

Molecular contributions to the frictional properties of fluorinated self-assembled monolayers

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The frictional properties of self-assembled monolayers (SAMs) formed from four different species (*n*-octyltrichlorosilane, 1H,1H,2H,2H-perfluorooctyltrichlorosilane, tridecanethiol, and 13,13,13-trifluorotridecanethiol) were measured on the molecular scale using atomic force microscopy (AFM). On this scale, monolayers containing partially fluorinated alkyl chains exhibited higher frictional properties than monolayers containing analogous fully hydrogenated alkyl chains. Systematic comparison of the frictional properties of these SAMs provided insight into the molecular contributions to the frictional response.

Keywords: self-assembled monolayers, atomic force microscopy, fluorinated molecules, boundary layer lubrication

1. Introduction

Fluorinated organic films have received much attention because of their chemical stability, anti-adhesive properties and unique wettabilities. In some applications, fluorinated organic films are found in tribological environments where their frictional properties are also important. An example of such an application is the use of molecularly thin perfluoropolyethers films as lubricants in disk drive storage technology [1]. Many studies have explored the physical properties and chemical reactivities of fluorinated organic systems [2,3]. In this letter, we explore the relationship between the molecular structure and the observed frictional behavior of model fluorinated monolayers.

Self-assembled monolayers (SAMs) have become popular choices for tribological studies as models of boundary layer lubricants. SAMs are thought to model boundary layer species because of the thickness of the film (monolayer) and the chemical anchoring of the film to the surface. Two types of self-assembled films have been widely studied: those derived from the adsorption and reaction of alkyltrichlorosilanes on the native oxide of silicon substrates and those formed from the adsorption of alkanethiols and disulfides on gold surfaces (for a recent review, see ref. [4]). An additional feature that makes these systems attractive for fundamental studies is the opportunity to synthetically control the chemical nature of the alkyl group and thus the composition of the film at the molecular level.

Just as self-assembled monolayers are being widely used in tribological studies of ultrathin films, scanning probe microscopies are being increasingly used to characterize the structure and physical properties of monolayer films. In the present study, we use the atomic force microscope (AFM) to simultaneously measure normal and lateral forces between microscopically sharp probe tips and the surfaces of SAMs. In relation to a tribologi-

cal interface, normal forces are related to load while lateral forces are ascribed to friction. With this approach, we have characterized the inherent frictional properties as a function of load of fluorinated and hydrogenated monolayers on silicon and gold substrates formed through two different self-assembly paths.

2. Experimental

Self-assembled monolayers were formed on the native oxide of silicon (100) surfaces from carbon tetrachloride solutions of 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PCR) and *n*-octyltrichlorosilane (PCR). Silicon substrates were prepared by etching in a piranha solution (70% H₂SO₄, 30% H₂O₂) for 30 s. The trichlorosilanes were used immediately upon receipt and without further purification. Monolayers were formed by immersing the silicon substrates in 0.1 mM solutions of the two trichlorosilanes for 24 h.

Self-assembled monolayers were formed on Au(111) substrates from 1 mM ethanolic solutions of tridecanethiol (Aldrich Chemical Co.) and 13,13,13-trifluorotridecanethiol; the synthesis of this partially fluorinated thiol will be reported elsewhere [5]. Crystalline gold substrates were prepared for this study by annealing gold wires 1 mm in diameter (Alfa Aesar, 99.9985%) in an H₂/O₂ flame until a small ball containing several (111) facets formed at the end of the wire [6]. These substrates were rinsed in HPLC grade water (Aldrich Chemical Co.), and then immediately immersed in the thiol solutions. Self-assembled monolayers were formed with an incubation time of 24 h.

An atomic force microscope (AFM) using a beam deflection technique and a four-quadrant photodiode detection scheme was used for these studies. Microfabricated silicon nitride cantilevers (tip F, Park Scientific Microlever) were used in the collection of the

data presented here. The normal force constant of these cantilevers was taken from manufacturer's specifications while the lateral force constant was obtained from mechanical modeling of cantilever torsion. To ensure precision, the same cantilever was used to probe the frictional properties of each set of monolayers compared, although different tips were employed for the two sets. Frictional properties of the films were measured and averaged over different regions of the surface and at different normal loads by procedures previously described [7]. These properties were also measured as a function of relative humidity; no dependence on humidity was, however, observed. Although from sample to sample some variation was observed in the magnitude of frictional forces, the general trends in frictional properties were consistent, and the data presented here are representative of the many sets of data collected.

3. Results and discussion

A comparison of the frictional properties of two self-assembled monolayers formed from alkyltrichlorosilanes is shown in figure 1. These monolayers were composed of alkyl chains eight carbons long: one was fully hydrogenated and the other was fully fluorinated in the outermost six carbons of the chain. Frictional forces were measured during sliding between a silicon nitride probe tip and the organic monolayer at low loads. Other work in our laboratory has shown no evidence of plastic deformation of SAMs at these loads using tips of similar size ($R \approx 600 \text{ \AA}$) [8]. Frictional forces are plotted here as a function of decreasing load; negative loads correspond to regimes of adhesion between the tip and the sample.

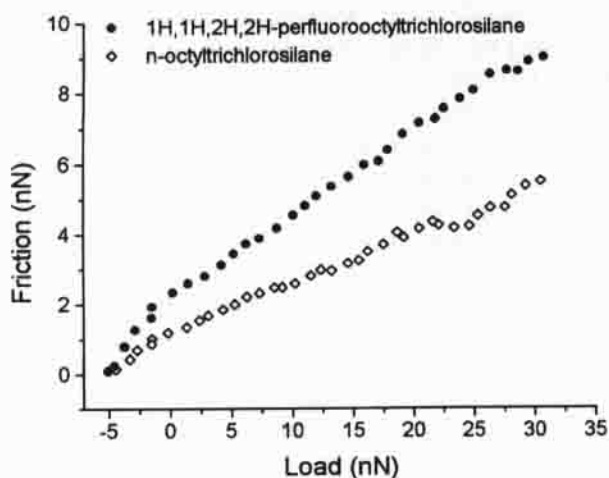


Figure 1. The force of friction is plotted as a function of applied load between a silicon nitride AFM probe tip and SAMs formed on the native oxide of silicon from solutions of *n*-octyltrichlorosilane (open diamond) and perfluorooctyltrichlorosilane (filled circle). Friction is plotted as function of decreasing load. At all loads, higher frictional forces are observed on the fluorinated monolayer.

As shown in figure 1, a measurably higher frictional force was observed at all loads on the fluorinated film. This result is consistent with other measurements of the frictional properties of hydrogenated and fluorinated monolayers [9–15].

Although the two SAMs formed from alkyltrichlorosilanes differ only by the substitution of fluorine for hydrogen, there are a number of consequences that this substitution can have on the film structure and consequently on the frictional properties. Potential consequences include changes in packing energy [9,10,15], packing density [10], film order [16] and molecular stiffness [15], all of which have been proposed to contribute to (or even dominate) the frictional properties of fluorinated monolayers [9–15]. We have discussed these issues elsewhere [17]. Because many of these film properties are interrelated, it is difficult to deduce from the preceding studies the molecular-level origin of the increase in friction observed for fluorinated films.

To simplify the possible interpretations, we synthesized and investigated a set of model films where many of the structural parameters were fixed, and the systematic introduction of fluorine could thus be readily evaluated. These films were formed through the self-assembly of alkanethiols on the (111) face of gold. The two thiols used for this study each consisted of linear 13-carbon chains: one molecule was fully hydrogenated (tridecanethiol) and the other was hydrogenated along the backbone of the chain and then terminated with a trifluoromethyl group (13,13,13-trifluorotridecanethiol). Thus, the monolayers formed from these two molecules should be identical with the exception of the substitution of fluorine in the terminal methyl group. The frictional properties of the SAMs formed from these alkanethiols,

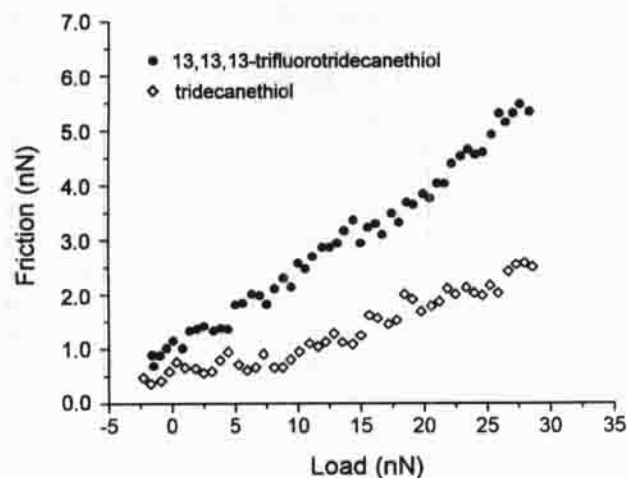


Figure 2. Frictional forces measured with AFM are plotted versus applied load (decreasing in this figure) for SAMs formed on Au(111) from solutions of tridecanethiol (open diamond) and 13,13,13-trifluorotridecanethiol (filled circle). The addition of fluorine to only the terminal methyl group produces a significant increase in the measured frictional forces.

measured by procedures analogous to those used for the first set, are shown in figure 2. As before, higher frictional forces were measured for the fluorinated interface at all loads.

From these data, insight into the molecular origins of the frictional properties of fluorinated films is possible due to the similarity of the two monolayers. Again, the only difference between the two thiols is trifluoromethyl versus methyl termination. Because the two molecules have identical backbone structures, we expect them to form films in which the packing energy, determined by the intermolecular interaction between chains, is approximately the same. In addition, the similarity in backbone structures suggests that the packing densities and thus the resultant film structures should be the same¹. We have verified this structural similarity in the two monolayers by measuring the lattice constant of the film structures from lateral force images. Within experimental error (± 0.2 Å), the monolayers formed from these two thiols exhibit the same lattice constant (4.9 Å), consistent with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbate structure on Au(111) [19]. The details of our measurements have been presented elsewhere [17]. We note that the lattice constant observed for both films is in good agreement with previous measurements of hydrogenated alkanethiols on gold, and is clearly distinguishable from the 5.7 Å lattice constant observed for monolayers formed from more highly fluorinated alkanethiols [20] or the 3.0 Å lattice constant of the underlying gold substrate [19]. We thus conclude that the trifluoromethyl terminal group, although estimated to have an approximately 30% larger cross sectional area than the methyl terminal group², represents an insufficient perturbation to induce a change in film structure from that of the fully hydrogenated monolayer [18].

In light of these structural similarities and the lack of significant differences in the adhesive interaction between the probe tip and these films (see negative load regime of figure 2), we propose that the frictional increase observed upon the systematic introduction of fluorine to the terminal group arises from the relatively larger barrier to rotation of the trifluoromethyl group. Rice and coworkers have performed molecular dynamics calculations of the energy barrier height between trans and gauche conformations of adjacent methylene and perfluoromethylene groups of linear alkanes [21]. Their work finds an approximately 50% increase in the barrier to rotation for the larger fluorinated methylene units relative to hydrogenated methy-

lene units. We propose that similar rotational barriers of the trifluoromethyl terminal group, coupled with increased steric interactions with neighboring chains further inhibiting molecular motion of the head group, are responsible for the observed increase in frictional properties. Experiments are currently being performed in our laboratory to elucidate the relative contributions of intra- and intermolecular barriers to molecular motion, and to examine how these barriers might influence measurements of friction.

Although the use of SAMs as lubricants is currently limited, the measurements presented here demonstrate the potential of controlling frictional properties on the molecular scale. Many current advanced tribological interfaces rely entirely on monomolecular layers of lubricants for control of frictional properties [22]. While lubricants are often chosen for desirable chemical properties, we believe that systematic choices of lubricant compositions and structures might also provide an additional level of control of the frictional properties in many advanced tribological applications.

4. Conclusions

In this study, we have measured with AFM the frictional properties of self-assembled monolayers generated from fluorinated and hydrogenated molecules. In the ultra-low load regime (tens of nanonewtons), we find that monolayer films containing predominantly fluorinated alkyl chains consistently exhibit higher frictional properties than those containing fully hydrogenated chains. Similarly, a comparison of trifluoromethyl- versus methyl-terminated films reveals higher friction for the fluorine-containing films. We propose that the frictional increase observed upon introduction of fluorine at this level is due to increased barriers to molecular motion within the films. Since these barriers are also present in predominantly or fully fluorinated molecules, it is likely that they are at least partly responsible for the higher frictional properties routinely observed for fluorinated thin films.

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¹ Results from the literature suggest that the CF_3 group can be substituted for the CH_3 group without perturbing the solid-state structure. See, for example, ref. [18].

² Using covalent C-H and C-F bond lengths, the van der Waals radii of hydrogen and fluorine, and the tetrahedral geometry of the terminal carbon atom, we calculate an effective area of the two terminal groups oriented normal to the C-C bond: 17.6 \AA^2 for CH_3 and 25.4 \AA^2 for CF_3 .

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