Atomic-Force-Microscope Study of Polymer Lubricants on Silicon Surfaces

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Atomic-force-microscope measurements of the forces on a sharp tungsten tip sliding across silicon substrates coated with perfluoropolyether polymers provide insight into how lubricants function at the molecular level. In particular, hydrodynamic lubrication is observed for tip-substrate separation distances as small as a few polymer chain diameters and a relatively small change in the composition of the polymer, namely, the addition of alcohol end groups, greatly increases the load required to compress and squeeze out the polymers from between the sliding surfaces.

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The friction and wear that occurs between two rubbing surfaces can be greatly reduced by separating the surfaces with a film of lubricating molecules. The key properties that enable a molecular film to provide good lubrication have been identified as low shear strength and resistance to penetrating asperities [1]. Nevertheless, a molecular picture of how molecules lubricate has yet to be developed. In this Letter, lubrication by polymer films is studied in detail by measuring the forces acting on a single asperity, in the form of a sharp tungsten tip, sliding across silicon surfaces coated with thin polymer films. The polymer molecules studied are linear chain perfluoropolyethers with and without alcohol end groups. These results not only illustrate the dynamics of these polymers between sliding surfaces, but demonstrate several important, previously unreported aspects for molecules in confined spaces: First, a relatively small change in the composition of the polymer, the addition of alcohol end groups, greatly improves the resistance of the molecules to being squeezed out from between the sliding surfaces. Second, polymer films behave as liquid films in that they have negligible shear stress to applied shear strains until the molecules are completely compressed or squeezed out from between the sliding surfaces, showing that hydrodynamic lubrication can occur for surfaces separated by only a few cross-sectional diameters of the polymer backbone. These results are contrasted with previous studies of the shearing of similarly thin polymer films using the surface force apparatus (SFA) where solidlike shearing of the films is usually observed [2–5].

The Si(100) substrates were cleaned by rinsing with ultrapure solvents followed by exposure to UV-created ozone. They have a 15-Å-thick surface oxide layer. The polymers were applied on the substrates to a 10 to 30 Å film thickness, as determined by ellipsometry. The perfluoropolyether polymer with relatively unreactive CF_3 end groups was $F_3CCF_2(OC_2F_4)_q(OCF_2)_pOCF_3$ (Fomblin Z-03 from Montefluos, molecular weight ∼3000, $q \sim p \sim 16$, chain length ∼100 Å, chain diameter ∼7 Å). The polymer with alcohol end groups [$HOCH_2$-$CF_2(OC_2F_4)_m(OCF_2)_nOCH_2OH$, Fomblin Z-Dol] has a somewhat smaller molecular weight ∼2000, but the same perfluoropolyether backbone. Experiments were conducted in ambient laboratory air.

The atomic-force microscope (AFM), shown schematically in Fig. 1, is similar to ones described previously [6–8], except it uses two optical fibers for independently measuring components of the force on the tip perpendicular and parallel to the substrate surface. The cantilever is constructed by bending a 50-μm-diam tungsten wire at a right angle, and then etching the end to a sharp point, typically 1000 Å radius. The perpendicular and parallel deflections of the wire are measured by optical interference, where the interference occurs between laser light reflected off the back and side of the wire and laser light reflected internally off the ends of the optical fibers. The force on the tip is determined by multiplying the deflections by the spring constant of the wire, typically 35 N/m.

Figure 2 shows the perpendicular force or load force acting on a tip as it is brought into contact with substrates covered with unbonded liquid films of the polymer molecules. At point M, a sudden attractive force is observed due to formation of a liquid meniscus around the tip. Similar force-versus-distance curves have been discussed previously [7,8], but here the focus is on tip-substrate separation distances < 25 Å. If the two surfaces are separated by the liquid polymer with unreactive end groups, the force becomes increasingly more attractive for decreasing separation distances. When hard wall contact is reached, the force quickly turns repulsive.

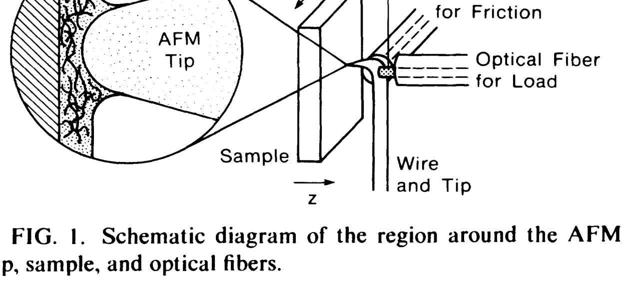

FIG. 1. Schematic diagram of the region around the AFM tip, sample, and optical fibers.

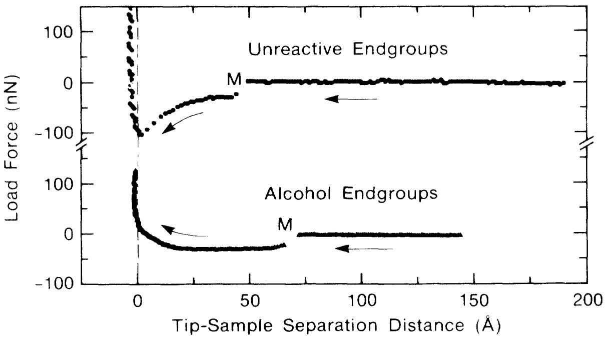

FIG. 2. Inward force-vs-distance curves comparing unbonded perfluoropolyether films on Si(100). The upper curve is for a 10-Å-thick film with unreactive end groups, while the lower curve is for a 30-Å-thick film with alcohol end groups. The tip-sample separation distance is defined as the difference between the Z sample and tip positions. A negative force indicates an attractive force.

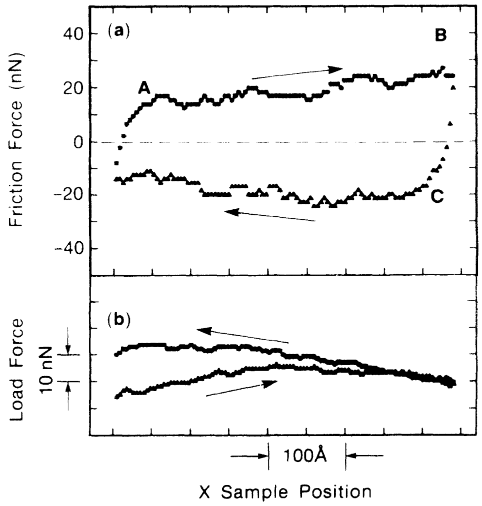

FIG. 3. The (a) friction and (b) load force on the AFM tip during sliding over an oscillation of the X sample position.

(Zero separation distance is set at the point where the tip and sample start to move together in hard wall contact.) Similar force-versus-distance curves were also observed for higher molecular weights (9000 and 14000) of this polymer, showing that the molecular weight of these molecules is relatively unimportant to the forces on the tip. The attractive force on the tip is the sum of the force from the liquid meniscus due to Laplace pressure [8] and solid-solid attraction, most likely van der Waals attraction [9,10], mediated by the liquid polymer.

If the two surfaces are separated by polymer with alcohol end groups, the load force is very different for separation distances < 25 Å. At this distance the net force becomes increasingly less attractive. The attractive forces acting on the tip are still present, but are counteracted by a repulsive force associated with the alcohol end groups. Recently, Rühe *et al.* [11] showed that these molecules with alcohol end groups have twice the heat of adsorption on silica surfaces as the molecules with unreactive end groups, with the extra heat of adsorption presumably coming from the polar or hydrogen bonding of the alcohol end groups with the oxide surface. The repulsive force on the tip would first come from the compression of the molecules underneath the tip followed by the force needed to overcome the hydrogen bonding so as to squeeze out the molecules from between the two surfaces. Consequently, an important effect of the alcohol end groups is to increase dramatically the load or contact pressure that a film of liquid polymer can support before solid-solid contact.

Friction experiments show that the alcohol end-group polymers maintain their load bearing capacity during sliding. In these experiments, the sample is moved rapidly back and forth in the X direction at a velocity of 1 μm/s, while the load on the tip is slowly increased to some maximum value, then decreased back to zero by moving the sample in the Z direction. No velocity dependence was found over the range of sliding velocities studied, 100 Å/s to 10 μm/s, indicating that viscous forces are negligible. Figure 3(a) shows an example of the parallel or friction force on the tip during one complete X oscillation of the sample. Initially, the tip moves with the sample, until, at point A, the wire exerts enough force to overcome the static frictional force, and the tip starts to slide across the surface. When the X sample direction is reversed at point B, the tip again moves with the sample until it starts to slide at point C. Figure 3(b) shows the perpendicular or load force on tip measure simultaneously with the friction force in Fig. 3(a). The upward shift over the cycle comes with the slight increase in load as the sample is slowly pushed up against the tip. The slight variations in load during the cycle correspond to a surface roughness of ~ 1 Å.

Figure 4 shows the average load and frictional force during sliding as a function of the Z sample position for the different types of lubricant films. Each data point in Fig. 4 represents the average over the sliding portion of a cycle in X like the one shown in Fig. 3. As the sample approaches the tip, contact with the lubricant occurs at point M, but for all the lubricant films the friction force is negligible until tip makes hard wall contact. For the liquid polymer films, Figs. 4(a) and 4(c) show that, just before hard wall contact is made, the load force during sliding becomes more attractive for the nonalcohol end-group polymer and less attractive for the alcohol end-group polymer in the same manner as when no sliding occurs (Fig. 2). When the sample is withdrawn, the friction force returns to zero when the hard wall contact is broken. Following the classical description of lubrication [1], the regime before hard wall contact is labeled hydrodynamic lubrication, where shearing of a liquid film takes place, and after hard wall contact, boundary lubrication,

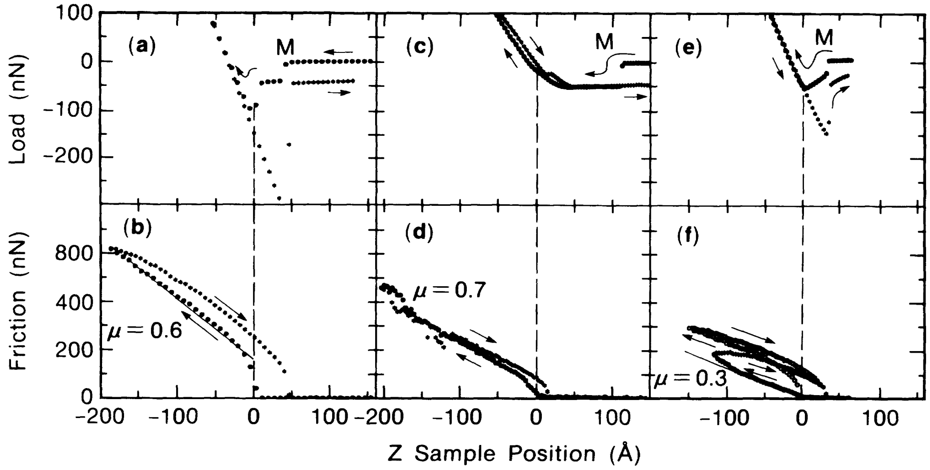

FIG. 4. The friction and load force vs the Z sample position for 30-Å-thick films on Si(100) of (a),(b) unbonded polymer with unreactive end groups, (c),(d) unbonded polymer with alcohol end groups, and (e),(f) bonded polymer. The open circles in (f) show the friction when the experiment is repeated in the same spot on the bonded polymer film.

where solid-solid shearing takes place. The transition between the two regimes is very sharp, requiring a change in separation distance less than a chain diameter.

The negligible friction before hard wall contact can be understood if it is assumed that the polymer films maintain their liquid character even for separation distances of only a few chain diameters. The friction force from shearing the liquid film can be approximated as $F \simeq A\eta v/D$, where A is the contact area, η the shear viscosity of the liquid, v the tip velocity through the film, and D a characteristic separation distance. If a 1000-Å radius tip penetrates a 30-Å-thick film, the maximum contact radius is 240 Å and the maximum contact area is 2×10^{-15} m^2. Using this contact area, the bulk viscosity for the alcohol ended polymer of 0.15 Pa s, $v=1$ μm/s, and $D=10$ Å, the viscous friction force would be ~0.3 pN, several orders of magnitude less than the detection limit of 1 nN for the experiment.

In the boundary lubrication regime, the friction for the liquid polymer films initially rises quickly, but soon increases linearly with load (friction coefficient μ in the range of 0.5 to 0.8). Similar friction coefficients are observed for unlubricated silicon surfaces, indicating that most of the unbonded polymers are squeezed out from between the rubbing surfaces, consistent with liquid polymers being poor boundary lubricants [1]. Some polymer molecules may still be trapped among the microasperities of the tip and contribute to the solid-solid shearing.

Polymers covalently bonded to surfaces are an important type of lubricant. Bonding of the alcohol ended polymer was achieved by heating at 150 °C for 1 h, in order to react the end groups with hydroxyl groups on the silicon oxide surface [7]. Figures 4(e) and 4(f) show the results from sliding on this bonded polymer film. At point M a slight attractive load force is observed when contact is made with the top of the bonded polymer layer. The attractive force increases gradually as the tip penetrates the film, increasing the area of contact and, correspondingly, the amount of attractive van der Waals interaction between the molecules and the tip. As was also the case for the unbonded polymers, no significant friction is observed until hard wall contact is made. So, even though the ends of the polymer are rigidly attached to the substrate, the backbone of the polymer apparently has enough flexibility to offer little resistance to the sliding tip except when rigidly compressed between the two surfaces.

For the bonded polymer the initial friction coefficient, $\mu=0.3$, is about half that for the unbonded liquid films. The lower friction indicates that significantly more molecules are trapped between the rubbing surfaces than for the unbonded polymer. With repeated traversals of the sliding tip, these attached molecules eventually wear away and the friction coefficient increases with increasing load. As the sample is retracted, the friction is substantially higher than on the inward approach. Further evidence for wearing away of the bonded polymer comes from repeating the sliding experiment in the same spot. In this case, the friction starts at a higher value than during the first experiment and has an even higher value when the sample is retracted. For unbonded polymer films, a slight hysteresis in friction is occasionally observed in the friction [for example, Fig. 4(b)] which may be due to a small amount of bonded surface contamination or burnishing of the sliding surfaces.

It is valuable to compare the results obtained here by AFM with those obtained using the SFA [2-5]. In SFA experiments, polymer films are sheared between two parallel, molecularly smooth mica surfaces with a typical lateral dimension of 100 μm. Consequently, a large number of molecules are confined to a narrow space. For films less than 50 Å thick, recent results of Hu, Carson, and Granick [5] indicate that this type of confinement leads to an increase in collective motions of the molecules with decreasing film thickness resulting in the effective viscosity of the films being dramatically enhanced by many orders of magnitude. For films thinner than about 5 molecular layers, the parallel nature of the two surfaces leads to layering of the molecules between the surfaces [2,3]. When these thinnest films are sheared, solidlike response is typically observed [2-4]. Results of Gee *et al.* [3] indicate that the solidlike shearing observed for these thin polymer films is intimately related to the layering of the molecules between the surfaces in that the more uniform the layering within the shear volume the more solidlike the shear force.

In contrast, in the AFM experiments presented here, polymer films can exhibit negligible shear force for separation distances as small as a few chain diameters with an effective viscosity no more than a few orders of magnitude greater than the bulk viscosity. This difference in behavior is most likely related to the vastly different geometries of the SFA and AFM experiments. For AFM, the geometry is one of spherical-shaped surface, rough on the molecular scale, sliding against a smoother flat surface. The sharp radius of curvature and the rough morphology of the AFM tip surface make it difficult for the polymer molecules to form layers between the sliding surfaces, which may partly account for the absence of solidlike shear for these thin polymer films. Also, the lateral dimension of the contact zone for the AFM tip is more than 10^3 times smaller than for the SFA experiments. The much smaller shear volume in the AFM experiments has two important potential effects: First, the relatively small number of molecules interacting with the tip sets an upper limit on the amount of collective motion and hence the degree that the effective viscosity can be enhanced by this mechanism [5]. Second, the molecules need travel only a short distance to escape from underneath the sliding tip. The importance of this second effect is illustrated by the AFM results for the polymers covalently bonded at both ends to the substrate surface. When the tip first contacts the top of the film, the bonded polymers have enough flexibility to bend out of the way of tip and offer negligible resistance to sliding; but, when the separation distance becomes small enough so that the bonded polymers become rigidly compressed under the tip, the shearing of the films becomes solidlike similar to that observed for polymer films in the SFA experiments. For the unbonded polymers, most of the molecules are able to escape from between the sliding surfaces with decreasing separation distance and solid-solid shearing occurs mainly from the tip sliding against the solid substrate.

The two types of experiments, AFM and SFA, probably represent two extremes for the confinement of liquid films. In AFM experiments, the smaller shear volumes and larger polymer-chain-length to asperity-radius ratio are most applicable to understanding actual lubrication applications, while the SFA experiments may be more applicable to other situations such as the liquids in porous media where a large number of molecules are confined to narrow spaces. The transition between these two regimes would provide an interesting area for future research.

To conclude, the forces on a sharp tip have been studied in detail as it penetrates polymer lubricant films during sliding. These results not only illustrate how these molecules lubricate surfaces, but also clearly show the importance of reactive or polar end groups to improve lubrication, as also observed in classical experiments in lubrication [1].

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[1] F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids* (Oxford Univ. Press, New York, 1950).

[2] J. Van Alsten and S. Granick, Phys. Rev. Lett. **61**, 2570 (1988).

[3] M. L. Gee, P. M. McGuiggan, J. N. Israelachvili, and A. M. Homola, J. Chem. Phys. **93**, 1895 (1990).

[4] A. M. Homola, H. V. Nguyen, and G. Hadziioannou, J. Chem. Phys. **94**, 2346 (1991).

[5] H.-W. Hu, G. A. Carson, and S. Granick, Phys. Rev. Lett. **66**, 2758 (1991).

[6] D. Rugar, H. J. Mamin, and P. Guethner, Appl. Phys. Lett. **55**, 2588 (1989).

[7] G. S. Blackman, C. M. Mate, and M. R. Philpott, Phys. Rev. Lett. **65**, 2270 (1990).

[8] C. M. Mate and V. J. Novotny, J. Chem. Phys. **94**, 8420 (1991).

[9] A. L. Weisenhorn, P. K. Hansma, T. R. Albrecht, and C. F. Quate, Appl. Phys. Lett. **54**, 2651 (1989).

[10] J. N. Israelachvili, *Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems* (Academic, New York, 1985).

[11] J. Rühe, S. Kuan, G. Blackman, V. Novotny, T. Clarke, and G. B. Street, in Applications of Surface Science and Advances in Tribology, ACS Symposium Series, edited by Y.-W. Chung, A. M. Homola, and G. B. Street (American Chemical Society, Washington, DC, to be published).