

Adhesion and friction of self-assembled organic monolayers

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Recent advances in the study of friction and adhesion using self-assembled monolayers (SAMs) include the use of microscopic measurements to investigate adhesion hysteresis and the effects of hydrogen bonding and acid-base interactions on this process. Also, recent molecular dynamics simulations have enabled several important observations to be made concerning friction between surfaces and the role that surface molecules play in systems.

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Abbreviations

AFM	atomic force microscopy
FFM	friction force microscopy
OTS	octadecylsilane
PDMS	polydimethylsiloxane
SAM	self-assembled monolayer

Introduction

Self-assembled organic monolayers are attractive model systems that can be used to conduct fundamental studies in wetting, adhesion and friction of surfaces. There is also the potential to apply these self-assembled monolayers (SAMs) to solve many practical adhesion- and friction-related problems. Interest in these systems stems from the ability of researchers to control the chemical as well as the physical properties (i.e. phase states) of these systems in systematic ways. In recent years, interest has been further intensified because of the availability of advanced surface analytical tools, sophisticated organic synthetic methods and a new understanding of the mechanics of interactions that prevails at surfaces. SAMs have provided a platform that promotes interaction between chemists and physicists in order to understand and solve adhesion and related problems. This brief review provides a simple roadmap showing how progress is currently being made in this important area of research, and highlights areas where more vigorous interaction between chemical and physical approaches is needed.

Adhesion

A starting point in studies of the adhesive properties of SAMs is the mechanics of contact of spherical objects, pioneered by Johnson, Kendall and Roberts (JKR) [1]. In this method, a spherical object is brought into contact with another sphere or flat plate under controlled loads. In the zone of contact, a deformation develops spontaneously that depends on the interfacial interaction and any external

load applied to the objects. A mechanical calibration of the load deformation data using the JKR theory affords estimation of the work of adhesion of the two surfaces. The contact deformations are measured by first increasing the load and then decreasing the load. Thus, two values of work of adhesion are obtained, the difference between which yields the hysteresis of adhesion. Adhesion hysteresis arises due to the irreversible processes occurring in the bulk and/or at the interfaces [2]. Elucidation of the origin of adhesion hysteresis is of fundamental importance in understanding adhesion as well as friction [3]. The interfacial origin of adhesion hysteresis in SAMs was confirmed by Whitesides and I [4]; we studied the adhesion of SAM-coated polydimethylsiloxane (PDMS) elastomers as a function of their chemical constitution. The surfaces of small hemispheres and flat sheets of PDMS elastomers were oxidized by an oxygen plasma, and were further modified with SAMs of hydrocarbon and fluorocarbon. JKR contact mechanics studies on these surfaces revealed that the hydrocarbon monolayers exhibited negligible adhesion hysteresis, whereas pronounced hysteresis was observed with the fluorocarbon monolayer. These studies further showed that adhesion hysteresis originates from the interfacial metastable processes of the type that also give rise to wetting hysteresis. A number of other studies [5,6] strengthened the above notion even further. Systematic studies carried out in [5,6] revealed that the adhesion hysteresis depends not only on the chemical constitution of the monolayer films, but also on the phase states of a given monolayer. Interdigitation of the monolayer films and the defect-induced pinning of surfaces were thought to be the factors contributing to these hysteresis phenomena.

In parallel with these macroscopic studies, several microscopic measurements, based on atomic force microscopy (AFM), have also provided evidence of adhesion hysteresis in SAMs. Joyce *et al.* [7] observed significant adhesion hysteresis between a tungsten tip and an alkane-thiol-modified gold substrate using an atomic force microscope. The authors proposed that the adhesion hysteresis is due to mechanical compaction of the monolayer and slow strain recovery. Earlier, molecular dynamic studies [8] showed that the SAMs recover almost elastically in standard loading-unloading cycles. More recent studies [9] are beginning to provide evidence that the mechanical compaction of the monolayers results in a change in their tilt angles, which may contribute to adhesion hysteresis. More definitive experimental and theoretical studies are, however, needed in order to estimate the relative contributions of the various plausible factors that give rise to adhesion hysteresis in SAMs. These include extension and relaxation of hydrocarbon chains, chain interdigitation, domain formation, reorientation of terminal

groups and inelastic deformation of the monolayer films. In the absence of adhesion hysteresis, the adhesion energies of SAMs correlate well with those predicted by Young's equation of contact angles as shown in [10,11].

Recently, several interesting AFM experiments [12,13*,14,15*,16] have been performed in order to elucidate the role of hydrogen bonding, as well as acid-base interactions, in adhesion. In these studies, the tips of the AFM probes were coated with gold and were subsequently modified with SAMs of alkane thiols having carboxylic acid or amine terminal groups. The adhesion of these modified tips to alkane thiol monolayers of various functionalities was studied. Using this method, several groups [13*,14,15*] have found evidence of significant acid-base interactions between amine and carboxylic acid groups. Han *et al.* [16] suggested that the energy of even a single hydrogen bond can be estimated using this method.

The basis for estimating the work of adhesion in many of these AFM experiments is an equation developed by Johnson *et al.* [1], which predicts that the force (P) required to pull a sphere out of another sphere or a flat plate is:

$$P = 1.5\pi RW \quad (1)$$

where, R is the radius of the sphere and W is the work of adhesion. Note that the elasticities of the substrates do not appear in this equation; W can therefore be estimated from a single measurement of the pull-off force. In most AFM experiments, Equation 1 or its variance has been widely used to estimate W with the assumption that the probe tip is spherical in shape. Caution should be exercised when using Equation 1 for several reasons. Firstly, some nonidealities in contact deformation may result due to the small radius of curvature of the AFM tip and due to its departure from the ideal spherical shape. The second reason is more subtle: Equation 1 is derived using a fracture mechanics criterion of elastic instability in an adhering system in which the work of adhesion is assumed to be uniform in the entire area of contact. In some contact mechanics studies [17,18], it has been found that the unloading branch of the load-deformation behavior deviates from the JKR prediction, although the loading branch behaves ideally. Several explanations, which are related to the lateral gradient of normal stress and the increasing rate of crack propagation (EJ Kramer, personal communication) as the center of contact is reached have been proposed to explain this non-JKR behavior. Due to the presence of these nonidealities, a gradient of W ($\partial W/\partial a$) is present at the interface which changes the balance of forces and shifts the elastic instability to such a degree that Equation 1 does not hold anymore. These nonidealities are particularly observed with the hydrogen bonding systems. AFM, in conjunction with the technology of organic self-assembly, is a beautiful technique to study adhesion. A proper analysis of the AFM data using a meaningful framework of fracture mechanics

would, however, enhance the elegance of this technique even further.

Friction

Much less is known about friction between surfaces than about adhesion. As adhesion and friction both involve the breaking of interfacial bonds, it is sometimes believed that these two phenomena are related. Two kinds of friction phenomena are observed: static and dynamic. Although arguments can be developed to show a relationship between static friction and adhesion for strongly interacting systems, the relationship between friction and adhesion for weakly interacting systems is quite complex [19,20**,21*]. For example, the fluorocarbon monolayers have considerably higher friction than the corresponding hydrocarbon monolayers [22–25] even though the fluorocarbons are known to have the lowest surface free energy of all organic materials.

In the case of sliding of one surface against the other, it is believed that the molecular collision processes lead to a transfer of mechanical energy into various vibrational modes, which is subsequently dissipated as heat [9,26,27]. It is this dissipation of mechanical energy that increases the friction between surfaces. In recent molecular dynamics studies [9], it was proposed that one significant mode of energy dissipation in SAMs is related to the oscillation of its tilt angle as the sliding surfaces pass over the potential energy minimum. Recently, Reiter *et al.* [28] conducted an adhesion measurement between two octadecylsilane (OTS) monolayers supported onto mica while the two surfaces slid past each other. They measured the surface energy of the OTS monolayer as 22 mJ m^{-2} in the absence of any shear force, a value that is typical of a methyl surface. Next they applied a shear force to the surfaces and measured the adhesion pull-off force while shearing continued at a constant frequency. As the shear amplitude was increased to about 10 nm, the adhesion energy suddenly decreased by about 40%. The authors speculated that the end groups of the SAMs are in a potential well formed by the opposing surface. Up to a critical shear, the end groups do not leave the potential well and the surfaces are in closest contact. Beyond a critical shear, the end groups are pulled out of the potential well and the adhesion energy is reduced. Based on these observations, one may ask several interesting questions regarding some empirical relationships that are found between friction and local segmental mobilities of organic surfaces [29]. In several studies [29,30], it has been observed that a segmentally mobile surface has lower friction than a rigid surface. Does the local mobility of molecules at surfaces reduce the effective height of the potential well thus providing a lesser frictional path to the surfaces? Within this scenario, does the stiffness of the molecules at surfaces, measured in terms of the bond rotational energy barrier, contribute to higher friction than those having smaller energy barriers? The energy barrier for the trans-gauche rotation [30] of

a C–C bond in a fluorocarbon monolayer (18.0 kJ mol^{-1}) is significantly higher than that ($12.34 \text{ kJ mol}^{-1}$) of a hydrocarbon monolayer, a trend that is consistent with the higher friction observed with the former surface. Hopefully, future experiments and simulations with SAMs of various terminal groups will provide answers to these questions.

Atomic force microscopic studies on SAMs are continuing to provide valuable information about the structure/property relationships in friction, as they are in adhesion [13*,14,15*]. Based on some earlier studies of Overney *et al.* [24], several investigators have used the lateral scanning of AFM tips [14,31*] to obtain chemical images of surfaces. The difference in the friction forces of the different chemical domains present on a surface provides the image contrasts needed in these FFMs.

Adhesion hysteresis and friction

About two decades ago, Roberts and Thomas [32] as well as Briggs and Briscoe [33] measured the shear forces between rubber hemispheres and flat glass surfaces. Sliding an object against rubber produces a lateral compressive stress, which causes a buckling in the rubber that traverses the contact zone as waves known as Schallamach waves [34]. During the propagation of such a wave, energy is lost in the trailing edge but it is gained in the wake of the wave. The difference between these two energies is the adhesion hysteresis. Using an energy criterion, these authors showed that the tangential shear stress (S) is proportional to the adhesion hysteresis (W) of rubber on glass as follows:

$$S = \Delta Ww/\lambda V \quad (2)$$

where, λ is the wavelength of the Schallamach wave, w is the wave velocity and V is the macroscopic sliding velocity. In the experiments reported by the authors, the energy gained at the wake of the wave is so much smaller than that lost in the trailing edge, that W was replaced by the receding work of adhesion. For weakly hysteretic systems, however, the difference in advancing and receding works of adhesion should be considered.

Equation 2 shows a direct relationship between adhesion hysteresis and friction. Some recent studies [25,35] with SAMs reiterated the plausible connection between adhesion hysteresis and friction, even though no macroscopic Schallamach waves were observed in these experiments. Owen and I [25] proposed that the frictional resistance of a fluorocarbon monolayer against a silicone elastomer originates from the significant adhesion hysteresis of the two surfaces. Yoshizawa *et al.* [35] carried out a systematic study of adhesion and friction for Langmuir–Blodgett films of various phase states and found that the friction forces are small for crystalline and liquid-like monolayers, but are

significant on a glassy amorphous monolayer. The authors proposed that the high friction of the glassy amorphous monolayer originates from the chain pull-out process that also manifests in the high adhesion hysteresis of this film. In the case of sliding monolayers, Yoshizawa *et al.* [35] proposed an equation of interfacial shear stress as follows:

$$S = \Delta W/\delta \quad (3)$$

where, δ is a characteristic molecular length. Note that Equation 2 converts to Equation 3 if $w=V$ and $\delta=\lambda$.

Earlier, Gittus [36] proposed that the frictional sliding between surfaces, in some cases, may be due to the propagation of Volterra dislocations (interfaceons). A Schallamach wave is a macroscopic example of such a dislocation motion. As the dislocations move, the strain concentration travels along with it. The mechanical hysteresis losses due to the associated stress-strain cycles are supplied by work done by the shear force. Although Gittus was aware of the effect of interfacial adhesion on frictional stress, he did not discuss this subject in any detail. The subject of adhesion in friction was covered by Roberts and Thomas [32] as well as Briggs and Briscoe [33] in the context of Schallamach waves. Briscoe and Evans [22] explicitly suggested the possibility that the sliding of two organic monolayers might occur via dislocation motion. If, indeed, the above is the case, then the shear stress should be related to the interfacial adhesion hysteresis, as some current studies indicate [25,35]. The complete problem, relating shear stress and dislocation movement, should, however, be worked out using a fracture mechanics approach, during which the associated strain energy release rate would involve dislocation speed, dislocation size, as well as the adhesion and bulk hysteretic properties of materials.

The role of friction in adhesion

A recent study of adhesion [37*] of a viscoelastic adhesive on several SAMs and polymer brushes revealed a complex relationship between adhesion and friction. It is commonly accepted that adhesive fracture toughness is proportional to the surface free energy. The experimental results of adhesion on the low energy monolayer films, however, showed that the contrary is true. Although the fluorocarbon surface has the lowest surface free energy of all the organic materials, it exhibited the higher adhesion toward a viscoelastic tape than the corresponding hydrocarbon surfaces. It was proposed that the separation of a viscoelastic adhesive from a surface occurs via a dewetting process. If the surface allows the adhesive to slip, then the shear and the associated extensional deformations in the adhesive are minimized and hence the adhesion strength is reduced. These studies revealed a situation where adhesion is controlled by friction. Here too, the interfacial friction, and thus adhesion, was found to decrease with the increased segmental mobility of the surfaces.

Technological advances

Several groups [38•–40•,41–45] have started investigating the practical utility of SAMs in the control of adhesion, friction and wear properties of materials. Bhushan *et al.* [38•] showed that chemically grafted SAMs have much larger wear resistance than the films produced by the Langmuir–Blodgett procedure. Tsukruk *et al.* [39•] found that the wear properties of SAMs are improved by chemically grafting C₆₀ fullerene molecules onto their surfaces. Deng *et al.* [40•] used SAMs to control the adhesion of micromotor parts in a microelectro-mechanical device. Fabianowski *et al.* [41] found that SAMs decrease the leakage current and enhance the hydrolytic stability of adhesive interfaces relevant to the electronic packaging applications.

Conclusions

In this brief review, we have summarized some of the recent trends in the research of adhesion and friction, where SAMs have been used as model systems. Several investigators are continuing to exploit the richness of the structures and compositions that the SAMs afford. These studies are certainly bringing the chemical and mechanical approaches used to study adhesion and friction problems much closer to each other, although stronger interaction between the two approaches is still desired for the development of a proper fracture mechanics framework needed to understand friction. In the next decade, we are likely to witness several major advances in these areas. We are likely to see a trend in attacking the adhesion and friction problems using microscopic, or even molecular-level, fracture mechanics as more sophisticated synthetic techniques and advanced experimental and theoretical tools continue to evolve. In this context, we are also likely to see major advances in the simultaneous measurements of mechanical responses and structural changes of thin organic films [46], a critical issue in understanding the transition from static to dynamic friction of surfaces. Technological applications of SAMs to control adhesion, friction and wear of materials are also likely to bloom; recent technological progresses [38•–40•,41–45] bear testimony to this fact.

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Force measurements between layers of amphiphiles, polyelectrolytes and biomolecules

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Force measurement techniques are providing increasing insight into the organization and properties of layers of organic molecules and biomolecules. Structural forces and forces of specific intermolecular interaction or recognition are being quantified for the first time using SFA and SFM methods. These data are essential for the rational design of biomolecular surfaces and bulk materials.

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Abbreviations

AFM	atomic force microscopy
JKR	Johnson-Kendall-Roberts
OTE	octadecyltriethoxysilane
PCMA	poly[2-(propionyl)ethyl]trimethylammonium chloride
SFA	surface force apparatus
SFM	scanning force microscopy

Introduction

Self-assembly of functional organic molecules is a versatile and effective route to fabricating interfaces with designed performance. Assessing the performance of interfaces with respect to properties such as adhesion, steric stabilization, friction and wettability is advanced substantially by direct measurement of intermolecular forces transmitted across interfaces. Methods for making these measurements are increasing in both number and power. The repertoire of techniques includes the surface force apparatus (SFA), scanning force microscopy (SFM), osmotic stress, interference reflection microscopy, optical tweezers and micropipette methods. Some of the recent developments and comparative advantages of these methods were discussed here last year by Evans and Parsegian [1], and, more recently, in the context of bioadhesion, by Leckband [2] and by Hammer and me [3•]. Dan [4] has analyzed the recent literature on dynamic, shearing and other time-dependent surface force interactions. Chaudhury's article [5] in this issue surveys surface force interactions measured by contact mechanics methods. A variety of papers concerning the role of surface forces in the physical and chemical mechanisms of tribology is available in recent issue of 'Langmuir' [6••].

This critical review is targeted at forces between layers of well defined structure assembled on solid interfaces in contact with liquid. Well defined structure can be

created and characterized more easily on large, flat surface areas. For those situations, SFA and SFM are the methods of choice; the other methods are better suited to particles or vesicles. In the same spirit, the pair of opposing, macroscopic surfaces in the SFA is the best platform for construction of well defined interfaces, if not the simplest experiment to perform, for the measurement of intermolecular forces. SFM has some advantages, particularly in ease of execution, and, where relevant, in ability to measure forces with excellent lateral, spatial resolution. This review will concentrate on new information over the past year by the SFA method, but will bring in SFM and other data where relevant or complementary to the SFA work. Some studies that will provide a basis for interesting, quantitative comparison between SFA and SFM on the same systems are beginning to appear [7]. The review will emphasize results that give new physical insight into a variety of complex materials, rather than papers that emphasize developments primarily of instrumentation or technique. There have also been some significant advances, however, along methodological lines [8,9].

This review will emphasize surface forces measurements on three categories of materials where there has been interesting progress during the past year, and which have not been the subject of other recent reviews. Luckham [10], Gast [11] and Szeleifer and Carignano [12] have surveyed interactions between adsorbed polymers, block copolymers and tethered polymer chains in nonaqueous media, building on earlier reviews [13-15]. Protein interactions at solid surfaces were thoroughly reviewed last year [16•], though studies in this and related areas are expanding rapidly. In this article, I will consequently emphasize work on three classes of molecules: amphiphiles, polyelectrolytes, biopolymers and biomolecular systems.

Surface forces in amphiphile systems

Interesting surface force data on amphiphiles have been obtained recently both on molecules layered on the surfaces of the SFA and on molecules confined in the solution space between the surfaces.

Langmuir-Blodgett, adsorbed, and chemisorbed layers

Wood and Sharma [17] have shown how to prepare a robust hydrophobic layer on mica, thereby producing a very useful foundation for the construction of more elaborate structures on top. In their method, the mica is made hydrophobic by the deposition of a prepolymerized Langmuir-Blodgett (LB) film of octadecyltriethoxysilane (OTE) on to mica that has been activated by exposure to