

INVESTIGATION OF INTERFACIAL COMPOSITION, STRUCTURE, AND TOPOGRAPHY ON
TRIBOMETRIC FRICTION

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Dissertation
Submitted to the Faculty of the
Graduate School of Vanderbilt University
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
in
Chemical Engineering
December, 2011
Nashville, Tennessee

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To my parents, who have always put my well-being in front of their own.

ACKNOWLEDGMENTS

I have been truly fortunate to work alongside gifted scientist and great people throughout my research career, at the Cleveland Clinic and also at Vanderbilt. My time at the Cleveland Clinic Lerner Research Institute was central to my development as a scientist and stoked my enthusiasm for research. Likang Chin was the ideal research mentor for an intimidated 20 year old entering his first research lab. She was intelligent, caring, made research fun, and took concern in my professional growth. I am grateful to call her a good friend even now. I would like to thank Andrew Baker for his guidance, patience, and most importantly for his friendship. I still have very fond memories of our dog training sessions we undertook. I would like to thank the other members of the Derwin lab: Diane Leigh, Amit Aurora, and Ryan Milks for their support and companionship.

My time at Vanderbilt has been immensely pleasurable due to the people I worked with everyday. Dr. Brandon Booth, Dr. Christopher Faulkner, Dr. Peter Ciesielski, Darlene Gunther, and Carlos Escobar helped create a great lab environment, productive, open to the exchange of ideas, and enjoyable. I would like to specifically thank Dr. Juan Tuberquia. Juan and I have been at each other's side for four straight years and I could not have asked for a better colleague and friend. His intelligence was always a great resource for me and I am grateful for his advice, loyalty, and compassion. Life as a graduate student can be trying, but my down days were very few and far between and that is a direct testament to the relationships I formed with my lab mates.

I would like to thank and acknowledge the various people around Vanderbilt who helped make my research possible. I would like to acknowledge Dr. Bridget Rogers for use of her ellipsometer and XPS, and Dr. David Cliffel for use of his the optical microscope. I would like to express my gratitude to Margarita Talavera, Mary Gilleran, Mark Holmes, and Rae Uson. I would like to thank Dr. Ben Schmidt and Bobby Harl for their help with the various analytical tools (XPS, AFM, profilometer, and ellipsometer) and also for their friendship. I would like to thank the various high school and undergraduate students who contributed to this project: Brion Lee, Nate Martin, Collen Leng, and Chris

Caswell. Their hard work and ideas were vital to this research. I would like to thank the members of the McCabe lab: Dr. Oleg Mazyar, Jose Riveria, and Ben Lewis for insightful discussions and their contributions to this research. I would like especially thank Dr. Clare McCabe for her role as my co-advisor. Her guidance and support strengthened the research and I learned a great deal from her counsel. I thank all the professors in the Chemical and Biomolecular Engineering Department for their expertise and teachings. I am especially grateful to my committee members, Dr. Paul Laibinis, Dr. Ken Debelak, and Dr. Deyu Li for their guidance and time. I would also like to thank my many friends who made my time at Vanderbilt memorable.

I send my deepest thanks to the two people who have contributed the most to my development as researcher: Dr. Kathe Derwin and Dr. Kane Jennings. I have been truly blessed to be mentored by brilliant scientific minds who are also wonderful role models. Dr. Derwin took a great interest in my growth as a scientist and was essential to my decision to pursue a Ph.D. Dr. Jennings has been the ideal graduate student advisor. His intellect and cleverness have been the driving force behind this thesis, but what makes Dr. Jennings stand out is his integrity. He always treats people with compassion and respect and he provides a great example on how to live a life. I have nothing but the upmost respect for Kane as a scientist and as a person.

Most importantly, I would like to thank my family. My parents have made large sacrifices for the good of their sons and daughters and I owe everything to them. My brothers and sisters have been crucial to my development as a scientist and as a person. From my eldest brother Mike I gained my inspiration to pursue a Ph.D and a enthusiasm for science. My brother Ed has shown me how to be passionate, hard working, and loyal. From my younger sister Kristen I have been shown the virtue of patience and sympathy. I am who I am because of my family.

Finally I would like to thank my various funding sources: the Office of Naval Research (N00014-06-1-0624 and N00014-07-1-0843), the State of Tennessee, and the Department of Education for a Graduate Assistance in Areas of National Need (GAANN) Fellowship (P200A090323).

TABLE OF CONTENTS

	Page
DEDICATION.....	iii
ACKNOWLEDGMENTS.....	iv
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
Chapter	
I. INTRODUCTION.....	1
References.....	7
II. BACKGROUND.....	11
Microelectromechanical Systems.....	11
Trichlorosilane Monolayers.....	12
Mixed Monolayers.....	14
Mathematical Models Describing Microscale Friction.....	16
References.....	19
III. EXPERIMENTAL PROCEDURES AND CHARACTERIZATION METHODS.....	22
Experimental Procedures.....	22
Materials.....	22
Synthesis of (1-trichlorosilyl undecyl) Trichloroacetate.....	22
Preparation of Silicon Substrates.....	23
Preparation of Silica Lenses.....	24
Formation of Alkyltrichlorosilane Monolayers.....	24
Preparation of Hydroxyl Monolayer.....	24
Formation of Fluorocarbon Trichlorosilane Monolayers	25
Formation of Alkyltrichlorosilane Mixed Monolayers.....	25
Characterization Methods.....	25
Spectroscopic Ellipsometry.....	25
Contact Angle Goniometer.....	27
Microscale Friction Testing.....	29
X-ray Photoelectron Spectroscopy.....	30
Scanning Electron Microscope (SEM).....	31
Atomic Force Microscopy (AFM).....	32
Profilometry.....	32

References.....	32
IV. SURFACE AND FRICTIONAL PROPERTIES OF TWO-COMPONENT ALKYLSILANE MONOLAYERS ON SILICON.....	36
Introduction.....	36
Experimental Methods.....	38
Formation of Alkyltrichlorosilane Monolayers.....	38
Microscale Friction Testing.....	38
Results and Discussion.....	39
Estimating Composition of Mixed Monolayers Based on Ellipsometric Data....	39
Oleophilicity of Mixed Monolayers.....	40
Effect of Monolayer Composition on Friction.....	42
Conclusions.....	46
References.....	47
V. MICROSCALE FRICTIONAL INVESTIGATION OF HYDROXYL-TERMINATED MONOLAYERS ON SILICON.....	49
Introduction.....	49
Experimental Methods.....	50
Formation of Alkyltrichlorosilane Monolayers.....	50
Microscale Friction Testing.....	50
Results and Discussion.....	51
Surface Energy of Hydroxyl Terminated Monolayer.....	51
Effect of Terminal Group on Friction.....	51
Conclusions.....	54
References.....	55
VI. FRICTIONAL PROPERTIES OF WELL-MIXED FLUOROCARBON / HYDROCARBON MONOLAYERS	54
Introduction.....	57
Experimental Methods.....	60
Formation of F6H2 Trichlorosilane	60
Formation of Fluorocarbon / Hydrocarbon Mixed Monolayers	60
Formation of Alkyltrichlorosilane Mixed Monolayers.....	61
Microscale Friction Testing.....	61
Results and Discussion.....	62
Mole Fraction Calculations from XPS.....	62
Surface Composition of Mixed Monolayers.....	65
Effect of Hydrocarbon Chain Length on Friction.....	71
Durability of Mixed Monolayer.....	76
Conclusions.....	79
References.....	81
VII. MICROSCALE FRICTION BETWEEN SLIDING MONOLAYERS.....	84
Introduction.....	84
Experimental Methods.....	86
Formation of Monolayers.....	86

Microscale Friction Testing.....	86
Humidity Testing.....	87
Results and Discussion.....	87
Substrate and Tip Monolayer Characterization.....	87
Effect of Probe Surface on Microscale Friction.....	89
Effect of Humidity on Microscale Friction.....	94
Conclusions.....	96
References.....	98
VIII. MICROSCALE FRICTION OF POLYMERS.....	102
Introduction.....	102
Experimental Methods.....	105
Preparation of Diazomethane.....	105
Preparation of Gold Substrates and Gold-Coated Tips.....	105
Formation of Monolayers	106
Formation of Polymethylene Films.....	106
Formation of Superhydrophobic Films.....	106
Microscale Friction Testing.....	106
Results and Discussion.....	107
Characterization of Surfaces.....	107
Polymer Friction.....	109
Effect of Testing Medium.....	114
Conclusions.....	117
References.....	119
IX. FRICTIONAL PERFORMANCE OF SILICA MICROSPHERES.....	121
Introduction.....	121
Experimental Methods.....	123
Deposition of Spheres.....	123
Functionalization of Microspheres.....	123
Quantitative Analysis of Coverage Area.....	124
Microscale Friction Testing.....	124
Results and Discussion.....	125
Sphere Dispersion and Confirmation of Rolling.....	125
Frictional Performance of Rolling-Element Lubrication Systems.....	127
Influence of Surface Coverage on Frictional Performance.....	133
Monolayer Functionalization of the Microsphere Systems.....	134
Conclusions.....	136
References.....	137
X. CONCLUSIONS AND FUTURE WORK.....	139
Conclusions.....	139
Future Work.....	143
Monolayer Friction.....	143
Polymer Friction.....	144
Rolling Lubrication.....	144
References.....	146

LIST OF TABLES

Table	Page
3.1 Reported advancing contact angles for water and hexadecane for a variety of densely packed monolayer surfaces	28
7.1 Advancing contact angle data for water and hexadecane on the various probe and substrate surfaces	88
7.2 Tribometric data from the various monolayer-monolayer tribology tests performed in ambient environments	94
8.1 Surface characterization data for the various films created on the probe and substrate surfaces	109

LIST OF FIGURES

Figure	Page
1.1 Representation of the molecular structure of mixed monolayers prepared from a n-alkyltrichlorosilanes of two different chain lengths	4
2.1 SEM images showing an indexing motor and comb-drive accelerometer	12
2.2 Scheme showing an idealized structure of monolayer films created from trichlorosilane precursors	14
4.1 Representation of the molecular structure of mixed alkylsilane monolayers	38
4.2 Effect of surface mole fraction of the long-chain component on the advancing hexadecane contact angles for two-component alkylsilane mixed monolayers	41
4.3 Effect of surface mole fraction of the long-chain component on the frictional properties of two-component alkylsilane mixed monolayers	43
4.4 Effect of ellipsometric thickness on the frictional properties of one-component and two-component C6/C18 alkylsilane monolayers	44
5.1 Effect of terminal group on the frictional properties of alkylsilane monolayers	52
5.2 Effect of terminal group and load on the frictional properties of alkylsilane monolayers	53
6.1 Molecular simulation snapshots of $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ and $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ mixed monolayers	58
6.2 Representation of the molecular structure of the perfluoroalkyl / alkylsilane mixed monolayers	59
6.3 XPS spectra of the C(1s) region for the various F/H mixed monolayers created by backfilling incomplete fluorocarbon monolayers.	63
6.4 Effect of the alkylsilane component surface mole fraction and chain length on the advancing hexadecane contact angles for perfluoroalkyl / alkylsilane mixed monolayers	67
6.5 Molecular simulation snapshot of a $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ mixed monolayer containing a 3:1 molar ratio between fluorocarbons and hydrocarbon components	70
6.6 Effect of the hydrocarbon chain length and load on the frictional properties of perfluoroalkyl / alkylsilane mixed monolayers at two different F/H ratios, 2:1 and 3:1	72

6.7	Effect of load on the on the frictional properties of perfluoroalkyl / alkylsilane and alkylsilane / alkylsilane mixed monolayers	74
6.8	Effect of load on the on the frictional properties of perfluoroalkyl / alkylsilane and alkylsilane / alkylsilane mixed monolayers	75
6.9	Molecular simulation snapshots of $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ monolayer-on-monolayer systems at two pressures, 0.05 mN / mm^2 and 2.5 mN / mm^2	76
6.10	Effect of composition on the durability of perfluoroalkyl / alkylsilane mixed monolayers	78
6.11	Effect of hydrocarbon chain length on the durability of perfluoroalkyl / alkylsilane mixed monolayers	79
7.1	Experimental data from the various monolayer-monolayer tribology tests performed in the ambient environment	89
7.2	Experimental results from the various monolayer-monolayer tribology tests performed at four different relative humidity levels and categorized based on the probes' and substrates' affinity for water	95
8.1	AFM images and line scans of the C18 monolayer, polymethylene film, and superhydrophobic film	103
8.2	SH interface in which water sits atop the polymer surface	105
8.3	Effect of substrate film on the frictional forces obtained with a 6 mm diameter borosilicate lens at a sliding speed of 0.1 mm/s and a 98 mN load	110
8.4	Effect of probe and substrate coatings on the friction force	112
8.5	Frictional effect of water submersion for the various C18 (a) and PM (b) probe systems	115
8.6	Optical image of the wear track (framed with the dotted line) obtained for the SH/SH system during underwater tribometry testing	116
8.7	Frictional effect of water submersion for the various control (a) and OH (b) probe systems	117
9.1	SEM images of the microsphere systems studied	126
9.2	Long-term frictional performance of the 2 μm diameter sphere system	128
9.3	SEM images of the wear track of the silicon surface after complete failure for the 2 μm diameter system	129
9.4	Effect of sphere diameter and load on the frictional performance of the silica sphere systems studied	130

9.5	Effect of sphere diameter and load on the wear life of the silica sphere systems studied	132
9.6	Long-term frictional performance of the 2 μm diameter sphere system at various loads	132
9.7	Effect of sphere surface coverage on the coefficient of friction	134
10.1	Summary of the lubrication systems studied	140
10.2	Example of a diacetylene-containing trichlorosilane adsorbate	143
10.3	Side view and top view of a proposed rolling lubricant system	145

CHAPTER I

INTRODUCTION

Future innovations in a wide range of fields, from telecommunications to biomedical devices, will further push the boundaries of miniaturization and create a greater demand for microelectromechanical (MEMS) and nanoelectromechanical (NEMS) systems^{1,2} (referred to by the generic term “MEMS” in this thesis). The benefits of miniaturization are numerous. The smaller size scales enable levels of precision never before achieved and make possible a whole new host of advanced applications, such as augmented reality or stealth data communication (Advanced MEMS systems for optical communication and imaging).¹⁻³ MEMS fabrication employs many of the high throughput techniques that are used to produce integrated circuits⁴ and these fast production rates, coupled with lower material requirements, provide an opportunity to dramatically decrease the cost of numerous devices, such as sensors, accelerometers, medical devices, and consumer electronics.^{1,2}

While the size scale of MEMS offers many advantages, the operation of scale and large surface-to-volume ratio create unique tribological issues as surface forces rather than bulk forces begin to play a dominant role in device performance.^{1,2,5} MEMS have surfaces that are separated by a few nanometers^{1,3,6} and can move with respect to each other at what can be modest velocities from a macroscopic point of view (cm/s) but which correspond to strain rates exceeding 10^9 s^{-1} .^{3,7} Since the operational forces of MEMS can be on the same scale as retarding forces, the increase in resistive surface forces such as adhesion and static friction can severely diminish device performance and in some cases, prevent devices from working.^{2,8-10} Traditional lubrication strategies, such as oils, are insufficient for MEMS devices as the microscale dimensions prevent viscous liquids from fully integrating into the device and do not provide ample wear protection or allow proper functioning. Due to the lack of sufficient lubrication schemes, the only MEMS devices that have been successfully implemented in commercial products have been those that have simple designs or avoid direct surface

contact (examples include digital micro-mirror devices and accelerometers).^{2,4} For MEMS devices to fulfill their vast potential, lubrication systems that allow direct surface contact, such as sliding or oscillation, and still provide long-term performance and reliability must be developed.

Numerous lubrication strategies have been investigated, but all have limited potential. Ultra-wear resistant polyethylene films,^{11,12} while proven to provide great frictional benefits, have micron thicknesses that are not viable for MEMS devices and cannot be deposited conformally between and underneath nano- and microscale components. Vapor-deposited films have shown to dramatically extend the wear-life of MEMS^{13,14} and are straightforward to apply, but generally adhere only weakly to the metal surface and are therefore easily removed, resulting in the need for a constant flow of lubricant molecules in the vapor phase to maintain the function of the lubricant.^{15,16} A variety of monolayer coatings have been investigated and are extremely attractive lubrication candidates due to their simple and cost-effective application.¹⁷⁻²¹ Unfortunately, the thin films are not sufficiently durable.^{22,23} Several other lubrication schemes (ionic liquids,²⁴ diamondlike coatings,^{25,26} nanopatterning^{27,28}) have been examined, but all have severe shortcomings. Further complicating the lubrication problem is the enormous diversity found in MEMS devices. Due to the range of dimensions and variety of mechanical components, several different lubrication schemes are likely required.

With the rapid advancements in microfabrication and nanotechnology, and the specific problem of lubricating MEMS, the field of tribology has reemerged as both an experimental and theoretical discipline. Tribologists are not only developing new lubrication schemes for the microscale,²⁹⁻³¹ but are investigating the molecular fundamentals of friction, wear, and lubrication.³²⁻³⁷ Extensive experimental work has been done using atomic force microscopy (AFM), surface force apparatuses (SFA), and microtribometers.^{5,35-38} AFM and friction force microscopy has been widely used to investigate atomic roughness, nanoscale friction, and intermolecular interactions between molecules.³⁵⁻³⁷ AFM experiments are conducted at sliding speeds ($\sim 1 \text{ m/s}$)^{37,39,40} that are several orders of magnitude lower than application speeds for MEMS devices (0.1 m/s to over 500 m/s)³

resulting in frictional properties that may not be in the correct regime for practical applications. In addition, AFM-based studies are limited to single-asperity contact, with contact radii of 1-40 nm,^{36,41} and lack the ability to investigate normal loads above 200 nN.^{37,42} Despite the low loads, the nanoscale contact area found in AFM creates contact pressures on the order of $\sim 10^9$ Pa. Microtribometers, while not as sensitive as AFM, allow tribologist rapid and adjustable frictional testing at testing parameters that are more applicable to MEMS devices.³ While AFM frictional testing is only single-asperity contact, microtribometers use a pin-on-disk configuration that better mimics the sliding contact area found in many MEMS devices.^{2,5} The use of a microtribometer also offers the ability to test tribological properties at mN forces and speeds that range from 0.01 mm/s to 10 m/s, while maintaining low to moderate surface pressures (30-200 MPa).^{4,43}

My thesis is focused on advancing lubrication at the microscale by performing both fundamental and applied research with a microtribometer. My investigation into mixed monolayers, for example, is motivated by developing a low-friction monolayers but offers the opportunity to investigate the influence of surface composition on monolayer friction. Mixed monolayers are molecular films that are created from two or more different components. Changing the length of the molecular precursors creates a monolayer that contains two distinct regions, a solid lower layer that is densely packed and a more mobile upper layer consisting of only the top portion of longer chain components, and presents a way to integrate a mobile, liquid-like layer into a bound film (Figure 1.1). Studies have shown that a combination of a mobile liquid layer and a bound solid film can greatly extend the lifetime of the lubrication scheme and also reduce the coefficient of friction.^{29,38,44} In Chapter IV, I determine if a liquid-like upper layer decreases monolayer friction by investigating a variety of hydrocarbon / hydrocarbon mixed monolayers (H/H). In this study I vary the length of the two hydrocarbon components and also vary the ratio of long and short chain molecules in order to investigate the effect of chain mobility and oleophilicity on monolayer friction.

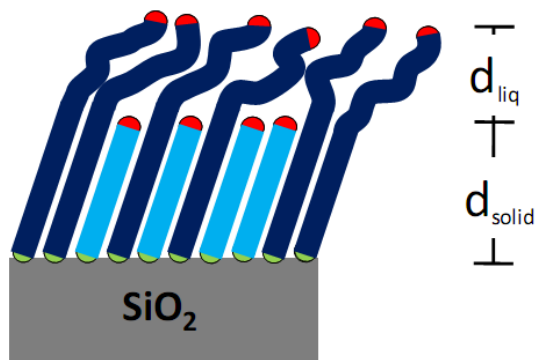


Figure 1.1. Representation of the molecular structure of mixed monolayers prepared from a n-alkyltrichlorosilanes of two different chain lengths. The films can be viewed as having two distinct regions, a solid base layer (d_{solid}) and a mobile upper layer (d_{liq}).

Chapter VI expands the study on mixed monolayers to include fluorocarbon / hydrocarbon mixed monolayers (F/H). By replacing the CH_3 -terminated base layer with a CF_3 -terminated surface, the interfacial interactions between the lower and upper regions would be considerably altered. The methylene and methyl groups present in H/H monolayers have similar interfacial interactions that would encourage the longer chains of the upper layer to collapse very near to the CH_3 base layer. Fluorocarbon monolayers, however, are oleophobic, and the hydrocarbon long chains would experience repulsive forces⁴⁵⁻⁴⁷ from the CF_3 -termini of the base layer and resist interaction with the fluorocarbon moieties. In Chapter VI, I present the effect of repulsive interfacial interactions on microscale friction and, with additional insight from surface characterization and molecular dynamic simulations, presents a physical interpretation of the findings. In addition, I investigate the effect of molecular packing and cross-linking on monolayer wear-life by comparing the cyclic tests of various F/H mixed films that differ in their F/H ratio.

Chapters V and VII discuss monolayer research that is more fundamental in nature. In Chapter V, I conduct tribometry testing with an OH-terminated monolayer. The polar behavior of an alcohol group is vastly different to that of fluorine or methyl and provides greater insight into the relationship between functional group exposure, adhesion, and coefficient of friction. While there

have been tribological investigations involving hydroxyl monolayers created from thiol adsorption,⁴⁸⁻
⁵¹ our work represents the first report of frictional properties of an OH-terminated monolayer on silicon. My investigation into monolayer friction is significantly shifted in Chapter VII, as this chapter discusses monolayer-on-monolayer friction and humidity-influenced adhesion. Interfacial interactions have been investigated with atomic force microscopy (AFM) using a wide range of probe surfaces, solvents, and humidity levels,^{36,37,52,53} While these AFM studies have significantly increased understanding of interacting surfaces at the nanoscale, very little is known on how the knowledge gathered through AFM studies translates to the microscale, which is the scale more relevant for many MEMS devices. Numerous research groups have investigated monolayer friction and their interfacial interactions on the microscale,^{11,27,54-57} but a large number of these microscale tribometry studies have been conducted in ambient air using microtribometers with unmodified probes, i.e., the probe surface is the native oxide surface of the probe material.^{28,43,54,56-59} Rather than testing with a stainless-steel probe in an ambient environment, the work presented in this chapter is conducted with monolayer-coated probes at a variety of humidity levels. Testing with various probe/substrate combinations allowed me to examine how probe surface energy and water vapor influences the frictional performance of various monolayers.

Chapter VIII describes additional testing with functionalized probes, but the focus is shifted to polymer friction. Compared to smooth monolayer surfaces, polymer / polymer friction presents different frictional mechanisms as contacting asperities, in addition to plowing, can penetrate into each other and can ratchet over each other. In Chapter VIII, I examine polymer/polymer friction and investigate the tribological effect of probe surface energy, plowing, and topography. The chapter also describes tribometry tests conducted while the substrate and probe were submerged underwater and the frictional effect of hydrophobic interactions and chemisorbed water layers is discussed.

Chapter IX describes my investigation on rolling friction. Introducing a rolling-element bearing between two contacting surfaces can greatly reduce friction, as objects move much more efficiently when they are rolling instead of sliding.⁶⁰ Rolling elements are used in numerous

applications that affect the functionality of your everyday life; everything from the cars people drive to the doors people open depends on rolling elements to provide a low-friction motion. Despite the well-known frictional benefits of rolling motion, few experimental investigations of rolling friction have been performed on the micro and nanoscale.⁶¹⁻⁶⁸ Prior investigations of rolling friction at the microscale or below have focused on rolling elements larger than 40 μm ^{62,65-69} and those of molecular dimensions.^{60,61,63,64,70,71} To assess the feasibility of microscale rolling friction at a key size range (200 nm to 10 μm) between these extremes that is compatible with MEMS and modern micro-fabrication technologies, I have developed a simple lubrication scheme based on a layer of silica spheres, with sphere diameters ranging in size from 0.5 to 4 μm , that are deposited onto a flat silicon substrate. I demonstrate that low friction rolling can be established at this size scale and also show that the coefficient of friction and wear life of the lubrication system are dependent on sphere diameter, surface coverage, and load. In the hope of improving the frictional performance of the sphere systems, I modified the sphere/substrate systems with molecular coatings of either hydrocarbon or fluorocarbon precursors and investigated the effect of surface composition on microscale rolling friction.

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CHAPTER II

BACKGROUND

Microelectromechanical Systems

Microelectromechanical systems (MEMS) are classified as devices that have a characteristic length of less than 1 mm and combine electrical and mechanical components.¹ A large majority of MEMS devices are built from silicon and are fabricated using the advanced, high throughput photolithography techniques that were developed for integrated circuit production.^{1,2} The fast production rates, low material requirements, and low power requirements to run MEMS devices provide an opportunity to dramatically decrease the fabrication and operational cost of numerous devices.² The advancements in microfabrication techniques have been enormous over the past two decades and we now have the ability to reliably build intricate MEMS devices (Figure 2.1 a) that have the potential to impact a wide range of fields from fluidics (pumps and valves), to communication and information technology (displays, data storage), to biomedical (lab-on-a-chip) and to automotive and aerospace industries where devices have been fabricated for applications such as sensors (acceleration, pressure, chemical), gear trains, gas turbines, switches, grippers, and tweezers.³ Unfortunately, lubrication technology has not been able to keep pace with our fabrication capabilities. Due to the lubrication challenges described in Chapter I, the most successful MEMS commercial products (such as accelerometers and pressure sensors)⁴ are simple in design and avoid direct surface contact (Figure 2.1 b). Advancing our knowledge of microscale friction is critically important toward the commercial realization and successful operation of MEMS devices.

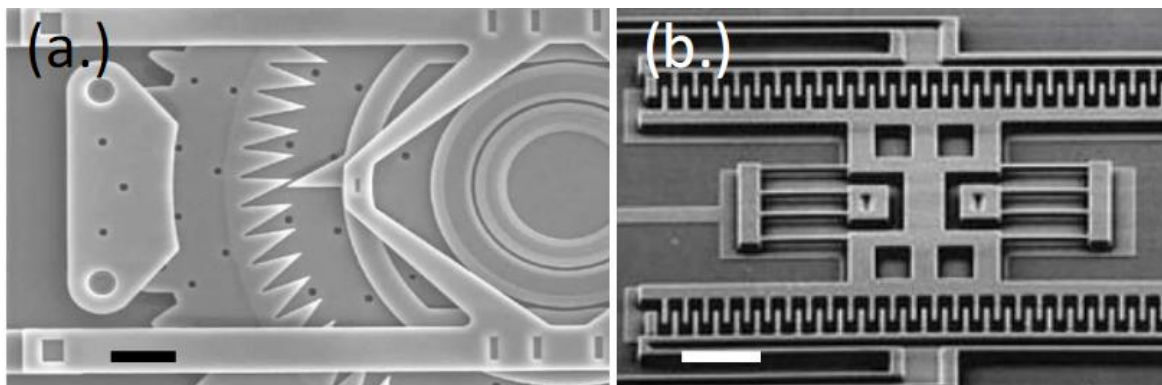


Figure 2.1. SEM Images showing an indexing motor (a) and comb-drive accelerometer (b). The scale bars represent a distance of 10 μm . The images were taken from www.sandia.gov (a) and www.eetasia.com (b).

Trichlorosilane Monolayers

Molecularly thin films can be formed on silicon substrates via exposure to a molecule containing a trichlorosilane head group, which undergoes a condensation reaction to covalently bind to a surface silanol group by way of siloxane linkages.¹ Since most MEMS devices are made from silicon substrates, the robust siloxane binding mode provides a straightforward way to apply molecularly thin films onto MEMS surfaces. Due to steric hindrances and the spacing of surface silanols, the alkyltrichlorosilane molecules react to form an average of ~ 1.5 bonds to the substrate surface.⁵ The remaining siloxane moieties can then bond together to form a cross-linked network throughout the monolayer film (Figure 2.2), creating an organized and stable thin film.⁵ The extent of cross-linking and the number of molecules that can occupy the surface are dependent on the size of the precursor backbone and termini, as bulkier functional groups can limit cross-linking and restrict access to surface sites (as discussed in Chapters V and VI).⁶ The binding mechanism of trichlorosilanes allows great flexibility, as the surface properties of the monolayer can be adjusted by altering the terminal group or composition of the molecule. Methyl, perfluoromethyl, phenoxy, biphenyl, trichloroacetate, and hydroxyl-terminated monolayers have all been created using trichlorosilane molecules.⁷⁻¹³ Furthermore, the molecular assembly mechanism for the alkylsilane

monolayers is ideal for MEMS applications, as the molecular adsorbates can penetrate into the nanometer wide gaps and crevices found in some MEMS devices.¹⁴

Hydrocarbon monolayers in particular have been studied as a potential solution to the MEMS lubrication problem. A well-ordered hydrocarbon monolayer creates a low-energy surface that greatly reduces the adhesion and friction associated with stiction caused by liquid adhesion and capillary condensation of water vapor from the environment.^{2,15,16} The lubricating properties of hydrocarbon monolayers have been used to alleviate microstructure release during the MEMS fabrication process,² but so far the monolayers have failed to provide adequate lubrication for MEMS operation. Monolayers consisting of n-octadecyltrichlorosilane (C18) can last thousands of cycles¹⁷ and have been used to extend the product life of MEMS devices, but continuous mechanical stress causes scission of the surface bonds¹⁷ and the monolayers gradually wear away and do not extend the lifetime of MEMS devices to acceptable levels.¹⁷⁻¹⁹ Furthermore, the degradation of monolayers quickens at higher surface pressures and C18 monolayers fail at ~20 cycles once surface pressures reach 400 MPa.

Additional monolayers have been investigated for tribological applications, most noticeably fluorocarbon monolayers.²⁰ Fluorocarbon monolayers are better at reducing adhesion and stiction than hydrocarbon monolayers,²¹⁻²³ but have shown to possess higher friction forces in a majority of studies.^{21,24-33} The poor frictional performance stems from the fluorocarbon monolayers' stiffness,²⁹ bulkier head group (causing increased steric interactions),^{30,31,34} and lower cohesion.³⁵ Fluorocarbon monolayers have also shown poor wear properties when compared against hydrocarbon monolayers of similar structure.^{17,28,33}

In addition to their lubrication properties, the ability for monolayers to tailor surfaces is being utilized for other MEMS technologies, such as molecular assembly and sensing applications. Monolayers will play a large role in advancing MEMS technologies and, therefore, it is important to increase our understanding of monolayer interactions and friction. Current monolayer research is focused on improving the durability of monolayers (through mechanisms such as

additional cross-linking³⁶, molecular coatings,³⁷ and multi-layering^{12,38}), enhancing their lubrication properties,^{39,40} and understanding their interfacial interactions.^{6,13,41} To help advance the understanding of monolayer friction and the molecular interactions between monolayers, I have undertaken a series of investigations. In Chapters IV and VI, I investigate potential improvements to monolayer lubrication. In an attempt to combine the properties of fluorocarbon and hydrocarbon monolayers, I develop a novel fluorocarbon / hydrocarbon mixed monolayer system (Chapter VI) and in Chapter IV I incorporate liquid-like regions into the hydrocarbon monolayers. In Chapters V and VII, I undertake more fundamental research as I investigate the influence of surface energy and testing environment on monolayer friction and interfacial interactions.

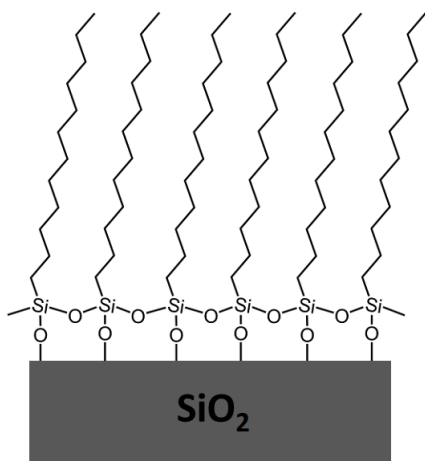


Figure 2.2. Scheme showing an idealized structure of monolayer films created from trichlorosilane precursors.

Mixed Monolayers

Driven by the complications of applying liquid lubricants to MEMS,^{39,42} there is an interest in creating solid thin films that possess liquid-like mobilities.^{43,44} Two-component mixed monolayers, in which the monolayer consists of two molecular components, represent a way to integrate a mobile, liquid-like layer into a bound film.^{39,43,44} By varying the chain lengths of the molecular components,

two distinct regions are created in the mixed monolayers: a solid lower layer that is densely packed and a more mobile upper layer consisting of only the top portion of longer chain components (Figure 1.2). The robust siloxane attachment minimizes molecular rearrangement and phase segregation on the surface and ensures a well-mixed structure for these films.¹⁰ Since there are fewer neighboring chains in the upper layer, the longer chains must cant from the surface normal into a liquid-like state in order to achieve interfacial interactions⁴⁴ and the extent of canting will depend on the specific interfacial interactions that occur between the longer chains of the upper layer and the base layer.

In this thesis, two different mixed monolayer systems are investigated, hydrocarbon / hydrocarbon mixed monolayers (H/H) and fluorocarbon / hydrocarbon mixed monolayers (F/H). In Chapter IV, I investigate numerous H/H monolayers that contain varying compositional ratios of short and long-chain molecules. The methylene backbone of the longer chain hydrocarbons and the methyl base layer have similar interfacial interactions that would encourage the longer chains of the upper layer to collapse into contact with the CH₃ base layer. The collapsing of the longer chains exposes the polymethylene backbone of the hydrocarbon molecules and creates a mixture of CH₃ and CH₂ groups at the monolayer/air interface.⁴⁴ Altering the compositional ratios and chain length difference will result in varying degrees of mobility and affect the exposure of the methylene backbone at the surface and the resulting oleophilicity of the surface. Varying the lengths of the short and long chains also alters the thickness of the solid base layer and liquid top layer, as well as total thickness of the film.

Chapter VI presents my investigation on F/H monolayers, where the shorter hydrocarbon component of the mixed monolayer is replaced with a fluorocarbon molecule. Fluorocarbon monolayers are oleophobic,⁴⁵ and thus, the interfacial interactions that occur between the top and base layer are altered considerably. Instead of canting down close to the base layer, the longer chain hydrocarbons will experience repulsive forces⁴⁶⁻⁴⁸ from the CF₃-termini of the base layer and resist interaction with the fluorocarbon moieties. Similar to the H/H study, in this investigation I alter the

chain lengths of the hydrocarbon components and vary the compositional ratio, thus creating different degrees of mobility in the top layer.

Mathematical Models Describing Microscale Friction

Analogous to the breakdown of classical physics for nanoscale dimensions, accepted laws for friction that work well in the macroscopic world become inadequate at the micro-scale and below.⁴⁹ The classic law of friction, Amonton's law, states that friction force (F_f) is proportional to normal force (F_n),

$$F_f = \mu F_n \quad (2.1)$$

where μ is the kinetic coefficient of friction. The coefficient of friction is a dimensionless number that allows quick comparison between lubrication schemes. The law maintains that friction is independent of contact area and velocity, which has proven to be untrue for certain microscopic systems. Various mathematical models have been developed to describe frictional behavior at smaller scales⁴⁹⁻⁵² and the appropriateness of each model is dependent on testing parameters and characteristics of the surfaces.

For molecularly smooth monolayer films, a commonly used model is the modified form of Amonton's law.⁵¹⁻⁵³ In this model, the friction force is defined by,

$$F_f = \mu F_n + F_o \quad (2.2)$$

where F_o is the residual force. F_o is a function of the adhesion between the surfaces and, therefore, is not accounted for by normal spring load. The residual force can be estimated by extrapolating frictional force vs. normal load plots to zero load. Higher energy surfaces have a stronger driving

force to achieve energetically favorable interactions with the probe and, therefore, will exhibit greater residual forces during frictional testing by tribometry. For low-energy surfaces residual forces are often negligible and the simpler equation (Equation 2.1) can be used to describe frictional behavior. In this thesis, Eq. 2.1 and 2.2 are both used to describe monolayer friction. Due to the low-energy surfaces of the H/H and F/H monolayers, Eq. 2.1 is used to model the friction of these films (Chapters IV and VII). When high-energy monolayers are investigated, such as OH-terminated monolayers, Eq. 2.2 is used (Chapters V and VIII).

Compared to smooth monolayers, polymer films present different frictional mechanisms due to their surface roughness. A common equation to describe model polymer friction is the Bowden and Tabor adhesion model,⁵⁴

$$F_f = \tau A_r + F_p \quad (2.3)$$

where τ is the shear strength of the surface, A_r is the real area of contact, and F_p is the plowing force due to the deformation of asperities.⁵⁴ In Chapter XIII, I investigate superhydrophobic films that contain microscale asperities and, consequently, ratcheting is an additional mechanism of friction that is possible for my polymer systems. Ratcheting occurs when one asperity has to climb over another one as they slide across each other and is prominent when microscale asperities are present.⁵⁵ The friction force for my polymer systems, therefore, arises from three main factors, adhesion which occurs at the real area of contact between the probe and substrate, plowing of asperities, and ratcheting.^{54,56,57} These frictional mechanisms are additive⁵⁷ can be related to friction force (F_f) through the equation,

$$F_f = \tau A_r + F_p + F_r \quad (2.4)$$

where τ is the shear strength of the surface, A_r is the real area of contact, F_p is the plowing force, and F_r is the ratcheting force.^{54,57} Eq. 2.4 is used in the polymer / polymer friction study presented in Chapter XIII.

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CHAPTER III

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION METHODS

Experimental Procedures

Materials

n-Docosyltrichlorosilane (C22), n-hexadecyltrichlorosilane (C16), and n-dodecyltrichlorosilane (C12) were purchased from Gelest. n-Octadecyltrichlorosilane (C18), decyltrichlorosilane (C10), (heptadecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (F8H2) and (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (F6H2) were purchased from United Chemical Technologies. n-Octyltrichlorosilane (C8) and n-hexyltrichlorosilane (C6) were purchased from Sigma-Aldrich. Trichloroacetyl chloride, trichlorosilane, methanol, undecylenyl alcohol, pyridine, anhydrous tetrahydrofuran, and chloroplatinic acid hydrate were all purchased from Sigma-Aldrich. Hydrogen peroxide (H_2O_2) 30%, ethyl acetate, sodium bicarbonate, sodium chloride, and toluene were purchased from Fisher Scientific. Sulfuric acid (H_2SO_4) and hexanes were purchased from EMD Chemicals, Inc. Hydrochloric acid (HCl) was purchased from EM Science. All reagents and chemicals were used as received. N-BK7 plano-convex lenses with a diameter of 6 mm and a radius of curvature of 15.5 mm were obtained from Thorlabs. Silicon (100) wafers were obtained from Wafer Reclaim Services, LLC.

Synthesis of (1-trichlorosilyl undecyl) Trichloroacetate

We prepared (1-trichlorosilyl undecyl) trichloroacetate via a two-step synthesis.¹ 6.6 mmol of undecylenyl alcohol and 9.9 mmol of pyridine were mixed for 30 min under nitrogen and then cooled to 0 °C by submerging the vessel into an ice bath. 14.5 mL of a 0.5 M solution of trichloroacetyl chloride in dichloromethane was then added drop wise to the mixture at 0 °C. The

mixture was then stirred for ~17 h at room temperature to create a dark yellow solution. The solution was then rinsed sequentially with distilled water, 1 M HCl (aq), saturated NaHCO₃ (aq), and 5 M NaCl (aq), followed by concentration using a rotary evaporator. The concentrate was then purified by column chromatography using an eluent consisting of 85% hexanes and 15% ethyl acetate, resulting in a product of trichloroacetic acid, undec-10-enyl ester. The terminal enyl group of this compound is then modified using 0.05 g of 0.12 M H₂PtCl₆ in 0.5 mL of dry tetrahydrofuran mixed with 0.5 mL of trichlorosilane and 6 mmol of trichloroacetic acid, undec-10-enyl ester in a N₂ glove box and then stirred for 4 h under nitrogen at room temperature. The resulting oily dark gray liquid was placed on a vacuum line for ~ 5 h and then further purified by vacuum distillation at 180 °C. The resulting product, (1-trichlorosilyl undecyl) trichloroacetate, is a colorless oily liquid. ¹H NMR, δ 4.37 (t, 2 H), 1.74 (quart, 2 H), 1.57 (quart, 2 H), 1.4 (quart, 2 H), 1.32 (quart, 14 H).

Preparation of Silicon Substrates

Silicon wafers were first cut into 4 cm x 1.3 cm pieces using a diamond-tip stylus. The silicon samples were sequentially rinsed with ethanol, water, and again with ethanol, dried in a stream of N₂, and then sonicated in ethanol for 30 min to displace any remaining contaminants. After sonication, the samples were rinsed sequentially with water and ethanol, dried in a stream of N₂, and placed in piranha solution (14 mL H₂SO₄:6 mL H₂O₂) for 30 min to hydroxylate the silicon oxide surface. The piranha-treated substrates were rinsed 3 times by submersion in water. All samples were rinsed once more in a stream of deionized water, briefly rinsed with ethanol, and thoroughly dried with N₂ before submersion in the precursor solution. Using an atomic force microscope, the root mean square roughness of the silicon substrate was determined to be 1.8 ± 0.7 nm over a 10 μm x 5 μm area.

Preparation of Silica Lenses

The lenses were rinsed sequentially with water and ethanol, dried in a stream of N₂, and placed in piranha solution (14 mL H₂SO₄:6 mL H₂O₂) for 30 min to hydroxylate the glass surface. The piranha-treated substrates were rinsed 3 times by submersion in water. All samples were rinsed once more with a stream of deionized water, briefly rinsed with ethanol, and thoroughly dried with N₂ before submersion in the precursor solution. Using an atomic force microscope, the root mean square roughness of the silicon substrate was determined to be 1.4 ± 0.3 nm over a 10 μm x 5 μm area.

Formation of Alkyltrichlorosilane Monolayers

Pure alkyltrichlorosilane monolayers were formed by immersing the piranha-treated substrates into 1 mM solutions of silane precursors in toluene. After 5 h, the samples were removed from the solution, rinsed in ~20 mL of toluene for 1 min, sequentially rinsed with ethanol, water, and again with ethanol, dried in a stream of N₂, and then stored in capped glass vials until characterization or testing was performed.

Formation of Hydroxyl Monolayer

Piranha-treated substrates were immersed in a 1 mM solution of (1-trichlorosilyl undecyl) trichloroacetate in toluene for 5 h. The samples were then removed from the solution, rinsed in 20 mL of toluene for 1 min, sequentially rinsed with ethanol, water, and again with ethanol, and then dried with N₂. The conversion of the trichloroacetate terminal group into a hydroxyl was accomplished by immersion into solution containing 10 mL deionized water, 10 mL methanol, and 0.15 g sodium bicarbonate for 15 min. The resulting hydroxyl-terminated monolayer sample was then sequentially rinsed with ethanol, water, and ethanol, then dried with N₂, and stored in a capped glass vial.

Formation of Fluorocarbon Trichlorosilane Monolayers

The fully formed fluorocarbon monolayers were formed by immersing the piranha-treated substrates into 1 mM solutions of F8H2 or F6H2 precursors in 20 mL of methylene chloride. After 15 min, the samples were removed, sequentially rinsed with methylene chloride, ethanol, water, and again with ethanol, and dried in a stream of N₂. The thicknesses and hexadecane contact angles of the monolayers were measured. If the measurements showed incomplete monolayer formation, the samples were again immersed in the precursor solution. Complete monolayer coverage, signaled by a HD contact angle of 80° and a thickness of ~1.4 nm, was achieved in 20 ± 5 min. Multilayer formation can occur if the samples are not removed shortly after a full monolayer has been formed. Once it was determined the monolayer was fully formed, the samples were removed from the solution, rinsed in 20 mL of methylene chloride for 3 min, sequentially rinsed with ethanol, water, and again with ethanol, dried in a stream of N₂, and then stored in capped glass vials until characterization or testing was performed.

Characterization Methods

Spectroscopic Ellipsometry

Ellipsometry allows measurement of thickness and refractive index of single films, layered stacks, and substrate materials with very high sensitivity.² Film thickness between 0.1 nm and 100 μm can be measured with a sensitivity better than 0.01 nm.² Linear polarized light in a specified wavelength range is reflected from a sample surface and changed into elliptically polarized light. Both the phase (Δ) and amplitude (Ψ) of the reflected light are collected by a detector and connected to the coefficient of reflection (ρ) through the fundamental equation of ellipsometry

$$\rho = \tan \Psi e^{i\Delta} \quad (3.1)$$

The coefficient of reflection is defined as the complex ratio of the Fresnel coefficient of reflection for the parallel (r_p) and perpendicular (r_s) components of the incident-plane-polarized electrical field vector

$$\rho = \frac{r_p}{r_s} \quad (3.2)$$

In order to extract meaningful information, model layers representing the film on the surface are used to fit theory to the measured data. A simple, effective model for transparent, thin organic films is the Cauchy Equation,

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots \quad (3.3)$$

where n is the film refractive index, A , B , and C are model fit parameters, and λ is the wavelength of incident light. A single parameter Cauchy model³ was used to determine ellipsometric thicknesses for all the monolayers created and the non-superhydrophobic polymethylene polymer film. In addition, ellipsometric thicknesses were used to estimate the compositions of the mixed alkylsilane monolayers, the procedure of which is described in Chapter IV.

Ellipsometric thicknesses were determined from a J. A. Woollam XLS-100 variable-angle spectroscopic ellipsometer. Thicknesses were fit to data taken at 75° from the surface normal over wavelengths from 200 to 1000 nm. The monolayers were modeled as a 0.5 mm Si substrate with an oxide layer and a Cauchy layer.⁴ The thickness of the oxide layer was approximated by measuring a piranha-treated silicon sample obtained fresh each time films were measured. The thicknesses of the alkylsilane monolayer films were calculated with an index of refraction set to 1.46 while the

fluorocarbon films were calculated with an index of refraction set to 1.38.⁵ For the polymethylene films created on the gold-coated substrates, the samples were modeled as gold substrates with a Cauchy layer. A fresh and uncoated gold substrate served as a baseline for thickness measurements and was used to determine the optical constants of the substrate and the index of refraction for the Cauchy layer was set to 1.52.⁶ All the thicknesses were calculated using the software's "normal fit" application and three separate thickness measurements were taken for each sample. The reported values and errors reflect the average and standard deviation of at least 4 independently prepared films.

Contact Angle Goniometer

Contact angles are sensitive to the outer half nanometer of film composition/structure and allow us to gain a semi-quantitative assessment of the surface properties of the various films.⁷ When a liquid is in contact with a solid surface in static equilibrium with a vapor, the liquid may form a contact angle (θ) with the surface. The contact angle is related to the interfacial tensions of the solid-vapor (γ_{SV}), solid-liquid (γ_{SL}), and liquid-vapor (γ_{LV}) interfaces through Young's Equation⁸

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (3.4)$$

The contact angle hysteresis (H), which is a quantity that provides additional information about a film surface, is defined as

$$H = \theta_A - \theta_R \quad (3.5)$$

where the advancing contact angle (θ_A) is measured after the liquid has been added to the drop, causing it to slowly advance across the surface, and the receding contact angle (θ_R) is measured after liquid has been removed from the drop, causing it to slowly recede across the surface. Hysteresis

increases with surface roughness and chemical heterogeneity.⁹ Water (H₂O) and hexadecane (HD) are generally used as contacting liquids to indicate the relative hydrophilicity/hydrophobicity and oleophilicity/oleophobicity, respectively, of a surface. H₂O will exhibit high contact angles if any hydrophobic material is present^{10,11} at the surface whereas HD has a greater sensitivity to specific chemical groups, especially in distinguishing CH₃ and CH₂ groups and hydrocarbon groups from fluorocarbon groups.¹²

Contact angles were recorded for all the films created. For the monolayer films, the measurements helped determine if a complete monolayer had been formed. Multilayering or loose-packing will create a non-homogenous surface and cause the advancing contact angle measurements to deviate from the accepted values shown in Table 3.1. Additionally, since HD contact angles can distinguish between methylene and methyl groups¹³⁻¹⁵ and also differentiate between hydrocarbon and fluorocarbon groups,^{16,17} contact angles were used to qualitatively assess the physical environment present on the mixed alkylsilane monolayers and fluorocarbon/hydrocarbon mixed monolayers. For the polymer films, water contact angles were used to assess the topography of the surface. Nanoscale and microscale asperities on the surface of the polymer can significantly increase the advancing water contact angle, as discussed in more detail in Chapter VIII.

Table 3.1. Reported advancing contact angles for water and hexadecane for a variety of densely packed monolayer surfaces.

Surface Moiety	$\theta_A(\text{H}_2\text{O})$	$\theta_A(\text{HD})$
CH ₃	111° ^{12,13}	45° ^{12,13}
-CH ₂ -	105° ¹⁴	< 10° ¹⁴
CF ₃	122° ¹⁵	81° ¹⁵
OH	28° ^{9,10}	< 10° ^{9,10}

Contact angles of water and hexadecane were measured with a Rame-Hart manual contact angle goniometer. Advancing and receding contact angles were obtained on both sides of $\sim 10\ \mu\text{L}$ drops with the syringe in the probe droplet during measurements. The reported values and errors reflect the average and standard deviation, respectively, of at least 4 independently prepared films.

Microscale Friction Testing

A Center for Tribology (CETR) UMT-2 Micro-Tribometer was used for all tribological tests. The use of a microtribometer offers the ability to test tribological properties at higher forces and speeds than AMF, while maintaining low to moderate surface pressures. While AFM frictional testing is only single-asperity contact, the microtribometers better mimic the sliding contact area found in many MEMS devices. Our microtribometer has two interchangeable sensors that allow the machine to apply loads ranging from 5 to 5,000 mN. The FVL sensor is capable of measuring forces from 1 to 100 mN in both dimensions with a resolution of 0.01 mN for an applied load between 5 and 30 mN, while the DFM-0.5 sensor can apply loads ranging from 50 to 5,000 mN and measure with a resolution of 0.25 mN. Single-pass tests were used to calculate the friction force for all of the lubrication schemes investigated, while extended cyclic tests were used to gauge monolayer durability and long-term performance of the rolling-friction system.

The tribological experiments presented in this thesis used a variety of probe attachments, as tests were performed with an assortment of ball bearings and also with convex silica lenses. The ball bearings were made of either stainless steel or sapphire and were attached to the sensor via a suspension-mounting cantilever. The FVL and DFM-0.5 sensors can be operated with balls ranging in diameter size from 1 to 9.8 mm. The root mean square roughness of the 4 mm balls, which was the predominant size used, was determined using an Olympus laser confocal microscope and was found to be $15 \pm 3\ \text{nm}$. The silica lenses were affixed to stainless steel posts (0.25 inch diameter and 0.75 inch length) using epoxy resin glue and were used with the DFM-0.5 sensor. The root mean square roughness of the silica lenses was determined using an atomic force microscope and was found to be

1.4 ± 1 nm. To estimate the mean contact pressure (p_m) of the probe tip on the surface, the Hertz equation^{18,19} for deformation of a flat surface by a sphere can be used,

$$p_m = \frac{1}{\pi} \left(\frac{4E_C}{3R} \right)^{\frac{2}{3}} F_N^{\frac{1}{3}} \quad (3.6)$$

where E_C is the composite elastic modulus of the two contacting materials, F_N is the normal load, and R is the tip radius. Using known values of elastic properties for silicon substrates ($E_{\text{SiO}_2} = 70$ GPa, $\nu = 0.17$)²⁰ and the contacting probe material, a surface pressure can be estimated. The contact pressures that are discussed in Chapters I, VI, VII, VIII and IX were derived using the above equation.

There are numerous mathematical models that attempt to connect microscale friction to a variety of parameters. As discussed in Chapter II, the appropriate equation to use depends on the characteristics of the surface and the testing protocol. In this thesis multiple lubrication schemes, which vary significantly in their surface properties, are investigated and various microtribometer testing protocols are used. Therefore, multiple microscale friction equations are used in this thesis. For clarity, the testing parameters and friction equation used for each individual study will be presented in the appropriate chapters.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is an ultra high vacuum technique where a material is irradiated with x-rays. The energy of the x-rays causes photoelectrons to be ejected from the material. The photo-emitted electrons that escape into the vacuum are those that originated from within the top 10 nm of the material, making XPS a surface-specific instrument.²¹ The deeper emitted electrons are either recaptured or trapped in various excited states within the material.²¹ The kinetic energy of the expelled electrons is dependent on the atom and the surrounding atomic environment

and, therefore, XPS can be used to determine the elemental composition, chemical state, and electronic state of the material surface.²¹ Data are typically reported as counts per second against binding energy. Binding energy (E_B) is related to the kinetic energy (E_K) by equation 3.7, where $h\nu$ is the energy of the incident photons and Φ is the work function of the spectrometer.²¹

$$E_K = h\nu - E_B - \Phi \quad (3.7)$$

XPS has the advantage of providing clear, distinct signatures for carbon in different bonding environments. For instance, the C 1s chemical shifts between CF₃, CF₂, and CH₂ groups can all be distinguished from one another, as the partially ionic nature of the C-F bond increases the binding energy of the electron.²² In Chapter VI, XPS was used to determine the compositions of the fluorocarbon/hydrocarbon mixed monolayers by comparing the intensities of the C1s peaks due to hydrocarbons and fluorocarbons. In addition, XPS can also be used to assess the orientation of sparse fluorocarbon monolayers. In sparse fluorocarbon monolayers, the molecular chains will tilt toward the surface, bringing them closer to the negatively charged silica surface. The molecular orbital energy of some of the fluorine atoms is raised by the proximity of the electron-rich silica surface, resulting in a smaller observed binding energy for the F 1s chemical shift.²² Frechette et. al showed that the F 1s peak of a sparse fluorocarbon monolayer can be fitted by two peaks, centered at about 687.5 and 689.1 eV, which can be attributed, respectively, to chains that are lying flat on the surface and chains that are all trans, proving that sparse fluorocarbon films consist of canted molecules that are loosely-packed rather than molecules that are contained in sporadic island formations.²²

X-ray photoelectron spectra (XPS) were obtained with a PHI 5000 VersaProbe spectrometer with use of a monochromatized Al K α X-ray source (square spot of 100 μ m x 100 μ m) and a concentric hemispherical analyzer (pass energy = 150 eV). The detector angle with respect to the surface normal was 45° and 5 total cycles were preformed. Peaks were fit with 70% Gaussian / 30%

Lorentzian profiles and a Shirley background. CasaXPS (Vamas) software was used to process the XPS data.

Scanning Electron Microscope (SEM)

SEM is an electron microscope that provides high resolution images (~1 nm limitation) by scanning a sample surface with a high-energy beam of electrons. As the electrons interact with the surface atoms, secondary electrons are ejected from the sample and scanning electrons are backscattered. Secondary electrons are electrons ejected from surface atoms due to inelastic collisions with scanning electrons, while backscattered electrons are scanning electrons that collide with nuclei and are reflected back. The secondary and backscattered electrons that are detected by the instrument form an image that provides compositional and topographical information about the surface. SEM was used to investigate the topography of the polymer films and confirm the rolling mechanism of the rolling lubrication system. Scanning electron images were obtained using a Raith e-Line electron beam lithography (EBL) system equipped with a thermal-assisted field emission gun at 10 keV.

Atomic Force Microscopy (AFM)

AFM is based on the measurement of changing deflections of a tiny cantilever holding a sharp tip, frequently made of Si_3N_4 or SiO_2 , as the tip is scanned over a surface.²³ Although various types of forces are encountered when a tip approaches the sample surface, signal generation in AFM is essentially based on interatomic repulsive forces that are extremely short range in nature. Since the interatomic repulsive force is influenced by the total electronic density around an atom, this force can be used to map the topology of the surface down to atomic dimensions.

AFM can be operated in contact, tapping or non-contact mode.²⁴ For a soft surface AFM is generally operated in tapping mode to eliminate lateral forces (i.e. scraping) across the sample that could potentially damage the surface and to achieve higher lateral resolution. The resulting AFM

image is a topographical representation of the sample surface, which can provide information regarding surface structure. The surface topography of the monolayers, polymers, and the probes were investigated via atomic force microscopy. AFM scans were also used to determine the root mean square roughness of these surfaces. AFM images were obtained with either a JEOL 5200 scanning probe microscope (SPM) or a Digital Instruments Nanoscan III atomic force microscope (AFM) under an ambient laboratory environment. Areas of 1.5-10 μm were scanned in tapping mode with a silicon nitride tip (~ 100 kHz frequency), and the images were plane-fitted and filtered to remove noise using the instrument software.

Profilometry

Profilometry is similar to contact mode AFM but is used to measure features on the order of tens of nanometers to hundreds of microns. The technique also employs a tip on the end of a cantilever and uses variations in the cantilever deflection to determine the topography of the sample as the tip is scanned. Unlike AFM in which the tip is rastered across the sample to produce a 3-dimensional image of the topography of the surface, profilometry is usually used to perform single line scans. In this thesis, profilometry measurements were performed in a Veeco Dektak 150 profiler, using 49 μN of force and the hills and valleys detection mode. Thicknesses of the superhydrophobic polyethylene film in Chapter VII were estimated by scratching the surface, scanning 1000 μm across the scratch and plane-fitting the scan results using the instrument software.

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CHAPTER IV

SURFACES AND FRICTIONAL PROPERTIES OF TWO-COMPONENT ALKYL-SILANE MONOLAYERS ON SILICON

Introduction

The complications of applying liquid lubricants to microelectromechanical systems (MEMS)^{1,2} have driven an interest in creating solid thin films that possess liquid-like mobilities (Chapter II).^{3,4} Two-component, mixed alkylsilane monolayers (H/H monolayers), in which the two alkylsilane components have different chain lengths, represent a way to integrate a mobile, liquid-like layer into a bound film.^{1,3,4} Given that the alkyltrichlorosilanes bind with similar efficiency regardless of chain length, the composition and structure of the mixed monolayers can be easily adjusted by varying the chain lengths and concentrations of the two adsorbates.^{1,3,5} As discussed in Chapter II, mixed monolayers can be viewed as having two distinct regions, a solid lower layer that is densely packed and a more mobile upper layer consisting of only the top portion of the longer chain components. Since there are fewer neighboring chains in this upper layer, the chains present in the upper layer must cant from the surface normal into a liquid-like state in order to achieve van der Waals interactions.^{1,4} The collapsing of the longer chains exposes the polymethylene backbone of the alkylsilane molecules and creates a mixture of CH₃ and CH₂ groups at the mixed monolayer/air interface.⁴ The mobile upper layer of the two-component mixed monolayers may prove beneficial for lubrication, as a variety of bound polymer films exhibit lower frictional forces when a liquid-like upper region is incorporated into the film.⁶⁻⁹

Recently, the frictional properties of H/H monolayers on silicon have been investigated by two research groups.^{1,3,4} Zhang et al.^{1,4} used AFM to compare the nanoscale frictional properties of pure monolayers and mixed monolayers of various short chain / long chain ratios. The authors

maintained that the mixed monolayers, due to the mobility of the upper region, will provide improved frictional performance if the films possess sufficient packing density to prevent contact between the AFM tip and substrate. More recently, Singh et al.³ performed a similar study on mixed monolayers but also included micro-scale friction tests along with the nano-scale AFM tests. Singh's³ AFM friction measurements agreed with the results previously achieved by Zhang⁴, but the micro-friction data exhibited different trends than the nano-scale results; at the higher loads, yet lower pressures of the tribometry tests, the mixed monolayers had a higher frictional force than the pure C18 monolayer. Singh et al.³ maintained that the nN and mN frictional behavior of the mixed monolayers could be explained by the number of monolayer chains in contact with the probe. They proposed that the AFM tip only contacts the long-chain molecules in the upper region while at the micro-scale, the counterface ball penetrates the upper region and comes into contact with the short chain components also. This frictional study by Singh et al. was limited to a 1:1 compositional ratio between the short and long chain components.

In this chapter, I used microtribometry to investigate mixed alkylsilane monolayers that contain varying compositional ratios of short and long-chain molecules. While a H/H monolayer containing a majority of long-chain components would result in a decrease in upper layer fluidity, the resulting enhancement in cohesion of this region through increased van der Waals interactions could provide sufficient support to prevent penetration of the probe while still providing some beneficial mobility. Singh's theory suggests that improved frictional performance would be observed if the probe only contacts the upper region.³ Zhang's premise is not dependent on tip contact with the lower layer and suggests that improved frictional performance would be observed if probe/substrate interactions can be prevented.^{1,4} Furthermore, altering the compositional ratios will result in varying degrees of spacing for the long chain molecules, which, upon collapse of the chains in the outer region, affect the exposure of the methylene backbone at the surface and the resulting oleophilicity of the surface. I also varied the lengths of the short and long chains to enable investigation of the effects

of thickness of the solid base layer and liquid top layer, as well as total thickness of the film, on interfacial friction (Figure 4.1).

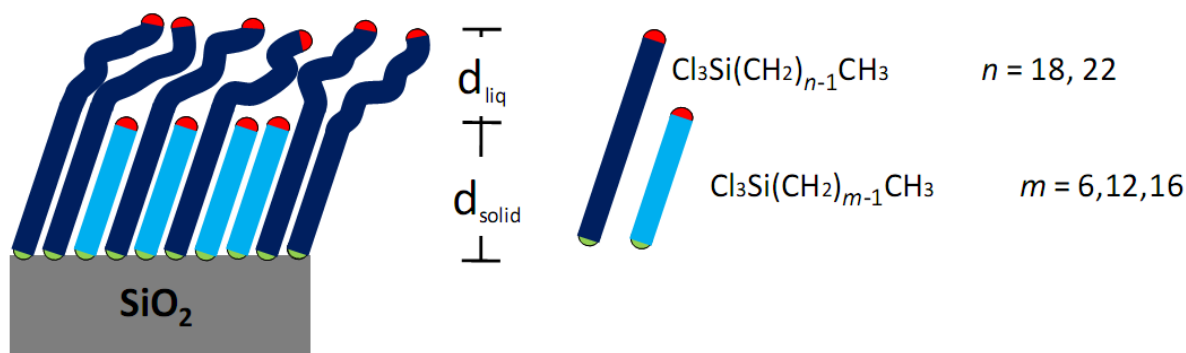


Figure 4.1. Representation of the molecular structure of mixed alkylsilane monolayers. The film can be viewed as having two distinct regions, a solid base layer (d_{solid}) and a mobile upper layer (d_{liq}). Long-chain components of 18 and 22 carbons (n) and short-chain components of 6, 12, and 16 carbons (m) were investigated in this study.

Experimental Methods

Formation of Alkyltrichlorosilane Monolayers

The alkyltrichlorosilane monolayers were formed by following the procedure outlined in Chapter III. The two-component alkyltrichlorosilane solutions were prepared individually by mixing in varying μL volumes of the two alkyltrichlorosilanes into 20 mL of toluene in 20 mL glass vials to obtain a total alkyltrichlorosilane concentration of 1 mM and then following the normal procedure for forming alkyltrichlorosilane monolayers.

Microscale Friction Testing

Microscale friction tests were performed with the 2-D FVL force sensor. The probe tip was a 1-mm diameter stainless steel ball firmly glued onto the end of an 8 mm long pin and attached to the sensor via a suspension mounting cantilever. The frictional force tests were performed under a

constant load of 9.8 mN and conducted in open air. The sliding speed and the scan length were maintained at 0.1 mm/s and 15 mm, respectively. Five single-pass tests were performed on each sample, with the reported coefficient of friction (μ) being determined by averaging the values measured during the five tests. The residual forces for the one-component and two-component alkylsilane monolayers were negligible during testing by tribometry (Chapter V); therefore, the coefficient of friction was related to the frictional forces using Amonton's law

$$F_f = \mu F_n \quad (4.1)$$

where the friction force (F_f) is proportional to the normal force load (F_n). The reported values and errors reflect the average and standard deviation of at least 5 independently prepared films.

Results and Discussion

Estimating Composition of Mixed Monolayers Based on Ellipsometric Data

To estimate the compositions of the mixed monolayers, I adopted a method based on thickness that has proven to provide similar results when compared to methods based on attenuation using X-ray photoelectron spectra.¹⁰ I assumed that the ellipsometric thickness of the mixed monolayer is a direct function of the binary composition of the monolayer through the equation

$$d_{total} = (1 - \chi_{lc})d_{sc} + \chi_{lc}d_{lc} \quad (4.2)$$

where d_{total} is the ellipsometric thickness of the mixed monolayer, d_{sc} and d_{lc} are the ellipsometric thicknesses of the one-component monolayers prepared from short-chain and long-chain adsorbates, respectively, and χ_{lc} is the surface mole fraction of the long-chain component in the mixed

monolayer. This correlation based on thickness assumes that the index of refraction (1.46) is unchanged for the liquid top layer and solid base layer.

The entire data set for a mixed system was compartmentalized to produce the lowest standard deviation within individual groups, or bins, of similar thickness, with each grouping consisting of at least 5 independently prepared films. The ellipsometric binning agrees well with the theoretical compositions based on the volumes of trichlorosilane precursors used to prepare the solutions. Categorizing the mixed monolayers based solely on the volumes of the solutions used to prepare the samples was not optimal because of the very small volumes (sometimes as low as 1 μL) used to create the 1 mM solutions, which resulted in inherent experimental error that would occasionally cause erratic and inaccurate groupings. An exception is the C16/C18 mixed system, for which I did rely on the solution concentrations for categorizing these films. The small chain length difference between the C16 and C18 molecules resulted in a narrow range of ellipsometric thicknesses that were often too close to distinguish, given the sensitivity of the ellipsometer ($\sim 1 \text{ \AA}$). I foresaw difficulty in segregating the C16/C18 data and only attempted to produce three different compositions (target χ_{lc} of 0.15, 0.50, and 0.85). I believe the large disparities between the target surface mole fractions are sufficient to overcome any experimental error and provide an accurate reflection of the data set. While I used solution concentrations to group the data for the C16/C18 mixed system, ellipsometric measurements were still used to determine χ_{lc} within each group to provide consistency between the various mixed monolayer systems.

Oleophilicity of Mixed Monolayers

As shown in Figure 4.1, the mobile upper layer of mixed monolayers only contains the longer chain molecules. Depending on the difference in chain length between the short and long-chain components and the composition of the monolayer, these upper layer chains may collapse into a liquid-like state to achieve favorable van der Waals interactions. The advancing contact angles for hexadecane (Figure 4.2) clearly demonstrate the effect that chain length difference and composition

have on the oleophilicity of the mixed monolayers. Having a mixed monolayer with a sparse upper layer and a large difference in chain length exposes more methylene groups, as the longer chains would have the molecular freedom and space to cant close to the lower layer. Molecular collapsing results in an interface consisting of both CH_3 and CH_2 groups, resulting in higher oleophilicity.^{1,4,11} Consistent with this molecular interpretation, the C6/C18 monolayers containing a majority of short chain molecules exhibit the highest oleophilicity. In contrast, a C16/C18 upper layer consists of only two carbons and lacks the length to collapse. The monolayer/air interface would consist of predominantly CH_3 moieties, and therefore, the contact angles for the C16/C18 mixed monolayers vary only a few degrees and are similar to the measurements achieved for organized one-component monolayers.¹

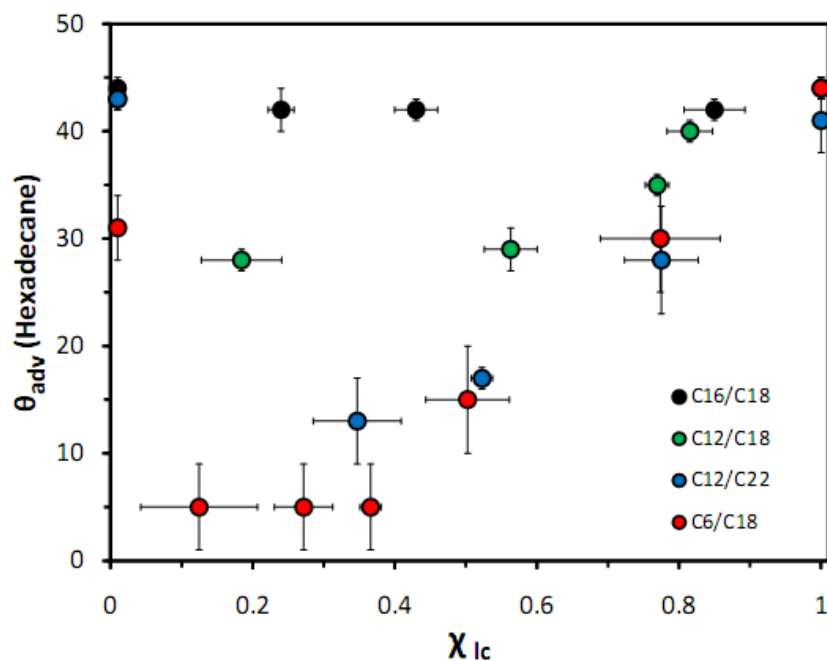


Figure 4.2. Effect of surface mole fraction of the long-chain component on the advancing hexadecane contact angles for two-component alkylsilane mixed monolayers. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The pure monolayers consisting of short chain components ($\chi_{lc} = 0$) were offset from the y-axis for clarity.

Advancing water contact angles showed only slight variances across the different mixed and pure monolayers. The one-component monolayers of C12, C16, C18, C22 all had $110^\circ \pm 1$ contact angles, which follow past results and signal the presence of a dense methyl surface.^{12,13} The one-component C6 monolayer is expected to contain a greater extent of gauche defects¹⁴ than the thicker pure monolayers and therefore, exhibits a lower contact angle of $106^\circ \pm 2$. The C6/C18 mixed monolayers with a lower density of long chains ($\chi_{lc} < 0.4$) have advancing water contact angles of $105^\circ \pm 1$, which agrees well with a predominantly CH₂ surface.¹⁵ For the other mixed monolayers, where the degree of collapsing is not as extreme and the chain length difference not as large, the water contact angles ranged between 108-110°. This result is expected, as previous studies show that water is relatively insensitive to the disorder of the top surface.¹¹

Effect of Monolayer Composition on Friction

Measurements of frictional properties for the mixed and one-component monolayers are shown in Figure 4.3. As discussed in the experimental section, the residual force was shown to be negligible for the one-component and two-component alkylsilane monolayers; therefore, the frictional force and coefficient of friction (μ) values are directly proportional for a constant normal load and can be used interchangeably when comparing the mixed monolayer systems. The C6/C18 system is the only set of films with a clear effect of composition on coefficient of friction, where the coefficient of friction decreases with an increase in C18 composition until a leveling off is reached at a χ_{lc} of 0.75. For the χ_{lc} of ~0.75 monolayers, the coefficient of friction value of 0.077 ± 0.008 is almost identical to the value obtained for the one-component C18 monolayer (0.076 ± 0.007). To further investigate the behavior of the C6/C18 system, I compared the C6/C18 monolayers with pure monolayers of varying chain lengths (Figure 4.4). The C6/C18 and one-component data follow the same general trend, a reduction in coefficient of friction for increasing thickness until a plateau is reached. This frictional behavior for the pure monolayers, complete with the minimum at C12, has also been observed in previous studies.^{14,16} I believe that the frictional data for one-component and C6/C18

mixed monolayers can be explained by the dependency of coefficient of friction on cohesive energy. One-component films with longer chain lengths and C6/C18 mixed monolayers with higher percentages of C18 have more intermolecular surface area available for van der Waals interactions and consequently, would have higher cohesive energies. The C6 and C8 one-component monolayers and the C6/C18 mixed monolayers with lower percentages of C18 are not sufficiently cohesive to prevent interaction of the probe with the underlying substrate, either through direct contact or non-contact forces. Once a monolayer has sufficient internal stability to prevent interactions between the probe and the substrate, the coefficient of friction remains relatively constant. The trend of thicker (and therefore more cohesive) films providing improved lubrication until a plateau is reached has also been observed by Mino et al.¹⁷ for perfluoroalkylsilane monolayers, Zarrad et al.¹⁸ for CH₃-terminated monolayers prepared from dimethyl aminosilane precursors, and us for alkanethiolate monolayers on gold substrates.¹⁹

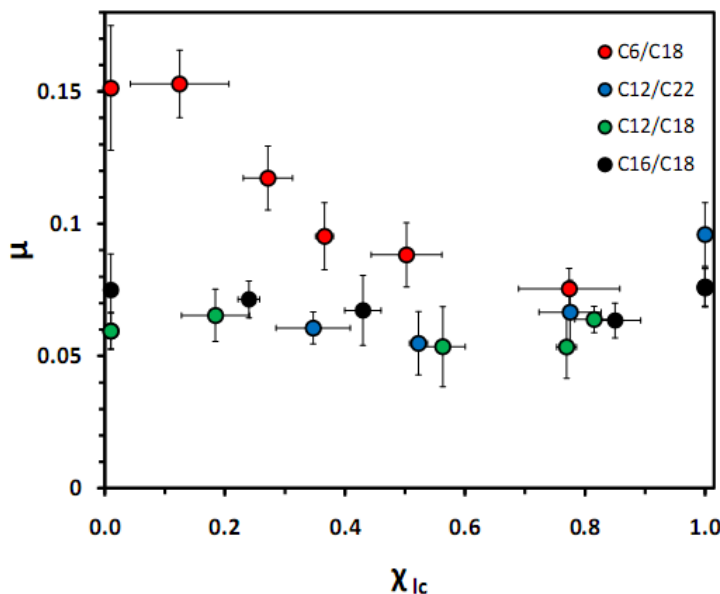


Figure 4.3. Effect of surface mole fraction of the long-chain component on the frictional properties of two-component alkylsilane mixed monolayers. Single-pass tribology tests were performed with a 1-mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The pure monolayers consisting of short chain components ($\chi_{lc}=0$) were offset from the y-axis for clarity.

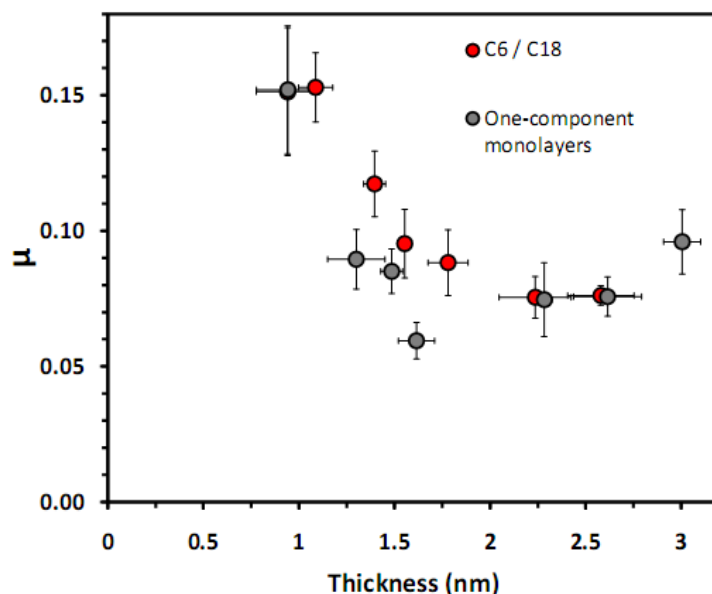


Figure 4.4. Effect of ellipsometric thickness on the frictional properties of one-component and two-component C6/C18 alkylsilane monolayers. Single-pass tribology tests were performed with a 1-mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The C6/C18 data points, going from thinnest to thickest, correspond to χ_{lc} of 0, 0.12, 0.27, 0.37, 0.50, 0.77, and 1.0. The one-component monolayers studied were C6 (0.94 nm), C8 (1.30 nm), C10 (1.49 nm), C12 (1.62 nm), C16 (2.28 nm), C18 (2.62 nm), and C22 (3.01 nm).

In Figure 4.4, the onset of the C6/C18 plateau in coefficient of friction occurs at a higher thickness than that of the one-component data. This offset in the plateau is consistent with the mixed monolayers having a liquid-like upper layer. For the C6/C18 films with $\chi_{lc} \leq 0.50$, the poorly oriented upper layer has a lower density and less cohesion between chains because it contains predominately the collapsed longer chain alkylsilanes. In addition, a C6/C18 film consisting of a majority of C6 molecules will have limited intermolecular surface area to form a dense base layer and offset the concentration of gauche defects that occur near the surface of the substrate.²⁰ When compared to a one-component film of equal thickness, the C6/C18 mixed monolayer would be less crystalline and would allow easier penetration of the probe, and therefore, a greater thickness is required to prevent probe-substrate interactions.

The H/H monolayers prepared from the other mixed systems (C12/C18, C16/C18, and C12/C22) have short chain components (C12 and C16) that are significantly longer than C6. The added length of the shorter molecules results in thicker and more robust base layers due to the increased van der Waals interactions so that all have ample internal stability to prevent probe-substrate interaction. Any difference in coefficient of friction for these mixed monolayers would be a result of top layer mobility or changes in oleophilicity due to exposure of CH₂ groups. The coefficient of friction values (Figure 4.3) for all the two-component monolayers are within a standard deviation of each other regardless of long chain composition or chain length difference. This insensitivity to composition indicates that surface composition (whether CH₂ or CH₃) and mobility of the top layer chains have little to no effect on coefficient of friction at the load and speed tested. Evaluating all the results on the friction of mixed monolayers, the critical factor determining the coefficient of friction is interchain cohesion while molecular mobility within the film and exposure of CH₂ groups at the surface are less significant at the loads and speeds tested.

The tribometer results obtained in our study do not compare well with those obtained by Singh et al.³ Specifically, they reported C6/C18 mixed monolayers ($\chi_{lc} = 0.50$) to give significantly higher coefficient of frictions than the pure C18 monolayer. Our results show only a slight increase in coefficient of friction between the C6/C18 ($\chi_{lc} = 0.50$) and pure C18 film. The differences could be attributed to the variances in testing protocol; while Singh et al. used a smaller load (4 mN vs. 9.8 mN), their sliding velocity was 10x greater (1 mm/sec vs. 0.1 mm/sec). Our tribometry study could not be performed with Singh's protocol because the parameters caused erratic and inconsistent data. As a consequence of achieving different tribometry results, the physical interpretation I present differs from the rationalization offered by Singh et al.³ Using AFM characterization as supporting evidence, Singh et al. reasoned that the micro-scale loads present in tribometry testing cause the counterface ball to come into contact with both the long and short components and therefore, the frictional forces of the mixed monolayers are found to be between the values obtained with the pure monolayers.³ Our explanation founded on cohesive energy and probe-substrate interactions, is based

on frictional measurements of four mixed monolayer systems at various compositions and the additional insight, provided by characterization of contact angles and thicknesses, of the physical environment present at the surface of the mixed monolayer.

Conclusions

Collectively, the results for the mixed monolayers and various one-component films indicate that monolayer thickness greatly affects the tribological properties of a monolayer but that molecular mobility within the film and interfacial oleophilicity are less important at the loads and speeds tested. C6/C18 was the only mixed monolayer system that showed a relationship between χ_{lc} and coefficient of friction, as the frictional properties remained relatively constant among the other mixed monolayers systems. Once a mixed monolayer has sufficient internal stability to prevent interactions between the probe and the underlying substrate, the tribological properties were indistinguishable from one-component monolayers.

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CHAPTER V

MICROSCALE FRICTIONAL INVESTIGATION OF HYDROXYL-TERMINATED MONOLAYERS ON SILICON

Introduction

The study on alkylsilane mixed monolayers in Chapter IV investigated the effects of upper layer mobility and oleophilicity on microscale friction. The CH_3 and CH_2 groups that make up the mixed monolayer / air interface have similar surface energy¹ and provide limited understanding on the influence of functional groups on monolayer friction as methylene and methyl groups allow only weak surface interactions through van der Waals forces. To compare functional groups with significantly different surface energies, I performed friction testing with a hydroxyl-terminated monolayer that was prepared by creating a trichloroacetate monolayer on silicon oxide and then cleaving the terminal ester² to form a hydroxyl surface.³ The hydroxyl monolayer must be created by modification of a pre-existing film because the OH group is synthetically incompatible with a trichlorosilane head group. The polar behavior of an alcohol group is vastly different to that of methylene or methyl, as hydroxyls may participate in hydrogen bonding and other dipole interactions with other surfaces, and provides greater insight into the relationship between functional group exposure, adhesion, and coefficient of friction. At the nanoscale, adhesion has a strong affect on frictional measurements⁴, even for low-energy surfaces such as CH_3 and CF_3 .⁵⁻⁷ Adhesive forces have such significance at the nanoscale that their detection via AFM is a common method to distinguish between functional groups on the surface.⁶⁻⁹ Adhesive forces are commonly neglected during microtribometry,^{10,11} but they can influence microscale friction.^{9,12} In order to develop a more complete understanding of the tribological properties of the monolayers, we have conducted frictional tests at multiple loads to determine the effect of adhesion on our tribometry tests, as adhesive forces

can be estimated by extrapolating frictional force vs. normal load plots to zero load. While tribological investigations have been performed on hydroxyl monolayers created from thiol adsorption,¹³⁻¹⁶ this work represents the first report of frictional properties of an OH-terminated monolayer on silicon.

Experimental Methods

Formation of Hydroxyl Monolayer

The hydroxyl monolayers were formed by following the procedure outlined in Chapter III.

Microscale Friction Testing

Microscale friction tests were performed with the 2-D FVL force sensor. The probe tip was a 1-mm diameter stainless steel ball firmly glued onto the end of an 8 mm long pin and attached to the sensor via a suspension mounting cantilever. To investigate the effect of adhesion on the tribological performance of the monolayers, friction tests were performed in open air at various loads (9.8 mN, 19.6 mN, 29.4 mN, and 39.2 mN). The sliding speed and the scan length were maintained at 0.1 mm/s and 15 mm, respectively. To account for potential residual forces (F_o), the modified form of Amonton's law^{4,17,18} was used. In this model, the friction force (F_f) is defined by,

$$F_f = \mu F_n + F_o \quad (4.1)$$

where μ is the kinetic coefficient of friction, F_n is the normal force and F_o is the residual force. F_o is the force that is not accounted for by normal spring load and can be estimated by extrapolating frictional force vs. normal load plots to zero load. Five single-pass tests were performed on each sample, with the frictional force being determined by averaging the forces measured during the five

tests. The reported values and errors reflect the average and standard deviation of at least 5 independently prepared films.

Results and Discussion

Surface Energy of Hydroxyl Terminated Monolayer

The hydroxyl monolayers were prepared by forming trichloroacetate-terminated monolayers (advancing water contact angle of $84 \pm 1^\circ$) from (1-trichlorosilyl undecyl) trichloroacetate and then cleaving the ester terminus into a hydroxyl by hydrolysis. The size of the trichloroacetate limits the packing of the molecules on the surface. Using the bond length between carbon and chlorine and the van der Waal radii of chlorine, the diameter of the trichloroacetate group can be estimated to be at least 5.73 Å, substantially larger than the 4.4 Å diameter of the siloxanol footprint at the substrate surface.¹⁹ Once the trichloroacetate is cleaved into a hydroxyl, the loosely packed monolayer would contain interchain spacing that allows methylene exposure and results in an intermediate surface energy. The advancing water contact angle ($64^\circ \pm 1$) is greater than that for densely packed OH monolayers but is almost identical with previous results by Berron et al. for loosely packed hydroxyl-terminated SAMs on gold.²

Effect of Terminal Group on Friction

Figure 5.1 compares the frictional data obtained with the OH monolayers with the data obtained from both a pure C12 monolayer and a “predominately CH₂” surface. The C12/C22 alkylsilane mixed monolayer group with the lowest mole fraction of long chain molecules (~0.35) is classified as the “predominately CH₂ surface” as these mixed monolayers represent a methylene rich surface with a sufficiently thick base layer that prevents probe-substrate contact. The significant collapsing of the upper layer chains and large exposure of methylene groups at the surface is evident by the low hexadecane contact angles ($13 \pm 3^\circ$) achieved for these monolayers (Chapter IV). Since

the monolayers presented in Figure 5.1 all have at least 12 atoms along the chain backbone, the effect of thickness on frictional force is eliminated. As noted in Chapter IV, frictional force (F_f) is insensitive towards methyl (F_f of 0.59 mN) versus methylene (F_f of 0.60 mN) surfaces as these functional groups have very similar interfacial interactions. When functional groups that exhibit higher surface energies are introduced, however, frictional force is increased greatly to $1.49 \pm .1$ mN for the trichloroacetate-terminated monolayer and $2.43 \pm .4$ mN for the hydroxyl-terminated monolayer.

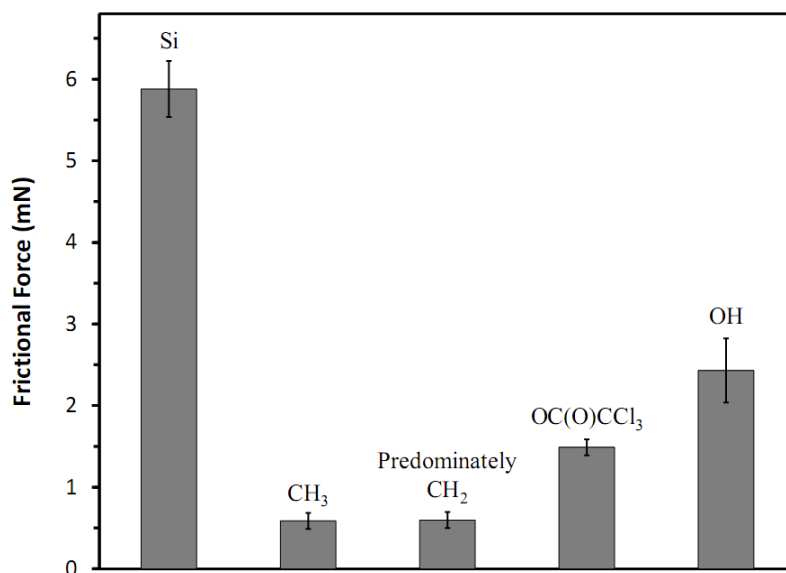


Figure 5.1. Effect of terminal group on the frictional properties of alkylsilane monolayers. Single-pass tribology tests were performed with a 1-mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The C12/C22 mixed monolayer group with the lowest mole fraction of long chain molecules (~ 0.35) is classified as the “predominately CH₂” surface.

The increased friction forces are a consequence of the higher energy surfaces having a stronger driving force to achieve energetically favorable interactions with the probe. These intermolecular interactions, in addition to capillary forces from physisorbed water vapor, create adhesion between probe and substrate that must be sheared during sliding²⁰⁻²³ and can increase the

linear coefficient of friction and residual force terms in the modified form of Amonton's law (Equation 5.1).^{4,17,18} Adhesive forces can scale at the same order of magnitude as normal force,²¹ making the modified form of Amonton's law relevant at the microscale. Figure 5.2 shows the effect of load force on the tribological performance of the various monolayers. The residual force can be estimated by extrapolating frictional force vs. normal load plots to zero load. The trichloroacetate-terminated monolayer showed negligible residual force, indicating that the increase in coefficient of friction is the primary cause for the higher friction forces. In contrast, the OH-terminated monolayer, in addition to an increase in coefficient of friction, displayed significant residual forces (~1.6 mN) during tribometer testing (Figure 5.2).

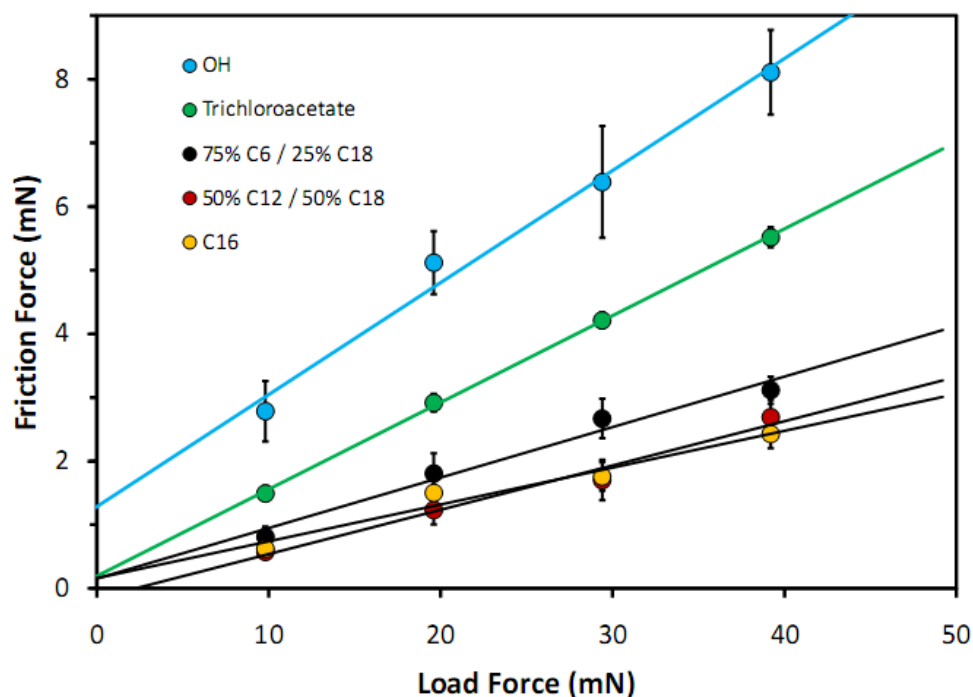


Figure 5.2. Effect of terminal group and load on the frictional properties of alkylsilane monolayers. Friction tests were performed with a 1 mm diameter stainless steel probe tip at various loads (9.8 mN, 19.6 mN, 29.4 mN, and 39.2 mN) at a sliding speed of 0.1 mm/s and a scan length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The residual force was estimated for each monolayer by performing a linear regression (solid lines) and extending the fit to the y-intercept. The R^2 values for the linear regressions were 0.986 (OH), 0.995 (Trichloroacetate), 0.974 (75% C6 / 25% C18), 0.978 (50% C12 / 50% C18), and 0.961 (C16).

Conclusions

Microtribometry tests were performed on various monolayers, which varied in their surface energy, to investigate the influence of functional group exposure and adhesion on microscale friction. The monolayers that contain CH_3 and CH_2 moieties had similar frictional performance (with friction forces of ~ 0.6 mN for a 9.8 mN load) and showed negligible adhesive forces. The trichloroacetate-terminated monolayer showed an increase in friction force (1.49 mN), but did not show a significant residual force, indicating that the increase in coefficient of friction is the primary cause for the higher friction forces. Introducing hydroxyl termini into the monolayer, however, resulted in a residual force of 1.6 mN and resulted in the highest frictional force of 2.43 mN.

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CHAPTER VI

FRICTIONAL PROPERTIES OF WELL-MIXED FLUOROCARBON / HYDROCARBON MONOLAYERS

Introduction

In Chapter IV, my study on H/H monolayers showed that liquid-like molecular mobility and exposure of CH₂ groups of the canted longer chains at the surface had no significant effect on friction.¹ Methylene and methyl groups have similar interfacial interactions that would encourage the longer chains of the upper layer to collapse into contact with the CH₃ base layer. If the shorter CH₃-terminated monolayer was replaced with a CF₃-terminated surface, the interfacial interactions would be considerably altered. The fluorocarbon monolayers are oleophobic, and thus, we would expect the longer hydrocarbon long chains to experience repulsive forces²⁻⁴ from the CF₃-termini of the base layer and resist interaction with the fluorocarbon moieties. Snapshots of molecular-dynamics simulations involving an H/H mixed monolayer (Figure 6.1a) and a F/H mixed monolayer (Figure 6.1b) demonstrate the aversion of the collapsed chains of the hydrocarbon from interacting with the CF₃ moieties. A mixed monolayer with repulsive interactions in the liquid-layer could possess unique frictional properties.

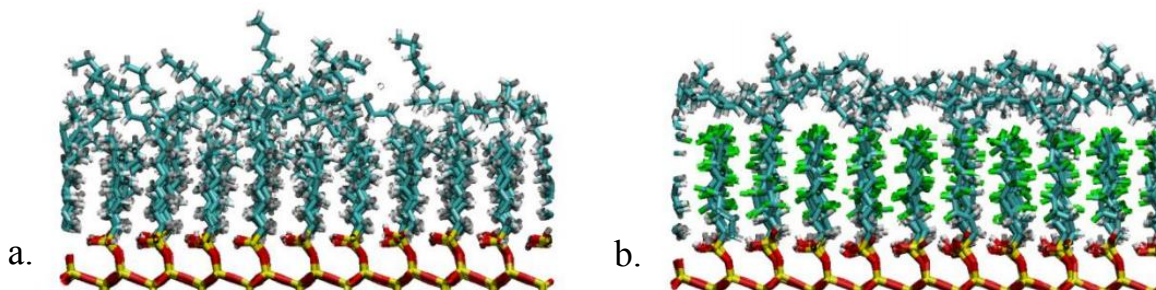


Figure 6.1. Molecular simulation snapshots of $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ (a.) and $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ (b.) mixed monolayers. The hydrogen atoms are represented in white, the carbon atoms are represented in blue, and fluorine atoms are represented in green. Simulations were developed and performed by Ben Lewis.

The incorporation of hydrocarbons into the solid base layer could also improve the lubricating properties of fluorinated films. Due to their ultralow surface energy, CF_3 -terminated monolayers have been investigated as a potential lubricant film in MEMS devices.^{5,6} Fluorocarbon monolayers, when compared to hydrocarbon monolayers, are better at reducing adhesion and stiction^{5,7,8} but have shown to possess higher frictional forces in a majority of studies.^{6,7,9-17} The fluorocarbon monolayers' stiffness,¹⁴ bulkier head group (causing increased steric interactions),^{6,15,18} and lower cohesion¹⁹ have all been cited as potential reasons for the poor frictional performance of these molecular films. Fluorocarbon monolayers have shown poor wear properties when compared against hydrocarbon monolayers of similar structure,^{13,17} as the size of the fluorocarbon head group limits the packing density and prohibits extensive cross-linking between molecules in the film. In attempts to combine the properties of fluorocarbon and hydrocarbon monolayers, mixed films of hydrocarbon and fluorocarbon precursors have been assembled from silanes,^{20,21} thiols,^{16,22} disulfides,^{22,23} and carboxylic acids.^{11,24,25} Differences in adsorption kinetics between hydrocarbon and fluorocarbon molecules^{26,27} and the tendency for fluorocarbons to phase separate from hydrocarbons^{10,11,23,24,28} has hindered the ability to produce F/H monolayers that are well-mixed and uniform. Prior frictional studies on F/H monolayers have all involved phase-separated Langmuir-Blodgett films,^{10,11,19-21,24} or chemisorbed monolayers on gold.^{22,23}

To assess the frictional performance of F/H monolayers, I have developed a protocol to create a well-mixed F/H monolayer that is chemically bound onto a silicon substrate. To circumvent the difficulties of forming a spontaneous, well-mixed F/H monolayer, I first create a sparse monolayer from (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane. Frechette et al. have shown through X-ray photoelectron spectroscopy that these fluorocarbon precursors, due to their limited ability for intermolecular cross-linking,^{29,30} create incomplete monolayers that are loosely-packed as opposed to creating sporadic closely-packed islands.²⁹ The loose-packing would result in molecular voids throughout the incomplete fluorocarbon monolayer. Alkyltrichlorosilanes of various lengths are then backfilled into the sparse monolayer, creating a well-mixed F/H monolayer (Figure 6.2). Depending on the hydrocarbon chain length ($n = 8, 12, 16, 18, 22$), the interfacial interactions will vary considerably for the F/H monolayers. For the shorter-chain alkylsilanes (8, 12), the fluorocarbon and hydrocarbon components will have similar heights and the resulting F/H monolayers will have CF_3 -moieties exposed at the surface. When longer-chain alkylsilanes are used, the F/H mixed monolayers will contain a mobile upper layer consisting of only the top portion of the longer chain alkylsilanes. The collapsing of the longer chains exposes the polymethylene backbone of these adsorbates, creating a mixture of CH_3 , CH_2 , and CF_3 groups at the mixed monolayer/air interface.

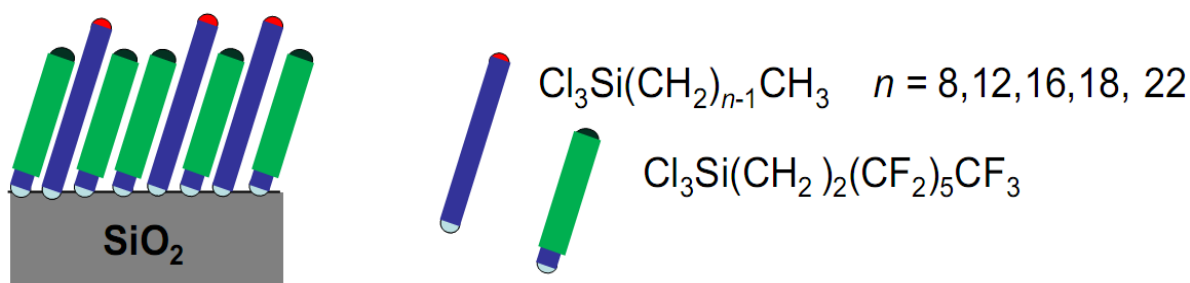


Figure 6.2. Representation of the molecular structure of the perfluoroalkyl / alkylsilane mixed monolayers. The films were prepared by creating a sparse fluorine monolayer from $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ and backfilling with $\text{CH}_3(\text{CH}_2)_{n-1}\text{SiCl}_3$, where $n = 8, 12, 16, 18, 22$.

Tribometry testing was completed at various loads for F/H monolayers and H/H monolayers of identical chain lengths. In addition, cyclic testing was performed to assess the wear properties of F/H monolayers. In this chapter, I show a significant reduction in the coefficient of friction of F/H mixed monolayers as compared to pure fluorocarbon monolayers when hydrocarbons of 8, 12, and 16 carbons are mixed into the fluorocarbon monolayer. Load-dependent frictional behavior is shown for F/H mixed monolayers containing 18 and 22 carbons. The extended wear tests show the benefit of cross-linking and cohesion for durability. With additional insight from surface characterization and molecular dynamics, we present a physical interpretation of the findings.

Experimental Methods

Formation of F6H2 Trichlorosilane Monolayers

The fluorocarbon monolayers were formed by following the procedure outlined in Chapter III.

Formation of Fluorocarbon / Hydrocarbon Mixed Monolayers

The F/H mixed monolayers from F6H2 silanes and alkylsilane molecules were prepared by first forming a sparse F6H2 monolayer and backfilling the surface with the alkylsilane molecules. The sparse F6H2 monolayers were formed by immersing the piranha-treated substrates into 1 mM solutions of perfluoroalkylsilane precursors in 20 mL of methylene chloride. Periodically, the samples were removed from the solution, rinsed in 20 mL of methylene chloride for 3 min, sequentially rinsed with ethanol, water, and again with ethanol, dried in a stream of N₂, and then hexadecane (HD) contact angles were measured. The two F/H monolayers systems that were the focus of our investigation were prepared using sparse fluorocarbon monolayers that achieved HD contact angles of $69^\circ \pm 2$ and $75^\circ \pm 1$ (vide infra). If the HD measurements showed insufficient monolayer formation, the samples were again immersed in the precursor solution. The total

submersion times were 7 ± 1 min and 12 ± 2 min, which corresponds to the 69° and 75° contact angles, respectively. Once the hexadecane contact angles confirmed monolayer formation was sufficient, the samples were again rinsed with ethanol, water, and again with ethanol, dried in a stream of N_2 , and placed into 20 mL of toluene containing 1 mM of the alkyltrichlorosilane precursor. After 5 h, the samples were removed from the solution, rinsed in 20 mL of toluene for 1 min, sequentially rinsed with ethanol, water, and again with ethanol, dried in a stream of N_2 , and then stored in capped glass vials until characterization or testing was performed. Mole fractions of the completed monolayers were calculated via XPS spectra to insure uniformity within the two F/H monolayer systems.

Formation of Alkyltrichlorosilane Mixed Monolayers

The H/H mixed monolayers were formed by following the procedure outlined in Chapter IV.

Micro-scale Friction Testing

Micro-scale friction tests were performed in open air with a ball-on-flat micro-tribotester (Center for Tribology, Inc.) using two separate sensors, a 2-D FVL force sensor and a DFM-0.5 force sensor. The FVL sensor was used to perform single-pass friction tests with a constant load of 9.8 mN. The probe tip was a 1-mm diameter stainless steel ball firmly glued onto the end of an 8 mm long pin and attached to the sensor via a suspension mounting cantilever. For the 98 mN loads, the DFM sensor was used and the probe tip was a 4 mm diameter stainless steel ball contained in a holder. All single-pass tests were conducted with a sliding speed of 0.1 mm/s and a scan length of 15 mm. The residual forces for the F/H and H/H monolayers were negligible during testing by tribometry; therefore, the coefficient of friction was related to the frictional forces using Amonton's law

$$F_f = \mu F_n \quad (6.1)$$

where the friction force (F_f) is proportional to the normal force load (F_n). Five tests were performed for each load on each sample, and the reported μ was determined by averaging the forces measured during the five tests. The reported values and errors reflect the average and standard deviation of at least 5 independently prepared films.

The long-term cyclic tests were done with the 4 mm diameter stainless steel ball, a normal load of 98 mN, a test length of 15 mm, and a slider speed of 1 mm/s. The tests were performed for 5 h, which corresponds to 1200 cycles, or until failure was evident. A film was considered to have failed once the friction force increased to 150% of its initial value. The reported values and errors reflect the average and standard deviation of at least 4 independently prepared films.

Results and Discussion

Mole Fraction Calculations from XPS

The F/H monolayers were prepared by forming an incomplete, loosely-packed fluorocarbon monolayer and then backfilling the film with hydrocarbon alkylsilanes. To insure consistency between the F/H monolayers, the surface composition achieved for the incomplete fluorocarbon monolayers was assessed using HD contact angles. My investigation was focused on mixed monolayers that were prepared using sparse fluorocarbon monolayers that achieved advancing HD contact angles of $69^\circ \pm 2$ and $75^\circ \pm 1$. Figure 6.3 displays the XPS spectra for the C(1s) region for the F/H monolayers that were prepared from the 69° group. The control sample, which is the incomplete fluorocarbon monolayer that was not backfilled, shows three distinct peaks at 285.5 eV, 291.5 eV, and 293.5 eV. The dominant peak at 291.5 eV corresponds to the CF_2 molecular backbone while the smaller peak at 293.5 eV represents the CF_3 terminal group. Despite not containing

alkylsilanes, the incomplete fluorocarbon monolayer still shows a significant hydrocarbon peak at ~ 285.5 eV due to the two CH_2 groups at the base of the perfluoroalkylsilane molecule (Fig. 6.2). This peak is rather broad due to the presence of at least two photoemissions, one from the first C atom (bonded to Si) and one from the second C atom (bonded to the first fluorinated carbon, which is denoted as $\text{CH}_2\text{-CF}_2$).²⁹ Intensity in this region can also originate from adventitious carbon that was not removed as the partial monolayer formed.²⁹

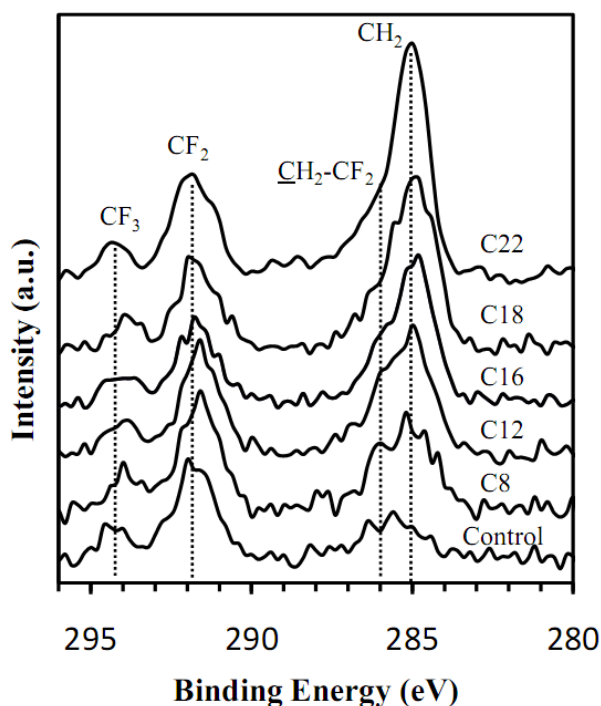


Figure 6.3. XPS spectra of the C(1s) region for the various F/H mixed monolayers that were prepared by forming an incomplete, loosely-packed fluorocarbon monolayer (giving a hexadecane contact angle of 69°) and then backfilling the film with hydrocarbon alkylsilanes that varied from 8 to 22 carbons in chain length. The control sample is the incomplete fluorocarbon monolayer that was not backfilled.

When hydrocarbon precursors are backfilled into the monolayer, the intensities of the two fluorocarbon peaks at 291.5 eV and 293.5 eV remain relatively unchanged. The uniform intensities of these peaks verify that the chemically bound fluorocarbon precursors are not displaced and the

hydrocarbons introduced into the film integrate into the voids present throughout the sparse fluorocarbon film. In addition, the stable intensities show that there is no significant signal attenuation from the longer-chain hydrocarbons. As opposed to the fluorocarbon peaks, the intensities of the hydrocarbon peaks are altered once the films are backfilled. The F/H mixed monolayers have an increased CH₂ peak at 285 eV and a shoulder peak, which corresponds to the $\underline{\text{C}}\text{H}_2\text{-CF}_2$ group, at ~286 eV.²⁹ We assume that the backfilled monolayers have sufficient packing density to eliminate adventitious carbon. The F/H mixed monolayers containing longer alkylsilanes have higher intensities for the CH₂ peak due to the increased number of carbons along their molecular backbones. The $\underline{\text{C}}\text{H}_2\text{-CF}_2$ peak, which stays constant among the F/H monolayers, is most pronounced for the F/C8 monolayer since this film has the least intense CH₂ peak.

Comparing the intensities between the fluorocarbon and hydrocarbon peaks allows a quantitative measurement of the mole fraction of alkylsilane molecules present in the F/H monolayers. Using the CF₃ and CF₂ integrated intensities from a control fluorocarbon monolayer, that is, a partial fluorocarbon monolayer that was not backfilled, and using the ratio of fluorinated/hydrogenated carbons present in the F6H2 precursors, we are able to estimate the CH₂ peak intensity due to the two methylene moieties on the F6H2 molecules. The hydrocarbon signal from the F6H2 molecules ($I_{\text{CH-F}}$) was then subtracted out of the CH₂/CH₃ spectra obtained from the mixed monolayers (I_{CH}). The normalized intensities of the alkylsilane components ($\bar{I}_{\text{CH}}$) was then determined by using the equation,

$$\bar{I}_{\text{CH}} = \frac{I_{\text{CH}} - I_{\text{CH-F}}}{n} \quad (6.2)$$

where n is the alkylsilane chain length. In a similar manner, the normalized intensities of the fluorocarbon components ($\bar{I}_{\text{CF}}$) was determined using,

$$\bar{I}_{CF} = \frac{I_{CF_2} + I_{CF_3}}{6} \quad (6.3)$$

where I_{CF_2} and I_{CF_3} are the intensities of the CF_2 and CF_3 peaks, respectively, and 6 is the number of fluorinated carbons in the F6H2 precursor. With $\bar{I}_{CH}$ and $\bar{I}_{CF}$ calculated, the mole fraction of alkylsilane molecules (χ_{CH}) present on the surface can be determined using the equation,

$$\chi_{CH} = \frac{\bar{I}_{CH}}{\bar{I}_{CH} + \bar{I}_{CF}} \quad (6.4)$$

Using Eq. 6.4, the F6H2 monolayers that exhibited an advancing HD contact angle of 69° were determined to have alkylsilane mole fractions of 0.34 ± 0.02 after backfilling. The denser fluorocarbon monolayers that achieved advancing HD contact angles of 75° have fewer vacancies where alkylsilane molecules can backfill into, thus decreasing the alkylsilane mole fraction to 0.23 ± 0.03 . The low standard deviations (0.02 and 0.03) demonstrate the consistency of our technique for forming the F/H mixed monolayers. For the remainder of this thesis, the fluorocarbon systems will be identified with the approximate ratio of F/H mole fractions of 2:1 and 3:1. To gain a true assessment of the surface behavior of F/H monolayers, the dimensions of the fluorocarbon and hydrocarbon components must be considered. The fluorocarbon molecules have cross-sectional areas ~ 1.8 times larger than the hydrocarbons.³¹ If the fluorocarbon and hydrocarbon chains are the same length, the 2:1 F/H monolayers would result in a fluorocarbon area fraction of 0.77, while the 3:1 F/H mixed monolayers mole would produce a fluorocarbon area fraction of 0.86.

Surface Composition of Mixed Monolayers

Advancing contact angles of hexadecane θ_{HD} and water θ_W were measured for all monolayers to assess the structure and surface composition of the films. Hexadecane is sensitive to

fluorocarbon, methylene, and methyl moieties, and θ_{HD} data can be used to gain insight into the molecular structure present on the surface of the films. The fully formed fluorocarbon monolayers had θ_{HD} of $80^\circ \pm 1$, which agrees with past reports and confirms the presence of a dense $-\text{CF}_3$ surface.³¹⁻³³ The loosely-packed fluorocarbon monolayers that were used to create the F/H monolayers contain significant amounts of canted chains and molecular vacancies that expose CF_2 groups, which results in lower θ_{HD} of $69^\circ \pm 2$ and $75^\circ \pm 1$. Once the molecular voids of the incomplete fluorocarbon monolayers are filled with alkylsilanes, the addition of hydrocarbon moieties, which are more susceptible to HD wetting,^{34,35} causes the θ_{HD} to diminish (Figure 6.4). When the chain length of the alkylsilane components exceeds the length of the F6H2 component by several carbons, the top portion of the hydrocarbon may collapse into a liquid-like state to achieve favorable van der Waals interactions. The longer hydrocarbon chains have more molecular freedom and would expose additional CH_2 groups; therefore, θ_{HD} decreases with increasing alkylsilane length.³⁴ If the F/H monolayers were completely phase-separated, their surface would contain only CF_3 and CH_3 domains. The C12, C16, C18, and C22 alkylsilanes would all form ordered methyl surfaces,^{36,37} and the CH_3 domains created from these molecules would have almost identical surface energies.^{38,39} The θ_{HD} values that would be achieved by these phase separated F/H monolayers (shown in Figure 6.4 as solid lines) can be estimated using Cassie's equation,

$$\cos \theta_{HD} = \chi_F \cos \theta_F + \chi_H \cos \theta_H \quad (6.5)$$

where χ_F and χ_H are the surface coverage of fluorocarbon and hydrocarbon molecules, θ_F is the contact angle of a fluorinated surface (80°), and θ_H is the reported HD advancing contact angle for the hydrocarbon components present on the surface (44°).¹ The dependency of the θ_{HD} on hydrocarbon chain length from Figure 6.4 suggests that the F/H monolayers are molecularly mixed and not phase-separated.

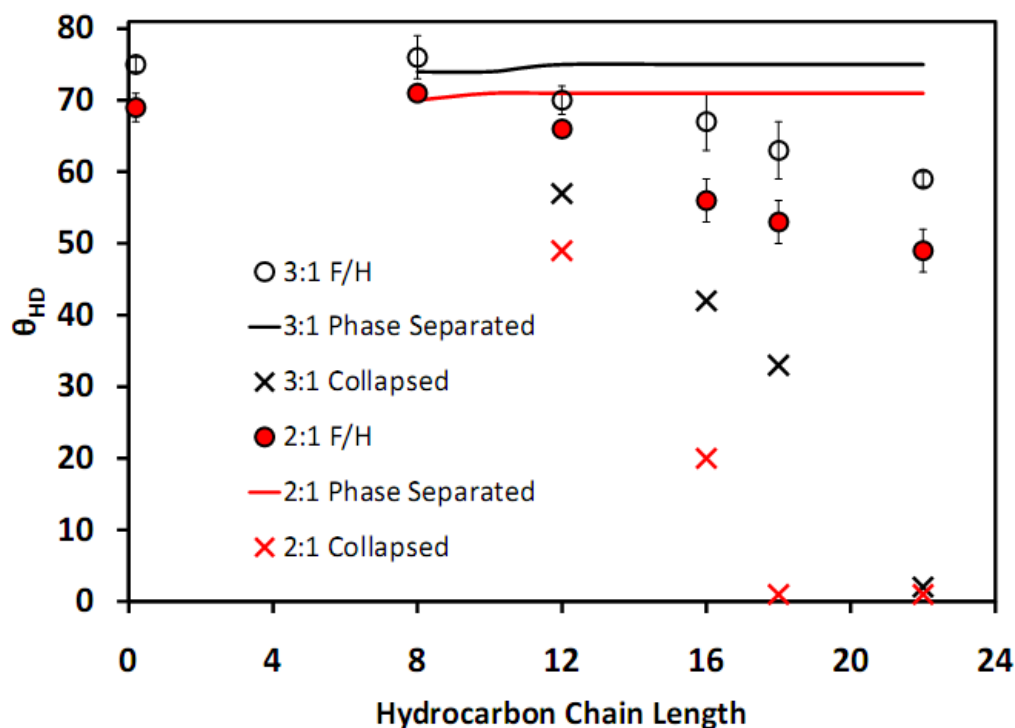


Figure 6.4. Effect of the alkylsilane component surface mole fraction and chain length on the advancing hexadecane contact angles for perfluoroalkyl / alkylsilane mixed monolayers. The solid lines represent the estimated contact angles that would be achieved for phase-separated monolayers, while the X markers represent the estimated contact angles that would be achieved if the longer-chain hydrocarbons fully collapsed to the surface. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films.

Due to the well-mixed structure of the F/H monolayers and the differences in alkylsilane chain length, the functional groups present on the surface of the F/H monolayers will vary. The F/H monolayers containing the longer-chain hydrocarbons (C12, C16, C18, C22), will have a surface composed of CF_3 , CH_3 , and CH_2 moieties, as the top portion of the longer chain alkylsilanes will cant from the surface and expose their polymethylene backbone. The F/C8 monolayers will have no significant collapsing, as the F6H2 molecules and the C8 alkylsilanes have the same number of carbons. The surface of the F/C8 monolayers will primarily consist of CF_3 and CH_3 functional groups which are molecularly mixed and, therefore, the Cassie equation is replaced with the Israelachvili and Gee equation⁴⁰

$$(1 + \cos \theta_{HD})^2 = \chi_F(1 + \cos \theta_F)^2 + \chi_H(1 + \cos \theta_H)^2 \quad (6.6)$$

which is used to assess the surfaces of molecularly mixed surfaces.^{41,42} To assess the F/C8 surface, Eq. 6.7 will take the form of

$$(1 + \cos \theta_{HD})^2 = \chi_F(1 + \cos 80^\circ)^2 + \chi_H(1 + \cos 36^\circ)^2 \quad (6.7)$$

where 36° is the reported HD contact angle for a CH_3 terminated surface created from C8 precursors.³⁹ Using Eq. 6.7, the fluorocarbon area fraction was calculated to be 0.80 for the 2:1 F/H monolayers and 0.90 for the 3:1 F/H monolayers. The area fraction estimations achieved from the Israelachvili and Gee equation for F/C8 monolayers and XPS analysis are both insensitive to molecular collapsing and allows us to directly compare the results. The two calculations, based on vastly different surface characterization techniques, produce similar results (0.77 vs. 0.80, 0.86 vs. 0.90) and validate our approaches.

As stated in the introduction and shown in Figure 6.1, the F/H monolayers containing the longer chain hydrocarbons (C12, C16, C18, C22) will contain partially collapsed chains that should resist interaction with the CF_3 -terminated base layer. Evidence of these repulsive forces is provided by comparing the HD contact angle of the F/H monolayers to the theoretical contact angles that would be achieved if the longer chain hydrocarbons completely collapsed to the fluorocarbon surface and exposed their entire methylene backbone. Here, the theoretical contact angle (θ_{th}) was determined using the Israelachvili and Gee equation, but θ_H is now the HD contact angle for methylene surfaces (0°),

$$(1 + \cos \theta_{th})^2 = \chi_F(1 + \cos 80^\circ)^2 + \chi_H(1 + \cos 0^\circ)^2 \quad (6.8)$$

The χ_H was calculated using the XPS-determined fluorocarbon area fractions of the 2:1 and 3:1 F/H monolayers (0.77 and 0.86 respectively) and then accounting for the surface area that would be occupied if the hydrocarbon chains totally collapsed to the surface once the molecular length was above 8 carbons (e.g. the F/H monolayers containing C16 would have a collapsed chain containing ~8 carbon atoms). The area occupied by the collapsed hydrocarbon chains was determined using the C-C bond length (1.25 Å)⁴³ and the excluded width of a CH₂ molecular backbone (4.2 Å).³¹ The theoretical model, represented by X symbols in Figure 6.4, shows a much larger drop in HD contact angles and a stronger dependence on chain length. The experimental data, which fall between the two extremes of phase-separated and collapsed hydrocarbon chains, are consistent with the F/H monolayer surface presented in the molecular simulations (Fig. 6.1), which is a well-mixed monolayer that contains partially collapsed chains due to repulsive interactions between fluorocarbon and hydrocarbon moieties.

In hydrocarbon mixed monolayers, methylene and methyl functional groups freely interact, and the long chains collapse down to the CH₃-terminated base layer (Figure 6.1). Our past study on alkylsilane mixed monolayers, presented in Chapter IV, showed that the extent of molecular collapse achieved in the upper layer of these films was dependant on the composition of the monolayer. Alkylsilane mixed monolayers with sparse upper layers exposed more methylene groups and achieved higher oleophilicities.¹ Consistent with this molecular interpretation, the C6/C18 monolayers containing a majority of short-chain components showed complete wetting of HD.¹ In contrast to the alkylsilane mixed monolayers, the F/H monolayers with sparser upper layers possess lower surface energies. The experimental data and the theoretical model both show the 3:1 F/H monolayers achieving higher HD contact angles than the 2:1 monolayers. The fluorocarbon base layer present in F/H monolayers is much more oleophobic than a CH₃-terminated surface. The increase in methylene exposure for the 3:1 monolayer, if there is any, is not enough to offset the increased exposure of oleophobic CF₃ moieties.

The aversion to molecular collapse of the longer chain alkylsilanes and the resulting exposure of CF_3 terminal groups is further supported by the advancing water contact angles. The fully formed fluorocarbon monolayers had advancing contact angles of $120^\circ \pm 1$. Every F/H monolayer, regardless of alkylsilane chain length, achieved θ_w between 112 - 118° . These angles are between the values shown by CF_3 films^{31,32,44} and hydrocarbon monolayers^{13,38}, providing evidence that the monolayer surface consists of both fluorocarbon and hydrocarbon groups. A molecular simulation snapshot of a 3:1 F/H monolayer supports the experimental data (Fig. 6.5). The image shows the considerable presence of the CF_3 termini on the surface (shown in green) despite the presence of partially collapsed hydrocarbon chains (shown in blue and white).

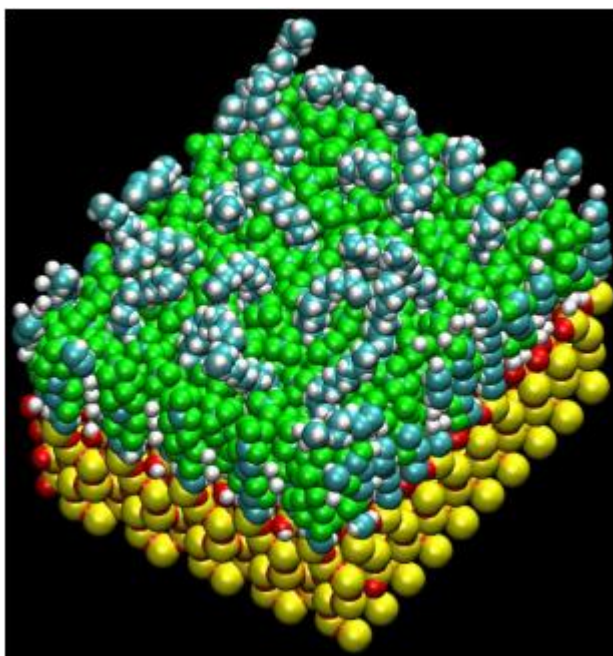


Figure 6.5. Molecular simulation snapshot of a $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ mixed monolayer containing a 3:1 molar ratio between fluorocarbons and hydrocarbon components. The hydrogen atoms are represented in white, the carbon atoms are represented in blue, and fluorine atoms are represented in green. Simulations were developed and performed by Ben Lewis.

Effect of Hydrocarbon Chain Length on Friction

Figure 6.6 shows the coefficient of friction at 9.8 mN and 98 mN for the two F/H monolayer ratios, 2:1 (a) and 3:1(b), and for fully formed, pure fluorocarbon monolayers. Fully formed fluorocarbon monolayers, compared to the loosely-packed fluorocarbon monolayers, allow a more accurate comparison with the F/H systems, as the sparse fluorocarbon monolayers used to create the F/H systems allow significant probe-substrate interactions. Compared to the fully formed fluorocarbon monolayers, the F/H monolayers containing C8, C12, and C16 alkylsilanes exhibit significantly reduced μ at both loads, with nearly identical trends for both the 2:1 and 3:1 monolayers. We attribute this reduction in μ to the F/H monolayers having increased packing, as the smaller radius of the hydrocarbon precursor allows the molecule to access surface sites on the substrate that the bulkier fluorocarbons cannot. The increased molecular density within the F/H monolayers will reduce probe/substrate interactions and therefore, lower the μ .¹

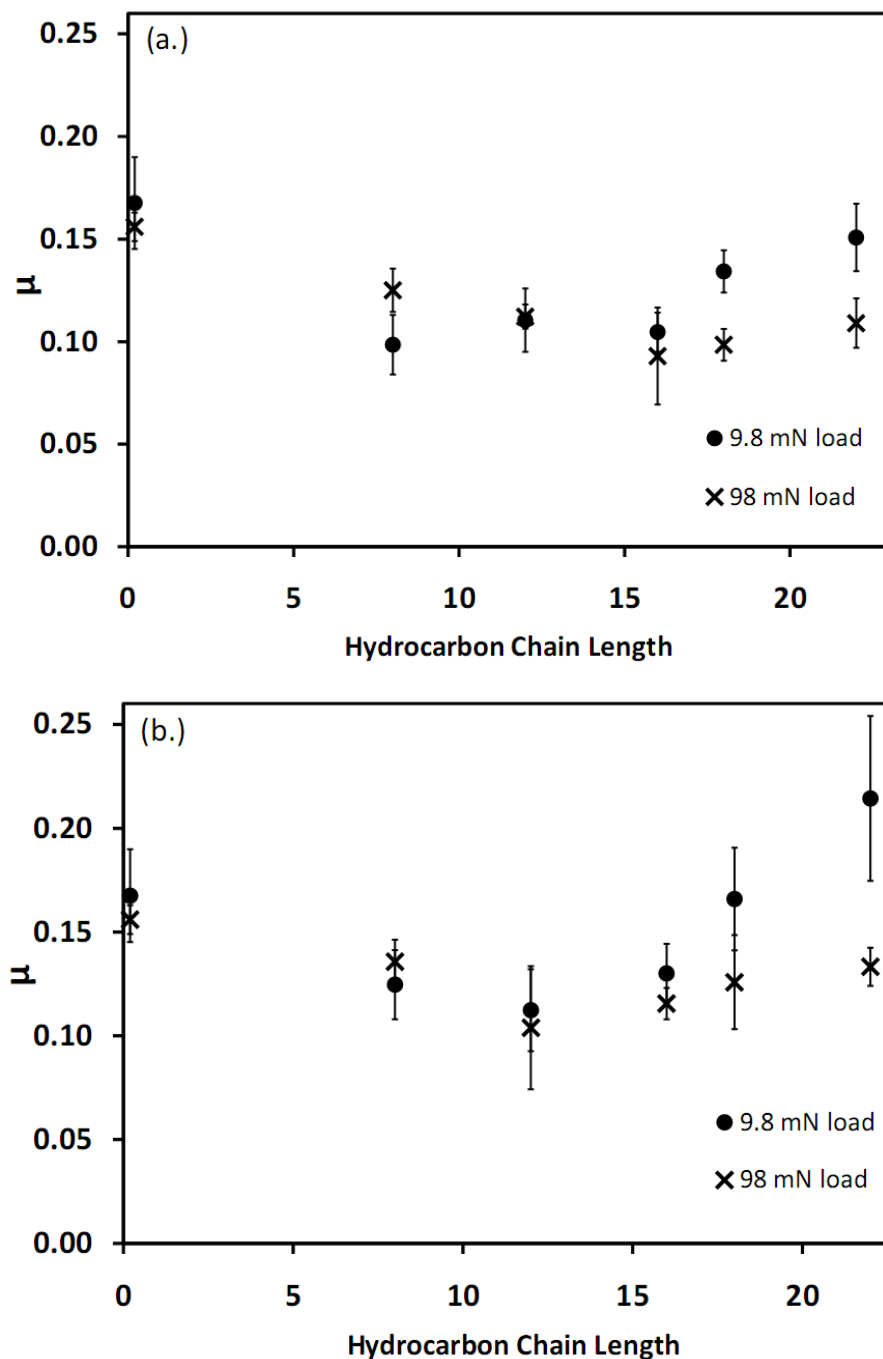


Figure 6.6. Effect of the hydrocarbon chain length and load on the frictional properties of perfluoroalkyl / alkylsilane mixed monolayers at two different F/H ratios, 2:1 (a) and 3:1(b). Single pass tribology tests were performed with a 1 mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films. The pure fluorocarbon monolayers (hydrocarbon chain length = 0) is offset from the vertical axis for clarity.

At the lower load of 9.8 mN, the longer-chain hydrocarbons (C18 and C22) have a significantly higher μ than the other mixed monolayers. Once a higher load is applied, however, the μ shows no dependence on hydrocarbon chain length, as the values for all the F/H monolayers are within a standard deviation of each other. The frictional dependence of the F/H monolayers on molecular freedom in the upper region is noteworthy because H/H monolayers showed no frictional dependence on mobility or CH₂ exposure at the surface (Chapter IV).¹ To further investigate the load-dependency of the F/C18 and F/C22 monolayers, additional tribometry testing was performed at 19.6 mN and 29.4 mN for the 2:1 F/H monolayers. Figure 6.7 displays the frictional response of these F/H monolayers against comparative H/H monolayers (C18/C10 and C22/C10 alkylsilane mixed monolayers with a ~2:1 long chain/short chain ratio). The trend of lowering μ with increasing load remains present for the F/H monolayers, while the H/H mixed monolayers show a relatively constant μ regardless of normal load. We believe that the load dependence for the F/C18 and F/C22 mixed monolayers is due to entanglement of the upper-layer hydrocarbons. As the mobile hydrocarbon chains resist interaction with the fluorocarbon base layer, they will seek out energetically favorable van der Waals interactions intramolecularly or with neighboring hydrocarbon chains.⁵ The entanglement will create cohesion among the hydrocarbon chains and result in a viscous liquid-like upper layer that resists shear and increases the friction force. The upper-layer hydrocarbon chains with greater length will allow additional entanglements and result in the greatest resistance to shear. As a consequence, the F/C22 monolayers show the highest μ . In contrast, the longer-chains in the H/H mixed monolayers freely interact with the methyl-terminated surface present in these films and would have a much lower driving force to interact with each other or themselves. During tribometry testing, the H/H mixed monolayers would possess a free-flowing upper layer and, therefore, show no chain-length effect or load-dependence.¹

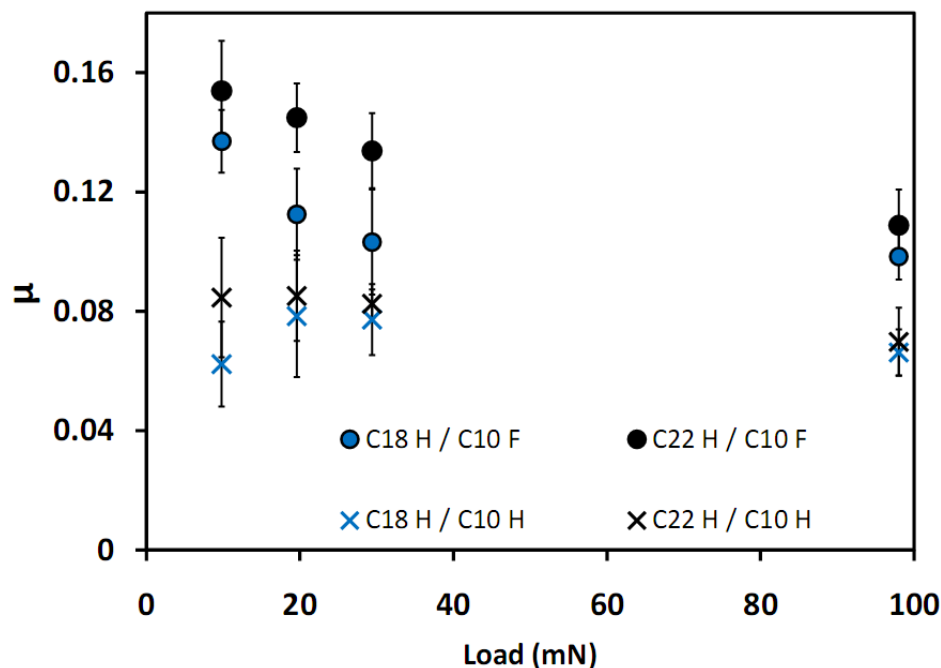


Figure 6.7. Effect of load on the on the frictional properties of perfluoroalkyl / alkylsilane and alkylsilane / alkylsilane mixed monolayers. Single pass tribology tests were performed with a 1 mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films.

Once the load is increased to 98 mN, the μ values are relatively constant among all the F/H monolayers (Figure 6.6). The increased normal force disrupts the entanglement among the upper-layer hydrocarbons of the F/C18 and F/C22 monolayers and, consequently, the hydrocarbon chains relax into a free-flowing state during tribometry testing. The F/C12 and F/C16 films show no frictional dependency on load, as seen in Figure 6.8, since the C12 and C16 hydrocarbons do not have the length to achieve appreciable intrachain or interchain interactions and therefore, behave like free-flowing chains even at the 9.8 mN load.

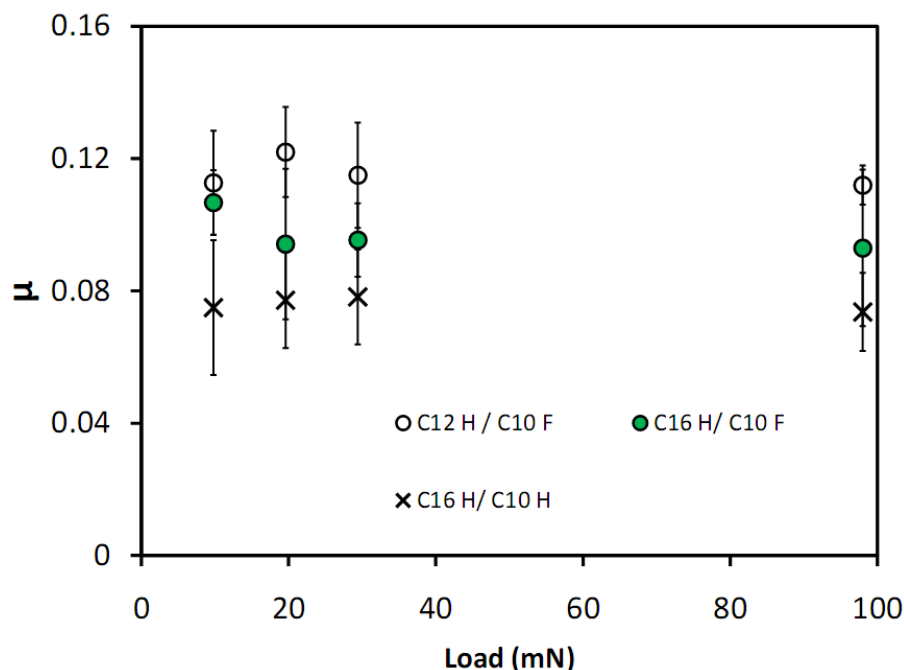


Figure 6.8. Effect of load on the on the frictional properties of perfluoroalkyl / alkylsilane and alkylsilane / alkylsilane mixed monolayers. Single pass tribology tests were performed with a 1 mm diameter stainless steel probe tip at 0.1 mm/s for a length of 15 mm. Reported values and error bars represent averages and standard deviations, respectively, based on at least 5 independently prepared films.

Molecular-dynamics simulations of a F/C18 monolayer-on-monolayer system support our interpretation for the load-dependent frictional properties found in F/H monolayers (Figure 6.9). The simulations, while modeling a different testing environment, verify the upper-layer hydrocarbons (shown in blue and white) desire to interact with each other and resist free-flowing behavior. At the lower pressure of 0.05 mN / mm² the simulations produced a μ of 0.30 and show a distinct separation of the hydrocarbons into an entangled region between the two fluorocarbon base layers. When a higher pressure of 2.5 mN / mm² is applied, the μ is reduced to 0.09, as the distinct segregation is eliminated and hydrocarbons act like a free-flowing liquid.

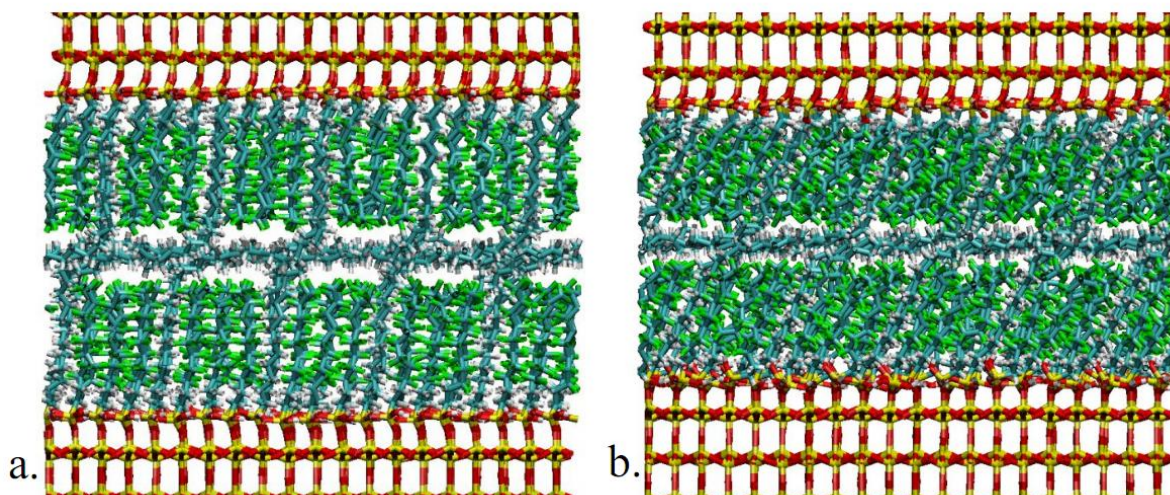


Figure 6.9. Molecular simulation snapshots of $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$ / $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ monolayer-on-monolayer systems at two pressures, $0.05 \text{ mN} / \text{mm}^2$ (a) and $2.5 \text{ mN} / \text{mm}^2$ (b). The hydrogen atoms are represented in white, the carbon atoms are represented in blue, and fluorine atoms are represented in green. Simulations were developed and performed by Ben Lewis.

Durability of Mixed Monolayer

Previous durability studies on perfluoroalkyl monolayers have shown that these films possess poor stability when compared to hydrocarbon monolayers.^{13,17} As discussed above, the fluorocarbons have a greater diameter than hydrocarbons, limiting the number of molecules that can occupy the surface. The increased size of the fluorocarbons also prohibits the extensive siloxane cross-linking found in alkylsilane monolayers.^{29,30} When covalent bonding does occur between neighboring fluorocarbon molecules, the bulk of the fluorocarbon will make these bonds highly strained.^{29,30} Integrating hydrocarbon molecules into a fluorocarbon monolayer could increase the wear life of the film. Hydrocarbons can access reaction sites on the substrate surface that the bulkier fluorocarbons cannot, which increases the packing of the film and cross-linking between neighboring molecules. The benefit of extensive cross-linking on durability has been clearly shown by our group when comparing the wear life of octyl-dimethylchlorosilane ($\text{H}_3\text{C}(\text{CH}_2)_7(\text{CH}_3)_2\text{SiCl}$) and n-

octyltrichlorosilane monolayers.⁴⁵ The trichlorosilane film withstood an applied load of 100 mN for 6x longer than the dimethylchlorosilane monolayers.

Figure 6.10 shows representative cyclic tests that were performed on a complete fluorocarbon monolayer, a pure C8 monolayer, and F/C8 monolayers of three different compositions (3:1, 2:1, and 1:5). The F/C8 system was chosen to test durability since the thickness of these films, due to the similar length of F6H2 and C8 precursors, are relatively insensitive to composition. The inset table of Figure 6.10 shows the increase in wear life as the mole fraction of hydrocarbon molecules increases within the film. The pure fluorocarbon monolayers and 3:1 monolayers, which have 84% of their surface covered by fluorocarbons, would have similar degrees of cross-linking and, therefore, show similar wear properties. As the fluorocarbon area fraction is decreased for the 2:1 F/H monolayers, the additional hydrocarbon molecules increase the stability of the films through intermolecular cross-linking. The 1:5 F/H films would allow even more cross-linking and have greater cohesion due to the substantial van der Waals interactions among the C8 chains.⁵ The added cohesion brought by extensive cross-linking and van der Waals interactions gives the 1:5 F/H films a wear life 6x longer than a pure fluorocarbon monolayer. The pure C8 monolayers show the greatest wear life as fluorocarbon molecules are not present to disrupt the cross-linking network. Besides containing the highest degree of cross-linking, the well-ordered C8 films have added stability due to the van der Waals interactions between hydrocarbon molecules and the absence of the repulsive fluorocarbon/hydrocarbon interactions.

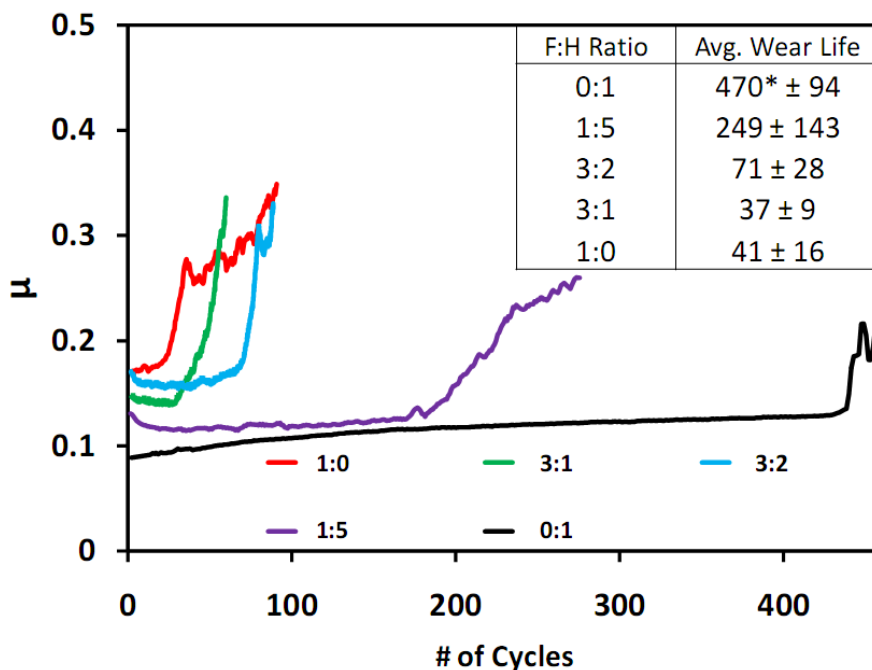


Figure 6.10. Effect of composition on the durability of perfluoroalkyl / alkylsilane mixed monolayers. Cyclic tribology tests were performed at 98 mN with a 4 mm diameter stainless steel probe tip at 1 mm/s for a scan length of 15 mm. A film was considered to have failed once the friction force increased to 50% of its initial value. Reported values and standard deviations were based on at least 3 independently prepared films. *Not all pure C8 monolayers experienced failure during testing. The average and standard deviation reported for these films are calculated from only the failed tests.

To investigate the influence of hydrocarbon chain length on durability, the wear life of the various 2:1 F/H monolayers, along with a pure C8 monolayer, were compared (Figure 6.11). Increased film thickness normally results in increased durability,⁴⁵ as a thicker film provides more molecular contacts for stabilizing van der Waals interactions. The F/H monolayers show no correlation between thickness and durability, as the F/H monolayers containing the longer chain hydrocarbons show no increase in wear life. This insensitivity to thickness is a result of the F/H mixed monolayers having two distinct regions, a packed lower layer and the mobile upper layer. The longer hydrocarbon chains within the upper region are sparsely distributed and will offer little resistance to probe penetration. The probe will contact the fluorocarbon base layer regardless of the

upper-layer thickness; therefore there is no enhancement in durability for the longer hydrocarbon systems.

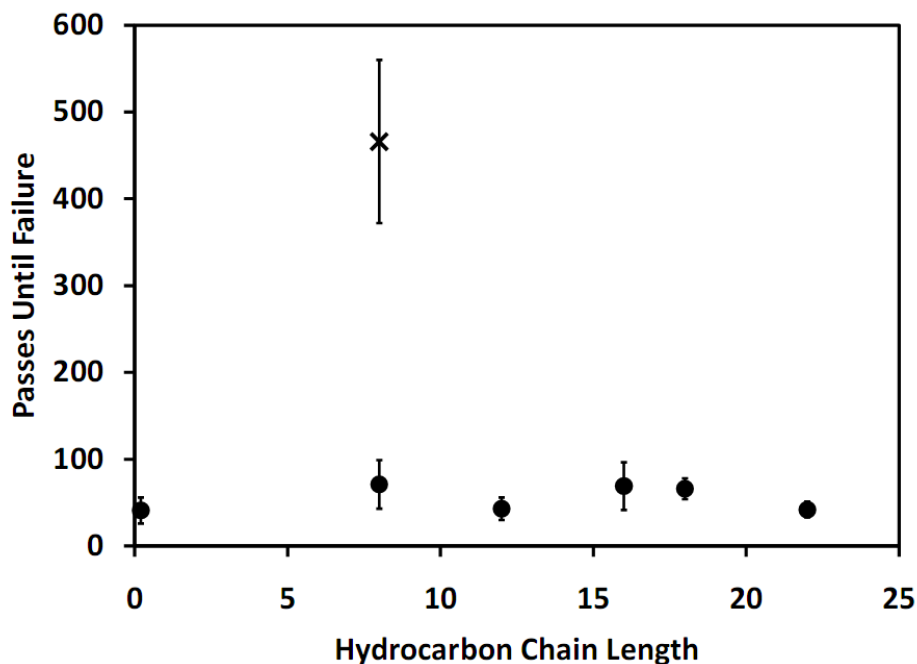


Figure 6.11. Effect of hydrocarbon chain length on the durability of perfluoroalkyl / alkylsilane mixed monolayers. Also shown are one-component F6H2 (chain length = 0) and C8 monolayers (signified by the X marking). Cyclic tribology tests were performed at 98 mN with a 4 mm diameter stainless steel probe tip at 1 mm/s for a scan length of 15 mm. A film was considered to have failed once the friction force increased to 50% of its initial value. Reported values and error bars represent averages and standard deviations, respectively, based on at least 4 independently prepared films. Not all pure C8 monolayers experienced failure during testing. The average and standard deviation reported for these films are calculated from only the failed tests.

Conclusions

Well-mixed F/H monolayers were created by forming a sparse fluorocarbon film and backfilling with alkylsilane molecules of various lengths. The frictional properties of monolayers containing F/H mole fractions of 3:1 and 2:1 were investigated at various loads. Compared to one-component fluorocarbon monolayers, F/H monolayers containing C8, C12, and C16 precursors

reduced the μ at all loads by at least 25%. The F/H films containing the longer hydrocarbons of C18 and C22 showed load-dependent behavior, as the μ for these monolayers decreases as higher loads are applied. At the highest load tested (98 mN), the μ values are indistinguishable among all the F/H monolayers. The load-dependant behavior was attributed to entanglement of the upper-layer hydrocarbons, which create a viscous liquid-like region on top of the F/H films. In addition, cyclic wear tests were performed on F/C8 monolayers of various compositions. An increase in hydrocarbon composition increased durability, showing that siloxane cross-linking among molecules and interfacial interactions among hydrocarbons greatly enhances the cohesion of films.

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CHAPTER VII

MICROSCALE FRICTION BETWEEN SLIDING MONOLAYERS

Introduction

Understanding the tribological interactions that occur between various monolayer surfaces is crucial for the proper engineering and design of surfaces at the microscale and below. At the nanoscale, interfacial interactions have been investigated with atomic force microscopy (AFM) using a wide range of probe surfaces, solvents, and humidity levels.¹⁻⁴ Conducting AFM in ambient air, which mimics the atmospheric conditions found in this work, Brewer et al. compared the performance of carboxylic acid-terminated tips and methyl-terminated tips on a variety of substrate monolayers.² When the carboxylic acid terminated tip was used, the hydroxyl and carboxylic acid monolayers showed coefficient of friction values that were 2x greater than the methyl-terminated monolayer.² In contrast, the highest friction for the methyl-terminated tip was achieved with the methyl surfaces.² The results agree with previous AFM studies showing that coefficients of friction are highest when similar surfaces (acid/acid and methyl/methyl) interact and lowest when dissimilar surfaces are in contact (acid/methyl and hydroxyl/methyl).^{2,5-8} This behavior was explained by adhesion, as adhesive forces are lowest when dissimilar groups that interact weakly are in contact.^{2,5-8} The work of Brewer, and additional chemical force microscopy studies by Clear et al.^{1,9,10} and others,^{2,6,7,11,12} have provided valuable insight into the influence of monolayer interactions and adhesion on frictional forces at the nanoscale.

In addition to monolayer interactions, the effect of humidity on friction has also been widely studied with AFM.^{3,4,13-18} At the nanoscale, humidity has been shown to significantly influence the adhesion and frictional properties of high energy monolayers^{17,18} and hydrophilic substrates.^{3,16} Zhang et al. showed that while adhesion increased, the friction coefficient decreased for hydrophilic

films as the relative humidity was increased up to 80%.¹⁸ The decrease in the coefficient of friction was attributed to adsorbed water molecules on the surface acting as a lubricant.^{18,19} In contrast, the frictional and adhesive forces for hydrophobic surfaces have been found to be insensitive to relative humidity at the nanoscale.^{13,18}

While the above studies have significantly increased understanding of interacting surfaces at the nanoscale, very little is known regarding how the knowledge gathered through these tests, which have a contact radius of 1-40 nm,^{1,20} translates to the microscale, which is the scale more relevant for many MEMS devices. Numerous research groups have investigated monolayer friction and their interfacial interactions on the microscale,²¹⁻²⁶ including our own,^{27,28} but a large number of these microscale tribometry studies have been conducted in ambient air using microtribometers and unmodified probes, i.e., the probe surface is the native oxide surface of the probe material.^{21,25-30} To our knowledge, microtribometer investigations utilizing coated probes have only focused on polymers³¹⁻³³ and the few investigations on the tribological effect of water vapor at the microscale have either focused on long-term performance^{34,35} or have been limited to low-energy thiol monolayers.³⁶ The effect of humidity on microtribometry has been studied by Bhushan et al., where it was shown humidity significantly affected plain silicon substrates,³⁶ but the only monolayer in this study was assembled from hexadecanethiol precursors on a gold substrate³⁶ and, therefore, little is known regarding how humidity-induced adhesive forces affect higher energy films at the microscale. In Chapter V we have shown that high energy monolayers can display significant residual forces during microtribometry²⁷ and, therefore, it is essential to quantitatively examine how water vapor influences microtribometer testing for a variety of monolayers.

The work in this chapter is the first microtribometer study to use monolayer-coated probes in the investigation of monolayer friction in order to investigate multiple monolayer/monolayer interfacial interactions and their effect on microscale friction. Monolayers were assembled from octadecyltrichlorosilane (C18), (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-1-trichlorosilane, and (1-trichlorosilyl undecyl) trichloroacetate on 6 mm borosilicate lenses and on flat silicon substrates. As

opposed to the chemisorbed thiol binding that is present in most chemical force microscopy studies,³⁷ in this work the monolayers contained on the probe lens are covalently bound to the surface and possess the ability for interchain cross-linking. Testing was done with all probe/substrate combinations at four different humidity levels, 3%, 37%, 75%, and 100%. The multiple humidity levels allow the effect of adhesive forces (such as capillary forces due to water vapor) on the microtribometry frictional measurements to be investigated.

Experimental Methods

Formation of Monolayers

The trichlorosilane monolayers were formed by following the procedures outlined in Chapter III.

Microscale Friction Testing

Microscale friction tests were performed either in open air ($37 \pm 2\%$ humidity) or within a humidity chamber. Testing was conducted with the DFM-0.5 force sensor. The probe tip was a borosilicate glass lens that was affixed to a stainless steel post (0.25 inch diameter and .75 inch length) using Weld epoxy resin glue from Loctite. All single-pass tests were conducted at a 98 mN load with a sliding speed of 0.1 mm/s and a scan length of 15 mm. Using Eq. 3.6 and the elastic moduli and Poisson's ratios (ν) of silica ($E = 70$ GPa, $\nu = 0.17$)³⁸ and borosilicate glass ($E = 63$ GPa, $\nu = 0.20$),³⁹ the mean contact pressure was calculated to be 30 MPa. While low-energy monolayers show negligible residual forces, we showed in Chapter V that OH-terminated monolayers displayed significant residual forces during tribometer testing.²⁷ To provide a clear comparison between the various monolayer-monolayer systems, the tribological data is reported as friction force using the equation,

$$F_f = \mu F_n + F_o \quad (7.1)$$

where μ is the kinetic coefficient of friction, F_n is the normal force and F_o is the residual force. Four tests were performed on each sample, and the reported frictional force (F_f) was determined by averaging the forces measured during the four tests. The reported values and errors reflect the average and standard deviation of at least 5 independently prepared films.

Humidity Testing

A humidity controller (PXR3 Model, Fuji Electric Systems) and a humidity chamber (Center for Tribology, Inc.) were used to control the humidity level of the air during tribometry testing. The humidity was consistently recorded during each tribometry test using a humidity sensor. The humidity controller and chamber were used to perform tribometry testing at three humidities: $3 \pm 1\%$, $75 \pm 5\%$, and $100 \pm 1\%$. The humidity chamber was not used for testing performed in ambient air ($37 \pm 2\%$ humidity).

Results and Discussion

Substrate and Tip Monolayer Characterization

Monolayers consisting of CH_3 , CF_3 , and OH termini were assembled on the borosilicate lenses and also on flat silicon substrates. Thickness and advancing contact angles of hexadecane (HD) and water were taken to qualitatively assess the structure of the monolayer films (Table 7.1). Ellipsometric thickness measurements of the flat silicon substrate monolayers were 1.4 ± 0.1 nm (OH), 1.7 ± 0.2 nm (CF_3), and 2.6 ± 0.2 nm (CH_3). Advancing contact angles were measured on both the lens and substrate monolayers. HD contact angles are more sensitive to surface composition and disorder of low-energy surfaces than is water⁴⁰ and provide a more complete assessment of the

structure of the films. For the CH₃ monolayers, the advancing HD contact angles of 43° (lens) and 44° (substrate) signals the presence of a dense methyl surface,^{27,41,42} while the advancing HD contact angles of 81° (lens) and 80° (substrate) for the CF₃ monolayers are consistent with the values obtained for fully formed fluorocarbon monolayers.⁴³⁻⁴⁵ The OH monolayers were prepared by forming trichloroacetate-terminated monolayers from (1-trichlorosilyl undecyl) trichloroacetate precursors and then cleaving the ester terminus into a hydroxyl group by hydrolysis.²⁷ The size of the trichloroacetate group limits the packing of the molecules on the surface and results in a loosely packed monolayer, where both OH and CH₂ groups are exposed at the surface.²⁷ The advancing water contact angle for the OH monolayers on the substrates (64° ± 1) is greater than that for densely packed OH monolayers but is almost identical with previous results by Berron et al. for loosely packed hydroxyl-terminated SAMs on gold that expose both hydroxyl and low energy methylene groups at the surface.⁴⁶ The OH monolayers formed on the lens possess slightly higher advancing water contact angles of 70° ± 3.

Table 7.1. Advancing contact angle data for water and hexadecane (HD) on the various probe and substrate surfaces.

	Tip		Substrate	
	Water	HD	Water	HD
Control	54 ± 3°	0°	-	-
CF ₃	120 ± 1°	81 ± 2°	120 ± 1°	80 ± 1°
CH ₃	111 ± 3°	43 ± 1°	110 ± 1°	44 ± 1°
OH	71 ± 3°	0°	64 ± 1°	0°

Effect of Probe Surface on Microscale Friction

Tribometry testing was completed with three different substrate monolayers (with termini of CH₃, CF₃, or OH) and four different probe surfaces (unmodified glass surface (control), CH₃ monolayer, CF₃ monolayer, or OH monolayer). In previous tribometric studies conducted at a 98 mN

load, which were performed in ambient air and with a 4 mm diameter stainless ball probe, we reported frictional forces of 7.6 ± 0.8 (CH₃), 15.7 ± 0.5 (CF₃), and 21.5 ± 1.4 mN (OH)²⁷ for these three substrate monolayers (Chapters IV, V, VI). To investigate the effect of the probe surface on microscale friction, we first focus on the tribometric data collected in ambient air. At ambient conditions ($37 \pm 2\%$ humidity), the effect of the probe surface on the friction force varied based on which substrate monolayer was being tested (Figure 7.1). The friction force remained low for the densely packed CH₃ substrate, regardless of the probe surface. The CH₃ (8.9 ± 0.9 mN) and CF₃ probes (9.2 ± 1.4 mN) produced nearly identical friction forces on the CH₃ surface and were within the standard error of the unmodified probe (10.6 ± 2.3 mN). The OH probe monolayer did produce a higher force of 12.7 ± 1.1 mN compared to the CH₃ and CF₃ probe monolayers for the CH₃ substrate monolayer.

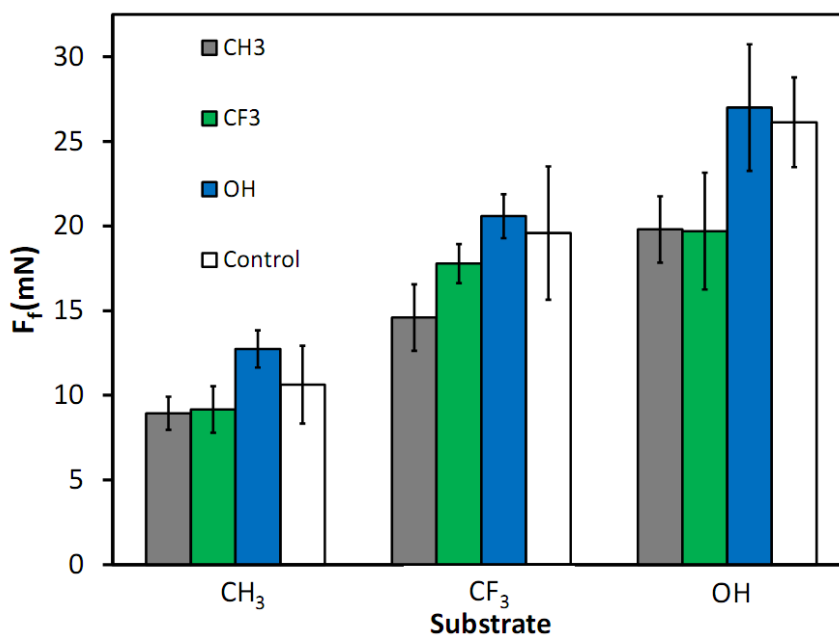


Figure 7.1. Experimental data from the various monolayer-monolayer tribology tests performed in the ambient environment (37% humidity). The single-pass tribology test was performed with a 6 mm diameter borosilicate glass lens affixed to a steel rod at 0.1 mm/s with a scan length of 15 mm. Testing of the three substrate monolayers (CH₃, CF₃, and OH) was done with an unmodified control lens and lenses modified with either a hydrocarbon monolayer, a fluorocarbon monolayer, or an OH monolayer.

The effect of the probe surface becomes greater for the CF₃ and OH substrate monolayers. For the CF₃ substrate, the lowest friction force was achieved with the CH₃ probe monolayer (14.6 ± 2.1 mN), followed by the CF₃ probe (17.8 ± 1.2 mN) and the control (19.6 ± 3.9), with the OH lenses producing the highest value of 20.6 ± 1.3 mN. Compared to the CH₃ substrate, the F_f values for each probe surface are significantly higher for the CF₃ substrate, which is in agreement with past studies^{13,29,42,47-54} that cite the stiffness²⁹ and bulkier head group of the fluorocarbon precursors^{51,53,55} as potential reasons for the increased frictional forces observed for these films. The bulkier head group lowers the cohesion per area⁵⁶ of the fluorocarbon film due to increased steric interactions^{51,53,55} and increased interchain spacing. To evaluate the molecular spacing within the film, a fully formed fluorocarbon monolayer was submerged in a hexadecyltrichlorosilane (C16) solution for 5 h and its oleophobicity reassessed. The advancing HD contact angle of the sample decreased from 81° to 70°, signaling that some CH₃ termini and methylene moieties from the C16 precursor are now exposed at the surface of the film and confirming that the fluorocarbon monolayer has molecular voids large enough for hydrocarbons to backfill into and bind to the silicon surface. This molecular porosity is related to the large steric bulk of the fluorocarbon chain and its stiffness that impede the molecule from filling molecular pinholes during monolayer formation. These pinholes allow for additional lateral motion of the chains under shear to elevate frictional forces beyond those observed for a dense CH₃-terminated monolayer. A control experiment with a fully formed C16 monolayer being submerged in a fluorocarbon precursor solution shows no evidence by wettability or x-ray photon spectroscopy of fluorocarbons backfilling into a hydrocarbon film.

The OH substrate attained the highest F_f values and, in addition, was the most affected by the probe surface. The CH₃ (19.8 ± 2.3 mN) and CF₃ probes (19.7 ± 3.5 mN) achieved significantly lower F_f values on the OH substrate than did the control (26.1 ± 2.6 mN) or OH probe (27.0 ± 3.7 mN). The higher friction forces are consistent with the low cohesion of the OH substrate monolayer and, more importantly, the higher surface energy of the OH groups that increases adhesion between

the substrate and probe. The hydroxyl moieties also provide opportunities for hydrogen bonding with the native oxide of the glass lens and the OH probe surface.²⁷ Comparing the data obtained with the unmodified lens probe with previous results achieved with a 4 mm diameter stainless steel ball, we observe that the control lenses produced higher frictional forces for all three substrate monolayers (7.6 vs 10.6 (CH₃), 15.7 vs. 19.6 (CF₃), and 21.5 vs. 26.1 (OH)).²⁷ The contact radius (A) achieved between the probe and the substrate can be estimated using the Hertz equation (Eq. 3.6) for a rigid sphere on a flat surface,

$$A^3 = \frac{3LR}{4E^*} \quad (7.2)$$

where L is the applied load (98 mN), R is the radius of the probe, and E^* is the combined modulus of the probe and substrate materials.⁵⁷ The elastic moduli and Poisson's ratios (ν) of silica ($E = 70$ GPa, $\nu = 0.17$)³⁸, stainless steel ($E = 200$ GPa, $\nu = 0.31$)⁵⁸, and borosilicate glass ($E = 63$ GPa, $\nu = 0.20$)³⁹ were used to determine E^* . The calculated contact radius of the lens probe, 32 μm , is 2x greater than the contact radius of the 4 mm steel ball (16 μm) and corresponds to a contact area that is 4x greater for the lens than the steel ball. At the microscale, friction is area dependent,^{36,59,60} and we believe the gradual curvature of the lens and the accompanying increase in probe/substrate contact area is responsible for the increased frictional forces.

Correlating the tribometric results with the thicknesses of the three substrate monolayers, one could argue that the increase in friction force is a result of decreasing monolayer thicknesses. In Chapter IV, we have shown that the frictional properties of CH₃-terminated films prepared from alkyltrichlorosilanes remain constant once the molecular precursors have 8 or more carbons along their backbone.^{27,28} To insure that monolayer thickness is not dictating our results, additional testing was performed with CH₃-terminated substrate monolayers formed from the dodecyltrichlorosilane (C12) precursors. The thinner monolayers prepared from C12, which were 1.6 nm thick and similar

to the thicknesses of the CF₃ and OH substrate monolayers, produced friction forces of 6.7 mN (CH₃ probe created from C18) and 7.9 mN (control probe). This slight decrease in friction forces for a 12 carbon CH₃-terminated monolayer as compared to an 18 carbon monolayer (which has been observed in previous studies^{61,62}, including our own²⁷) provides evidence that the frictional performances of the various monolayers in this study are not biased toward higher thicknesses.

Collectively, the results demonstrate that the probe surface does influence microtribometry testing. The high energy probe surfaces of the unmodified glass and the OH monolayer increase the friction force due to an increase in adhesive forces and interfacial interactions. This effect is most significant when the substrate is also high energy (OH substrate), as a high energy substrate has a higher affinity to achieve energetically favorable interfacial interactions. The consistent trend of higher energy probe surfaces producing higher friction forces, even on low-energy surfaces, is in contrast to previous chemical force microscopy investigations that show that frictional forces are largest when similar surfaces are in contact.^{2,5-8} Hydrogen bonding and adhesion brought on by water vapor affects tribometric testing, while dispersive forces, which are significant during AFM testing,^{2,5-8} appear to have little influence during these microscale tests.

In addition to investigating the impact of the probe surface on tribological testing, the data presented in Figure 7.1 also reveal which surface, the probe or the substrate, has a larger impact on frictional behavior. The observation of a tribological system being dependent on which surface (the probe or substrate) contains a specific monolayer has been observed in prior frictional studies. Using AFM, Flater et al. observed different frictional forces for a C18 probe / silicon substrate system than for a silicon probe / C18 substrate system.⁶³ From Table 7.2 we note that the frictional forces are shown to have a greater variation when the probe surface is held constant than when the substrate is constant. A straightforward quantitative assessment of the importance of the two surfaces on F_f values can be made by comparing the average of the variances. The average variance in the F_f values for altering the probe surface, and keeping the substrate constant, is 6, while the average variance for altering the substrate, and keeping the probe surface constant, is substantially higher at 29. As

discussed above, the probe surface does affect the tribological tests to a certain degree, but the substrate dominates the frictional behavior. In other words, a microtribometer system that puts two different monolayers in contact will give different F_f values depending on which monolayer is on the substrate and which is on the probe.

Table 7.2. Tribometric data from the various monolayer-monolayer tribology tests performed in ambient environments (37% humidity).

	Tip			
	CH ₃	CF ₃	OH	Control
CH ₃				
F_f (mn)	8.9	9.2	12.7	10.6
Stdev	0.9	1.4	1.1	2.3
CF ₃				
F_f (mn)	14.6	17.8	20.6	19.6
Stdev	2.1	1.2	1.3	3.9
OH				
F_f (mn)	19.8	19.7	27.0	26.1
Stdev	2.3	3.5	3.7	2.6

Effect of Humidity on Microscale Friction

To examine the influence of humidity on microscale friction testing, experimental trials were performed at four different humidity levels, 3, 37, 75, and 100%. In Figure 7.2 I present the humidity data from the four tips on the three substrate monolayers and categorize the results based on the hydrophobicity or hydrophilicity of the probe and substrate. Focusing on the systems that contain a low-energy probe and substrate (either CH₃ or CF₃), Figure 7.2a shows consistent friction force values, suggesting a lack of dependence on humidity for low-energy monolayers. If a higher energy probe (OH or unmodified) is used on a CH₃ or CF₃ substrate, a dependence on humidity begins to emerge for extremely dry conditions, as the lowest friction force values for these systems all occur at 3% humidity (Fig. 7.2b). The most significant effect was observed with the OH/CH₃ system, for which the value decreased from 12.7 in ambient conditions to 7.8 at 3% humidity. For the OH

substrate (Fig. 7.2c and d), the influence of humidity can be seen for all four probes, as the dry environment resulted in the lowest friction force values. The decrease was greatest for the OH and unmodified probes, as the F_f values obtained in the dry environment were 25% lower than the values achieved in ambient air (Fig. 7.2d). Collectively, the data show that low-energy surfaces are relatively insensitive to humidity, while the friction forces of higher energy surfaces are reduced in extremely dry conditions.

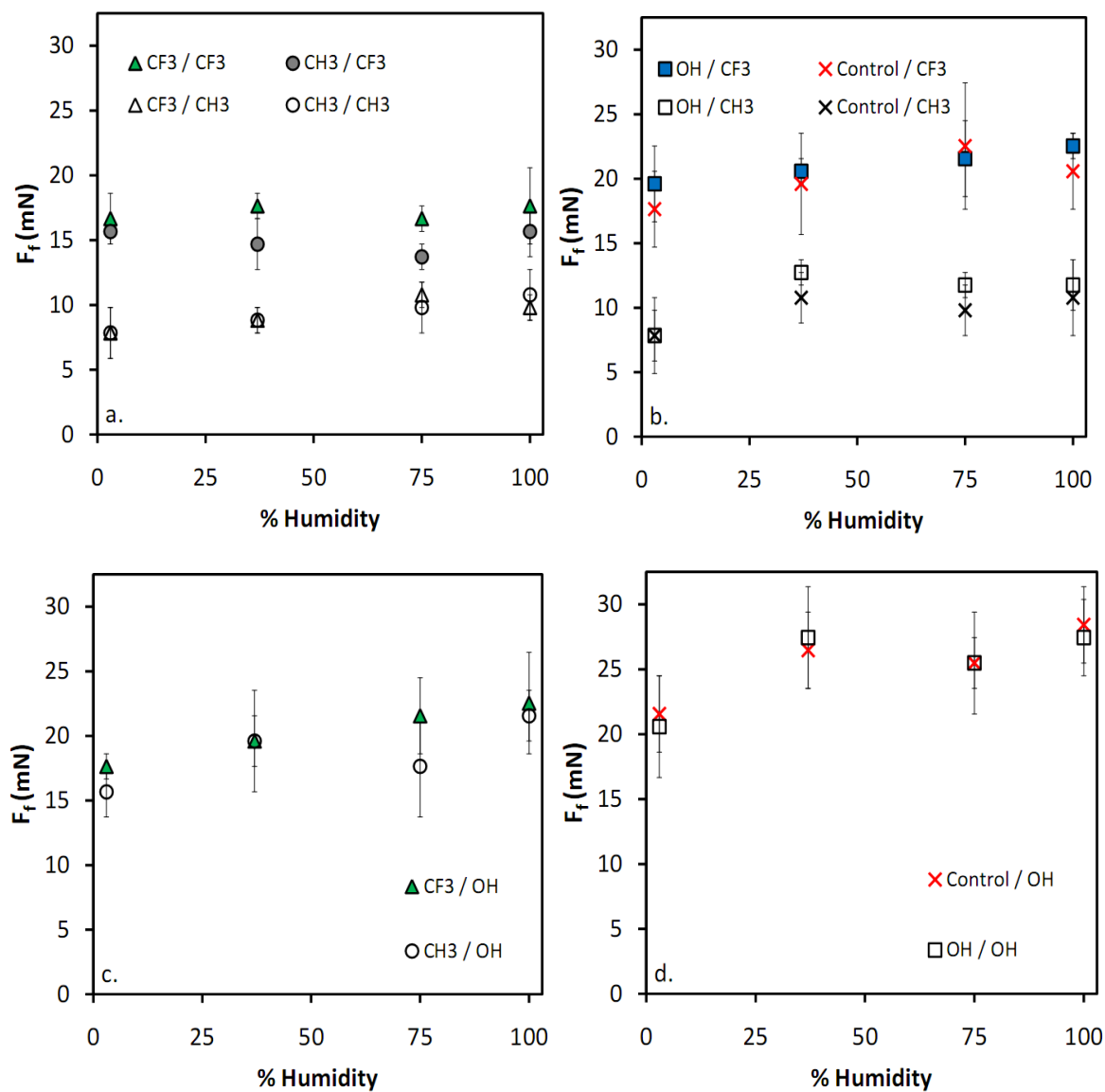


Figure 7.2. Experimental results from the various monolayer-monolayer tribology tests performed at four different relative humidity levels (3, 37, 75, 100%) and categorized based on the probe's and substrate's affinity for water. The plots display probe / substrate combinations of (a) hydrophobic / hydrophobic, (b) hydrophilic / hydrophobic, (c) hydrophobic / hydrophilic, and (d) hydrophilic / hydrophilic. The single-pass tribology test was performed with a 6 mm diameter borosilicate glass lens affixed to a steel rod at 0.1 mm/s with a scan length of 15 mm.

Multiple studies with AFM have shown that increased humidity increases adhesion on hydrophilic surfaces.^{17,18} Humidity-induced adhesion has also been observed on the microscale by Bhushan et al. for high energy silicon substrates.³⁶ The results here suggest similar behavior as the OH substrate, OH probe, and unmodified probe would be susceptible to adhesion brought on by physisorbed water between the probe and substrate that must be sheared during sliding.^{6,36,64,65} These adhesive forces can increase the linear coefficient of friction and residual force terms in the modified form of Amonton's law (Equation 7.1).^{1,27,66,67} The results, however, do not show the lubricating effects of water vapor that have been shown in nanoscale friction studies^{3,16,18} and also by Bhushan et al.³⁶ Once the humidity level increased over 50%, Bhushan showed a decrease in the friction force for the plain silicon substrate, attributed to adsorbed water molecules on the surface acting as a lubricant.^{18,19,36} The frictional performance of the OH substrate monolayer stays consistent at $\geq 37\%$ humidity, suggesting that the sparse OH monolayer is not sufficiently hydrophilic or that the loads and speeds present during the tests do not allow adsorbed water vapor to provide a lubrication benefit. For the hydrophobic monolayers, CF_3 and CH_3 , the results agree with AFM studies that show capillary forces for these hydrophobic surfaces to be negligible even at 100% humidity.^{14,18} A monolayer/monolayer system containing two hydrophobic surfaces, therefore, will be unaffected by humidity. If the system contains one high energy surface (OH probe, OH substrate, or unmodified probe), however, the friction is decreased at the driest condition (3% humidity).

Conclusions

Microtribometry tests were performed on various monolayer-coated silicon substrates with functionalized probes to investigate the interfacial interactions between monolayers on the microscale. In contrast to CFM studies where higher friction has been measured when probe and substrate have the same terminal group, we found at the microscale that CH_3 probes and substrates

produced the lowest friction forces, regardless of the other mating surfaces. The CF_3 substrate monolayer, despite being of lower energy than the CH_3 substrate monolayer, produced friction forces that were 1.5 – 2x higher than the methyl-terminated surface. This increase in friction force was attributed to the molecular porosity of the fluorocarbon film that allows additional lateral motion of the chains under shear. My results show that the higher energy probes increase friction forces during testing, most noticeably for the OH monolayer substrate. The substrate surface was shown to have a greater impact on frictional performance than the probe. In addition, the effect of water vapor on microtribometry was investigated by performing the microtribometry tests at various humidity levels. The driest environment (3% humidity) produced the lowest F_f values for any probe/substrate system that contained a high energy surface. The frictional forces in the driest environment can be reduced by as much as 25% and is due to the reduction of adhesive forces.

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CHAPTER VIII

MICROSCALE FRICTION OF POLYMERS

Introduction

Surface roughness is an inherent property of many thin polymer films, as the nature of surface-initiated polymerization lends itself to uneven morphology since reaction sites are unevenly dispersed along the surface. Polymer surfaces have generally shown poor frictional performance¹ due to their surface roughness, which results in deformation of asperities and is commonly referred to as plowing.^{2,3} A majority of microscale frictional investigations involving polymers have been conducted with smooth probe surfaces, usually a metal ball or polymer pin,^{1,4,5} and little is known regarding how surface morphology influences the tribological properties of two polymer surfaces sliding across each other. Compared to a smooth probe, a rough polymer probe contacting a polymer surface presents different frictional mechanisms as contacting asperities can penetrate into each other and can ratchet over each other. Little is known how ratcheting and the plowing of asperities affect microscale friction.

To examine polymer/polymer friction and investigate the tribological effect of plowing and topography, we have conducted tribometry with a variety of probe and substrate films. In addition to the unmodified probe, which is an unmodified silica lens, three hydrocarbon films, which vary in their thickness, were created on the probe and substrates; a solid-like monolayer prepared from octadecyltrichlorosilane molecules (C18) that has an average thickness of 2.6 nm, a polymethylene film (PM) that has an average thickness of 76 nm, and an extremely rough superhydrophobic polymethylene film (SH) that has an average thickness of 1,721 nm. The C18, PM, and SH films are all created from low-energy hydrocarbon groups but vary immensely in their topography and surface properties. The C18 film is a molecularly smooth monolayer that is a densely packed crystalline

film.⁶ In contrast, the polymers are semi-crystalline films that contain amorphous domains. All testing was completed at room temperature (22°C), which is much greater than the glass transition temperature for polymethylene (-120 °C)⁷, and, therefore, the polymer film will contain chains that have liquid-like movement.^{8,9} Instead of being smooth, the PM film contains nanoscale asperities, while the SH surface contains features that are close to a micron in size (Figure 8.1).

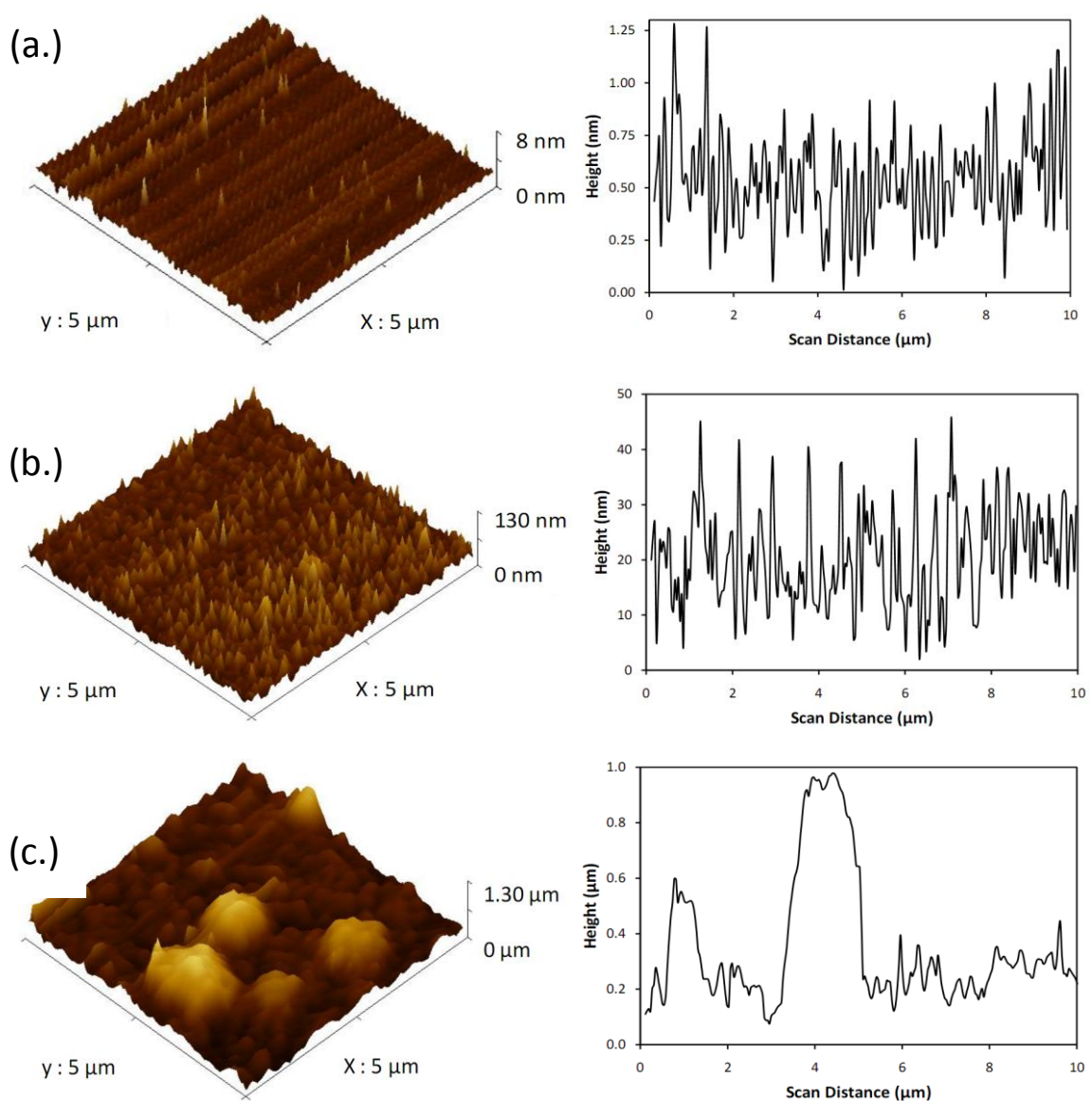


Figure 8.1. AFM images and line scans of the C18 monolayer (a), polymethylene film (b), and superhydrophobic film (c). AFM was conducted under tapping mode.

Frictional testing was also performed while the substrates were submerged in water. Underwater testing allows us to investigate multiple issues: the influence of hydrophobic interactions on microscale friction, the effectiveness of an entrapped air lubrication layer at the SH interface, and the frictional benefit of a chemisorbed water layer. Numerous chemical force microscopy studies have shown the large role hydrophobic interactions have at the nanoscale,^{10,11} but little is known whether the hydrophobic effect is prominent for microtribometry. Testing with the C18 and PM surfaces, which are both hydrophobic, allow us to assess the importance of the hydrophobic effect on microtribometry. The SH films, while also hydrophobic, provide a vastly different interface than the C18 and PM films. When submerged in water, the SH films will contain a micron-thick film of air, creating a polymer/water interface that consists mainly of entrapped air (Figure 8.2).¹² As two superhydrophobic surfaces come into contact underwater, pockets of air form between the two surfaces.¹³ At the nanoscale, these air pockets have significantly influenced the tribological properties of hydrophobic substrates.^{13,14} Our investigation will determine if the entrapped air can prevent contact between mating surfaces and provide an ultra-low frictional system at the microscale. Lastly, the hydrophilic unmodified probe provides an opportunity to investigate the influence of a chemisorbed water layer on microtribometry. Thin films of water are effective lubricating layers¹⁵ and introducing water into the lubrication systems could reduce frictional forces and provide additional insight into polymer friction.

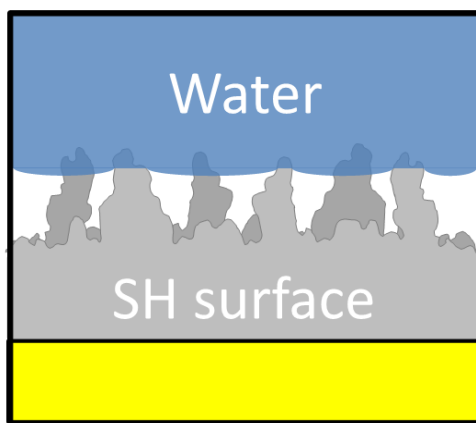


Figure 8.2. A SH interface in which water sits atop the polymer surface. Scheme provided by Juan Tuberquia.

Experimental Methods

Preparation of Diazomethane

Diazomethane (DM) was carefully synthesized according to literature¹⁶ to produce a ca. 16 mM solution in diethyl ether and stored at -17°C. The concentration of DM was determined by titration with benzoic acid.¹⁶ Caution: diazomethane is toxic and potentially explosive and should be handled carefully.

Preparation of Gold Substrates and Gold-Coated Tips

Silicon (100) wafers and silica lenses were rinsed with water and ethanol and dried in a stream on N₂ prior to placing in a metal atom evaporator and reducing the pressure to 4×10^{-6} Torr with a diffusion pump. Then, chromium (100 Å) and gold (1250 Å) were evaporated in sequence onto the wafers and lenses at rates of 1-2 Å s⁻¹. The chamber was then brought to atmospheric pressure and the gold-coated silicon wafers and silica lenses were removed. The wafers were then cut into 1.2 cm x 4 cm samples. The gold-coated substrates and lenses were rinsed with ethanol and dried with N₂ before use.

Formation of Monolayers

The C18 and hydroxyl monolayers were formed by following the procedure outlined in Chapter III. Using an atomic force microscope, the root mean square roughness (RMS) of the C18 monolayer-coated substrate was determined to be $1.7 \pm .5$ nm over a $10 \mu\text{m} \times 5 \mu\text{m}$ area.

Formation of Polymethylene Films

PM films were prepared by immersing the gold-coated silicon substrate and gold-coated silica lenses in a 16 mM DM solution in ether for 24 h at -17°C . Upon removal from the solution the samples were rinsed with ethanol and dried in a stream of nitrogen. Using an atomic force microscope, the RMS roughness of the film was determined to be 14 ± 3 nm over a $10 \mu\text{m} \times 5 \mu\text{m}$ area.

Formation of Superhydrophobic Films

The SH films were prepared by first assembling a vinyl-terminated self-assembled monolayer (SAM) on the gold-coated substrates and lenses by immersing the samples for 12 h in a 1 mM undec-10-ene-1-thiol solution in ethanol. After removal from the thiol solution, the samples were rinsed with ethanol and dried with nitrogen. The vinyl monolayer was then exposed to a 0.1 M solution of borane. The substrates were then exposed to a 16 mM solution of diazomethane in ether to initiate polymerization from the borane sites. A detailed protocol of the polymerization process can be found in a previous work from our group.¹⁷ Using an atomic force microscope, the RMS roughness of the films was determined to be 161 ± 87 nm over a $10 \mu\text{m} \times 5 \mu\text{m}$ area.

Microscale Friction Testing

Micro-scale friction tests were performed either in open air or with the sample immersed in water. Testing in water was accomplished by creating a custom-made container that allows the sample to be anchored to the tribometer stage while submerged under a depth of ~ 5 mm of water.

Single-pass testing was conducted at a constant load of 98 mN with a sliding speed of 0.1 mm/s and a scan length of 15 mm. The probe tip was a borosilicate glass lens that was affixed to a stainless steel post (0.25 inch diameter and .75 inch length) using Weld epoxy resin glue from Loctite. Three tests were performed for each load on each sample, and the reported frictional force (F_f) was determined by averaging the forces measured during the three tests. The frictional model used in this chapter is described in the Results section. The reported values and errors reflect the average and standard deviation of at least 3 independently prepared films.

Results

Characterization of Surfaces

Three different hydrocarbon films were created on the probe lenses and substrate surfaces, a monolayer film assembled from octadecyltrichlorosilane (C18), a polymethylene film assembled from diazomethane precursors (PM) on gold via a surface-catalyzed polymerization, and a microscopically rough superhydrophobic polymethylene film (SH) assembled by a surface-initiated polymerization. In addition, a hydroxyl-terminated probe monolayer was used in the water lubrication study. The monolayers were formed on the glass probe and silicon substrates by hydroxylating the surfaces and immersing them in a solution containing the trichlorosilane precursor. The two different polymerization processes required a gold surface and, therefore, the glass lenses and silicon substrates were coated with a 125 nm gold layer before the PM and SH films were assembled onto the surfaces. Thicknesses and contact angles were taken to assess the structure of the films, and these values are shown in Table 8.1. Thicknesses of the probe films could not be taken due to the curvature of the lenses. The ellipsometric thickness of the C18 substrate monolayer was $2.6 \pm .2$ nm and the advancing (adv) and receding (rec) contact angles for the substrate were $110 \pm 1^\circ$ (adv) / $103 \pm 2^\circ$ (rec) for water and $44 \pm 1^\circ$ (adv) / $41 \pm 1^\circ$ (rec) for HD. The probe C18 monolayer exhibited angles of $110 \pm 1^\circ$ (adv) / $102 \pm 2^\circ$ (rec) for water and $43 \pm 2^\circ$ (adv) / $40 \pm 2^\circ$ (rec) for HD. The contact

angles signal that dense and oriented monolayers were formed on both the substrate and probe surfaces.¹⁸⁻²⁰ The OH monolayers, as discussed in Chapter V, were prepared by forming trichloroacetate-terminated monolayers from (1-trichlorosilyl undecyl) trichloroacetate precursors and then cleaving the ester terminus into a hydroxyl group by hydrolysis.²⁰ The size of the trichloroacetate group limits the packing of the molecules on the surface and results in a loosely packed monolayer where both OH and CH₂ groups are exposed at the surface.²⁰ The exposure of both hydroxyl and low energy methylene moieties results in intermediate contact angles of $69^\circ \pm 2$ (adv) and $52^\circ \pm 2$ (rec) for the probe monolayer.²¹

The two polymethylene films differ considerably from each other in thickness and in topography. The ellipsometric thickness of the PM substrate films was measured as 76 ± 10 nm. The water contact angles for the substrate and probe PM films were $120 \pm 5^\circ$ (adv) / $61 \pm 4^\circ$ (rec) and $122 \pm 3^\circ$ (adv) / $62 \pm 5^\circ$ (rec), respectively, while the HD contact angles were 0° for all. The elevated advancing water contact angles and high hysteresis are consistent with a surface that features nanoscale asperities, in agreement with Figure 8.1b. This wetting analysis agrees with the AFM image (Figure 8.1b), which shows a surface made up of nanoscale roughness and features asperities that are 10-50 nm in height. The SH films were too thick for ellipsometric measurements and, therefore, profilometry was used to determine the thickness of these films. The average thickness of the SH films was determined to be $1,721 \pm 115$ nm. The water contact angles for the SH films are considerably higher than the PM films, as the SH substrate had values of $164 \pm 3^\circ$ (adv) / $160 \pm 3^\circ$ (rec), while the probe SH surface had values of $157 \pm 2^\circ$ (adv) / $152 \pm 3^\circ$ (rec). The SH films possess a combination of micrometer- and nanoscale features (Fig. 8.1c) that gives the films their superhydrophobic properties. When a drop of water is placed onto the surface, a majority of the polymer interface is occupied by air pockets, resulting in the water drop contacting less than 5% of the polymer interfacial area (~95% air) based on analysis with the Cassie equation.¹⁷

Table 8.1. Surface characterization data for the various films created on the probe and substrate surfaces.

	Thickness (nm)	θ_W		θ_{HD}	
		adv	rec	adv	rec
Unmodified Tip	-	$54 \pm 3^\circ$	$31 \pm 4^\circ$	0°	-
OH Tip	-	$69 \pm 2^\circ$	$52 \pm 2^\circ$	0°	-
C18 Substrate	2.6 ± 0.2	$110 \pm 1^\circ$	$103 \pm 2^\circ$	$44 \pm 1^\circ$	$41 \pm 1^\circ$
C18 Tip	-	$110 \pm 1^\circ$	$102 \pm 2^\circ$	$43 \pm 2^\circ$	$40 \pm 2^\circ$
PM Substrate	76 ± 10	$120 \pm 5^\circ$	$61 \pm 4^\circ$	0°	-
PM Tip	-	$122 \pm 3^\circ$	$62 \pm 5^\circ$	0°	-
SH Substrate	$1,721 \pm 115$	$164 \pm 3^\circ$	$160 \pm 3^\circ$	0°	-
SH Tip	-	$157 \pm 2^\circ$	$152 \pm 3^\circ$	0°	-

The thicknesses of the C18 and PM films were determined from ellipsometry, while the thickness of the SH film was determined using profilometry.

Polymer Friction

To investigate the tribological interactions of two mating polymer surfaces and the role of surface roughness on polymer friction, microtribometry testing was performed with a variety of probe tips and substrates in ambient air (Table 8.1). A common equation to describe polymer friction is the Bowden and Tabor adhesion model,²²

$$F_f = \tau A_r + F_p \quad (8.1)$$

where τ is the shear strength of the surface, A_r is the real area of contact, and F_p is the plowing force due to the deformation of asperities.²² Due to the microscale asperities of the SH film, ratcheting is an additional mechanism of friction that is possible. Ratcheting occurs when one asperity has to climb over another one as they slide across each other and is prominent when microscale asperities are present.²³ The friction force for the polymer systems, therefore, will arise from three main factors, adhesion which occurs at the real area of contact between the probe and substrate, plowing of

asperities, and ratcheting.^{22,24,25} These frictional mechanisms are additive²⁵ can be related to friction force (F_f) through the equation,

$$F_f = \tau A_r + F_p + F_r \quad (8.2)$$

where F_r is the ratcheting force.²⁵ The effects of plowing and ratcheting can qualitatively be observed in the test profiles obtained from the polymer substrates. Figure 8.3 shows the test profiles obtained with an unmodified probe of the C18, PM, and SH films, along with a plain silicon substrate. Rather than the continuous smooth sliding profile that is achieved with monolayer friction, the polymer data are more erratic.

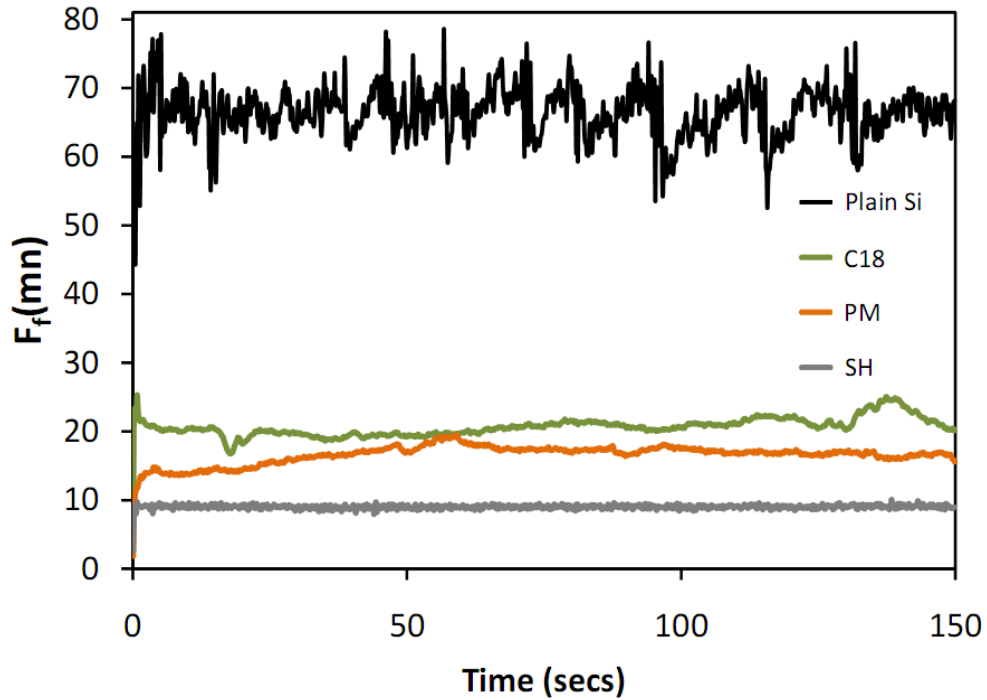


Figure 8.3. Effect of surface film on the frictional forces obtained with a 6 mm diameter borosilicate lens at a sliding speed of 0.1 mm/s and a 98 mN load for silicon substrates. The tribological test represents a single pass along a 1.5 cm line.

The tribometry results for all four probe surfaces (unmodified, C18, PM, and SH) on the three substrate films are compared in Figure 8.4. The frictional data obtained with the unmodified and C18 probes will be discussed first, as these surfaces have similar material properties and are both molecularly smooth (with RMS values > 2 nm), allowing us to isolate the influence of the surface energy of the probe on polymer friction. In Chapter VII, I examined the influence of the probe surface on monolayers by performing tests with a variety of monolayer-functionalized probe lenses. The C18 probe monolayer, when compared to the unmodified probes, did produce lower frictional forces for the CF_3 and OH substrate monolayers, but the effect was barely noticeable for the C18 substrate monolayer (the friction forces achieved on the C18 substrate were 8.9 ± 0.9 mN for the C18 probe versus 10.6 ± 2.3 mN for the unmodified probe). For the present study, comparing the results obtained with the unmodified probe and C18 probe (the white and gray bars, respectively, in Fig. 8.4) shows that the surface energy of the probe has a much more significant influence when the substrate is a polymer film. For the PM films, the friction force is reduced from 17.4 ± 2.7 mN to 11.2 ± 1.0 mN when a C18 probe is used rather than an unmodified probe. The SH films show an even greater decrease, as the friction is reduced from 18.7 ± 3.9 mN (unmodified probe) to 9.6 ± 0.9 mN (C18 probe). Even though the C18 and the polymer films are all low-energy hydrocarbon films, the polymer substrates have a greater dependence on probe surface energy because of the differences in morphology. The smooth and crystalline C18 monolayer²⁶ does not undergo significant deformation, which creates a low shear surface that undergoes negligible plowing. In contrast to the well-ordered^{6,27} and solid-like C18 monolayer,²⁶ the polymer films are semi-crystalline (with a crystalline content of $\sim 70\%$)¹⁷ and will contain amorphous domains. Tribometry testing was conducted at room temperature, which is substantially greater than the glass transition temperature for polyethylene (-120 °C),^{7,28} and, therefore, the chains in the amorphous domain of the polymer material are in a liquid-like state^{8,9} and allow greater penetration of the probe into the film,²⁹ increasing the shear strength.² More significantly, the polymer films (Fig. 8.1) contain asperities that will deform during sliding and drastically increase the friction force due to plowing.²³ Since the polymer films have

higher shear strength and undergo plowing, the probe surface energy has a greater significance. Therefore, the well-known lubricating properties of the C18 probe monolayer^{20,30-32} diminish the plowing force and shear strength, resulting in decreased frictional forces when compared to the unmodified probe.

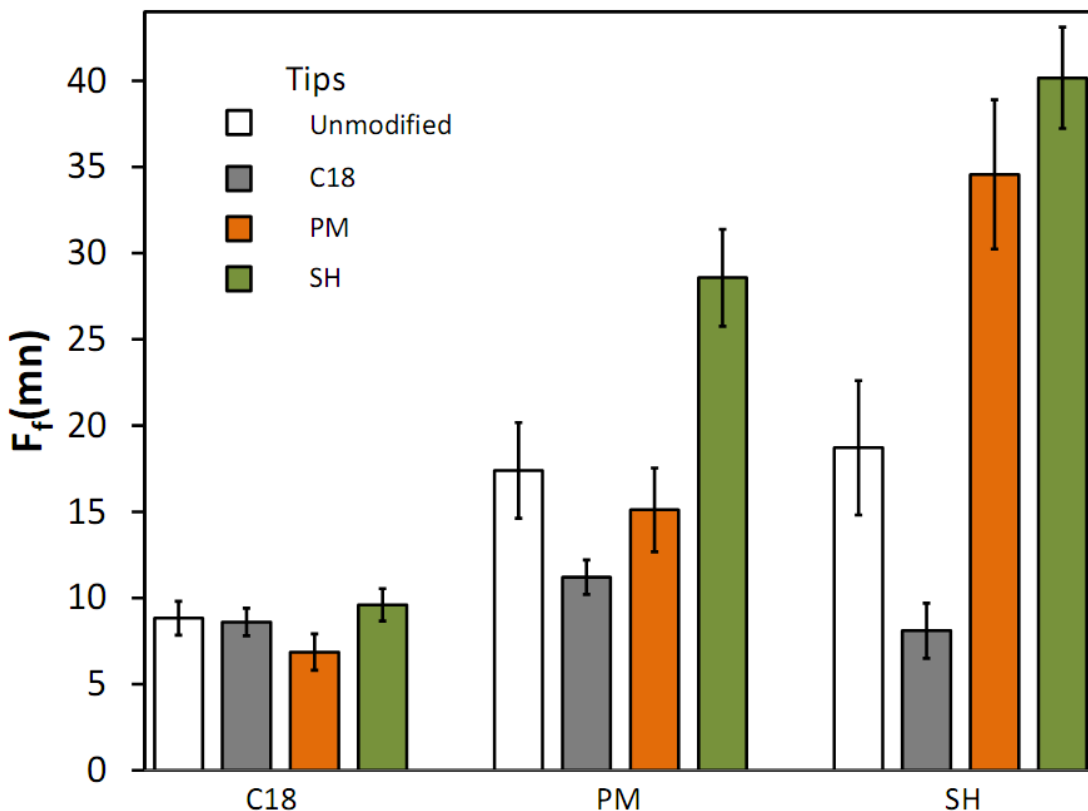


Figure 8.4. Effect of probe and substrate coatings on the friction force. The single-pass tribology tests were performed with at 0.1 mm/s with a scan length of 15 mm. Tests on the three hydrocarbon substrate films (C18 monolayer, PM film, and SH film) was done with either an unmodified lens or a lenses coated with one of the three hydrocarbon films. Reported values and error bars represent averages and standard deviations, respectively, based on at least 3 independently prepared films.

The SH films are substantially rougher than the PM films and contain microscale asperities (Fig. 8.1c), yet the friction force values obtained with the unmodified probe for the SH and PM films are statistically indistinguishable. Furthermore, the SH films actually achieve lower frictional forces than PM films when the C18 probe is used (8.1 ± 1.6 mN vs. 11.2 ± 1.0 mN). Here, the microscale

asperities of the SH film are limiting the real contact area between the probe the SH film since the probe will only contact the summit of the asperities.²³ The decrease in real contact area will decrease adhesion^{33,34} and would off-set the increase in plowing force brought on by the asperities, resulting in similar friction force values for the PM and SH substrates.²³

Compared to the smooth unmodified and C18 lenses, testing with probes containing polymer films will provide significantly different surface contacts and interfacial interactions. The topography of the polymer probes is drastically rougher than the smooth silica lens, which has a root mean square roughness of only $1.4 \pm .3$ nm. In Figure 8.4 the effect of the polymer probe on the frictional forces depends on the contacting substrate. The SH substrates exhibit the largest dependence on the probe, as the PM probes produced a friction force of 34.6 ± 4.3 mN and the SH probes resulted in frictional forces of 40.2 ± 2.9 mN, which are much higher than the friction force measured with the unmodified probe (18.7 ± 2.9 mN). The PM substrate achieves similar friction forces with the unmodified and PM probe (17.4 ± 2.7 and 15.1 ± 2.4 mN respectively), but the SH probe produces a significantly higher friction force of 28.6 ± 2.8 mN. Unlike the polymer substrates, the frictional performance of the C18 substrate was relatively insensitive to the probe surface, as the frictional forces are between 6.9-9.6 mN for all substrates.

The frictional behavior for the polymer-coated probes is driven by the plowing of asperities and the ratchet mechanism. The plowing force will be increased for polymer / polymer systems since both surfaces contain asperities.³⁵ The ratcheting effect would be more prominent when microscale asperities are present;²³ thus, the highest friction forces occur for the SH (probe) / SH (substrate) system, followed by the PM / SH and SH / PM systems. When the ratcheting effect is negligible, as it would be for the PM / PM, SH / C18, and PM / C18 systems, the polymer probes produce much lower frictional forces. For the PM substrate, the PM probe produces a slightly lower friction force than the unmodified probe and provides evidence that the reduction in adhesion between two low-energy PM surfaces is significant and offsets, or even surpasses, the increase in plowing force due to the addition of another rough polymer surface. Compared to the polymer/polymer systems, tests

conducted on the C18 substrate would have decreased plowing forces since only one surface would contain asperities. This decrease in plowing and the low-energy surfaces of the polymer probes allows the SH probe to achieve similar friction forces as the unmodified probe (9.6 ± 0.9 and 8.8 ± 1.0 mN, respectively) and the PM probe to achieve the lowest friction forces at 6.9 ± 1.1 mN. Considering the combined results of the C18 probe and C18 substrate, the frictional benefit of a solid, smooth, and low energy monolayer^{20,30} when the other contacting surface is a polymer is clearly shown.

Effect of Testing Medium

To examine the tribometric influence of a chemisorbed water layer and to determine whether entrapped air and hydrophobic interactions have a significant influence on microtribometry results, frictional tests were also performed on selected systems while the substrates were submerged under ~5 mm of water. For the C18 and PM probes, underwater testing will involve two hydrophobic surfaces coming into contact underwater and, therefore, the hydrophobic effect may cause additional adhesion.¹⁰ At the nanoscale, adhesive forces from different testing mediums can differ by 2 orders of magnitude¹⁰ and can have a considerable influence on atomic force microscopy frictional measurements.¹⁰ The results shown here demonstrate that the testing environment has little or no influence on the frictional results, as the frictional forces are nearly identical in water and in air for all substrates (Fig. 8.5a,b), and demonstrate that hydrophobic interactions are insignificant at the higher loads and larger size scale of microtribometry.

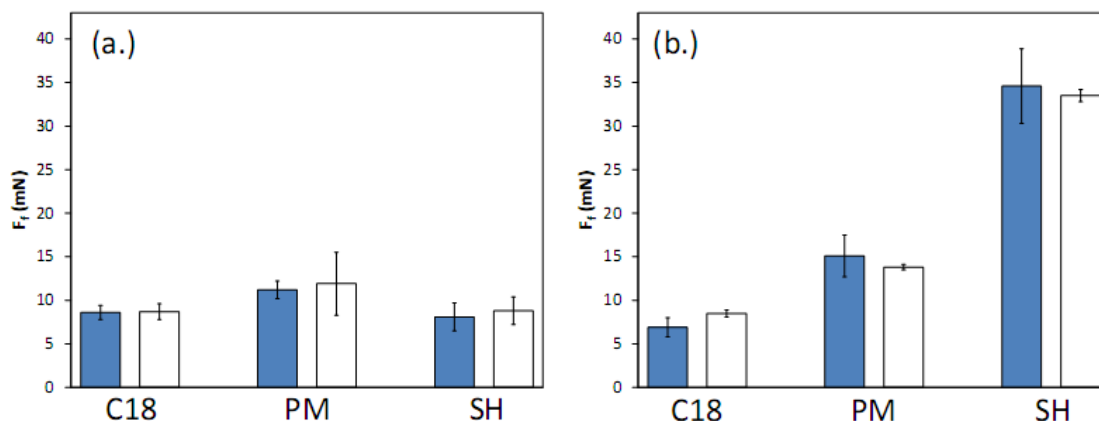


Figure 8.5. Frictional effect of water submersion for the various C18 (a) and PM (b) probe systems. The single-pass tribology tests were performed at 0.1 mm/s with a scan length of 15 mm. Testing on the three hydrocarbon substrate films (C18 monolayer, PM film, and SH film) was done either in ambient air (blue) or with the substrate submerged in water (white). Reported values and error bars represent averages and standard deviations, respectively, based on at least 3 independently prepared films.

The superhydrophobic properties of the SH probe will create a different interface than the C18 or PM probe. As discussed previously, the micron asperities of the SH film creates air pockets when the surface is in contact with water and, therefore, air will be entrapped between the water and polymer interface once the superhydrophobic film is submerged underwater.¹² At the nanoscale the air pockets have significantly influenced the tribological properties of superhydrophobic substrates^{13,14} and these surfaces have been used to achieve low-friction fluid flow.^{36,37} In an attempt to create an ultra-low lubrication scheme based on an entrapped air layer, I tested the SH / SH system underwater. The frictional forces that were obtained with the submersed system, 33.3 ± 0.7 mN, were slightly lower than the open air testing (40.2 ± 2.9 mN), but the similarities in water and air testing suggest that, at the loads and speeds tested, the air pockets do not show noteworthy beneficial lubrication properties and do not prevent the substrate and probe from mating, as extensive wear tracks can be seen with an optical microscope (Figure 8.6).

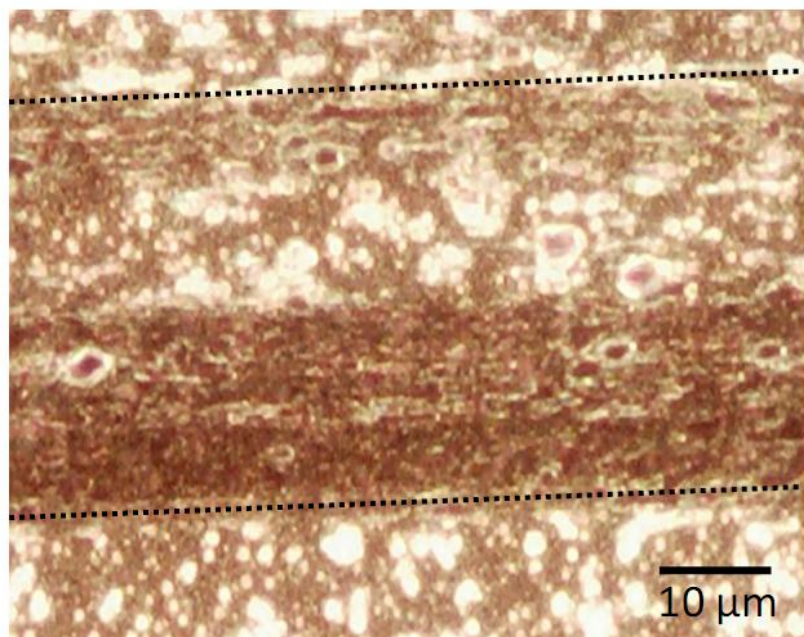


Figure 8.6. Optical image of the wear track (framed with the dotted line) obtained for the SH/SH system during underwater tribometry testing. The single-pass tribology test was performed at 0.1 mm/s with a scan length of 15 mm.

In contrast to the hydrocarbon film-coated probes, water has a significant effect for polymer films being tested with the unmodified probe, which is hydrophilic. In water, the friction of the PM substrate is decreased from 17.4 ± 2.7 mN to 12.7 ± 2.9 mN, while frictional forces for the SH substrate decreased from 18.7 ± 3.9 mN to 10.5 ± 1.6 mN (Fig. 8.7a). Water can form a lubricating film and separate sliding surfaces,³⁸ and we believe a chemisorbed water layer adheres to the unmodified probe during the underwater testing. This water layer would lower the shear and decrease the adhesion between the probe and substrate,³⁹ lowering the shear strength and plowing forces. Fluid lubrication due to water has been reported for microtribometry, as friction was decreased for a polymer brush system when testing was performed in water rather than in dry N₂.³⁹ The unmodified / C18 substrate system was unaffected by the water layer, since the C18 monolayer already provides a smooth low-shear surface. To confirm the frictional benefit of chemisorbed water, additional testing was done with an OH-monolayer probe. As shown in Table 8.7b, the friction force decreased for all three substrates when they were submerged in water. The OH-monolayer is not as hydrophilic as the

unmodified probe (Table 8.1), and the water molecules will not have as strong of an affinity to the surface as they would have for the unmodified silica probe. As a consequence, the frictional benefit of the water layer is not as large for the OH probe.

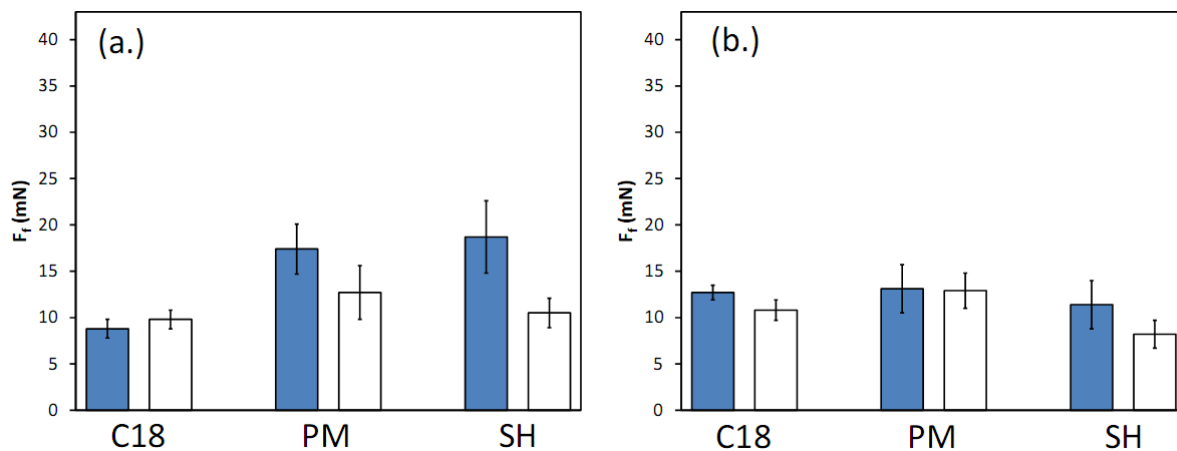


Figure 8.7. Frictional effect of water submersion for the various control (a) and OH (b) probe systems. The single-pass tribology tests were performed with at 0.1 mm/s with a scan length of 15 mm. Testing on the three hydrocarbon substrate films (C18 monolayer, PM film, and SH film) was done either in ambient air (blue) or while the substrate was submerged in water (white). Reported values and error bars represent averages and standard deviations, respectively, based on at least 3 independently prepared films.

Conclusions

Microtribometry tests were performed on various polymer-coated substrates to examine polymer/polymer friction and investigate the tribological effect of plowing and topography. As opposed to hydrocarbon monolayers, the frictional performance of the PM and SH films were dependant on the surface energy of the probe, as the lubricating properties of the C18 probe monolayer^{20,30-32} diminished the plowing force and shear strength. When polymer probes were used on the polymer substrates, the ratcheting mechanism was the dominant influence, as highest friction forces occurred when microscale asperities were present. In addition, tribometry tests were performed with the substrates submerged under water to examine the influence of hydrophobic

interactions on microscale friction, the effectiveness of an entrapped air lubrication layer at a SH/SH interface, and the frictional benefit of a chemisorbed water layer. For the C18, PM, and SH probes, the water environment had little influence on the frictional results, suggesting that, at the loads and speeds tested, hydrophobic interactions do not influence the lubrication properties and entrapped air at the water/SH film interface does not prevent the substrate and probe from mating. The unmodified probe, in contrast, showed decreased frictional forces for the polymer substrates in the water environment. This decrease was attributed to a chemisorbed water layer on the hydrophilic probe which lowered the shear and decreased the adhesion between the probe and substrate.

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CHAPTER IX

FRICTIONAL PERFORMANCE OF SILICA MICROSPHERES

Introduction

Introducing a rolling element between two contacting surfaces can greatly reduce friction, as rolling can produce frictional forces that are $10^2 - 10^3$ times lower than those due to sliding.¹ Despite the well-known frictional benefits of rolling motion, few experimental investigations of rolling friction have been performed on the micro and nanoscale.¹⁻⁸ In contrast to macroscopic studies where adhesion is relatively unimportant and rolling friction dominates, interfacial interactions grow in importance as the dimensions of the rolling element shrink to the microscale and below, and friction can be composed of both rolling and sliding.^{9,10} Furthermore, the pressure and contact areas inherent in a microscale system are different than those seen on the macroscale.¹¹

Prior investigations of rolling friction have focused on rolling elements larger than $40\text{ }\mu\text{m}$ ^{2,5-8,12} and those of molecular dimensions.^{1,3,4,13-15} Beerschwinger et al.⁵ reported coefficient of friction values of 0.05 for $40\text{ }\mu\text{m}$ diameter glass spheres rolling between two flat surfaces, and Ghodssi et al.⁶ reported a 0.01 value for a tribological system containing $285\text{ }\mu\text{m}$ diameter stainless steel ball bearings. More recently, Sinha et al.⁸ reported coefficients of friction as low as 0.005 for $53\text{ }\mu\text{m}$ glass microspheres contained between two rotating silicon plates. At the nanoscale, experimental investigations of rolling friction have focused on hollow nanoparticles such as C_{60} fullerenes³ or fullerene-like supramolecules consisting of WS_2 or MoS_2 .⁴ While all these studies have demonstrated the advantages of rolling over sliding in reducing frictional forces and wear, a key size range (200 nm to $5\text{ }\mu\text{m}$) between these extremes that is compatible with MEMS and modern micro-fabrication technologies has not been explored.

In this chapter, we present a simple lubrication scheme based on a layer of silica spheres that are deposited onto a flat silicon substrate. To investigate the effect of sphere size and load on frictional performance, the diameters of the spheres were varied (4 μm , 2 μm , or 500 nm), and testing was done at multiple loads with the microtribometer. A 10-50 μm contact radius exists between the sample and the spherical probe tips used during testing, creating microscale contact areas similar to those which would be found in MEMS devices.¹⁶ The goal of the work was to demonstrate that low friction rolling can be established at this size scale and to identify critical parameters, such as the surface coverage of the spheres, which need to be satisfied for effective lubrication. Sphere confinement suitable for extended cyclic testing, which has been achieved at larger dimensions,⁶ is outside the scope of the present work. To confirm that rolling friction is being achieved, a simple test based on the deposition of a thin gold coating onto the microsphere system was developed and introduced. In this chapter we show that the coefficient of friction and wear life of the lubrication system are dependent on both sphere diameter and load, as the individual spheres need to be able to withstand the contact pressures applied during testing.

In addition, the silica spheres and silicon substrate can be modified by the addition of monolayer films to investigate the effect of surface composition on microscale rolling friction. Molecularly thin films can be formed on the spheres and surrounding surfaces with trichlorosilane precursors, as the trichlorosilane moieties covalently bind to the spheres and substrate through siloxane linkages.¹⁷⁻¹⁹ As discussed in chapter II and as shown in previous chapters, trichlorosilane monolayers assembled on top of silicon substrates can decrease friction forces by an order of magnitude¹⁷ and significantly reduce stiction.^{19,20} In the hope of improving the frictional performance of the sphere systems, we have developed a protocol to functionalize the sphere/substrate systems with molecular coatings of either octadecyltrichlorosilane (C18) or (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (F6H2) precursors. While there have been numerous studies that spray coat ball bearings,²¹⁻²³ our work represents the first report of the molecular functionalization of a rolling friction system.

Experimental Methods

Deposition of Spheres

10 mL of a water solution containing a 5% mass fraction of silicon oxide spheres, with diameters of 4, 2, or 0.5 μm , were obtained from Corpuscular Inc. The coefficients of variation for the spheres were $< 2\%$ for the 4 and 2 μm spheres and $< 3\%$ for the 0.5 μm spheres. The 5% solution was diluted 1:60 with distilled water, creating an aqueous solution containing a 0.08% sphere mass fraction. 400 μL of the well-mixed aqueous 0.08% solution was deposited on the piranha-treated silicon substrates with a pipette. The samples were then placed in a vacuum chamber and put under a reduced pressure of 0.03 Torr for 10 min. The 10 min time period was found to be adequate to allow the spheres suspended in the solution to adhere to the substrate surface, but is sufficiently brief to prevent bubble defects from forming. The samples were then removed from the chamber and the excess water on the substrates was then siphoned off the surface with a micropipette. The samples were then once again placed under pressure for 10 min to evaporate any remaining water. Finally, all samples were sequentially rinsed with a gentle stream of ethanol and water, and then thoroughly dried with N_2 (the particles remain adhered to the surface throughout the rinsing and drying process). The samples were stored in Petri dishes until testing or functionalization was performed.

Functionalization of Microspheres

The trichlorosilane monolayers were formed by immersing the substrates, which were already layered with 2 μm diameter silicon oxide spheres, into 1 mM solutions of either the C18 or F6H2 precursors (the detailed procedure for monolayer formation can be found in Chapter III).

Quantitative Analysis of Coverage Area

Microscope images of the samples were acquired using an Olympus BX41 microscope with Pixera camera and Pixera Viewfinder Pro software. Two magnification lens were used (10x and 25x) to produce the images. Quantitative analysis of coverage area was achieved by using Image J software. The color contrast within the optical images was maximized and the sphere coverage was determined using the contrast distribution analysis tool. The coverage areas were determined by averaging the results of at least 3 separate images. The reported values and errors reflect the average and standard deviation of at least 4 independently prepared samples.

Microscale Friction Testing

The microtribometer was used to perform cyclic friction tests at multiple loads (9.8, 98, 245, 490, and 980 mN). For the lowest load tested, 9.8 mN, the probe tip was a 1 mm diameter stainless steel ball firmly glued onto the end of an 8 mm long pin and attached to the sensor via a suspension mounting cantilever. For the higher loads, the probe tip was a 4 mm diameter stainless steel ball contained in a holder. The contact radii achieved during testing are estimated using SEM images of the probe paths and found to be between 10-50 μm . All tests were conducted with a sliding speed of 1 mm/s and a scan length of 10 mm. Unless specified, the frictional tests were terminated once the coefficient of friction reached 0.20. Three tests were performed for each load on each sample. The coefficient of friction (μ) was determined using Amonton's law

$$F_f = \mu F_n \quad (8.1)$$

where the friction force (F_f) is proportional to the normal force load (F_n). The reported coefficients of friction (μ) were determined by averaging the forces measured during the low-friction rolling

stage. The reported values and errors reflect the averages and standard deviations of at least 4 independently prepared samples.

Results and Discussion

Sphere Dispersion and Confirmation of Rolling

To create the submonolayer coatings of silica spheres, a sphere / water solution was pipetted onto the silicon substrates, and then, the entire sample was placed under a reduced pressure. To prevent bubble defects from forming, the samples were returned to atmospheric pressure after 10 min and any remaining water on the surface was mechanically drawn off. The samples were then once again placed under vacuum to evaporate any remaining water. Using optical images, the coverage area for the three sphere sizes were estimated to be $56\% \pm 8\%$ (4 μm dia.), $51\% \pm 5\%$ (2 μm dia.), and $46\% \pm 4\%$ (0.5 μm dia.), whereas perfect 2-D hexagonal sphere packing would result in 90% coverage. Attempts to increase the surface coverage above the reported values, by increasing the sphere concentration or volume of the solution, resulted in multi-layering and vertical aggregates.

During the evaporation process, the silica spheres aggregate due to adhesive interactions between the silica spheres while in the water solution.²⁴ These microscale clusters are shown in the SEM images presented in Figure 9.1 (a-c). The attractive forces between the spheres become more significant with decreasing diameter²⁵ and, therefore, clustering is more pronounced for the smallest sphere size (Figure 9.1 (c)). During frictional testing, the rolling motion of the spheres disrupts the adhesive interactions, and the aggregates disperse to create a more microscopically uniform coverage (Figure 9.2 (a)). To confirm that rolling motion is occurring during frictional testing, we sputtered a ~ 10 nm thick coating of gold onto a 4 μm microsphere system. The coated samples were then tested with the tribometer and imaged with a scanning electron microscope. Since the underside of the spheres will not be exposed during sputtering, janus (or “two-faced”) spheres are created that contain a gold-coated region and a relatively bare silica region, which will become visible as the janus

spheres roll during frictional testing. SEM imaging shows the bare silica regions of the spheres (Figure 9.1 (d)), which confirms that rolling motion does occur. Furthermore, the weakly-adhered gold coating on the sphere was occasionally worn away upon probe-sphere contact. Figure 9.1 (d) clearly shows wear patterns that extend around the circumferences of the spheres, providing additional support that the sphere is rolling as it contacts the probe.

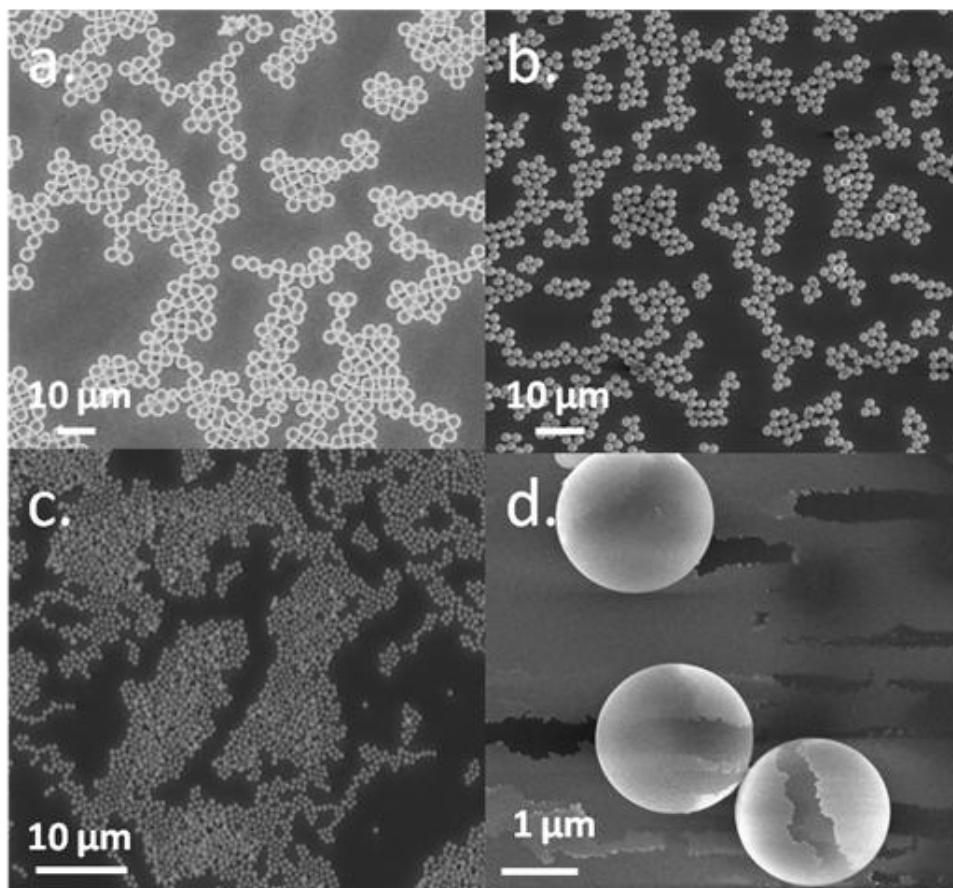


Figure 9.1. SEM images of the microsphere systems studied. Images (a-c) show the dispersion of the 4 μm diameter (a), 2 μm diameter (b), and 0.5 μm diameter (c) microsphere systems before frictional testing was performed. Image (d) displays the exposure of the uncoated “bottom” and the circumferential wear-tracks of the 4 μm spheres coated with 10 nm of gold, which demonstrates that rolling friction is being achieved.

Frictional Performance of Rolling-Element Lubrication Systems

Figure 9.2 shows a typical frictional test at a load of 98 mN for the 2 μm sphere system. As can be seen in the figure, an immediate decrease in friction is observed for the first few cycles, followed by an extended period of low friction, and then, an eventual rapid increase in the coefficient of friction. We believe that the higher frictional forces observed during the first few passes are due to the collisions occurring between the closely packed sphere clusters. To investigate the effect of close packing, microsphere systems that have lower initial surface coverages ($34 \pm 4\%$) than the reported averages were tested. These sparser systems did not exhibit the initial high friction forces, which supports our claim that the collisions between the spheres resists the initial rolling motion¹³ and results in slightly higher friction. After a few passes the dispersion of the spheres (Figure 9.2 (b)) allows unhindered rolling to be established. The substrate is devoid of any confinement barriers and, therefore, the wear track continually widens during testing as the spheres become more dispersed (Figure 9.2 (a,b)). Once the surface coverage decreases below a critical threshold (discussed further below), the pressure on the individual spheres becomes too great; instead of rolling, spheres begin to experience excessive compression and fracture (Figure 9.2 (c,d)), which increases the coefficient of friction. As testing continues, the remaining intact spheres experience even greater stress and eventually all the silica spheres are either crushed or dispersed, resulting in probe-substrate contact and a dramatic increase in the coefficient of friction. Complete failure occurs once the sphere fragments are pushed towards the ends of the wear track (Figure 9.3). At this phase the probe is scratching the silicon substrate, and the coefficient of friction values increase to ~ 0.6 , which corresponds to the values achieved for a bare silicon substrate.

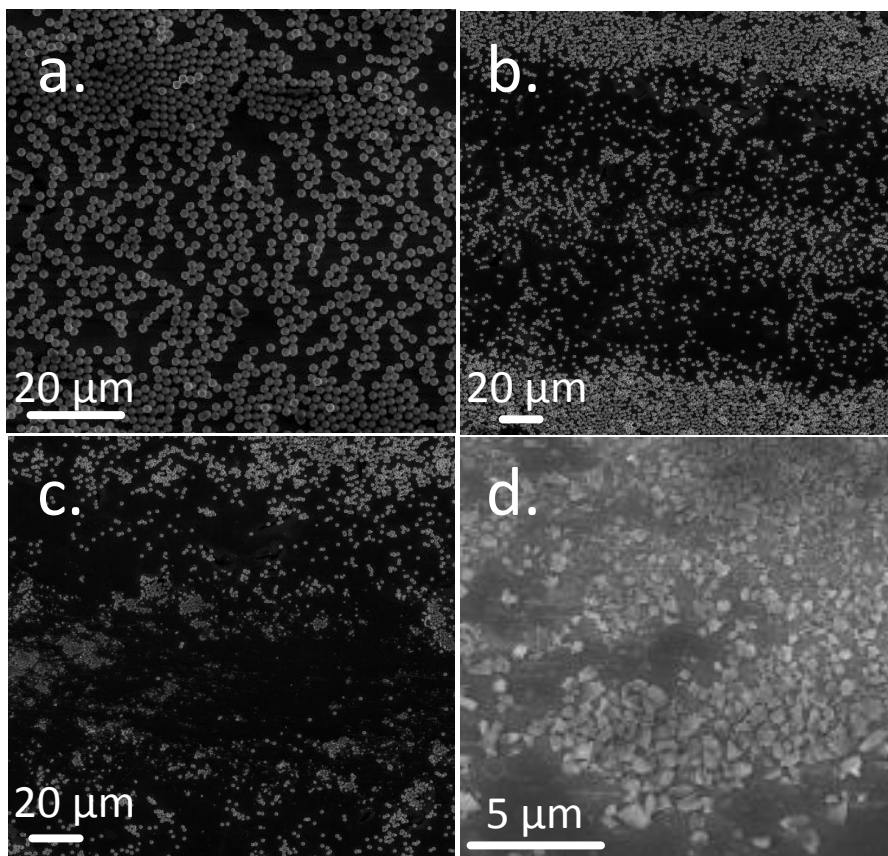
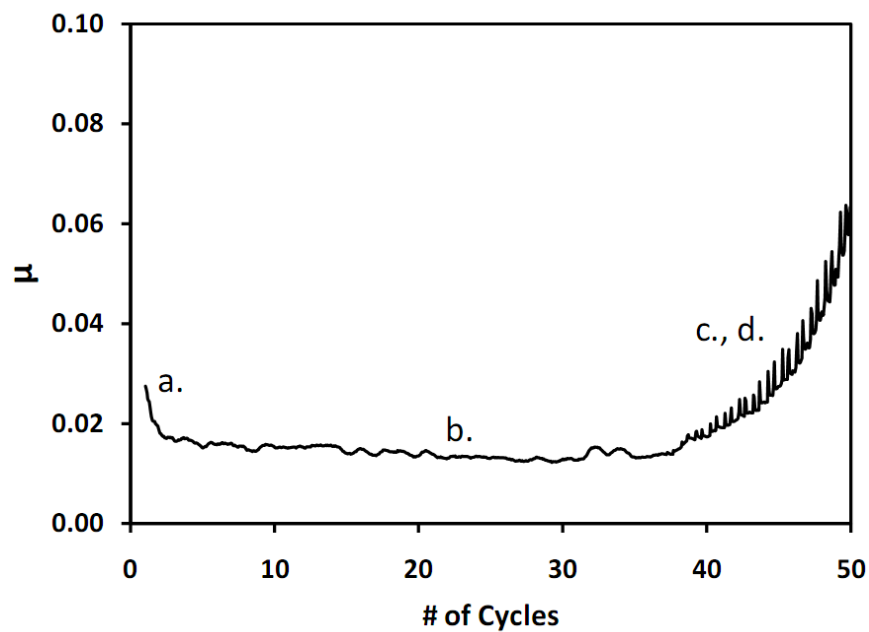


Figure 9.2. (Top) Long-term frictional performance of the 2 μm diameter sphere system. The cyclic tribology test was performed with a 4 mm diameter stainless steel ball contained in a holder at 1.0 mm/s with a scan length of 10 mm. (Bottom) SEM images of the 2 μm diameter sphere system show areal coverage during different stages of the cyclic test. Once the sphere coverage decreases to a critical level the pressure of the probe causes fragmentation of the individual sphere elements (d).

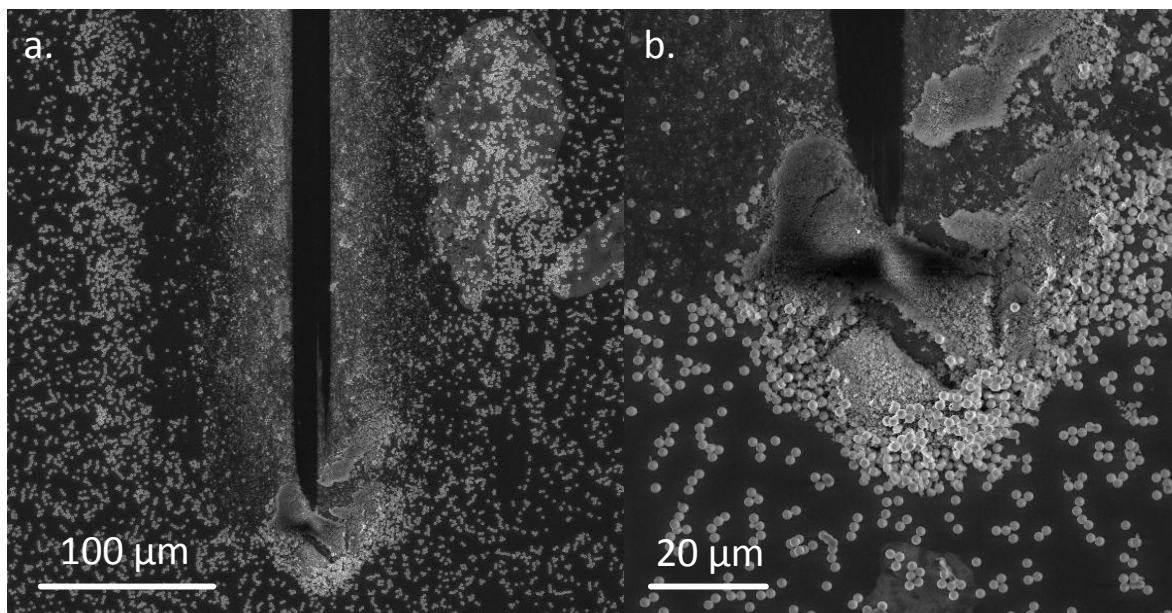


Figure 9.3. SEM images of the wear track of the silicon surface after complete failure for the 2 μm diameter system. Image (b) is a magnified image at the end of the wear track and displays the buildup of microspheres, microsphere fragments, and debris from the underlying silicon substrate.

To investigate the influence of load and sphere diameter on microscale rolling friction, we tested the three sphere systems at five loads: 9.8 mN, 98 mN, 245 mN, 490 mN, and 980 mN. The reported coefficients of friction (μ) were determined by averaging the forces measured during the low-friction rolling stage. As shown in Figure 9.4, the frictional performance is dependent on load and sphere diameter. The 0.5 μm system, which will be discussed further below, only achieved rolling friction at the lowest load tested, while rolling friction was established up to 980 mN for the 4 μm and 2 μm systems. At the 9.8 mN, 98 mN, and 245 mN loads, the 4 μm and 2 μm sphere systems produced test profiles very similar to Figure 9.2 and achieved extremely low coefficients of friction that were statistically indistinguishable from each other. Specifically, the 4 μm system had coefficient of friction values of 0.021 ± 0.006 (9.8 mN), 0.021 ± 0.004 (98 mN), and 0.020 ± 0.005 (245 mN), while the 2 μm system had coefficient of friction values of 0.020 ± 0.004 (9.8 mN), 0.019 ± 0.003 (98 mN), and 0.021 ± 0.004 (245 mN). The frictional benefit of rolling over sliding is considerable; the ~ 0.02 values achieved for the silica spheres is 30x less than the value achieved for

tribometer testing on a flat silicon surface.¹⁷ When the load is increased to 490 mN the coefficient of friction increases to 0.026 ± 0.005 (4 μm) and 0.035 ± 0.009 (2 μm) as the increased testing load puts a greater contact pressure on the spheres and begins to hinder the rolling motion.^{13,26} At 980 mN the rolling motion is severely affected and the coefficients of friction increase significantly to 0.08 ± 0.036 (4 μm) and 0.12 ± 0.035 (2 μm).

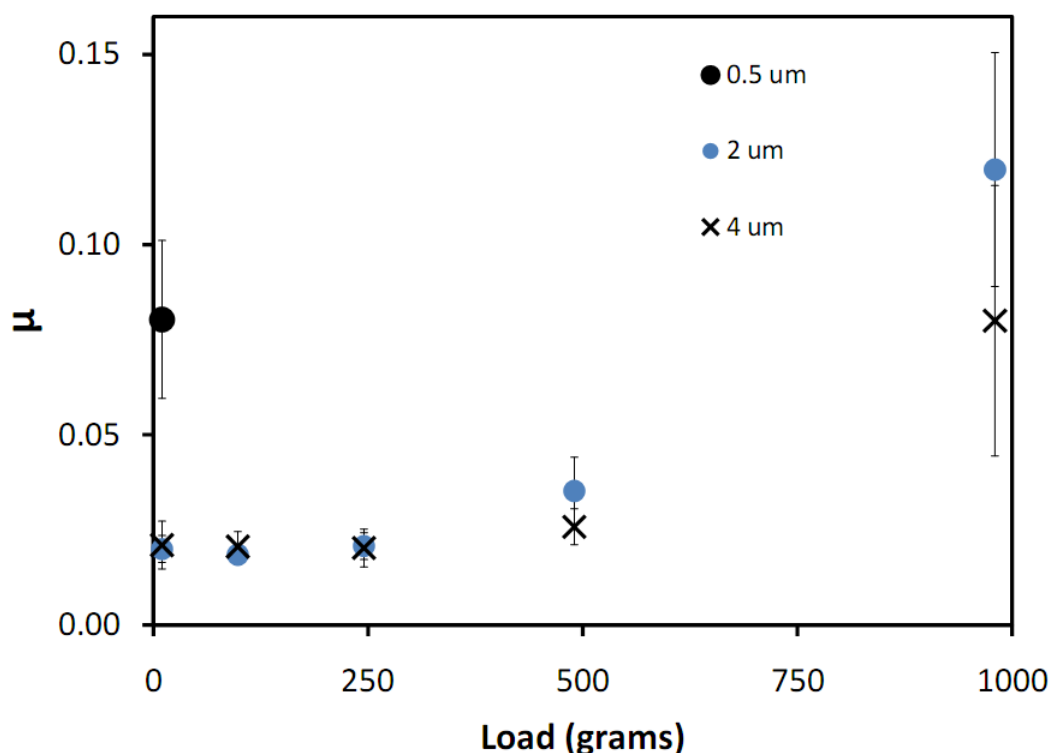


Figure 9.4. Effect of sphere diameter and load on the frictional performance of the silica sphere systems studied. Cyclic tribology tests were performed with a 1 mm diameter stainless steel probe tip for the 9.8 mN loads, while all other loads used a 4 mm diameter stainless steel ball contained in a holder. Test speed was at 1.0 mm/s with a scan length of 10 mm. The coefficient of friction was determined by averaging the forces measured during the low-friction rolling stage. The 0.5 μm diameter spheres only achieved rolling friction for the 9.8 mN load, and, therefore, there is only one data point for that diameter. Reported values and error bars represent averages and standard deviations, respectively, based on at least 4 independently prepared films.

The wear life of the sphere systems was also investigated and is presented in Figure 9.5. Failure was easily identified by a sudden spike in coefficient of friction and a dramatic increase in data noise (Figure 9.6). The trends are similar for the 4 μm and 2 μm systems, as the 9.8 mN and 98 mN loads resulted in comparable cycle lives followed by a decrease in wear life with increasing loads. The 4 μm system achieved wear life values of 33 ± 2 cycles (9.8 mN), 32 ± 2 cycles (98 mN), 15 ± 8 cycles (245 mN), 4 ± 2 cycles (490 mN), and 1 ± 0 cycles (980 mN), while the 2 μm system achieved values of 28 ± 16 cycles (9.8 mN), 31 ± 11 cycles (98 mN), 10 ± 2 cycles (245 mN), 4 ± 1 cycles (490 mN), and 1 ± 0 cycles (980 mN). The lack of confinement within the microsphere systems is responsible for the failure; the continuous dispersal of the spheres away from the probe track results in increased pressures on the individual spheres which remain in contact with the probe and eventually the contact pressure experienced by the spheres exceeds their material strength and fragmentation occurs. At higher loads the critical pressure is reached earlier and, therefore, the spheres are fragmented sooner (Figure 9.5). The wear life is almost identical at 9.8 mN and 98 mN loads, which would appear to disagree with our analysis. However, the 9.8 mN load was applied with a 1 mm diameter probe, while the 98 mN load was applied with a 4 mm probe. If the applied pressure is estimated with a simplified sphere-on-flat Hertz equation^{27,28} the 9.8 mN tests and 98 mN tests would produce similar pressures and, therefore, results in comparable cycle lives.

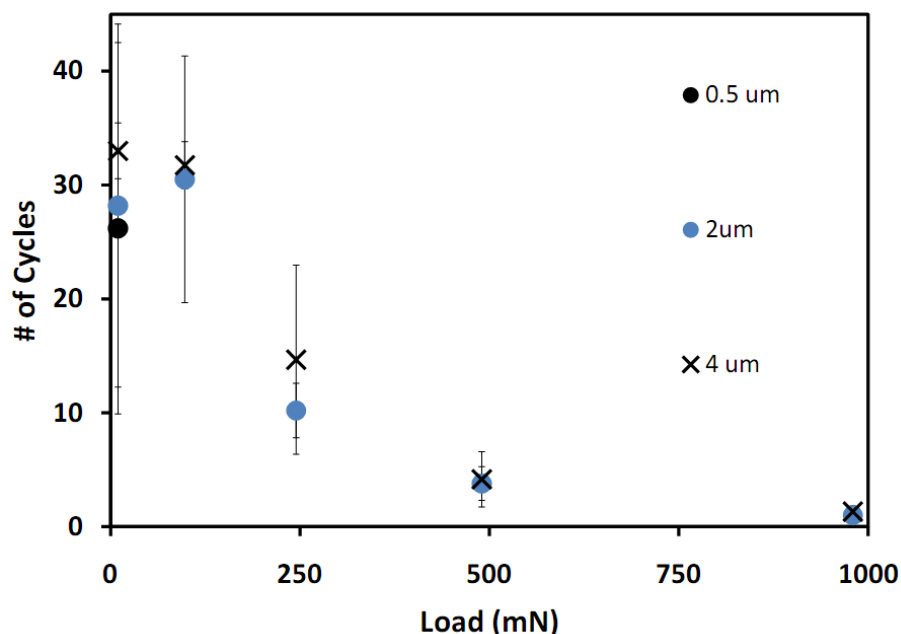


Figure 9.5. Effect of sphere diameter and load on the wear life of the silica sphere systems studied. Cyclic tribology tests were performed with a 1 mm diameter stainless steel probe tip for the 9.8 mN loads, while all other loads used a 4 mm diameter stainless steel ball contained in a holder. Tests were performed at 1.0 mm/s with a scan length of 10 mm. Failure was easily identified by a sudden and drastic increase in friction and an increase in signal noise (Figure 8.6). The 0.5 μm diameter spheres only achieved rolling friction for the 9.8 mN load, and, therefore, there is only one data point for that diameter. Reported values and error bars represent averages and standard deviations, respectively, based on at least 4 independently prepared films.

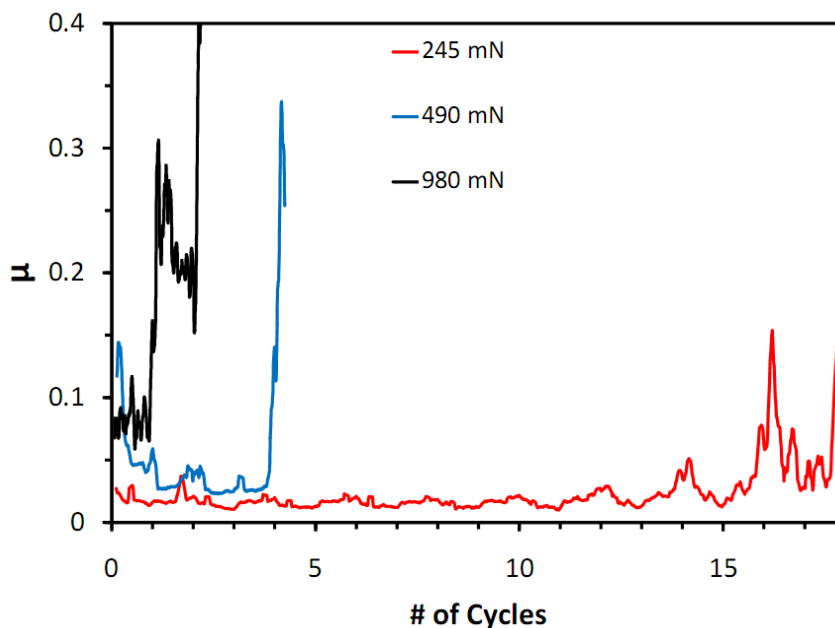


Figure 9.6. Long-term frictional performance of the 2 μm diameter sphere system at various loads. The cyclic tribology test was performed with a 4 mm diameter stainless steel ball contained in a holder at 1.0 mm/s with a scan length of 10 mm.

The performance of the microsphere systems is dependent on sphere radius, as larger spheres result in lower coefficients of friction and longer wear lives for a given load. The size effect was only marginal between the 4 μm and 2 μm systems (a difference in coefficients of friction was only observed at the 490 mN and 980 mN loads, while the differences in cycle-life were insignificant) but was evident for the 0.5 μm spheres. While the 4 μm and 2 μm systems were able to achieve rolling friction up to 980 mN, the 0.5 μm spheres were able to support rolling motion only at the lowest tested load of 9.8 mN, achieving a coefficient of friction of 0.080 ± 0.02 with an average cycle-life of 26 ± 16 . Even though the 98 mN load should provide a similar pressure as the 9.8 mN tests, the additional load of 98 mN was found to scatter the 500 nm spheres to a greater extent (most likely due to the increased loading rate). This additional dispersion reduced the contact area, thereby increasing the pressure above the yield strength of silica.

Influence of Surface Coverage on Frictional Performance

To confirm and further investigate the effect of sphere coverage on frictional performance, a series of 98 mN frictional tests with the 2 μm sphere system were performed and terminated at various times. The surface coverage of the spheres was estimated using SEM images and the coefficient of friction determined by averaging the friction force over the last full cycle before the test was terminated. As shown in Figure 9.7, a large increase in friction force occurs for the 2 μm system once the surface coverage of the spheres drops below 15 %. The surface coverage was found to decrease from the initial value of 51 % to 36 % after only two cycles. After the first couple of passes the rate of sphere dispersion slows considerably, as it took an average of 31 cycles (Figure 9.5) to reach the critical failure threshold of 15 % coverage. These results support our explanation of the frictional results; the continual scattering of the spheres gradually increases the contact pressure due to decreased contact area between the spheres and the probe tip. The increased pressure hinders the motion of the spheres, increasing the coefficient of friction, and eventually, the pressure exceeds the yield strength of the spheres and the spheres crack and fragment. In addition, the identification of the

minimum coverage needed offers important guidance for the development of advanced lubrication schemes that use containment of 2 μm silica ball bearings.

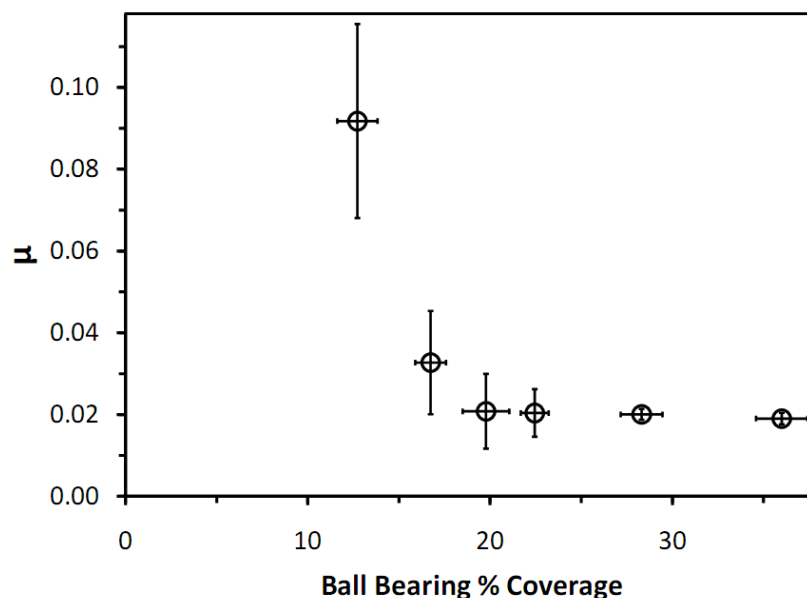


Figure 9.7. Effect of sphere surface coverage on the coefficient of friction. Cyclic tribology tests, which were terminated at various times, were performed with a 4 mm diameter stainless steel ball contained in a holder with a test speed of 1.0 mm/s and a scan length of 10 mm. The areal coverage of the spheres was determined using SEM images and the coefficient of friction calculated by averaging the friction force over the last full cycle before the test was terminated. The entire data set was compartmentalized to produce the lowest standard deviation for sphere coverage within individual groups, with each group consisting of at least 3 data points.

Monolayer Functionalization of the Microsphere Systems

In an attempt to reduce adhesive forces and improve the performance of the microsphere system, the 2 μm sphere system was coated with monolayers consisting of C18 or F6H2 molecules. The 2 μm spheres were first deposited on the silicon substrate and then the entire surface (substrate plus spheres) was coated by immersing the sample into 1 mM solutions of the precursor molecule. The resulting coatings, which would be partially incomplete due to the inaccessible regions where there is direct sphere-substrate contact, will contain either CH_3 (C18) or CF_3 (F6H2) termini. Surface coverage, using optical images, was calculated before and after the functionalization process and was

determined to be unchanged. The presence of the monolayer coating was confirmed using water contact angles. Before functionalization, the 2 μm sphere samples achieved advancing contact angles of $23 \pm 10^\circ$ and receding contact angles of $5 \pm 5^\circ$. After the CH_3 or CF_3 -terminated monolayers were formed the advancing contact angles rose to $142 \pm 6^\circ$ (CH_3) and $136 \pm 12^\circ$ (CF_3), signaling a dramatic decrease in the surface energy. The high advancing contact angles achieved for the samples are greater than those reported for flat monolayers (111° for CH_3 ^{29,30} and 120° CF_3 ³¹) due to the surface roughness provided by the deposited spheres.³² The surface roughness also caused high contact angle hysteresis, as the functionalized samples achieved receding contact angles of $77 \pm 5^\circ$ (CH_3) and $63 \pm 19^\circ$ (CF_3).

The frictional performance of the functionalized samples was tested with a 98 mN load and the minimum coefficient of friction achieved for the functionalized samples was found to be similar to the unmodified samples. Specifically, the C18 monolayer samples achieved a coefficient of friction of 0.023 ± 0.0026 and the F6H2 monolayer samples resulted in a value of 0.020 ± 0.0040 . The coated monolayers, however, did have significantly shorter wear lives. While the unmodified samples required 31 cycles (Figure 9.5) to fail, the coated sphere systems failed in 6 ± 3 cycles (CH_3) and 12 ± 4 cycles (CF_3). The lower cycle lives of the functionalized systems suggest that the sphere coverage decreased more rapidly during testing. The low-energy surfaces achieved by functionalization would dramatically reduce the adhesive interactions between the spheres and the substrate and, thus, promote quicker dispersal of the spheres beyond the probe track. Despite the poor wear life shown by the coated samples, functionalization of the sphere/substrate system may prove beneficial in next generation lubrication schemes as shearing surfaces which confine the spheres and ball bearing systems would benefit from lower energy surfaces and easier dispersion of spheres. The monolayer coatings can greatly reduce stiction caused by liquid adhesion and capillary condensation of water vapor from the environment.^{19,20,33} In addition, functionalization could be used to increase the wear life of microball bearing systems, as numerous studies at larger size scales have shown that surface coatings can delay failure.^{21-23,34,35}

Conclusions

We have investigated the frictional performance of lubrication systems based on rolling silica spheres. Silica spheres, either 4 μm , 2 μm , or 0.5 μm in diameter, were dispersed on silicon substrates by drop casting from an aqueous solution at reduced pressure. A simple test, involving a deposition of gold onto the microsphere system, was introduced to confirm that rolling motion has occurred. The coefficient of friction and wear life of the lubrication systems were investigated at numerous loads with a ball-on-flat microtribometer. The 4 μm and 2 μm systems performed similarly, with the 4 μm spheres achieving slightly lower coefficients of friction at higher loads than the 2 μm spheres. The dependence on sphere diameter was clearly seen with the 0.5 μm system, which failed immediately at loads above 9.8 mN. The lubrication systems tested in this paper did not attempt to confine the rolling spheres and, therefore, failure was brought on by the continual dispersion of the spheres. The decrease in the surface coverage of the spheres created higher contact pressures that ultimately increased enough to fragment the individual spheres. In addition, functionalization of the sphere systems was accomplished using C18 or F6H2 precursors. The molecular coatings decreased the surface energy of the spheres and substrate, allowing the spheres to be dispersed beyond the probe track quicker during tribometry testing. Overall, the 0.02 coefficient of friction values achieved with the 4 μm and 2 μm systems for numerous loads offers promise that rolling friction, if properly confined, can be utilized as a lubrication scheme for microscale devices.

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CHAPTER X

CONCLUSIONS AND FUTURE WORK

Conclusions

One of the most widely used lubrication systems for microscale applications are hydrocarbon monolayers, as these thin films create a low-energy surface that significantly reduces friction and stiction.¹⁻⁴ The focus for this thesis has been two-fold: developing novel lubrication schemes that look to improve upon the frictional performance of hydrocarbon monolayers and advancing the understanding of thin film lubrication by investigating the interfacial interactions of various thin films systems. Figure 10.1 displays the numerous lubrication schemes that I investigated and the coefficient of friction values they achieved when tested at a load of 98 mN and with unmodified probes. As can be seen in Figure 10.1, I was able to achieve μ values that are substantially lower than the those obtained with the best performing hydrocarbon film by developing a microsphere system that contains rolling elements. This lubrication system is based on a layer of silica spheres, which varied in diameter size (4 μm , 2 μm , or 500 nm), that are deposited onto a flat silicon substrate. In Chapter IX, I showed that the μ and wear life of the rolling lubrication system are dependent on sphere diameter and identified critical values of surface coverage and load which need to be satisfied for effective lubrication. In the hope of improving the frictional performance of the sphere systems, I modified the sphere/substrate systems with molecular coatings of either C18 or F6H2 precursors and showed that the monolayers caused quicker dispersal of the spheres.

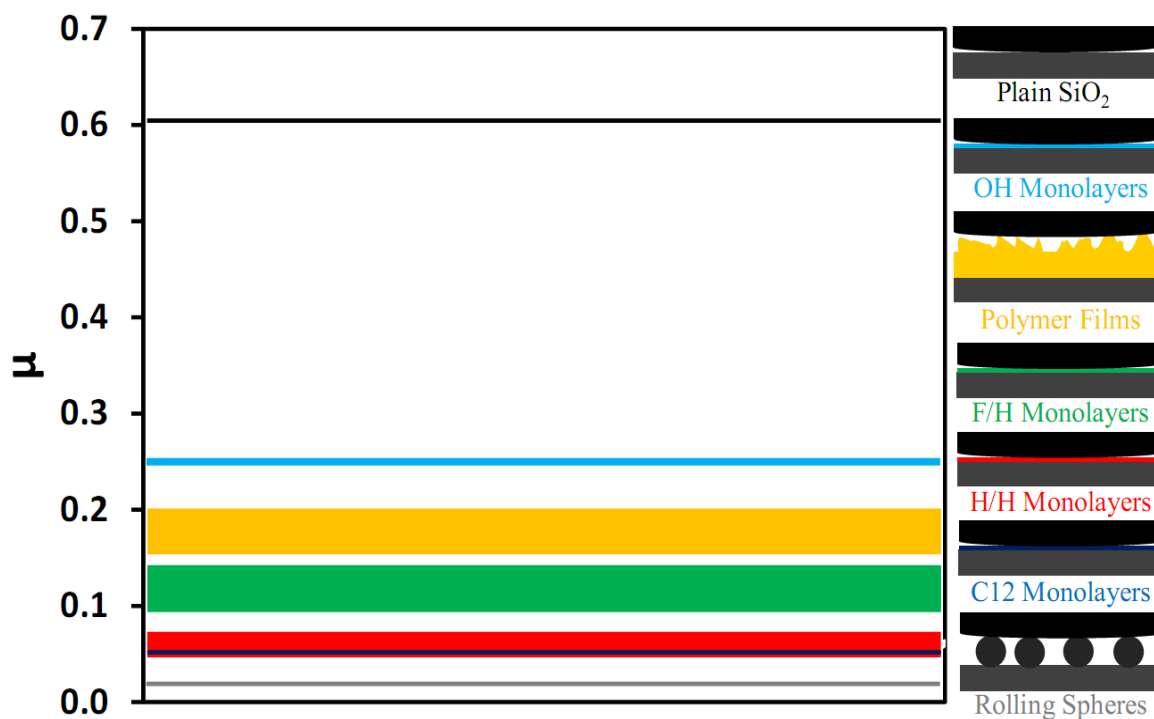


Figure 10.1. Summary of the coefficient of friction values obtained for the various lubrication systems studies at a 98 mN load and an unmodified probe.

Improving upon sliding friction, however, proved to be difficult. In Chapter IV, I investigated a variety of hydrocarbon / hydrocarbon (H/H) films and discovered that a liquid-like upper layer does not improve the frictional properties of monolayer films. In the study I varied the length of the two hydrocarbon components and also varied the ratio of long and short chain molecules in order to investigate the effect of chain mobility and oleophilicity on monolayer friction. The results indicated that monolayer thickness greatly affects the tribological properties of a monolayer but that molecular mobility within the film and interfacial oleophilicity are less important at the loads and speeds tested. Once a H/H mixed monolayer has sufficient internal stability to prevent interactions between the probe and the underlying substrate, the tribological properties were indistinguishable from one-component monolayers. The investigation into mixed monolayers was expanded in Chapter VI to include well-mixed F/H monolayers, which were created by forming a sparse fluorocarbon film and backfilling with alkylsilane molecules of various lengths. F/H

monolayers containing C8, C12, and C16 precursors significantly reduced the μ when compared to one-component fluorocarbon monolayers, but did not improve on the frictional performance of pure hydrocarbon monolayers (Figure 10.1). Interestingly, the F/H films containing the longer hydrocarbons of C18 and C22 showed load-dependent behavior, as the μ for these monolayers decreases as higher loads are applied. The load-dependant behavior was attributed to entanglement of the upper-layer hydrocarbons, which create a viscous liquid-like region on top of the F/H films.

Rather than attempting to improve the frictional performance of monolayers, Chapters V and VII focused on understanding thin film lubrication. In Chapter V, I conducted tribometry testing with various monolayers, which varied in their surface energy, to investigate the influence of functional group exposure and adhesion on microscale friction. The monolayers that contain CH_3 and CH_2 moieties had similar frictional performance and showed negligible adhesive forces. The trichloroacetate-terminated monolayer showed an increase in friction force, but did not show significant adhesion, indicating that the increase in coefficient of friction is the primary cause for the higher friction forces. The OH-terminated monolayer, however, resulted in a significant increase in adhesion and resulted in the highest frictional forces. My investigation into monolayer friction was significantly shifted in Chapter VII, as I conducted testing with monolayer-coated probes rather than stain-less steel probes. In contrast to CFM studies where higher friction has been measured when probe and substrate have the same terminal group, I found at the microscale that CH_3 probes and substrates produced the lowest friction forces, regardless of the other mating surfaces. The results showed that higher energy probes increase friction forces during testing, most noticeably for the OH monolayer substrate. In addition, the effect of water vapor on microtribometry was investigated by performing the microtribometry tests at various humidity levels. The driest environment (3% humidity) produced the lowest F_f values for any probe/substrate system that contained a high energy surface. The reduction in frictional forces was attributed to the reduction of adhesive forces.

Chapter VIII presented microtribometry tests performed on various polymer-coated substrates. To gain insight into the influence of topography on polymer / polymer friction, I tested

various substrate films that varied in their surface morphology. As opposed to hydrocarbon monolayers, the frictional performance of the PM and SH films were dependant on the surface energy of the probe, as the C18 probe monolayer diminished the plowing force and shear strength. When polymer probes were used on the polymer substrates the ratcheting mechanism was the dominant influence, as highest friction forces occurred when microscale asperities were present. In addition, tribometry tests were performed with the substrates submerged under water. For the C18, PM, and SH probes, the water environment had little influence on the frictional results and suggests that, at the loads and speeds tested, hydrophobic interactions do not show any beneficial lubrication properties and does not prevent the substrate and probe from mating. The control probe, in contrast, showed decreased frictional forces for the polymer substrates in the water environment. This decrease was attributed to a chemisorbed water layer on the hydrophilic probe that lowered the shear and decreased the adhesion between the probe and substrate.

An overarching conclusion from the experimental results for the monolayer and polymer investigations is that the lubricating performance of monolayers is difficult to improve upon. Liquid-like mobility, which has been shown to improve polymer friction,^{5,6} had no influence on the performance of the hydrocarbon monolayers. Incorporating fluorocarbon molecules, which create an ultra-low energy surface,⁷ into hydrocarbon monolayers did not improve the frictional properties. Lowering the ambient humidity close to zero or incorporating water into the lubrication system had no significance when both the probe and substrate were hydrocarbon monolayers. Once a hydrocarbon monolayer is thick enough to prevent probe-substrate interactions, smooth hydrocarbon monolayer is an extremely effective lubricant that can negate influences, such as plowing and capillary forces, that are usually detrimental to effective lubrication.

Future Work

Monolayer Friction

As discussed in Chapter I and II, monolayers prepared from trichlorosilane molecules have proven to extend the product life of MEMS devices, but they do gradually wear away and are not sufficiently robust to extend the lifetime of MEMS devices to acceptable levels. As shown in this thesis, hydrocarbon monolayers have superior lubricating properties and are difficult to improve upon: research should therefore be focused on extending their durability. The tribological stability of monolayers scales with chain length,⁸ but the longest chain length studied has only been 22 carbons in length⁹ (molecules longer than this are commercially unavailable). A longer molecule can be synthesized to prepare “thicker” silane monolayers. The increased cohesive energy of the film¹⁰ should extend the wear life of the monolayers considerably. Another strategy to promote further stability is to incorporate UV cross-linking into a monolayer film. Molecular precursors containing diacetylene units and trichlorosilane moieties can be synthesized (Figure 10.2). Diacetylenes have the ability to cross-link with each other when exposed to UV light. Monolayers created from diacetylene-containing trichlorosilanes have the potential to yield a highly robust surface due to the intermolecular cross-linking brought on by the diacetylene groups.

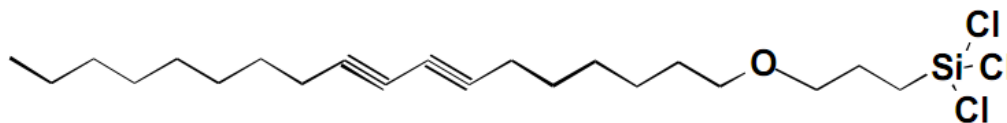


Figure 10.2. Example of a diacetylene-containing trichlorosilane adsorbate.

Polymer Friction

Advanced research into polymer friction is focused on a variety of areas, with the effect of surface alignment, novel composites, and mechanochemistry being a few of the active fields of research.¹¹⁻¹⁴ Rather than pursue another area of polymer friction research, I would continue to investigate the role of asperities and try to construct a more quantitative model linking topography and other surface properties to polymer friction. Additional polymer / polymer testing can be performed with different polymer films (PTFE, PDMS, etc) of varying morphologies in an attempt to isolate the influence of various parameters, such as surface energy and surface roughness, on polymer friction. Additional characterization of the polymer surface can also be done. SEM and AFM images of the polymer surfaces can be taken after the tribological tests have been performed to assess the topography changes and quantify how much deformation occurs.

Rolling Lubrication

For the rolling friction investigation I used a flat silicon substrate that did not attempt to confine the microspheres. Any practical rolling scheme must confine the rolling elements and provide long-term performance. To confine the spheres, microchannel arrays (Figure 10.3) can be fabricated using e-beam lithography or by an anisotropic etch of silicon in KOH.¹⁵ The height of the channel would be $\sim \frac{1}{2}$ height of the rolling element and the channel will be closed on each end. Methods will then need to be developed to disperse the silica microspheres in the channels to achieve uniform coverages. One can examine various solvents as well as the surface composition of the balls and at the tops and within the channels to aid the filling of the channels with particles.

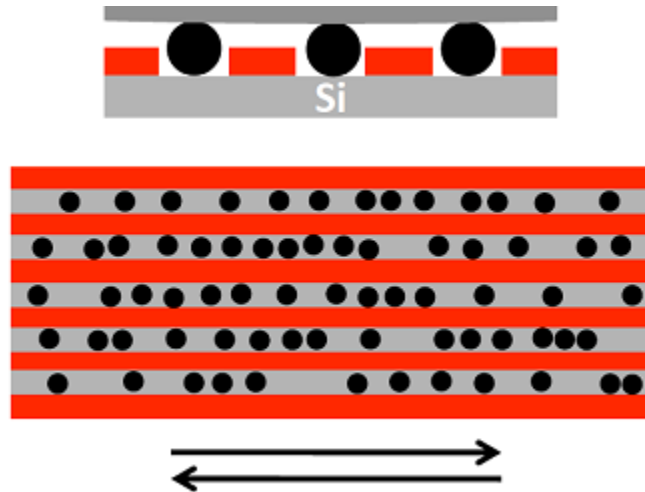


Figure 10.3. Side view (top) and top view (bottom) of a proposed rolling lubricant system. The sliding force atop this surface is directed in the plane of the page (top) and left/right (bottom).

Once the confined system has been developed, numerous investigations can be undertaken. Through experiments and modeling, the range of particle coverage within the channels that achieves the lowest frictional coefficients can be identified. The channel surfaces can be modified with lubricant films, such as ionic liquids or monolayers, to investigate the effect of mobile lubricant on the frictional performance and longevity of the particle. When the most promising system has been identified, the rolling scheme can be instituted in a real MEMs system.

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