

FRICITION AND ADHESION MEASUREMENTS BETWEEN A FLUOROCARBON SURFACE AND A HYDROCARBON SURFACE IN AIR

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The friction and adhesion between a fluorocarbon monolayer-coated surface against a hydrocarbon monolayer-coated surface has been directly measured. The friction was found to be lower than the friction between a hydrocarbon monolayer against a hydrocarbon monolayer and a fluorocarbon monolayer against a fluorocarbon monolayer. No stick-slip sliding was observed for speeds from 0.8 $\mu\text{m/s}$ to 2.6 $\mu\text{m/s}$. The fluorocarbon–hydrocarbon interface was adhesive, with the energy of interaction measured to be $14.9\text{ mJ/m}^2 \pm 1.0\text{ mJ/m}^2$. As predicted from theory, the magnitude of the adhesion of a fluorocarbon monolayer against a hydrocarbon monolayer is between that measured for a fluorocarbon monolayer against a fluorocarbon monolayer and a hydrocarbon monolayer against a hydrocarbon monolayer. One may note that the interfacial energy, γ , follows the general trend $\gamma_{\text{FC/FC}} < \gamma_{\text{HC/FC}} < \gamma_{\text{HC/HC}}$, whereas the shear stress, τ , varies according to $\tau_{\text{FC/HC}} < \tau_{\text{HC/HC}} < \tau_{\text{FC/FC}}$.

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INTRODUCTION

Hydrodynamic or fluid lubrication has been extensively studied since the experimental work of Tower and theoretical work of Reynolds [1, 2]. These fluid lubricant films are often hundreds of nanometers thick. Current technological devices, such as magnetic storage drives and microelectromechanical systems (MEMS), operate in a regime where the required lubricant is only a few molecular layers in thickness [3]. In these confined systems, the properties of the confined fluid are often quite different from the bulk properties, and the liquid film can behave more like a solid [4].

Due to their technological importance, extensive experimental and theoretical studies of monolayer films have been conducted in recent years to determine the molecular origin of adhesion and friction and to understand how the structure of the monolayer film determines these properties [5–11]. Many of these lubricating monolayer films consist of an anchoring group that attaches the molecule to the surface and an alkyl tail that provides the lubrication. Self-assembled monolayers (SAMs), such as alkylsilanes on silicon oxide and alkanethiols on gold, readily react with the solid surface and orient with the alkyl tail directed away from the surface [12]. Surfactant monolayers, either adsorbed from solution or applied onto the solid surface *via* the Langmuir-Blodgett technique, can also give an oriented monolayer film.

The state of the monolayer film (either solid, amorphous, or fluid) has been found to influence the measured friction and adhesion hysteresis [5, 13–15]. For fully packed, well-ordered monolayers, the friction has been found to be lower than that measured for less ordered, amorphous monolayers. For solid monolayer films, atomic force microscopy (AFM) measurements find a chain-length dependence on the friction with shorter chain molecules generally giving higher friction than longer chain molecules [11, 16, 17]. The friction force was also found to depend on the domain orientation with respect to the sliding direction as well as the specific orientation of the terminal group [18, 19].

Molecular modeling of self-assembled monolayers has given insight into the structure of monolayer films and how this structure affects the friction and adhesion [20–23]. In shear simulations, stick-slip motion is observed for well-ordered monolayer sliding. This motion can lead to the formation of gauche defects in the monolayer [20].

A number of techniques have measured the friction of monolayer films, including the surface forces apparatus (SFA) [9, 24–26], the AFM [6, 27], and a pin-on-disk apparatus [15, 28]. Some of the

investigations involve a solid surface being slid over a single monolayer (as is generally the case with AFM experiments where an uncoated tip slides over the monolayer) and others involve two identical monolayers being slid against each other (as is generally the case with SFA experiments). In both of these configurations, the friction of a fluorocarbon monolayer is *higher* than the friction of a hydrocarbon monolayer [8, 26, 29].

In most of the experiments where a monolayer is slid against another monolayer, the surfaces are symmetric, *i.e.*, a hydrocarbon monolayer is slid against another hydrocarbon monolayer of a similar packing density. In this experiment, the friction of a fluorocarbon (FC) monolayer against a hydrocarbon (HC) monolayer is measured. Because the FC and HC monolayers are chemically incompatible, one might expect there to be little interpenetration of the opposing chains. Hence, the friction between dissimilar monolayers might be expected to be less than the friction between similar monolayers. The results show that the shear stress between a HC and FC monolayer film is indeed less than half the shear stress measured between either FC or HC films measured against a similar surface. The adhesion, however, is between that measured for a FC/FC interface and a HC/HC interface.

MATERIALS AND METHODS

A SFA with a lateral sliding attachment was used to measure the shear forces [30, 31]. The lateral sliding attachment slides two surfaces past each other. The technique generally uses mica surfaces that were cleaved to obtain molecularly smooth surfaces. Each mica sheet was silvered on the backside to allow interferometry measurements and glued onto silica support disks. One disk was mounted onto a rigid steel plate that was connected through two vertical double-cantilever springs to a translation stage. A variable-speed motor-driven micrometer was pressed against the translation stage to regulate motion. One of the vertical springs contained an attached semiconductor strain gauge connected to a chart recorder that recorded the lateral force. Another disk was mounted onto horizontal double-cantilever springs that measured the normal force. The spring constants of the normal and lateral force-measuring springs were $100 \text{ N/m} \pm 10 \text{ N/m}$ and $30 \times 10^2 \text{ N/m} \pm 3 \times 10^2 \text{ N/m}$, respectively. For the adhesion measurements, a normal spring constant of $1.1 \times 10^4 \text{ N/m} \pm 0.1 \times 10^4 \text{ N/m}$ was used. Unless otherwise noted, the \pm represents uncertainties of the measured values and represents one standard deviation of the observed value.

Besides measuring the shear and normal forces, the SFA simultaneously measures the surface separation and contact area *via* observation of the optical interferometric fringes. Typical values of the sliding velocity, v , applied normal loads, L , contact areas, A_{real} , and lateral forces, F , in this study were $0.8 \mu\text{m/s}$, from 0 – 100 mN , from 0.0025 – 0.01 mm^2 , and from 0 mN to 10 mN , respectively. The velocity and applied loads have an estimated relative standard uncertainty of $\pm 5\%$ of the measured values, whereas the friction force and contact area have an estimated relative standard uncertainty of less than $\pm 10\%$ of the measured values. The surface separation can be measured to $\pm 0.1 \text{ nm}$.

The surfaces were prepared by Langmuir-Blodgett deposition of surfactant monolayers on molecularly smooth sheets of muscovite mica. A Nima Technology Ltd trough (Type 622; Coventry, England) was used for the deposition. Each monolayer was prepared separately.

The HC monolayer was prepared using a double-chained cationic surfactant, dioctadecyl dimethyl ammonium bromide (DODABr), obtained from Aldrich (St. Louis, MO, USA). The structure of the surfactant is shown in Figure 1a. The surface properties of this monolayer have been studied previously [32]. DODABr was spread from a heptane-ethanol mixture (92:8 by volume) onto a water subphase. The solvent was allowed to evaporate for 20 min and the monolayer was compressed at a rate of $100 \text{ cm}^2/\text{min}$ until a surface pressure of 25 mN/m was reached, giving a packing density of the HC at the air–water interface of about $0.68 \text{ nm}^2/\text{molecule}$. The mica was brought through the air/water interface at a rate of 4 mm/min . A pressure of 25 mN/m was maintained during the transfer. The advancing (θ_a) and receding (θ_r) contact angles of water on the HC-coated mica surfaces were $93^\circ \pm 2^\circ$ and $50^\circ \pm 2^\circ$, respectively.

The FC monolayer was prepared using a double-chained cationic surfactant (N-(α -(trimethylammonio)acetyl)-O-O'-bis(1H,1H,2H,2H-perfluorodecyl)-L-glutamate chloride, $(\text{C}_8\text{F}_{17}\text{-C}_2\text{H}_4)_2\text{-L-Glu-Ac-N} + (\text{CH}_3)_3\text{Cl}^-$ (TAFC), obtained from Sogo Pharmaceuticals, Ltd., (Tokyo, Japan). The structure of the surfactant is shown in Figure 1b. The surface properties of this monolayer have been studied previously [33]. TAFC was spread from a chloroform-ethanol mixture (98:2 by volume) onto a water subphase. The solvent was allowed to evaporate for 20 min and the monolayer was compressed at a rate of $100 \text{ cm}^2/\text{min}$ until a surface pressure of 20 mN/m was reached, giving a packing density of the fluorochemicals at the air–water interface of about $0.65 \text{ nm}^2/\text{molecule}$. The mica was brought through the air/water interface at a rate of 4 mm/min . A pressure of 20 mN/m was maintained during the transfer. The advancing (θ_a) and receding (θ_r)

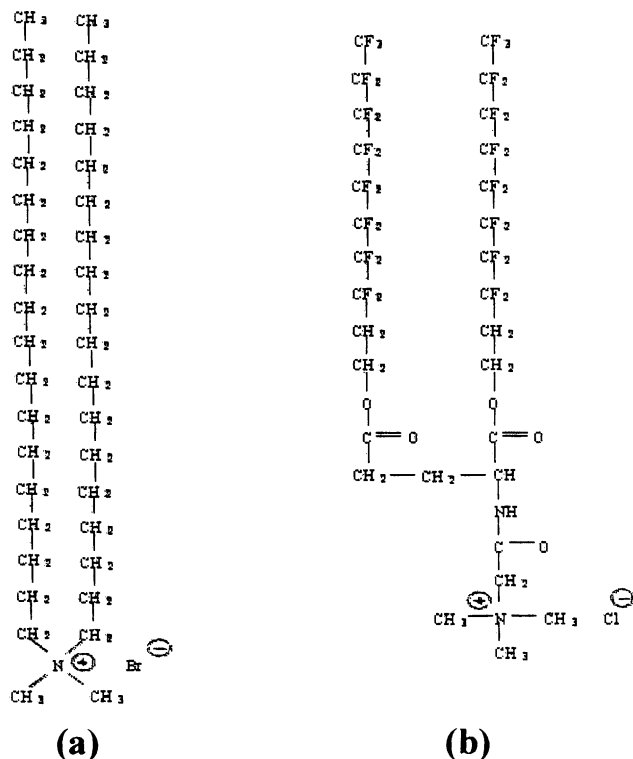


FIGURE 1 Chemical structure of (a) the HC monolayer DODABr and (b) the FC monolayer TAFC.

contact angles of water on the FC-coated mica surfaces were $113^\circ \pm 2^\circ$ and $55^\circ \pm 2^\circ$, respectively. At this pressure, the monolayer is in the liquid expanded state.

The surfaces were placed inside the SFA chamber that was then purged with dry nitrogen. A small container filled with P_2O_5 was placed in the chamber of the SFA to extract residual moisture from the atmosphere. The surfaces were allowed to jump into contact and the friction, load, and surface separation were simultaneously measured. Sliding was maintained in one direction until a steady friction was observed. The direction was reversed and the steady-state friction was again measured. The load was then increased gradually, and the friction and surface separation were measured after each increase. All experiments were carried out at a temperature of $23^\circ\text{C} \pm 1^\circ\text{C}$ and a sliding velocity of $0.8\text{ }\mu\text{m/s}$. At least three repeat measurements were performed.

RESULTS

The shear strength between two surfaces is related to the adhesion and adhesion hysteresis between the surfaces [5, 13]. Therefore, the adhesion between dissimilar surfaces will first be discussed followed by friction measurements.

For nonpolar materials, the reversible work of adhesion between two materials with surface energies γ_1 and γ_2 can be given by [34, 35]

$$W_A = 2(\gamma_1\gamma_2)^{0.5} \approx 2\gamma_{12}. \quad (1)$$

Hence, the interfacial energy, γ_{12} , can be predicted by knowing the surface energies of the two individual materials. The surface energies of various materials are given in Table 1 [36]. Inserting the data from Table 1 into Equation (1), the works of adhesion between a HC/HC interface, a HC/FC interface, and a FC/FC interface are expected to be about 60 mJ/m², (29 to 42) mJ/m², and (15 to 30) mJ/m², respectively. Hence, the interaction between a HC and a FC surface is expected to be *adhesive* and the magnitude of that adhesion is *between* that measured for similar HC/HC or FC/FC interfaces.

The interfacial energy of a material can be directly measured from the pull-off force. According to Johnson-Kendall-Roberts (JKR) theory, the pull-off force, L_{ad} , of a sphere (radius R) near a flat surface is related to the interfacial energy, γ_{12} , between two surfaces [37],

$$\gamma_{12} = -L_{ad}/3\pi R. \quad (2)$$

In this experiment, a FC monolayer was brought into contact with a HC monolayer and the pull-off force was measured. From pull-off force measurements, γ_{12} was measured to be 14.9 mJ/m² \pm 1.0 mJ/m². Thus, the work of adhesion between a FC monolayer and HC monolayer is 29.8 mJ/m² \pm 2.0 mJ/m², as predicted from Equation (1).

According to Amontons' laws on friction, the friction force, F , needed to slide one surface past another surface is independent of their macroscopic area of contact and proportional to the normal load, L [38].

TABLE 1 Material Properties

Outermost surface composition	Surface energy, γ_s (mJ/m ²)	Critical surface tension, γ_c (mJ/m ²)	Polymer sliding on polymer coefficient of friction, μ
—CF ₃	7–14.5	6	
—CF ₂ —CF ₂ —	22.6	18	0.04–0.08
—CH ₃	23–30.5	22	
—CH ₂ —CH ₂ —	35.9	31	0.1

However, for adhesive surfaces there may be friction even when $L \leq 0$. In this case, F/L diverges and it is common to associate the friction coefficient, μ , with the derivative of the force *via*

$$\mu = dF/dL \quad (3)$$

The measured friction between a HC and a FC surface is shown in Figure 2. There was a finite friction force at zero load, indicative of adhesive surfaces. The friction force increased monotonically with load, and the coefficient of friction $\mu = dF/dL$ was measured to be 0.027 ± 0.007 . The surfaces exhibited smooth sliding and no stick-slip motion was observed.

The friction between two HC-coated surfaces was also measured, and stick-slip motion was observed at $v = 0.8 \mu\text{m/s}$. During stick-slip motion, the force rises to a maximum and then dips rapidly to a

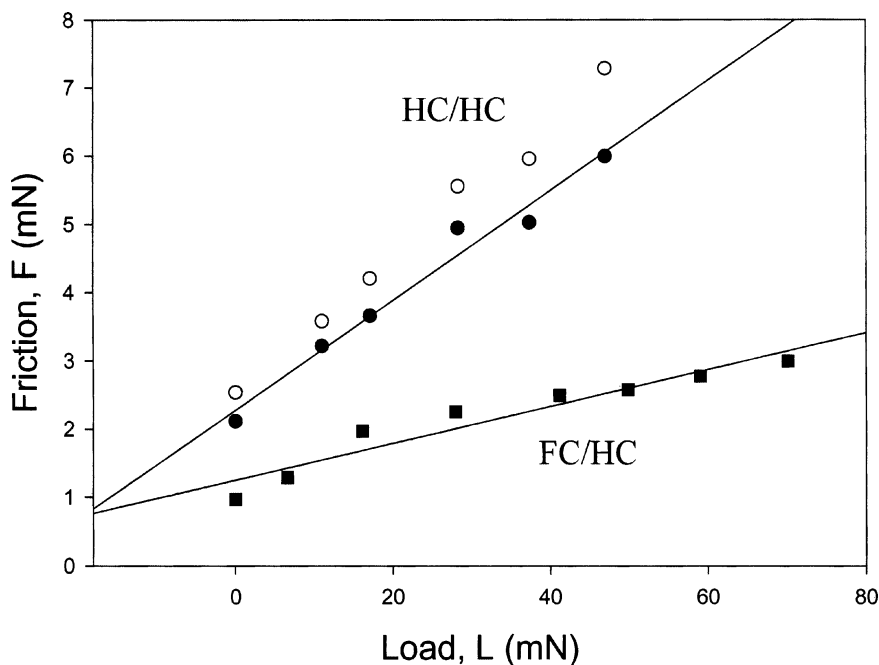


FIGURE 2 Measured friction forces as a function of the applied load. Data for the hydrocarbon monolayer includes both kinetic (●) and static (○) friction forces. The solid lines are least-squares fit to the kinetic data. The slope of the data gives $\mu = 0.08 \pm 0.015$ for the HC/HC interface and $\mu = 0.027 \pm 0.007$ for the FC/HC interface. The friction force has an estimated relative standard uncertainty of less than $\pm 10\%$ of the measured values.

minimum. As in previous work, we associate the maximum with the static friction and the minimum with the kinetic friction. The average force could also be taken as the kinetic friction, but this would not change the results significantly. In order to compare directly the kinetic friction values between the FC/HC and HC/HC surfaces, the velocity of sliding was increased in an attempt to go beyond the critical velocity. However, the surfaces usually were damaged before the stick-slip motion disappeared ($v > 5 \mu\text{m/s}$), hence, the data for the HC/HC friction (shown in Figure 2) includes both kinetic (shown as solid circles) and static (shown as open circles) friction measurements. The measured friction between HC/HC surfaces increased monotonically with load and the kinetic coefficient of friction $\mu_k = dF/dL$ was measured to be 0.080 ± 0.015 . Clearly, the friction of a HC/HC interface is higher than the friction of a FC/HC interface.

The SFA allows independent measurement of the true area of contact so that the shear stress, τ , at the interface can be determined. In many cases τ increases linearly with external pressure, P . Note that τ_0 leads to friction at zero load as observed for adhesive surfaces. In this case, the friction force, F , is proportional to the “real” area of contact, A_{real} , according to [39]

$$F/A_{\text{real}} = \tau = \tau_0 + \alpha P, \quad (4)$$

where τ_0 and α are constants.

As shown in Equation (3), it is the shear stress that is more applicable for adhesive surfaces. The shear stress τ (F/A) *versus* pressure P (L/A) is shown in Figure 3. The shear stress for the FC/HC interface was constant with pressure, at least for pressures below 10 MPa, with $\tau_{\text{HC/FC}} = 0.23 \text{ MPa} \pm 0.07 \text{ MPa}$. The measured shear stress of the HC/HC interface increased with pressure. The slope of the data in Figure 3 gives $\alpha_{\text{HC/HC}} = 0.044$. Note that a similar value of α was previously obtained for single-chained HC monolayers [8]. For pressures less than 6 MPa, $\tau_{\text{HC/HC}} = 0.7 \text{ MPa} \pm 0.05 \text{ MPa}$.

DISCUSSION

Previous pull-off measurements have found the interfacial energy between symmetric HC and FC monolayers to be $\gamma_{\text{HC}} \approx 30 \text{ mJ/m}^2$ and $\gamma_{\text{FC}} \approx$ (from 7 to 15) mJ/m^2 , respectively [26, 40]. According to Equation (1), the interfacial energy of a FC monolayer against a HC monolayer should be between 14.5 mJ/m^2 and 21.5 mJ/m^2 . From pull-off measurements, the interfacial energy was measured to be $14.9 \text{ mJ/m}^2 \pm 1.0 \text{ mJ/m}^2$, as predicted from Equation (1). Hence, the

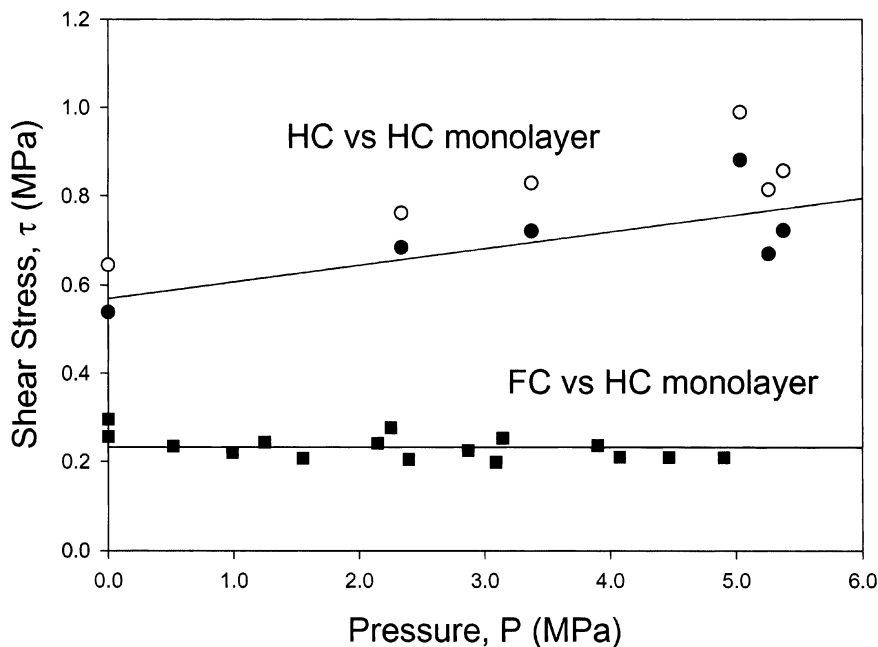


FIGURE 3 Measured shear stress, τ , as a function of pressure, P , for HC/HC (●) and HC/FC (■) interfaces. The open and closed circles represent static and kinetic measurements for the HC/HC interface, respectively. The solid lines are least-squares fit to the kinetic data. The shear stress has an estimated relative standard uncertainty of $\pm 20\%$ of the measured values.

measured interfacial energy is adhesive and between that measured for symmetric HC and FC interfaces. The adhesion between the surfaces is primarily due to dispersive forces and the magnitude of that adhesion follows predictions from theory, *i.e.*, $\gamma_{\text{FC/FC}} < \gamma_{\text{HC/FC}} < \gamma_{\text{HC/HC}}$. Because there is a strong correlation between the measured results and theoretical predictions, it is unlikely that there is a large degree of charge transfer between the surfaces, which has been found between other dissimilar surfaces [41].

The measured friction between the monolayers does not follow the same trend as that measured for adhesion. Previous measurements have found $\tau_{\text{FC/FC}} = 1.0 \text{ MPa} \pm 0.2 \text{ MPa}$, and $\mu_{\text{FC/FC}} = 0.05$ to 0.15 [8, 26]. For the measurements presented here for the FC/HC interface, $\tau_{\text{FC/HC}} = 0.23 \text{ MPa} \pm 0.07 \text{ MPa}$, and $\mu_{\text{FC/HC}} = 0.027 \pm 0.007$, and for the HC/HC interface $\tau_{\text{HC/HC}} = 0.70 \text{ MPa} \pm 0.05 \text{ MPa}$, and $\mu_{\text{HC/HC}} = 0.080 \pm 0.015$. Hence, for the friction measurements, $\tau_{\text{FC/HC}} < \tau_{\text{HC/HC}} < \tau_{\text{FC/FC}}$. This implies that it is not a chemical effect

that determines the friction force, but due to the state of the monolayer films and the interdigitation of the surfactant tails.

The state of the monolayer film (either solid, amorphous, or fluid) has been found to influence the measured friction and adhesion hysteresis. For fully packed, well-ordered monolayers, the friction has been found to be lower than that measured for less ordered, amorphous monolayers [13]. The packing of the FC and HC monolayers on the mica surface at surface pressures of 20 mN/m and 25 mN/m, respectively, results in monolayers with a packing density of $0.6 \text{ nm}^2 \pm 0.1 \text{ nm}^2$ and $0.50 \text{ nm}^2 \pm 0.04 \text{ nm}^2$ for FC and HC monolayers, respectively [32, 33]. Two chains are on each molecule, and the cross section per chain occupied by hexagonally packed perfluorinated alkanes and HC alkanes is 0.25 nm^2 and 0.20 nm^2 , respectively [42]. Hence, the FC monolayer appears to be more tightly packed than the HC monolayer. In spite of this, the ability of a FC chain to produce a solid film generally does not occur until 10 or more CF_2 groups are present, due to the weak interaction between the adjacent chains [42]. A possible configuration of the monolayers is shown in Figure 4. The monolayer was modeled using Cerius2 software by Accelrys, Inc. (San Diego, CA, USA). The packing of the headgroup was set to that obtained on the LB trough and was held constant during the modeling.

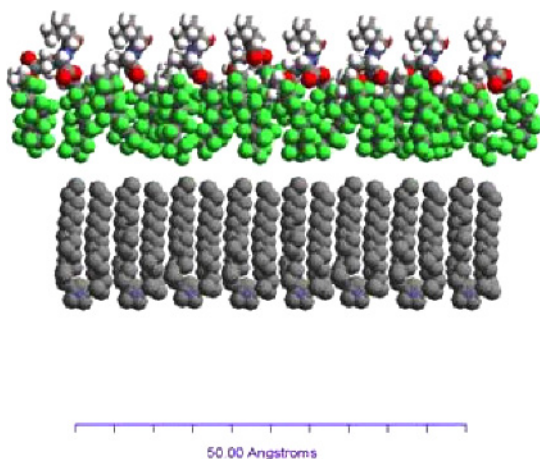


FIGURE 4 Schematic representation of a possible configuration of the HC monolayer DODABr against the FC monolayer TAFC. The density of the headgroups is similar to the packing of the headgroups in the experiment. For clarity, the HC and FC chains were arbitrarily separated (see Color Plate I).

The state of the monolayer affects the degree of interdigitation; a high degree of interdigitation gives rise to higher friction. The extent of interdigitation will depend on the balance between the intermolecular forces and the intramolecular forces as well as the packing density. Since the lateral adhesion within the HC monolayer is greater than the adhesion between the HC/FC monolayer, little interdigitation is expected to occur. A proposed schematic model of the interaction between a FC/HC interface and a HC/HC interface is shown in Figures 5a and 5b, respectively. It is proposed that the HC/HC interface has a slightly lower packing density and interdigitation is more energetically favorable than for the FC/HC interface. If no interdigitation occurs, one might expect to measure superkinetic friction [43]. This was not observed for the sliding velocity of $0.8 \mu\text{m/s}$ but may become evident at higher velocities.

The state of the monolayer also affects relative monolayer stiffness. In general, a FC chain is stiffer than a HC chain. This is believed to be the main reason for the higher friction of a close-packed FC monolayer. However, if the monolayer is not close packed, then the chains might easily tilt or splay away from the contact zone. This is likely the case for many AFM experiments where the chains can move away from the small contact zone. The intermolecular forces or lateral adhesion between the chains is of primary importance in determining the ability to dissipate energy. It should also be noted that the fluorinated monolayer used in these experiments is not only composed of eight FC per chain but contains two methylene groups, an ether linkage, an amide link, and a carbonyl group, as shown in Figure 1. These groups are more flexible than the FC tail and could further act to decrease the strain energy [23].

Some FC monolayers have been found to form ordered domains or islands on a water subphase [44]. These domains are randomly

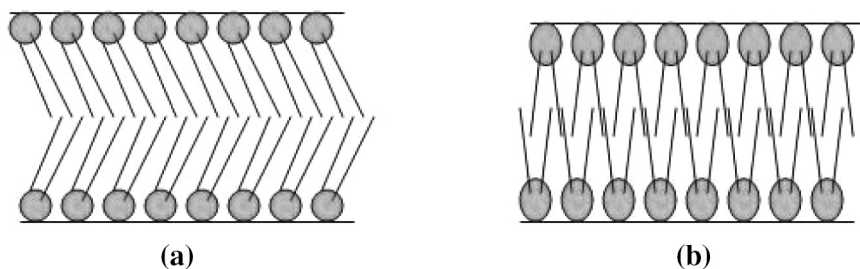


FIGURE 5 Proposed interdigitation of the monolayer tails for the (a) the HC DODABr monolayers and (b) the HC monolayer against the FC monolayer.

oriented and are separated by a more dilute disordered phase. It is possible that the presence of a dilute disordered phase allows for enhanced energy dissipation of the monolayer films under shear and, hence, lower friction. There have been some reports of domain formation occurring for the fluorinated monolayer used here [33]. The large contact area of the SFA implies the measurements are made over multiple domains and defects. Recent quartz crystal microbalance experiments of alkanethiols on gold suggest that the number of defects present in these films affects energy dissipation within the films and, hence, the measured friction should decrease [45].

The stick-slip dynamics are a special occurrence that requires commensurability of the two sliding surfaces. It is perhaps not surprising that stick-slip dynamics were not observed in the FC/HC interface as the surfaces were not commensurate, and, if defects were present, a small percentage of defects could break this commensurability. Defects in the surface structure can dramatically change the dynamics and strongly affect how energy is dissipated under shear.

The friction of a HC monolayer against a FC monolayer ($\mu = 0.027 \pm 0.007$) is similar to the friction of a Poly(tetrafluoroethylene) (PTFE) film ($\mu = 0.04\text{--}0.07$). For a PTFE film, however, the friction mechanism is believed to be quite different from the boundary friction of the monolayers [46, 47]. For PTFE, extensive interfacial reordering occurs with sliding in addition to a PTFE transfer layer being readily deposited on the countersurface. For the monolayers, adhesion between the terminal groups must be overcome to initiate sliding, and transfer does not readily occur.

The results have implications for industrial issues. In polymer processing, for example, processing aids (antioxidants, fluorochemicals) are routinely added to the polymer prior to extrusion. Some processing aids, such as antioxidants, protect the polymer during high temperatures, and others coat the extruder, thereby reducing the interaction of the polymer with the surface. The results presented here show that by coating the interior wall of the extruder, the fluorochemical reduces the shear stress at the extruder surface.

CONCLUSIONS

The interfacial energy of a HC monolayer against a FC monolayer was measured to be $14.9 \text{ mJ/m}^2 \pm 1.0 \text{ mJ/m}^2$. As predicted by theory, this value is between that measured for HC monolayer against HC monolayer ($\gamma_{\text{HC}} \approx 30 \text{ mJ/m}^2$) and a FC monolayer against a FC monolayer ($\gamma_{\text{FC}} \approx (\text{from } 7 \text{ to } 15) \text{ mJ/m}^2$). The measured friction between the monolayers does not follow the same trend as that measured for

adhesion. For the friction measurements, $\tau_{\text{FC/HC}} < \tau_{\text{HC/HC}} < \tau_{\text{FC/FC}}$. The measured shear stress of a FC monolayer against a FC monolayer was $\tau_{\text{FC/HC}} = 0.23 \text{ MPa} \pm 0.07 \text{ MPa}$, less than half that measured between HC/HC monolayers.

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