Chain Pullout and Mobility Effects in Friction and Lubrication

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The interfacial shear stress that occurs when a network of a polymer that is highly mobile at the segment level (an elastomer) is slid over a smooth surface of an immobile (glassy) polymer has been measured. The glassy material is covered by a thin layer of end-attached chains of the mobile material. The experiment was designed so that there were no free chains at the interface; the slip occurred between network chains on the one side and rigid material plus end-attached mobile chains on the other side. Two main results were obtained. (i) The interfacial shear stress is strongly affected by the segment mobility of the materials on both sides of the slip plane, and considerably lower stress is observed when the materials on both sides of the interface are highly mobile. (ii) Very thin layers of tethered chains can increase the interfacial friction. Both results are relevant to the understanding of a number of practical situations that range from the operation of thin layers of lubricants, such as those found in magnetic storage devices, to the problem of wall slip and melt fracture in polymer processing.

The study of tribology and friction is complicated for most systems by the difficulty of measuring the real area of contact and hence the true interfacial shear stress. Interfacial shear stresses have mainly been measured with variants of the surface forces apparatus, where the substrates are atomically smooth bent mica sheets. Measurements have been obtained with thin layers of hydrocarbon, fluorocarbon, and silicone lubricants between the mica sheets and also on lubricant layers that were deposited by self-assembly and Langmuir-Blodgett techniques on the mica (*1–6*). The values obtained this way for interfacial shear stress have been mainly in the range of 5×10^5 to 10^7 Pa. However, it should be noted that, in all cases, the presence of the mica probably has a strong influence, through both adsorption and constraint effects, on the mobility of the interfacial layer.

An alternative to the mica technique for obtaining a known true interfacial area is the use of a cross-linked elastomer with a smooth, curved surface as one of the two substrates. The low modulus of the elastomer ensures the equality of the real and apparent contact areas if the other substrate is not too rough. This technique, which was originated by Roberts and Tabor to study squeeze film lubrication (*7, 8*), has been used by a number of researchers concerned with the friction of elastomers (*9, 10*). A disadvantage of this technique, with respect to the crossed mica devices, is the difficulty of monitoring lubricant film thickness during slipping (*8*). However, the technique is free of the constraint and adsorption problems that influence the results obtained with mica substrates.

In the experiment considered here, a smooth lens-shaped slider made of a cross-linked siloxane (polydimethyl siloxane or PDMS) rubber network is slid over a flat, smooth substrate coated with the glassy polymer, polystyrene (PS). On top of the PS is a very thin layer of a PS-PDMS diblock copolymer—that is, a layer where each molecule consists of a chain (block) of PS covalently bonded to a block of PDMS. The copolymer layer thickness was between 0 and 18 nm for most systems. Each molecule of the diblock copolymer is organized so that its PS block is mixed with the PS underlayer and so that its PDMS block is on top. We are concerned therefore with three effects: (i) the slippage of elastomeric PDMS chains of the network on glassy PS, (ii) the slip between PDMS chains without penetration, and (iii) the effects on the slip process of the penetration of the tethered PDMS chains of the diblock into the PDMS network. Very little is known about the slip of a mobile (really liquid, at the segment level) material on a rigid material even for the simple situation considered here, where the interaction between the materials is mainly by dispersion forces. There has been speculation that the presence of the immobile material might slow the molecular motions of the mobile material close to the interface and hence increase the interfacial shear stress (*11, 12*). The slip of a network across a layer of tethered, penetrating chains has recently been analyzed theoretically by Ajdari, Rubinstein, and co-workers (*12, 13*). They argue that at very low speeds, the pullout of the tethered chains from the network will have a very high effective friction coefficient that is related to the very long relaxation time of an end-tethered chain in a network. The situation is similar to the diffusion of star-shaped polymers. They suggest that at intermediate speeds the tethered chains will begin to stretch so that only a section toward the free end of the chains can relax, forming a "plume." At high speeds, the whole chain is stretched. They thereby predict the existence of three main regions: (i) a region at very low velocity, where the shear stress increases linearly with slip speed; (ii) an intermediate velocity region, where the shear stress is independent of slip speed; and (iii) a high-speed region, where the shear stress again increases linearly with crack speed. Some experimental evidence for this model is to be found in both experiments on wall slip in flow (*14*) and on adhesion (*15*).

The interfacial shear stress was measured as a function of slip velocity by mounting a small lens-shaped PDMS slider at one end of a spring that had a high compliance in both the vertical and one horizontal direction. The other end of the spring was attached to a micrometer manipulator. The slider was lowered until it jumped into contact with a polymer-coated silicon wafer that was mounted on the stage of an optical microscope. The contact patch could be monitored by looking through the clear PDMS slider. In most of the experiments, no normal load was applied and so the contact diameter was controlled just by the work of adhesion at the interface, together with the radius of curvature and elastic modulus of the slider. The slider was moved over the substrate with the manipulator to give a small, rapid horizontal translation to the base of the spring. The position and area of the contact patch, which then translated slowly across the field of view of the microscope, were recorded with video techniques. The slider velocity could be obtained directly and the shear force obtained from the slider position as the stiffness of the spring was known. The small lens-shaped sliders were made by the technique developed by Chaudhury (*16*), who has used them previously for the study of both adhesion and friction. Sliders were made from vinyl-ended PDMS chains of molecular weight 6000, cross-linked with a hydrosilane cross-linking agent and a platinum catalyst.

The substrates were made in a manner similar to that described previously (*15*). A silicon wafer was coated with a 16-nm layer of end-attached PS, and then a layer of PS-PDMS diblock copolymer (with blocks of molecular weight 40,000 and 68,000, respectively) was spin-coated on the PS. The substrate was annealed at 170°C for 1 hour to ensure that the PS block mixed with the PS underlayer, leaving the PDMS block at the air surface. Layer thicknesses were measured with ellipsometry. The contact angle of water on the diblock-coated substrates was between

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103° and 106°, similar to that of water on PDMS. Angle-resolved x-ray photoelectron spectroscopy (XPS) measurements on a sample whose PDMS layer was nominally 1.2 nm thick were consistent with a model of a 1.1-nm-thick layer of pure PDMS over pure PS. Both contact angle and XPS results confirm that the PDMS was mainly at the air surface.

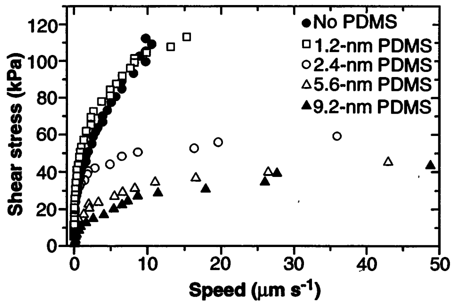

Fig. 1. Variation of the true shear stress with slip velocity for a range of thickness of the tethered PDMS layer. The values of Σ range from 0.007 chains per square nanometer for the 1.2-nm-thick layer to 0.055 chains per square nanometer for the 9.2-nm-thick layer.

Figure 1 shows the variation of true shear stress with slip velocity for a range of thicknesses of the tethered PDMS layer on the substrate. The same results are shown on a more expanded scale in Fig. 2. It is clear that for layer thicknesses greater than 1.2 nm, the shear stress at the higher slip speeds tends to decrease with increasing thickness of the PDMS layer. At low slip speeds there was no difference between the shear stress on 0-nm-thick PDMS (uncovered PS) and 2.4-nm PDMS substrates. However, the 5.6-nm and 9.2-nm layers decreased the shear stress over the whole range of slip velocities. For a 1.2-nm-thick layer of the tethered PDMS, there was an increase of the shear stress for slip speeds less than about 10 μm s^{-1} over that observed with no tethered PDMS chains. The observed shear stress was in the range of 1 to 100 kPa [consistent with previous results with elastomer sliders (*9*, *10*)] and thus lower than the shear stress seen with lubricant layers between mica sheets. Evidently, the lack of mobility induced by the constraint and adsorption of the mica sheets profoundly influences the resistance to sliding.

Let us consider first the results obtained with the thicker layers of tethered chains. There is little driving force for the tethered chains to penetrate deep into the network, whose elastic free energy resists swelling. Hence, one would expect the situation, as sketched in Fig. 3, where the PS remains covered with tethered PDMS chains. The slip therefore is between tethered PDMS chains on the one side and the PDMS network on the other. Comparison of the shear stress obtained with 5.6-nm and 9.2-nm layers with that obtained with no tethered PDMS layer shows that the shear stress of PDMS on PDMS is significantly less than that of PDMS on PS. This large difference occurs in spite of the fact that there is little difference in the van der Waals interaction and work on adhesion of the interface. Clearly, the mobilities of the materials on both sides of the interface affect the friction. This result suggests that the rigidity of the PS slows down the molecular motion of the adjacent PDMS segments, giving direct evidence that a thin layer of mobile material becomes less mobile when adjacent to a solid.

Let us turn now to the results obtained with the 1.2-nm-thick layer. If the network is not present, the tethered chains are in a situation where they are severely compressed normal to the interface and stretched parallel to the interface with respect to their relaxed Gaussian shape, as suggested in Fig. 4. When the network is present, the tethered PDMS chains may be expected to expand from the PS surface and enter the network. Hence, most of the PDMS units in contact with the PS are part of the cross-linked network. Sliding the interface requires both (i) sliding the network over the PS and (ii) pulling the tethered chains through the PDMS network. The latter process causes an increase of the friction over that on the bare PS substrate.

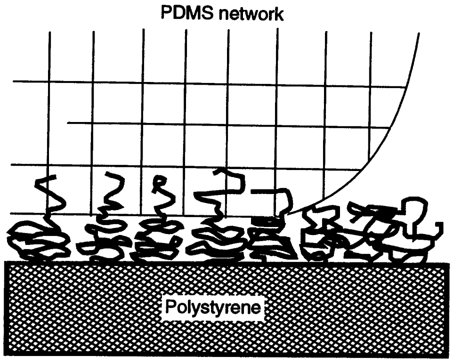

Fig. 3. A sketch of the situation when the tethered PDMS layer was relatively thick and so the network did not contact the PS. The tethered chains are represented by the bold lines, and the network is shown, very schematically, above.

The theory of Ajdari, Rubinstein, and co-workers (*12*, *13*) describes just this situation of pulling chains through a network, so it is valuable to compare the experimental results with their predictions. In the intermediate speed, constant stress regime, they predict the pullout stress is given by $\sigma_p = \Sigma kT/D_e$, where Σ is the areal density of tethered chains, k and T are the Boltzmann constant and temperature, respectively, and D_e is the mesh size of the network. Hence, for the 1.2-nm layer, assuming a D_e value of 5 nm, they predict a pullout stress of 5.8 kPa. This number should be compared with the difference between stresses obtained with the 0-nm-thick and 1.2-nm-thick layers. This difference is about 5 kPa at a slip speed of 0.02 μm s^{-1} and increases slowly to a maximum of about 10 kPa at a speed of about 2 μm s^{-1} then decreases to 0 at about 10 μm s^{-1}. Hence, there is a regime at speeds below 2 μm s^{-1} where the stress difference varies very slowly, as it changes only by a factor of 2 while the speed changes by two orders of magnitude. Considering the approximations involved in the theory and the assumption of complete chain penetration in the experimental analysis, there is good agreement between the theoretical prediction of a constant stress of 5.6 MPa and the experimental results.

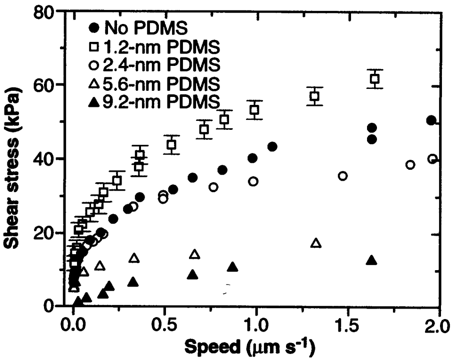

Fig. 2. The results of Fig. 1, expressed here at an expanded scale to show the low slip-speed region. The error bars shown for the 1.2-nm layer are typical for all the substrates.

As the slip velocity increases above about 7 to 10 μm s^{-1}, the shear stress with a 1.2-nm-thick PDMS layer decreases below that with no PDMS. With increasing slip velocity, less of the grafted layer is in the network so the number of network-to-PS contacts decreases, thereby decreasing the friction. Two separate effects contrib-

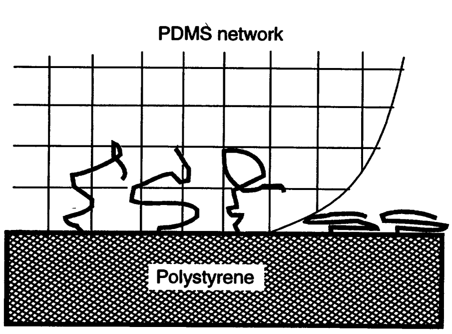

Fig. 4. Sketch of the situation when the PDMS layer was only 1.2 nm thick and there was no slip, showing the tethered chains penetrating well into the lens.

ute to the amount of tethered chain between the PS and the network. First, the chain will pull out of the network and remain on the substrate until the penetrated length reduces to the size of the relaxed plume, which acts as an anchor. As the plume decreases in size with increasing slip speed, the fraction of the tethered chain on the substrate will increase with slip speed. Second, the kinetics of the penetration of an end-grafted chain into a network, which has been studied theoretically (*17*) and by simulation (*18*), will have an effect. Initially, penetration is very rapid until the patch of chain on the substrate (between the tether point and the point of entry to the network) becomes stretched. However, complete penetration is a very slow process, and it is reasonable that it might not occur in the time scales observed here, about 0.5×10^{-3} s.

At low speeds, the 2.4-nm layer showed friction similar to that of the 0-nm and 1.2-nm layers but much lower friction at high speeds. Presumably, much of the tethered chains can again penetrate the network at low speeds, but a slip speed of only about 1 μm s^{-1} is required to start forming a layer of the tethered chains on the PS. For the 5.6-nm layer, the friction was reduced from that observed for the 2.4-nm layer over the whole experimentally accessible speed range. The shear stress at the lowest observable velocity, 0.01 μm s^{-1}, was reduced by a factor of 2. The measurements were not taken over a long enough time scale to test for the existence of a finite shear stress as the velocity tended to 0, but none of the thinner layers showed linear, viscous-like slip at low velocities. Compared to the 5.6-nm layer, the 9.2-nm layer showed only a small decrease in shear stress at high velocity but at low velocity showed a considerable decrease in shear stress so that the stress apparently tended to 0 at 0 velocity. Hence, the slip showed liquid-like characteristics. Presumably, the network chains did not contact the PS.

It is valuable to consider the absolute values of the shear stress observed with the 9.2-nm layer, as the slip appeared to show liquid-like properties at low velocities. At the lowest stresses, the shear stress varies approximately linearly with the slip rate with a gradient (slip coefficient) of about 2×10^{10} Pa·s m^{-1}. A simple lower bound estimate for the slip coefficient would be $\zeta_1 a^{-2}$, where ζ_1 is the monomer friction coefficient (*19*) and a is a monomer size. This value might be observed between PDMS layers that show no penetration. Assuming $a = 0.48$ nm and $\zeta_1 = 8.9 \times 10^{-12}$ N·s m^{-1}, this lower bound value for the slip coefficient is 3.7×10^7 Pa·s m^{-1}, much lower than that observed. Clearly there is some penetration between the end-tethered layer and the network. The slip coefficient can also be compared with the value expected if the chains penetrated the network fully, but the friction was just simple segmental friction rather than the enhanced friction predicted by Ajdari, Rubinstein, and co-workers. These simple segmental friction assumptions give a coefficient of $\Sigma\zeta_1 Z = 4.5 \times 10^8$ Pa·s m^{-1} (where $Z = 919$ is the degree of polymerization of the tethered chains), still 50 times smaller than the value observed. Clearly the simple models based on segmental friction are not consistent with our results. Hence, even with thick layers friction is enhanced by the chain pullout effects described by Ajdari, Rubinstein, and co-workers (*12*, *13*).

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29 October 1993; accepted 26 January 1994

Differential Adhesion of Cells to Enantiomorphous Crystal Surfaces

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Interactions during cell adhesion to external surfaces may reach the level of discrimination of molecular chirality. Cultured epithelial cells interact differently with the {011} faces of the (*R,R*) and (*S,S*) calcium tartrate tetrahydrate crystals. In a modified version of the classical Pasteur experiment, the enantiomorphous crystals were sorted out from a 1:1 mixture by the selective adhesion of cells to the (*R,R*) crystals. This stereospecificity results from molecular recognition between chiral components on the cell surface and the structured crystal surface. Crystals may allow experimental differentiation between distinct stages in cell substrate contacts, providing mechanistic information not readily attainable on conventional heterogeneous surfaces.

Adhesion to exogenous surfaces has profound effects on the structure and behavior of cells, especially of anchorage-dependent cells (*1*). Cell substrate adhesion is commonly viewed as a molecularly complex and diversified multistage process, which includes cell attachment and spreading (*2*), focal adhesion formation, extracellular matrix deposition, and rearrangement (*3*). In general, cell attachment to and spreading on surfaces may occur through two distinct but highly interdependent mechanisms: specific binding mediated by adhesive extracellular matrix proteins and direct association with the underlying solid surface (*4*). The former interactions occur through specific proteins such as fibronectin, vitronectin, and surface integrin receptors. However, little is known about the nature of direct interactions with the substrate.

To address this issue, it is helpful to use substrates that are homogeneous and structurally defined at the molecular level. Specific molecular and organizational parameters that cannot be defined on heterogeneous substrates such as glass and tissue culture plastics can be thus characterized. We examined the manner in which crystals operate as substrates for cell adhesion.

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