of bulk fluid rheology measurements would greatly enhance development efforts. The velocity dependence is strikingly similar to that of a wide variety of fluids confined in the surface forces apparatus, strongly supporting the notion of a universal behavior of tribological fluids.

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References

- (1) Gee, M. L.; McGuigan, P. M.; Israelachvili, J. N. *J. Chem. Phys.* **1990**, *93*, 1895.
- (2) Yoshizawa, H.; McGuigan, P.; Israelachvili, J. *Science* **1993**, *259*, 1305.
- (3) Reiter, G.; Demirel A. L.; Granick, S. *Science* **1994**, *263*, 1741.
- (4) Luengo, G.; Schmitt, F.-J.; Hill, R.; Israelachvili, J. *Macromolecules* **1997**, *30*, 2482.
- (5) Ruths, M. R.; Ohtani, H.; Greenfield, M. L.; Granick, S. *Tribol. Lett.* **1999**, *6*, 207.
- (6) Demirel A. L.; Granick, S. *Phys. Rev. Lett.* **1996**, *77*, 2261.
- (7) Flory, P. J. *Pure Appl. Chem.* **1984**, *56*, 305.
- (8) Schirmeisen, A.; Jansen, L.; Holscher, H.; Fuchs, H. *Appl. Phys. Lett.* **2006**, *88*, 123108.
- (9) Hammerschmidt, J. A.; Gladfelter W. L.; Haugstad, G. *Macromolecules* **1999**, *32*, 3360.
- (10) Fetters, L. J.; Graessley, W. W.; Kiss, A. D. *Macromolecules* **1991**, *24*, 3136.
- (11) Richter, D.; Arbe, A.; Colmenero, J.; Monkenbusch, M.; Farago, B.; Faust, R.; *Macromolecules* **1998**, *31*, 1133.
- (12) Farago, B.; Arbe, A.; Colmenero, J.; Faust, R.; Buchenau, U.; Richter, D. *Phys. Rev. E* **2002**, *65*, 051803.
- (13) Yamada, S. *Tribol. Lett.* **2002**, *13*, 167.
- (14) Yamada, S. *Langmuir* **2003**, *19*, 7399.
- (15) Reiter, G.; Demirel, A. L.; Peanasky, J.; Cai, L. L.; Granick, S. *J. Chem. Phys.* **1994**, *101*, 2606.
- (16) Thompson, P. A.; Grest, G. S.; Robbins, M. O. *Phys. Rev. Lett.* **1992**, *68*, 3448.
- (17) Frick, B.; Dosseh, G.; Cailliaux A.; Alba-Simionesco, C. *Chem. Phys.* **2003**, *292*, 311.

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