Design of nanocomposite polymer coatings for MEMS applications

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Design of nanocomposite polymer coatings for MEMS applications

by

Duangrut Julthongpiput

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For the Major Program
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ABSTRACT

The recent evolution in microelectronics of combining electrical and mechanical functions has brought about the exciting field of microelectromechanical system (MEMS). As the dimensions of the components shrink, adhesion, stiction, friction, and wear become a significant technological barrier for the successful development of durable microdevices. In this thesis, we investigate wear-resistant, nanocomposite, molecular coatings from advanced polymers with controlled nanomechanical and nanotribological properties from the prospective of long-term applications for MEMS. We discuss fundamentals governing the mechanical and tribological properties on a micro scale associated with the morphology and microstructure of these molecular coatings.

In order to fabricate wear-resistant and superelastic molecular coatings, several types of the molecular designs are proposed and tested in this work. All designs are based on chemical attachment of the polymer layers onto a functionalized silicon surface. We focus on developing two different kinds of molecular coatings: reinforced elastomeric layers from grafted block-copolymers and polymer brush layers grown by the “grafted to” technique. A more complicated design included bilayered nanocomposite coatings consisting of a hard polymer layer placed on the top of an elastomeric layer to regulate surface adhesion and to increase surface stiffness of nanocomposite bilayers. Another design incorporates a paraffinic oil component to assure the presence of highly mobile molecules inside of the elastomeric phase. This oily fraction can be a source of an instant supply of mobile lubricant to a deformed contact area, thus providing potential self-lubrication and self-healing mechanisms for surface areas affected by excessive deformation. We observed that the interfacial assemblies, as presented in this paper, exhibited very low friction coefficient, low stiction, and better wear stability as compared to other, non-structured, non-tethered, or non-reinforced organic molecular lubrication coatings widely used as boundary lubricants. These results have interesting implications for the use of ultrathin grafted polymers as molecular lubricants.
CHAPTER 1

INTRODUCTION

1.1. General Introduction to Nanolubrication

The integration of miniaturized mechanical components with microelectronic components has spawned a new technology, known as microelectromechanical systems (MEMS).\(^1\) It promises to extend the benefits of microelectronic fabrication to sensing and actuating functions.\(^2\)\(^,\)\(^3\)\(^,\)\(^4\) One of the core technological processes underlying MEMS is termed surface micromachining which involves the fabrication of micromechanical structures from deposited thin films.\(^5\)\(^,\)\(^6\) Historically, silicon has formed the basis for the well-established integrated-circuit (IC) technology. As a consequence, polycrystalline silicon (polysilicon) is the most commonly used structural material in surface micro machining. However, silicon displays high stiction that prevents the free, non-destructive motion of microparts. In addition, their short operation lifetime is caused by high surface energy and the brittleness of a silicon oxide surface layer with well-developed nanograin surface texture.\(^7\) High surface energy of such a surface is due to the high concentration of silanol (Si-OH) groups, which results in a hydrophilic surface (low contact angle, close to 0° for clean surfaces). This leads to complete surface wetting under normal air/fluid conditions, and to the formation of very strong capillary forces between micrometer-sized parts.\(^8\)

Integration of sensing and computing to actuation is currently in its embryonic stage. Rapid actuation requires fast moving contacting surfaces. Frictional heating associated with moving parts requires innovative materials as well as creative design. Adhesion and stiction of silicon become the dominant issues for durability and reliability of MEMS devices.\(^11\) To reduce stiction, new materials are required to modify surface properties of silicon. Molecular lubricants with ultimate thickness less than 10 nm should provide reduce surface energy, low shear modulus and static friction coefficient, and tailored dynamic behavior, along with the ability to self-repair, sustain variations of temperature and humidity, and have long shelf-life.
A variety of organic molecular films were used as prospective boundary lubricants including adsorbed organic layers, Langmuir monolayers, grafted polymer brushes, fluidic layers, and organic self-assembled monolayers (SAMs). Langmuir-Blogett (LB) was, indeed, the first technique to provide the chemist with the practical capability to construct ordered monolayer assemblies. A monolayer film can be deposited on a flat surface using a single molecular type. There have been many surface science studies on molecular interactions, surface forces, and molecular organization using LB technique to deposit surfactant molecules (amphiphiles) on mica, glass, gold, or silicon. The technique utilizes the ability of the surfactant molecules to pack closely at an air-liquid interface with an ordered monolayer structure. When a substrate is moved through the water-air interface, a monolayer can be transferred during emersion (retraction or upstroke) or immersion (dipping or downstroke). A monolayer usually will be transferred during retraction when the substrate surface is hydrophilic, and the hydrophilic head groups interact with the surface. On the other hand, if the substrate surface is hydrophobic, the monomer will be transferred in the immersion, and the hydrophobic alkyl chains interact with the surface. Over the years, many molecules have been studies, such as fatty acid, silane, thiols, phospholipids, and polymeric films. Most of these films behave like a solid, the molecules are tightly packed. However, when they are under contact stress, the film fractures and breaks down. Hence the durability of the films is relatively low. LB films can also be deposited as liquid and mixed solid-liquid state on well-defined surfaces. However, non-polar molecules or high molecular weight polymers are difficult to deposit uniformly on a surface.

The traditional LB technique only works well in a system that is well defined, i.e., purity of molecule, hydrophobic functional head group, and well-defined surfaces. When it comes to depositing complex mixtures of molecular weights, mixed functional groups, dip coating is better suited. Vapor phase deposition of molecule in vacuum is also feasible if the vapor pressure of the molecule to be deposited is low enough. Spin coating can also be done. However, all these techniques have problems in depositing mixed molecules especially in controlling the film thickness and surface concentrations. The success of depositing different molecules on a surface at a monolayer level with different molecular weights, functional
groups, and molecular structures depends largely on how the molecules pack together (geometric compatibility, orientations, size, shape). If the molecules are not anchored through chemical bonding, then surface reorganization often takes place forming various islands of molecular aggregations of various thicknesses. The deposition area needs a lot of research to define the parameters necessary to control thickness and surface concentrations.  

1.2. Current Developments in Nanolubrication

1.2.1. Alkyl-based Self-Assembled Monolayers (SAM)

To overcome low wear resistance of physisorbed organic monolayers, SAMs were proposed as prospective candidates for robust molecular lubrication (Figure 1). These nanometer-thick monolayers have been introduced in the 1980s for surface modification through chemical adsorption of functional organic molecules with the formation of chemical bonds between end reactive groups and surfaces. The two most popular compounds for this use are alkyl-silanes and alkyl-thiols, which bind to oxide layers of silicon/metals and gold surfaces, respectively. These monolayers are indeeded much more mechanically stable than classic physisorbed monolayers, and show greatly reduced friction coefficients. A great technological advance with regard to these molecular lubricants is that self-assembling processes are technologically compatible with wet-chemistry processes in the microfabrication industry.

SAMs with chemical composition similar to conventional LB films (long alkyl chains) are observed to be much more stable against shear stresses while showing similar friction coefficient and low adhesion. Both thiol- and silane-base SAMs, show comparable nanotribological behavior, with silane layers being more stable. Typical value of friction coefficient for SAMs against silicon/silicon nitride counterparts is in the range from 0.02 to 0.1, and the reduction of friction forces in comparison with bare substrates by a factor of 5 to 10 is usually reported.
Significant variation of friction forces with different lengths of alkyl chains was observed for several SAMs (Figure 2). Increasing the number of atoms in alkyl tails from 2 to 18 resulted in a 5-fold decrease in friction forces. This phenomenon was attributed to very different microstructure of tethered monolayers composed of short and long chains. For short chains, disordered monolayers are formed with a high concentration of conformational defects. Long-chain molecules form more ordered monolayers with tight packing of alkyl tails. Disordered states along with possible larger contact areas result in higher level of energy dissipation during sliding process for short-chain SAMs. Long-chain SAMs are tightly packed, and allow little indentation due to increased modulus. They dissipate little energy, which results in low friction coefficient and higher wear resistance. Large reversible deformation of molecular packing was observed in experiments with the nanotip piercing through a whole monolayer and probing the underlying gold surface. Therefore, unlike conventional LB films, chemically tethered monolayers are capable of significant elastic deformation, and can restore their shape after varying intrusive micromechanical contact.

Among these classes of films, the most widely used in today industry is the octadecyltrichlorosilane-based SAM (OTS). This coating film permits the wide-ranging control of surface properties, from completely hydrophobic (contact angle of 100-110°) with
low capillary forces to completely hydrophilic. A greatly reduced friction coefficient is usually observed.\textsuperscript{18} Although these SAM coatings have been shown to effectively alleviate release and in-use stiction, the limitations of the chlorosilane SAM coating arise from the coating procedure. The coating process is somewhat cumbersome in that the SAM solution must be freshly made and appropriately conditioned immediately before each coating. This is due to the sensitivity of the SAM solution to ambient humidity and the tendency of the SAM precursors to polymerize. As a consequence, great care and control are needed for the coating process to be successful.

Figure 2. General trends in variation of adhesion force, friction forces and elastic modulus of monolayers composed of molecular chains of different lengths.\textsuperscript{16}
1.2.2. Functional SAMs

SAMs with functional surfaces are formed by chemisorption of molecules with two reactive ends. Their microstructure is similar to conventional SAMs with terminal reactive groups located predominantly at the monolayer surface (Figure 3). Such surface groups are capable of selective interactions and can be used for the grafting of molecules with appropriate functionality. To date, a variety of functional SAMs have been fabricated with carboxyl, hydroxyl, amine, sulfate, epoxy, and other chemical groups.

The general formula of a functional SAMs shows two types of functionality, $R_nSiX(4-n)$. Silicon (Si) is the center of the silane molecule, which contains an organic functional group (R) [ex: vinyl, amino, chloro, epoxy, mercapto, etc.], with a second functional group (X) [ex: methoxy, ethoxy, etc.]. The functional group (R) will attach to an organic resin while the alkoxy group (X) attaches to an inorganic material or substrate to achieve a "coupling" effect.

Figure 3. Schematic of an organic monomolecular film functional SAMs. The circles indicate chemical bonding and triangles indicate reactive surface groups. (b) Molecular model and (c) chemical structure of the 3-aminopropyltrimethoxysilane SAM.
Silane coupling agents are predominately used as mediators, binding organic materials to inorganic materials. As a result, silanes will improve the electrical and mechanical strength properties of materials in wet or dry conditions. The inorganic group (X) of the silane molecule will hydrolyze to produce silanol, which forms a metal hydroxide or siloxane bond with the inorganic material. The organic group (R) of the silane molecule will react with the organic material to produce a covalent bond. As a result the organic material and the inorganic material are tightly bound together after heating.

**Functionalization of SAMs on glass and silicon wafer**

The use of trichlorosilanes for the preparation of SAMs on hydroxyl-terminated surfaces (e.g. glass and oxidized silicon wafers) was first reported by Sagiv in 1980.\(^{22}\) Since then, the simple n-alkyltrichlorosilane SAMs have been investigated extensively, and have been reviewed by Ulman.\(^{23,24}\) One of the main interests is the formation of multilayers and their use in non-linear optical devices.\(^{25,26}\) Other fields of interest are the use of SAMs on glass for biological and chemical sensing.\(^{27}\) Recently, Reinhoudt et al. have shown the chemisorption of 3-aminopropyltriethoxysilane on hydroxylated surfaces and the terminal amino groups were reacted with a variety of reagents to introduce the desired functionality as illustrated in Figure 4.\(^{28}\)

![Figure 4. Schematic representation of the preparation of functionalized SAMs.\(^{48}\)](image-url)
1.2.3. Grafted polymer layers

An alternative approach to surface modification is the formation of molecularly thick layers from adsorbed macromolecular chains (Figure 5). Physically absorbed polymer layers with nanoscale thickness form weakly adhered coatings with poor surface stability and a tendency to dewet at elevated temperatures and shear stresses. Introduction of functional groups as terminal reactive ends or multiple reactive centers into flexible backbones promotes much higher surface stability. Chemical or other strong attachment of macromolecular fragments to solid substrates stabilizes polymer layers and prevents dewetting phenomena. If surface tethering allows a certain degree of mobility, such layers possess enhanced long-term wear resistance caused by the replenishment of the worn areas from surrounding intact areas.

![Figure 5. Possible configurations of polymer macromolecules with one, two, and multiple reactive groups grafted to a surface.](image-url)

The application of this approach was demonstrated for a number of grafted polymer layers. Polymer layers were grafted to mica, carbon, gold, silicon, silica, biomedical surfaces, polymer films, and fibers. These layers possessed low adhesion, intermediate friction coefficient, and remarkable wear resistance to surface damage far exceeding one for physisorbed films or bare surfaces.
Grafted block copolymer layers

The block copolymers with immiscible blocks form phase-segregated nanostructures that determine the whole set of their properties. Recently, the attention has been drawn to the study of organized thin films from block copolymers, because of their potential for such applications as organized coatings, adhesives, lubricants, and templates for lithography. The block copolymers are observed to form microphase morphologies in very thin films. These films undergo series of structural reorganizations with decreasing film thickness. The surface microdomain morphology depends upon the t/d ratio where t is the film thickness and d is the equilibrium spacing of the microdomain structure. Great deal of the works in this area is devoted to the thin thermoplastic elastomer films composed from ABA block copolymers where A constitutes thermoplastic material (e.g. polystyrene (PS)) and B elastomer (e.g. polybutadiene or ethylene/butylenes copolymer). These polymers, composed of thermoplastic and elastomeric blocks are called thermoplastic elastomers (TPE). In such materials, the mechanical performance of the reinforced rubber is combined with the straightforward processing of thermoplastics due to the physical network of flexible chains.

Van Dijk and van den Berg studied thin films of poly [styrene – b - butadiene - b-styrene] (SBS) triblock copolymer with the film thickness ranging from 30 to 150 nm. It was found that these films possessed microstructure close to the one for the bulk material, where PS phase formed cylindrical microdomain network. The orientation of PS cylinders depended on film thickness. Motomatsu et al. used atomic force microscopy for the investigation of microphase domains of poly-[styrene – b - (ethylene-co- butylene) - b- styrene] (SEBS) triblock copolymer film with 170 nm thickness. The surface of the film exhibited characteristic cylindrical morphology typical for the TPE materials with similar composition. To date, only relatively thick (>30 nm) films from block copolymers were obtained by spin-coating and solvent casting and their microdomain structure was studied.
*Grafted polymer brush layer*

Another surface modification involves the chemical attachment (grafting) of the polymers with functional terminal groups in the form of polymer brushes.\(^{43}\) Polymer brushes attracted attention in 1950s when it was found that grafting polymer molecules to colloidal particles was a very effective way to prevent flocculation.\(^{44}\) In other words, one can attach polymer chains, which prefer the suspension solvent to the colloidal particle surface; the brushes of two approaching particle resist overlapping and colloidal stabilization are achieved. Subsequently, it was found that polymer brushes could be useful in other applications such as new adhesive materials\(^{45}\), protein-resistant biosurfaces\(^{46}\), lubricants\(^{47}\), and polymer surfactants\(^{48}\).

Polymer brushes refer to an assembly of polymer chains which are tethered by one end to a surface or an interface (Figure 6)\(^{49}\) Tethering is sufficiently dense that the polymer chains are crowded and forced to stretch away from the surface or interface to avoid overlapping, sometime much farther than the typical unstretched size of a chain. These stretched configurations are found under equilibrium conditions; neither a confining geometry or an external field is required. This situation, in which polymer chains stretch along the direction normal to the grafting surface, is quite different from the typical behavior of a flexible polymer chain in solution where chain adopts a random-walk configuration.\(^{50}\)

To characterize the polymer layer, several parameters should be evaluated.\(^{51}\) The amount of grafted polymer, \(\Gamma (\text{mg/m}^2)\), is calculated from the ellipsometry and AFM thickness of the layer \(h\) (nm) by the following equation:

\[
\Gamma = h \rho
\]  

(1)

where \(\rho\) (1.05 g/cm\(^3\)) is the density of PBA.
The grafting density, $\Sigma$ (chain/nm$^2$), i.e., the inverse of the average area per adsorbed chain, is determined by:

$$\Sigma = \frac{\Gamma N_A \times 10^{-21}}{M_n} = \frac{6.023 \times 100}{M_n}$$

(2)

where $N_A$ is Avogadro’s number and $M_n$ (g/mol) is the number-average molecular weight of the grafted polymer.

The distance between grafting sites, $D$ (nm), is calculated using the following equation:

$$D = \frac{1}{4\pi\Sigma}^{1/2}$$

(3)

The mean square end-to-end distance ($h_\Theta$, nm) of a non-disturbed polymer chain in bulk state is calculated from

$$h_\Theta = k M_w^{0.5}$$

(4)

where $k$ is 0.068 for PS and PBA and the radius of gyration, $R_g$, is calculated from

$$R_g = h_\Theta/\sqrt{6}$$

(5)

Alexander studied the structure of brushes under variable solvent condition in the moderate-density regime in which the chain strongly interact with their neighbors. The thickness of the brush would be related to the dimensionless grafting density $\sigma$, and the chain length $N$ through the following scaling laws:

$$h \approx N\sigma$$  (in a poor solvent)  

(6)

$$h \approx N\sigma^{1/3}$$  (in a good solvent)  

(7)
where $\sigma = (a/D)^2$ is the dimensionless grafting density and assume $a \approx 0.6$ for PBA taking the account of similar flexible polymer chains with PS. 53

![Figure 6. (a) Schematic representation of two neighboring grafted chains and definition of the radius of gyration, $R_g$ and (b) end-grafted polymer brush.](image)

The grafted brush layer can be produced from either solution or melt. It is commonly observed that only a limited layer thickness can be obtained by adsorption of polymer from solution, since after some chains have become attached, incoming chains have to diffuse against a concentration gradient to reach the solid surface. In addition, there is an entropy loss arising from the change in conformation of both the incoming and the adsorbed polymer to accommodate another chain. For these reasons, typically only a few milligrams of polymer per square meter adsorbs onto a solid surface from a good or $\theta$ solvent, regardless of whether the chains become chemically bound to the surface or only physisorbed. 58

1.3. Nanolubrication and Its Requirements

Generally, all of these developments substantiate the idea that surface modification can be an effective means of controlling the surface properties of MEMS. If an organic film can perform effectively, the issue is how to keep the film intact impact and if damaged, how
to repair it or to resupply molecules for the film to repair itself. When the lubricant molecules are removed from a location either by shear or oxidation/evaporation, molecules from other location can move in to cover the surface, this can be defined as self-repairing. Under typical high-speed contacts, asperity temperatures are high. So molecules will have to withstand thermal decomposition and oxidation. The vapor pressure and volatility therefore need to be extremely low. Resistance to oxidation and decomposition will need to be high.\textsuperscript{11}

To summarize, lubrication at nanoscale (control of adhesion, stiction, friction) requires lubricant molecules with are non-volatile, oxidation, and thermal decomposition resistant, and self-repairing or self-regeneration. In addition, the nanolubricating films should have strong adhesive strength and cohesive strength to resist shear stresses. Organization of such films, whether single molecule species or mixed species, has profound influence on film performance. The most important property of the film is its bonding characteristics with the surface (adhesive strength of the film).\textsuperscript{11}

1.4. Goal

The ultimate goal of this project is the understanding of the effective ways for the development of wear-resistant, nanocomposite, molecular coatings from advanced polymers with controlled nanomechanical and tribological properties to enhance the performance of micro- and nanodevices such as bio/chemo-fluids (biochips), and provide new capabilities that include large reversible local deformations, adaptive surface mechanical properties, and self-healing mechanisms. Relationship between microstructure and surface properties is a primary form of this work.

1.4. Objective

In order to fabricate wear-resistant and superelastic molecular coatings, we focus on several critical steps:

- Fabrication of epoxysilane SAMs as a binding layer.
Fabrication of a nanocomposite/reinforced rubber on silicon surface.

Fabrication of bi-layer coatings composed of compliant interlayer and hard capping layer for the improvement of microtribological properties of elastomeric nanolayers.

Enhancement of nanotribological performance of elastomeric nanolayers by introduction of paraffinic oil within the layer.

Fabrication of two-component polymer brushes.

Understanding the morphology and microstructure of these molecular coatings.

Understanding the mechanical and tribological properties on a micro-scale.

Testing the limits of mechanical and thermal stability of these layers under local mechanical shearing.

1.6. Approaches

In order to fabricate wear-resistant and reinforced molecular coatings, the chemical attachment of the polymer layers onto the functionalized silicon surface will be explored. There are several critical elements in the molecular design of these layers. First, the polymer itself should possess highly reversible elasticity typical for rubber phases and should easily adapt to any complicated 3D nanoscale surface topography. Secondly, the surface stiffness of this layer should be relatively high to prevent penetration of a sharp asperity through a whole layer. Thirdly, the layer should be strongly attached to a silicon surface. Fourthly, its thermal stability should be reasonably high to prevent layer deterioration during local thermomechanical stresses. And finally, the advanced design of such layers should include potential self-healing and self-lubricating mechanisms.

With these requirements, we propose several prospective molecular designs that will be targeted in the project (Figure 7):

1. Epoxy-terminated SAMs-molecular glues for polymer layers (Figure 7(a)).
2. Grafted reinforced rubber layer (Figure 7(b)).
3. Capped layer (Figure 7(c)).
4. Oil enhanced layer (Figure 7(d)).
5. Homo and binary composite polymer brushes (Figure 7(e)).

Figure 7. Various designs of nanocomposite/reinforced elastomeric films chemically grafted to the silicon substrate via reactive interfacial SAM.
CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Surface Modification and Preparation

Highly polished single-crystal silicon wafers of {100} orientation (PureSilicon, Inc.) were cut in pieces of approximately 1.5 by 2 cm before modification. Any surface modification and preparation consists of four stages: (1) oven-dried glassware preparation; (2) ultrasonic bath and piranha treatment; (3) SAM formation; and (4) polymer layer formation.

2.1.1 Oven-dried glassware preparation

All glassware was first cleaned by detergent and rinsed with water. Chromic sulfuric acid solution was prepared by mixing 1:10 of potassium dichromate with super saturating sulfuric acid. The glassware were submerged in Chromic sulfuric acid solution for roughly 30-40 minutes, rinsed with water, and additional rinsed with high purity water (18 MΩcm, Nanopure). Then, clean glassware was dried in 100°C oven.

2.1.2 Ultrasonic bath and piranha treatment

The substrates were first placed in Nanopure water and cleaned in an ultrasonic bath for 10 minutes, and placed in a hot piranha solution. Piranha solution was prepared by mixing of 30% of H₂O₂ (30% solution in water) added slowly with 70% concentrated sulfuric acid (97%). The substrates were placed in the 90°C heated piranha solution for roughly 1 hour. Then, the substrates were removed from the solution and rinsed six times with high purity water (18 MΩcm, Nanopure). After that, the substrates were dried under a stream of dry nitrogen, placed into 15 ml-tubes, filled with nitrogen firmly closed with teflon caps, and then immediately taken the nitrogen-filled glove box.
2.1.3 SAM formation

An epoxysilane compound, (3-glycidoxypropyl) trimethoxysilane (Table 1) was purchased from Gelest Inc. ACS grade toluene and ethanol were obtained from Aldrich and were used as received. The epoxysilane solution in toluene of different concentration (from 0.1-1 volume %) was prepared in oven-dried glassware in a nitrogen-purged glove box, because the epoxysilane is very moisture sensitive. For 10 substrates modification, 50 ml of 1% solution was prepared by mixing 0.5 ml epoxysilane with 50 ml toluene. After the solution preparation, the clean substrates were immersed in the solution for different periods of deposition time (from 1 minute to 24 hours) as illustrated in Figure 8. After the deposition was completed, the modified substrates were removed from the solution, and rinsed four times with toluene. Additionally, the substrates were placed in toluene in the ultrasonic bath for 10 minutes. The SAMs formed were dried under a stream of dry nitrogen inside a cleanroom 100 facility. After preparation, samples were stored in desiccators to prevent moisture in air.

![Figure 8. Schematic of SAM process.](image)

2.1.4 Polymer layer formation

*Polystyrene and poly (butyl acrylate) homopolymer brushes*
Carboxyl-terminated polystyrenes (M\(_n\) = 4,500 to 672,000) and carboxyl-terminated poly (butyl acrylate) (M\(_n\) = 6,500) were obtained from Polymer Source, Inc (Table 1). All samples possessed a relatively narrow molecular weight distribution with M\(w\)/M\(_n\) in the range 1.05-1.4. The initial PS and PBA polymer film is spin-coated from 1 wt % toluene solution onto the wafers modified by the epoxysilane SAM. The specimens were placed in a vacuum oven at 150 °C to enable the end groups to graft to the epoxy-terminated substrate. At high temperature, carboxylic groups were able to react with the epoxy groups of the monolayer. The mechanism of the reaction between the anhydride group and the epoxy group is also quite well understood.\(^{59}\) It is caused by the reaction of impurities with the second component. Hydroxy impurities react with the anhydride of a dicarboxylic acid monoester. The resulting free carboxylic group reacts with an epoxy group of an ester, creating a new hydroxy group, which can react again with an anhydride. In this manner, the reaction continues. For carboxyl-terminated PS, we expect to avoid the multiple anchorings due to the fact that all chains are monofunctional (Figure 9). In addition, at given grafting conditions, PS and PBA monomeric units are incapable of reacting with SAMs. The unbounded polymer is removed by multiple washing with toluene, including washing in an ultrasonic bath.

![Figure 9. Microstructure of homopolymer brush grafted to epoxy-terminated surface.](image)
Table 1. Materials, chemical formulas, and molecular weights.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical Formula</th>
<th>Mn (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxysilane</td>
<td>$C_9H_{20}O_5Si$</td>
<td>236.34</td>
</tr>
<tr>
<td>PS-COOH</td>
<td></td>
<td>4.5K 16.9K 28.5K 45.9K 143.0K 672.0K</td>
</tr>
<tr>
<td>PBA-COOH</td>
<td></td>
<td>6.5K</td>
</tr>
<tr>
<td>SEBS</td>
<td>Poly(ethylene-co-butylene)</td>
<td>41.0 K</td>
</tr>
<tr>
<td>PPP</td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td>Epoxy</td>
<td></td>
<td>NA</td>
</tr>
</tbody>
</table>
Polystyrene / poly (butyl acrylate) binary brushes

The initial PS/PBA (Table 1) polymer film was spin-coated from 1 wt % toluene solution onto the wafers modified by the epoxysilane SAM. The thickness of the polystyrene film measured by ellipsometry was about 40 ± 3 nm. The coated wafers were annealed for 18 h in a vacuum oven at 150°C to enable the end groups to graft to the substrate. The polymer that had not grafted was removed by multiple washings with toluene and additional washing in an ultrasonic bath.

Poly [styrene – b - (ethylene-co- butylene) - b- styrene] (SEBS)

SEBS copolymer was Kraton 1901 (Shell) with styrene and maleic anhydride (MA) content 29wt% and 2wt%, respectively (M_n=41,000 g/mol, M_w/M_n=1.16 (Figure 10). The SEBS copolymer films were deposited on the epoxy-terminated SAM from toluene solution and melt. The MA groups of the rubbery block poly (ethylene-co-butylene) (PEB) were able to react with the epoxy groups of the monolayer, thus anchoring the rubber block to the surface. For grafting from the solution, the epoxysilane modified silicon wafers were immersed in the copolymer solutions of different concentrations (from 0.25 to 8 wt %) for 24 hours.

For the grafting from the melt, the initial polymer film was spin-coated from the 1.5 wt. % toluene solution onto the wafer modified with the epoxysilane SAM. The thickness of the spin-coated film measured by ellipsometry was 60 ± 6 nm. The specimen was placed in a vacuum oven at 150°C for 45 – 360 minutes to enable the MA groups to diffuse and graft to the epoxy-terminated substrate. In all experiments, the unbounded polymer was removed by multiple washings with toluene, including the washing in an ultrasonic bath. After nine washes, the thickness of the layer did not decrease with additional treatment in an ultrasonic bath. The samples were dried under the stream of dry nitrogen.
SEBS/oil nanocomposite polymer gel layer

SEBS (see above) has been used for grafted polymer layer. The paraffinic oils, \( \text{C}_{15}\text{H}_{32} - \text{C}_{24}\text{H}_{50}, \) (Aldrich) were used as lubrication additives (Table 2). Grafted polymer layers with 8 nm thickness were placed in a sealed tube and kept for saturation with oil vapor at 60 °C for 24 hours. The swelling of bulk SEBS block copolymers in paraffinic oil was performed at 60 °C. The circular SEBS specimens with a radius of 3 mm and a thickness of 1.5 mm were immersed in an oil bath. After specified time of swelling, the specimens were removed from the oil, blotted, and weighted on an electronic balance. Volume swelling for specimen was estimated as the ratio of the final weight to the initial weight of the sample. The thickness of the swollen samples was measured by using the digital caliper and the value of thickness changed from 1.5 mm to 3.5 mm after 35 hours of swelling. The sample thickness was required for calculation of value of diffusion coefficient as discuss in Chapter 6.

![Chemical Structure of the SEBS with FEB (69%), PS (29%), and MA (2%)](image)

Figure 10. Chemical Structure of the SEBS with PEB (69%), PS (29%), and MA (2%).
Table 2. Chemical formulas, molecular weights, and melting points of different paraffinic oils.

<table>
<thead>
<tr>
<th>Paraffinic oil</th>
<th>Chemical formula</th>
<th>Formular weight (g/mol)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentadecane</td>
<td>( \text{C}<em>{15}\text{H}</em>{32} )</td>
<td>212</td>
<td>9.9</td>
</tr>
<tr>
<td>Octadecane</td>
<td>( \text{C}<em>{18}\text{H}</em>{38} )</td>
<td>254</td>
<td>29</td>
</tr>
<tr>
<td>Eicosane</td>
<td>( \text{C}<em>{20}\text{H}</em>{42} )</td>
<td>282</td>
<td>37</td>
</tr>
<tr>
<td>Tetracosane</td>
<td>( \text{C}<em>{24}\text{H}</em>{50} )</td>
<td>338</td>
<td>50</td>
</tr>
</tbody>
</table>

**EP/PPP composite layer**

The EP was Novolac resin D.E.N. 431™ provided by Dow Chemical. The amino functionalized PPP, kindly supported by Dr. Valerie V. Sheares, was prepared in a two-step synthesis. First, poly (4'-fluoro-2, 5-diphenylsulfone) (PI) was synthesized via Ni (0) catalyzed coupling of 2,5-dichloro-4'-fluorodiphenylsulfone. Nucleophilic aromatic substitution of PI with 4-aminophenol gave the amino functionalized PPP.

To estimate the bulk properties of EP/PPP material, EP was mixed and reacted with an equivalent amount of PP (EP/PPP = 0.9/1.0 (wt./wt.)) at 150 °C for 1 hour and 200 °C for 6 hours. The resulting cross linked material has excellent solvent resistance to DMAc, m-cresol and THF, with no weight gain after a 24-hour immersion period in each solvent. Differential scanning calorimetry showed a glass transition temperature of 175 °C. Thermogravimetric analysis of the amino PPP cured epoxy had 5 and 10% weight loss values in air of 392 and 408 °C, respectively. The EP/PPP layers were deposited by spin coating of the EP/PPP mixture (0.9/1.0 (wt./wt.)) dissolved in THF. Different concentrations (0.15% - 0.7%) of EP/PPP solution were used to produce top layers with the thicknesses from 4 nm to
22 nm as was measured by ellipsometry. The specimens were cured in a vacuum oven at various temperatures (45 – 110 °C) (Figure 11).

![Diagram](image)

Figure 11. Microstructure of capped layer grafted to epoxy-terminated surface.

### 2.2 Characterization Methods

#### 2.2.1 Contact angle measurement

Contact angle technique is sensitive to the chemical composition of the top molecular layer and is a relative simple, inexpensive, and popular technique for characterizing surfaces (Figure 12). There are two types of the contact angle; static and dynamic. A static angle, which is determined by the equilibrium of interfacial tension, is formed at a stationary liquid front. A dynamic contact angle, which is determined by the balance of the interfacial driving force and the viscous retarding force, is formed at a moving liquid front. Hence, dynamic contact angle is rate-dependent. Static contact angle was used in this project and can be analyzed in the terms of "apparent" surface coverage or the fraction of silicon surface screened by a film, $\beta$. The Cassie equation assumes a simple "two-phase" model of surface structure and provides the relationship.
\[ \cos \theta_m = \beta \cos \theta_L + (1 - \beta) \cos \theta_{si} \]  

(8)

Where \( \theta_m \) is measured contact angle, \( \theta_L \) is contact angle for a complete layer, and \( \theta_{si} \) is contact angle of bare silicon.

In this work, film surfaces were examined by static contact angle (sessile droplet) measurements using a custom-designed optical microscopic system. Droplets (1.5 - 2 \( \mu l \)) of Nanopure water were placed randomly over the surface. Contact angles were determined within one minute after droplet deposition. All reported values were an average of at least six measurements. The shape of the drop was observed with a microscope equipped with a CCD camera, and the contact angle was measured at a monitor screen (Figure 13).

Figure 12. A water contact angle picture.

Figure 13. Schematic drawing of contact angle measurement.
2.2.2 Ellipsometry

Ellipsometry is a non-destructive optical technique, which deals with the measurement and interpretation of changes of the polarization state of polarized light undergoing oblique reflection from a sample surface. The quantities measured by an ellipsometer are ellipsometric angles $\Psi$ and $\Delta$ which are related to the complex ratio of the Fresnel reflection coefficients $R_p$ and $R_s$ for light polarized parallel (p) and perpendicular (s) to the plane of incidence such as

$$\rho = R_p / R_s = \tan \Psi \exp(i \Delta) \quad (9)$$

The complex reflectance ratio $\rho$ is completely determined by an amplitude ($\tan \Psi$) and a phase $\Delta$ and characterizes the differential changes in amplitude and phase. These changes are related to a transformation of a shape and orientation of the ellipse of polarization, respectively.

Figure 14 illustrated schematic diagram of ellipsometry and sample structure model. In order to deduce unknown parameters of a sample under investigation, a model for the sample structure is first constructed with initial estimates of the parameters. These parameters (e.g. thickness and refractive index) are then varied to generate a set of calculated $\Psi^{\exp}$ and $\Delta^{\exp}$. The initial parameters of the model parameters are transformed finally into true parameters of the sample, such as thickness and optical constants.

In this project, the film thickness was determined by ellipsometry with the angle of incidence of $70^\circ$. The silicon oxide thickness was measured for each silicon wafer after the piranha solution treatment and before film deposition. The thickness of the silicon oxide layer was determined to be within 0.8 - 1.2 nm for different wafers. The index of refraction of the epoxysilane monolayer and silicon oxide was considered to be equal to the "bulk" value of 1.46$^{63}$ and 1.429$^{64}$ respectively. The refractive index for SEBS was estimated via additive
molar contributions. All reported thickness values were averaged over six measurements from different areas of the substrate.

![Ellipsometry diagram](image)

**Figure 14.** (a) Schematic diagram of ellipsometry measurement (InOmTech, Inc.). (b) A model of the sample layer structure.

### 2.2.3 Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectra were collected on an FTIR-8300 spectrometer (Shimadzu) equipped with an attenuated total reflectance (ATR), which probes the surface layer in the range ~0.5-3 μm. The sample is held in optical contact with prism. For oil enhancement experiment, the SEBS/C15D32 films were prepared by spin-coating on a silicon wafer, and the coated silicon wafer was attached to the ATR crystal by using a clamp. FTIR spectra were recorded every
20 minutes after deposition. IR absorption bands for both SEBS and C_{15}H_{32} are located around 2864-2968 cm\(^{-1}\) due to the chemical identity of the hydrocarbon-based polymer and the paraffinic oil. Thus, it was impossible to determine the oil concentration within the SEBS films. As a replacement fluid for these experiments, we used a deuterated analog of the paraffinic oil, C_{15}D_{32}. Its characteristic IR absorption bands are located in the different range of the spectrum, at 2094 and 2194 cm\(^{-1}\). Therefore, the deuterated oil, C_{15}D_{32}, can be used for the monitoring of the amount of oil inside the polymer.

2.2.4 Atomic Force Microscope (AFM) measurement

AFM is a powerful and advanced technique, which is used to measure the morphology, microroughness, and material differentiation of surfaces. Also, AFM is used to study mechanical, adhesive, and frictional properties of the materials. The basic principles of AFM technique are that the probe is scanned over the surface in an X-Y raster pattern. A laser focused on the cantilever is reflected on to a segmented photodiode detector to monitor the deflection of the cantilever due to surface topography (Figure 16.). A feedback loop maintains a constant force on the sample by adjusting the height of the cantilever to compensate for topographical feature. The result is a three-dimensional map of the sample surface.\(^{66}\)

![Figure 15. Picture of an AFM.\(^{66}\) ](image-url)
Figure 16. The scanning force microscope takes advantage of atomic interaction to map out molecular features of a surface.

Two basic AFM modes that were used in this project were tapping mode and contact mode. They were used for some time with varying success for a range of materials. Each has limitations, which are discussed below.

**Tapping Mode**

Tapping mode imaging is a key advance in AFM of soft, adhesive or fragile samples. This patented technique allows high-resolution topographic imaging of sample surface that is easily damaged, loosely held to their substrate. Tapping mode imaging overcomes the limitations of the conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever’s resonant frequency using a piezoelectronic crystal (Figure 17). The piezo motion causes the cantilever to oscillate with
high amplitude (the free air amplitude, typically greater than 20 nm) when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000 to 500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillating is necessary reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is due to identify and measure surface features.66

Figure 17. Tapping cantilever in free air (a) and on sample surface (b).66
Height and phase image

The tapping mode scan provides topography data, such as height and phase image as illustrated in Figure 18. Phase imaging is an extension of the tapping mode. By mapping the phase of the cantilever oscillation during a scan, it goes beyond topographical data to detect variations in composition, adhesion, friction, viscoelasticity, and other properties. Applications include contaminant identification, mapping of components in composite materials, and differentiating regions of high and low surface adhesion or hardness. For this work, silicon tips with spring constant 50 N/m were used. Imaging was done at scan rates in the range of 1-2 Hz and 90° scan angle. The images were scanned at scale ranging from 0.5*0.5 μm to 20*20 μm.

![Figure 18. The scanning force microscope image of epoxysilane monolayer, (a) Height Image, (b) Phase Image.](image)

Light and Hard Tapping image

During the scanning in the tapping mode the cantilever oscillates vertically near its resonance frequency and tip makes contact with the sample surface only briefly in each cycle of oscillation. When the tip contacts the surface, the vibrational characteristics of the cantilever vibrations change due to the tip-sample interaction. The feedback mechanism of the tapping mode is controlled by the set-point amplitude ratio $r_{sp} = A_{sp}/A_0$, where $A_0$ is the amplitude of the free oscillation and $A_{sp}$ is the set-point amplitude such that during scanning...
the observed amplitude of oscillation is maintained at $A_{sp}$ by adjusting the vertical position of the cantilever. $A_0$ was chosen about 40 nm. For the "light" and "hard" tapping, the set point amplitude ratio, $r_{sp}$, was 0.9±0.05 and 0.45±0.05, respectively, as recommended in Ref. 68.

**Contact Mode**

In conventional contact mode, the probe tip is simply dragged across the surface and the resulting image is a topographical map of the surface of the sample. While this technique has been very successful for many samples, it has some serious drawbacks. The dragging motion of the tip and the surface can cause substantial damage to both sample and probe and create artifacts in image data.66

Figure 19 illustrates the basic principle of contact mode imaging. The AFM system is comprised of two main components: 1) the scanner; 2) the AFM detection system. The scanner houses the piezoelectric transducer. The piezo element physically moves the sample in the X, Y and Z direction. The detection system consists of a laser which generates a spot of light that is reflected off of a microfabricated cantilever onto a mirror and finally into a pair of photodiodes. The position of the spot is determined by circuitry, which generates a voltage from the difference between the two photodiodes (A-B). The circuit outputs a voltage ranging from +10V to -10V depending on the position of the spot on the two photodiodes.66

The AFM system maintains the tip at the end of the cantilever in contact with the sample surface. The sample is scanned under the tip in X and Y. Features on the sample surface deflect the cantilever, which in turn change the position of the laser spot on the photodiodes. This position change is read by the feedback loop. The feedback loop moves the sample in Z to restore the spot to its original position.66
Figure 19. Contact AFM Concept. (a) The tip scans a flat position, maintaining the laser beam at the center of the photodiode array. (b) As the tip encounters a raised feature, the cantilever is pushed up, deflecting the laser beam upward. (c) The Z piezo retracts, the cantilever recenters the laser beam onto the photodiode array. (d) Tip encounters a decline in the sample topology, the cantilever is pushed down, deflecting the laser beam downward. (e) The tip is pushed down until the laser beam recenters on the photodiode array (A=B).

**Thickness Measurement**

For thickness evaluation from AFM data, we used a "scratch" test. Scratches were produced with a sharp steel needle at different loads or by multiple scanning with a stiff tip with a high normal load (several μN). The surface were scanned in the 4*4 μm scan size and
scratched at the middle in 1*1 μm as illustrated in Figure 20. This approach is used frequently for AFM measurement of organic and polymer layers and produces reasonable results.\textsuperscript{69}

Figure 20. Scanning force microscope image of PS films, which was scratched by multiple scanning with a stiff tip in contact mode.

Adhesive measurement

Adhesion between the tip and sample can develop for a number of reasons. Under ambient air conditions, most surfaces are converted by a layer of adsorbed gases, which are typically several nanometers thick. When the scanning tip touches this layers, capillary action causes a meniscus to form and surface tension pulls the cantilever down into the layer. Trapped electrostatic charge on the tip and surface can contribute additional adhesive forces. Adhesive forces were measured from force-distance curves as pull-off forces. Pull-off forces were determined from the cantilever deflection (point B, Figure 21) in a retraction mode of a
force-distance curve. The number of data points collected in one approaching-retracing cycle varied from 128 to 256 with increments in the range 2-4 nm. Elimination of the capillary forces was achieved by scanning in fluid. For these experiments we used a 1-mL drop of aqueous solution placed on the substrate surface.70

Figure 21. Force-distance curve and different regimes of the tip-surface contact: (A) jump-in contact (designated as a point of physical contact in the AFM technique); (B) pull-off (adhesive force); (C) loading part (compliance). Inset shows the long-range repulsive forces. Separation distance is defined by using point A as a reference point with zero coordinate.70

**Micromechanical measurement**

Force volume mode, which utilizes the collection of the force distance curves (FDC) over selected surface areas, was used for micromechanical analysis (MMA) of polymer layers. A single FDC records the forces acting on the tip as it approaches to and retracts from a point on the sample surface (Figure 21).71 Force volume mode allows for the micromapping of the mechanical properties of polymer surfaces with nanometer scale resolution, while obtaining topographical information simultaneously.72, 73 Typically, we used 64x64 pixels within 1x1 μm surface areas to do micromapping with a lateral resolution of 15 nm. Data collected were processed using an MMA software package developed in our lab which provides means for calculation of localized elastic modulus, depth profile of elastic
modulus, reduced adhesive forces, and surface histograms of elastic moduli and adhesive forces from experimental images as described elsewhere.\textsuperscript{74} Spring constants of cantilevers were determined from a resonant frequencies and the tip-on-tip method according to the procedures described earlier.\textsuperscript{75, 76} Tip radii were evaluated with scanning of reference gold nanoparticle specimens and a deconvolution procedure.\textsuperscript{77}

### 2.2.5 Microtribometer

An oscillating friction and wear tester (microtribometer) is used to characterize the frictional characteristics of the polymer gel layers (Figure 22). The 3 mm diameter steel ball with a smooth surface (microroughness less than 10 nm) is mounted in a carrier head and oscillated against a stationary planar specimen with an applied load of 0.3 N and 1.8 N, which correspond to the Hertzian pressure of 300 MPa and 1.2 GPa, respectively. Sliding speed is 4.43 mm/sec with a stroke length of 3 mm.

![Schematic drawing of Microtribometer](image)

Figure 22. Schematic drawing of Microtribometer.\textsuperscript{78}
2.2.6 Auger Electron Spectroscopy (AES)

AES is used primarily for identifying chemical constituents at the surface and interfaces of conducting and semiconducting materials. The analysis depth for most transitions of interest is 1-5 nm. With the recent introduction of field emission sources, single point probe size < 10 nm can be achieved. Alternatively, the electron beam can be rastered over much larger areas (0.5 mm$^2$) to obtain average surface compositions. In addition to the secondary electron images that provide topographic information, the spectra, depth profiles, element specific line scans, and maps can be obtained and stored for subsequent computer processing.\(^79\)

The sample size for Auger analysis can range from a few millimeters to about 1-2 centimeters. Conducting materials such as metals and semiconductors can be analyzed directly. Insulating samples (glasses, polymers, etc.) are much more difficult to analyzed because of charging effects. They may require a thin conductive coating to prevent electrical charging of the specimen.

In AES the excitation source is a finely focused electron beam that impinges on a sample surface. The interaction of the primary electron beam with the surface results in the generation of Auger electrons via the Auger process, along with secondary electrons. Scanning the electron beam over the surface provides topographic information through secondary electron imaging (see section 2.2.7 on scanning electron microscopy).\(^79\)

In this work, the physical and elemental characteristics of the surface are investigated by PHI-670 Auger electron spectroscopy. AES surface analysis is performed using a field emission gun with an accelerating voltage of 5 kV and a current of 0.0211 μA. The working potential for depth sputtering is 1 kV using Ar-ion. Under this working condition, the sputtering rate is 0.5 nm/min when calibrated against SiO$_2$. 

2.2.7. Scanning Electron Microscopy (SEM)

The primary use of SEM is the study of the surface topography of solid samples. The resolution of these instruments is typically between 1.5 and 3.0 nm, approximately two orders of magnitude better than optical microscopes and one order of magnitude less than transmission electron microscopes, thereby bringing the gap between these related techniques.

In SEM, an electron beam passing through an evacuated column is focused by electron magnetic lenses onto the specimen surface. The beam is then rastered over the specimen in synchrony with the beam of a cathode ray display screen. The (inelastically scattered) secondary electron emission from the sample (determined to a large extent by the surface topography) is then used to modulate the brightness of the cathode ray display screen, thereby forming the image, the image contrast is determined largely by compositional differences of the sample surface rather than topographic features.79
CHAPTER 3

EPOXY-TERMINATED SELF-ASSEMBLED MONOLAYERS:
MOLECULAR GLUES FOR POLYMER LAYERS

Epoxysilanes are classical compounds that have been used to enhance the stability and integrity of polymer/inorganic interfaces. They are applied widely to a variety of glass-fiber reinforced polymer composite materials. These compounds also have found application in the biomedical sciences to provide a strong binding of biological polymers to glass surfaces for biocompatibilization of inorganic surfaces. However, their ability to form table, smooth, and homogeneous monolayers has not yet been proven. Usually, for ordinary composite materials, relatively thick (several hundred nanometers) films of these compounds are applied to fabricate effective bonding conditions at interfaces. In several recent studies, attempts to build epoxysilanes monolayer films by either dip-coating or vapor deposition have lead to the formation of films composed of at least aggregated molecular layers with unknown surface morphology and microstructure. For example, in Ref. 85 the thickness of a dip-coated epoxysilane film was determined to be 1.7 nm, which is much greater than the extended molecular length. In addition, no detailed morphological studies on these layers were performed to prove their integrity and homogeneity. The formation of disordered and chemically heterogeneous molecular layers is a common problem for functional silanes due to the complicated hydrolysis/interaction/adsorption/reactivity competition of the head-end reactive groups with the hydroxyl-terminated silicon oxide surfaces. The questions of completeness, smoothness, and ordering of chemisorbed layers from silanes with terminal functional groups should be addressed to prove their ability to serve as coupling agents for molecular layers.

In this chapter, we report on the fabrication of truly monolayer epoxysilane films appropriate for chemical binding of composite molecular layers on silicon substrates. We especially focus on the surface morphology and microstructure of these SAMs as a function of fabrication conditions as a means to optimize the self-assembly process. Results of testing the
epoxysilane SAMs surface morphology, microstructure, shear properties, and ability to tether functional terminated polymers are discussed.

3.1. Results and Discussion

3.1.1. The kinetics of the formation and morphology of epoxysilane SAMs

Epoxysilane films were prepared by using toluene solutions with epoxysilane volume concentrations from 0.1% to 1%. In the project, we limit ourselves to discussion of only the 1% concentration. At other concentrations, significant aggregation and formation of inhomogeneous films occur due to prepolymerization of silane molecules in bulk solution, as will be discussed in detail elsewhere. Low-concentration epoxysilane solutions lead to the formation of tiny molecular aggregates composed of hundreds to thousands of molecules packed in bi- and trilayers instead of smooth monolayer films. These aggregates are loosely packed, which causes a high heterogeneity on a molecular scale. Aggregate formation arises from the presence of an excess amount of water per epoxysilane molecule in the bulk and occurs at epoxysilane concentrations lower than 0.5%. This conclusion is supported by several recent studies showing that an optimal ratio of water in the bulk/surface is required to form a complete homogeneous monolayer. For the short chain epoxysilanes studied here, we observed that hydrolization/polymerization in bulk toluene solution is a major reason for the formation of inhomogeneous surface coverage.

Contact angle measurements show typical kinetics of molecular adsorption from solution (Figure 23). The contact angle rises very quickly within the first 10 min from close to zero (<5°) for clean silicon wafer to 42° and then gradually increases to 52° at 24 h of deposition time. This value was slightly lower than 62°, which was obtained for thick (and presumably disordered) epoxysilane films. The "apparent" surface coverage or the fraction of the silicon surface screened by the attached monolayer, \( \beta \), can be calculated from contact angle model of surface structure as described in Eq (8): Calculations according to Eq. 8 show that the "apparent" surface coverage increases very quickly reaching 70% within the first 10 min and then gradually increases within the next several hours.
Figure 23. Variation of contact angle and calculated “apparent” surface coverage of the epoxysilane film versus deposition time.

The “apparent” thickness of the epoxysilane monolayer is measured from ellipsometry data assuming a double-layer model (silicon substrate + silicon oxide layer + epoxysilane layer) and homogeneous dense molecular packing (Figure 24). The “apparent” thickness increases gradually up to 0.85 ± 0.1 nm after 24 h of deposition. Obviously, small thicknesses at the initial stage of SAM formation reflect either the incompleteness of the monolayer (partial surface coverage as derived from contact angle data) or its lower density. These two possibilities are defined by a mode of monolayer growth. The difference between the AFM and ellipsometry thicknesses for homogeneous SAMs at intermediate stages of growth (see below) means that the density of the epoxysilane film is lower than its bulk density. Since for all ellipsometric measurements the bulk refractive index of the
epoxysilane is used, for these monolayers the “apparent” ellipsometry thickness is underestimated.

Figure 24. Variation of film thickness obtained from ellipsometry and AFM data and surface microroughness versus deposition time.

As can be concluded from topographical AFM images, epoxysilane SAMs obtained from 1% solution are complete, very smooth, and homogeneous with a light grainy surface morphology (Figure 25(a)). Friction force microscopy and phase images (not shown) confirm the homogeneous surface composition of monolayers. The microroughness of the monolayers is virtually constant after 5 min of deposition time and is $0.22 \pm 0.05$ nm within a $1 \mu m \times 1 \mu m$ area. The microroughness is close to the roughness of the supporting silicon substrates ($rms = 0.1 \pm 0.02$ nm). This indicates that the grainy surface topography in Figure 25(a) is composed of areas with elevation fluctuations of the order of one bond in the molecular backbone. The grainy morphology observed for epoxysilane films is typical for SAMs with functional groups and is caused by partial lateral aggregation within monolayers and mismatch of cross-sectional areas of terminal groups. The difference in the cross-
sectional areas of terminal silanol groups and epoxy groups inevitably should lead to formation of frustrated molecular packing (Figure 25(b)). The lateral sizes of the grain textures do not exceed 10-20 nm, as can be estimated from images, taking into account tip shape. Only at extremely short deposition times (<2 min) is the formation of isolated islands of epoxy layers of nanometer sizes observed. Therefore, the epoxysilane SAMs, beyond the first several minutes of adsorption, form complete layers and possess molecularly smooth surfaces. Experimental data for these deposition times can be interpreted in terms of simultaneous growth of a complete monolayer with gradually increasing density of molecular tethering.

Figure 25. (a) AFM image of the epoxysilane monolayer after a 1.5 h deposition time; the vertical scale is 4.0 nm. (b) Sketch of the molecular ordering of epoxysilane molecules within the SAM; triangles indicate epoxy cycles, and circles indicate chemical bonding of silane molecules with the substrate.

3.1.2. Surface microstructure and chemical composition of epoxysilane SAMs

Film thickness is measured with the AFM technique at local grooves and holes produced either with a sharp steel needle or by multiple scanning over the same area with a by stiff AFM tip with high local forces (several microNewtons). This approach is used
frequently for AFM measurements of organic and polymer layers and produces results, which correlate closely with X-ray and neutron reflectivity data. However, all epoxysilane SAMs formed here are extremely stable under multiple scanning with high forces. Only at two locations did we succeed in removing a small fraction of the SAM with the AFM tip and in measuring its thickness. Scratches produced with a sharp needle complemented these measurements. The thickness of the layer was determined at 10 locations along several different scratches produced for films at 30 min and 24 h of deposition. The values determined from different measurements and for different films were very consistent and equal to 0.8 ± 0.15 nm (Figure 24).

The average thicknesses for complete SAMs determined from both AFM and ellipsometry (0.85 ± 0.15 nm) are very close to the molecular dimensions estimated from computer models for the fully extended conformation (0.9-1.0 nm). This allows for the following two conclusions. First, molecules within complete monolayers are predominantly oriented along the surface normal and prevent their extended conformation. Second, complete monolayers are tightly packed with a refraction index (and density) very close to the known value for bulk packing. A sketch of the molecular microstructure of epoxysilane SAMs is presented in Figure 25(b).

Fabrication of stable and dense SAMs from silane molecules with two terminal functional groups capable of forming covalent bonding with silanol groups on a silicon oxide surface is not trivial. Concurrent adsorption and reaction between two functional groups may lead to the formation of thick (multilayer) films. However, we can argue that hydrolization of methoxysilane groups and epoxy cycles followed by fabrication of either Si-O-Si or Si-O-C bonds, respectively, possesses very different reaction rates, as is demonstrated for aqueous epoxysilane solutions. In the second stage of the reactions, formations of Si-O-Si or Si-O-C bonds have very comparable rate constants with a 50% conversion time of 10 days for the 2% solution for given conditions. Finally, hydrolization of methoxysilane bonds is much faster than opening epoxy cycles at given conditions: 2 h versus 8 days for 50% conversion, respectively. Taking into account the fact that we had a
water layer present only at the silicon surface and in an extremely small amount in toluene solvent (<0.03%), one could expect that, under the given deposition conditions, epoxy groups are not able to be hydrolyzed. Therefore, the vast majority of chemical bonding to the surfaces is formed by Si-O-Si bonds, allowing epoxy cycles to be concentrated on a film surface.

The presence of a high concentration of epoxy groups at SAM surfaces, which correlates with fabrication kinetics, is confirmed by XPS studies.\textsuperscript{88, 89} These data confirm the predominant presence of epoxy terminal groups at the SAM surface and not trimethoxysilane groups (Figure 26). They indicate a significant increase of the carboxyl group concentration in the uppermost surface layers at longer deposition times. Meanwhile, the content of silanol groups at the surface remains relatively constant. If trimethoxysilane groups of silane molecules would be exposed at the SAM surface, multiple rinses with water-containing solvents after fabrication would result in their hydrolysis and a dramatic increase of surface silanol group content for longer deposition times. XPS data display that this is not the case. In addition, a high contact angle (52°) serves as another indication of the presence of closed epoxy cycles and not silanol groups on a surface.

Finally, adhesive forces between the AFM tip and the epoxysilane SAM are significantly higher (~2 times) than those for a bare silicon oxide surface. As known for AFM measurements, a significant part of the adhesive interactions in humid air is related to capillary forces. Obviously, these forces are much lower for a more hydrophobic SAM surface. Therefore, the observed increase should be associated with a higher contribution of chemical interactions due to the presence of reactive surface groups. On the other hand, adhesive forces for epoxysilane SAMs are much higher (five to 10 times) than those for methyl-terminated SAMs, which also indicate a strong presence of the functional groups on the SAM, surface. Strong tethering of polymer brushes with carboxyl terminal groups to epoxysilane SAMs is also observed, as will be discussed in the Chapter 7.
Figure 26. XPS spectra for the carbon 1s region of epoxysilane monolayers deposited 10 min (a) and 24 hours (b).
3.2. Conclusions

We fabricated homogeneous and molecularly smooth epoxysilane SAMs on silicon substrates. An optimal combination of self-assembly parameters allows fabrication of truly monomolecular and complete films. Epoxysilane molecules complete monolayers of 0.85 nm thickness are predominantly oriented along the surface normal and are in their extended conformation. Terminal epoxy groups are mainly located at the surface of the SAMs. In addition, the complete monolayers are tightly packed with a refractive index (and density) very close to the known value for bulk packing. The presence of epoxy groups at the SAM surface promotes higher adhesive forces despite a lower contribution of capillary forces, which is indicative of and the strong reactivity of the functional SAMs. The organic epoxysilane monolayer chemically attached to the silicon surface significantly reduces the shear strength and dissipation of mechanical energy at the interface in a manner that is comparable with the behavior of other functional SAMs. These results may have some important technological applications since the epoxysilane SAMs may serve as a molecularly smooth template for chemical tethering of composite polymer layers as described in the next section.
CHAPTER 4

GRAFTED REINFORCED RUBBER LAYERS

In this chapter, we discuss robust ultrathin SEES films by melt/solution grafting to a chemically reactive silicon surface functionalized with epoxy-terminated SAM as described in chapter 3. We concentrate on the ultrathin block copolymer layers with \( t/d \ll 1 \). The purpose of this study is to reveal the morphology and properties of the nanometer thick tri-block copolymer layers as a function of the thickness. In particular, this work is an attempt to answer the question: how thick should be the copolymer film to demonstrate the phase segregated microstructure typical for tri-block copolymers with immiscible blocks and avoid the dewetting? It is necessary to note that scaling down the film thickness to the limit \( t/d < 1 \) (or to a truly nanometer scale) is a challenging task. Such ultrathin films have tendency to dewett a surface because of their inherently unstable nature at \( t < D \), where \( D \) is the size of unperturbed macromolecules.\(^{102}\)

We use the triblock copolymer of poly(styrene – b - (ethylene-co- butylene) - b-styrene] functionalized with 2% of maleic anhydride (MA) in the hydrocarbon chains (SEBS) as a thermoplastic elastomer material. The epoxysilane SAM deposited on a silicon wafer is used as an anchoring interface. We previously demonstrated in the chapter 3 that the epoxy SAM is homogeneous with terminal epoxy groups mainly located at the SAM surface.\(^{103,104}\)

4.1. Results and Discussion

4.1.1. Grafted reinforced rubber layers to a functionalized silicon surface

Thickness and contact angle

Figure 27(a) demonstrates the thickness of SEBS film grafted from solution versus concentration. The layer height gradually increases with the concentration reaching 2.7 nm at 8%. Grafting from the melt results in much thicker films (8.4 – 9.1 nm) (Figure 27b). The thickness of the films deposited from the melt depends slightly on
the time of the grafting. However, the principal amount of the copolymer (90-95 %) is
grafted during the first 45 minutes. Figures 27a and 27b also present the thickness of the
films scaled with the spacing of microdomain structure, d. For the estimations of the ratio
t/d, we use d=28 nm, since this value is reported for a similar SBS block copolymer with
very close composition. Indeed, the combination of the grafting from the melt and
solution allows us to vary film thickness in a wide range of t/d from 0.05 to 0.33, thus,
keeping the target condition t/d << 1.

Figure 28 presents the contact angle variation for the SEBS films. The contact angle
varies from 93° for the thinnest film to 100 ± 2° for films with t > 1.7 nm. These values are
within the range reported for PS surface (90°) and polyethylene surface (99 ± 3°). Since
the chemical composition and surface energies of polyethylene and polybutylene are very
close, for their copolymer, PEB, we can expect contact angle to be close to 99°. Therefore,
the contact angle value indicates that the surface of the block copolymer films is completely
occupied by PEB chains except for the thinnest layer. Such phenomenon, when block with
lower surface energy covers the topmost surface, is common for the block copolymer
films. The lower contact angle for films with t < 1.7 can be caused by the
predominant surface location of PS phase. The presence of PS chains on the surface of the
thinnest film can be connected to the fact that the ethylene-co-butylene chains are confined
due to surface tethering through MA groups. When the surface concentration of the grafted
polymer is low (as in the case of the thinnest film), the probability that each chain made
multiple ties with the substrate is higher. Consequently, the multiple connections may
prevent the PEB segments from migration to the air/film interface. For higher film thickness,
fraction of PEB segments (PEB possesses lower surface energy) is located in topmost layer
covering PS blocks.
Figure 27. SEBS film thickness as measured by ellipsometry, AFM microroughness and the film thickness reduced to $d$ versus concentration of SEBS in solution (a) and time of the grafting from melt (b).
On the other hand, if SEBS film is adsorbed directly on a bare silicon surface from solution under similar conditions, contact angle does not reach values for tethered films. Maximum values that can be reached are only 83° that is much lower than either contact angle for PS or PEB. The microroughness for the adsorbed film is about 1.2 nm and much higher than the one for the grafted film. This difference indicates that physically adsorbed films are definitely incomplete as was confirmed by microscopic observations (image not shown).

![Graph showing contact angle vs. thickness]

Figure 28. Contact angle for the SEBS monolayers versus the thickness of the film. Line is guide for eyes.

*AFM images recorded at high set point ("light" tapping)*

Figures 29 and 30 present topographical and phase images of the SEBS films with different thickness. The images were recorded using the tapping mode at the highest set point value (the lowest forces) that permitted a reproducible imaging ($r_{sp} = 0.9 \pm 0.05$, "light" tapping). From the dependence of the amplitude and phase shift on the distance between the sample and the tip (not shown), it reveals that, in this case, we scanned in attractive
interaction regime, and, consequently, the topography image reflects the morphology of the topmost layer. At such "light" tapping, the tip-sample interaction is strongly influenced by adhesion attractive forces. An attractive force can be considered as a reduction of the effective spring constant of the cantilever-sample system. Consequently, the phase of oscillating cantilever at a fixed drive amplitude is shifted to lower value. The shift is greater on the surface areas with higher adhesion, because the duration of tip-sample contact is longer for these parts of the surface.

Figure 29. AFM topographical ((a) and (c)) and phase ((b) and (d)) images of SEBS films with thickness of 1.35 nm (t/d = 0.05) ((a), (b)) and 1.8 nm (t/d = 0.07) ((c), (d)).
Vertical scale is 7.0 nm and 20 degree for topography and phase modes, respectively. Bright parts correspond to higher features and phase shifts. "Light" tapping.

The microroughness of the films measured by AFM under "light" tapping conditions within 1μm x 1μm is 0.26 ±0.04 nm that is much lower than their thickness (Figures 27 and 28). For thin films with the thickness 2.7 nm and lower (t/d ≤ 0.1), the topographical images show that the copolymer forms densely packed, nanometer-scale clusters distributed homogeneously and completely covering the surface (Figures 29a and 29c). Figure 30a demonstrates the topography of the film with t/d ≥ 0.3. This image reveals light surface waviness on a generally smooth film surface. Additionally, small cavities randomly distributed on the surface can be observed. The cavities are 0.4 ±0.1 nm dip.

Figure 30. AFM topographical, (a) and phase, (b) images of SEBS film (t/d ≥ 0.3) with thickness 8.9 nm. Vertical scale is 7.0 nm and 20 degree for topography and phase modes, respectively. Bright parts correspond to higher features and phase shifts. "Light" tapping.

Under selected scanning conditions (r_sp = 0.9±0.05), bright sections correspond to the areas with higher tip-sample adhesion. The thin (t/d ≤ 0.1) and thick (t/d ≥ 0.3) films display very different distribution of adhesive forces on the surface. For thin films, the
surface areas with higher and lower adhesion are randomly distributed (Figures 29b and 29d). The difference in adhesion between these areas is more pronounced for the thinnest film, where, according to the contact angle measurements, both PS and PEB chains are located on the surface (Figure 28). Figure 31 shows the root mean square deviation (RMSD) of phase shift in image area for the thin samples. For the “light” tapping, RMSD reflects the level of adhesion fluctuation over the film surface. Indeed, RMSD has the highest value for the thinnest film, indicating the highest fluctuation of local chemical composition. RMSD practically levels off for $t > 1.7$ nm ($t/d > 0.06$) that reflects more homogeneous surface composition.

Figure 31. Root mean square deviation (RMSD) of phase shift versus the thickness. “Light” tapping. Line is guide for eyes.
For thick films (t/d ≥ 0.3), the phase image clearly shows the microphase separation typical for the ABA tri-block copolymers with immiscible blocks \(^{117}\) (Figure 30). Small circular and cylindrical domains with a diameter of 8-12 nm are regularly dispersed in the matrix. Modest widening of the microdomain structure is presented due to the tip contribution, which can be estimated as adding 20 - 30% of the total width for tips with R = 5-10 nm. Therefore, one can estimate the actual lateral dimensions of domains as less than 10 nm. The domains form a pseudohexagonal close-packing within the matrix and the nearest-neighbor distance determined from the 2D Fourier-transformation is about 28 ± 2 nm that is close to interdomain spacing observed for bulk material.\(^{105}\) It is necessary to note that the location of the tiny cavities on the topographical image corresponds to the position of dark domains on the phase image. In view of the fact that the surface of the film is occupied by PEB chains, the difference in surface adhesion can be connected to the variation in the tip-sample contact area. It is worth to note that more dense areas with higher adhesion should appear brighter on the phase image under the scanning conditions used (r\(_{sp}\) = 0.9 ± 0.05).\(^{116}\) The variation in the adhesion of the topmost layer can be connected with the presence of PS domains located underneath of the PEB layer. Figure 31 displays RMSD for the thick (t/d > 3) films versus their thickness. The value of RMSD is rather low and stays practically the same for all “thick” films studied. It reveals that the variation of the tip-sample interaction is very small for different areas.

**AFM images recorded at low set point (“hard” tapping)**

Figures 32 and 33 present topographical and phase images of the thin and thick SEBS films, respectively. The images were recorded in repulsive mode (r\(_{sp}\) = 0.45 ± 0.05), as controlled by the dependence of the amplitude and phase shift on the distance between the sample and cantilever. This type of tapping at high forces, allows observation of microphase separation that forms underneath the topmost soft polymer layer.\(^{109}\) The tip squeezes the rubbery part of the film and hard domains appear brighter in the height image.\(^{109, 118, 116}\) For the “hard” tapping the elastic forces due to the deformation of the sample can be described by an additive term to the spring constant of the cantilever-sample system.\(^{114, 119}\) As a
consequence of the higher effective spring constant the resonance frequency increases, which keeps the drive frequency constant, and the phase shift increases. For a soft sample the phase shift is lower than for a stiff sample. Accordingly, hard domains of the block copolymers appear brighter in the phase images. \textsuperscript{109, 116}

Figure 32. AFM topographical ((a) and (c)) and phase ((b) and (d)) images of SEBS films with thickness of 1.35 nm (t/d = 0.5) ((a), (b)) and 2.6 nm (t/d = 0.1) ((c), (d)). Vertical scale is 7.0 nm and 100 degree for topography and phase modes, respectively. Bright parts correspond to higher features and phase shifts. "Hard" tapping.
Figures 32a and 32b show typical image for thin films. The topographical images are essentially featureless. There are no evidences for the microphase separation typical of the block copolymer materials. When the film thickness increases up to 2.6 nm ($t/d = 0.1$), both topography and phase images display initial stages of microphase separation within the film (Figures 32c and 32d). The small circular PS domains can be clearly observed.

Figure 33. AFM topographical ((a) and (c)) and phase ((b) and (d)) images of SEBS films ($t/d \geq 0.3$) with thickness of 8.4 nm ((a), (b)) and 9.1 nm ((c), (d)). Vertical scale is 7.0 nm and 100 degree for topography and phase modes, respectively. Bright parts correspond to higher features and phase shifts. “Hard” tapping.
Figure 34 shows RMSD of phase shift for thinnest films. For the “hard” tapping, RMSD reflects the fluctuation in repulsive forces and indicates the level of elastic heterogeneity within the polymer layer. Generally, RMSD and, consequently, the film heterogeneity is virtually constant for small film thickness. Very low RMSD level indicates the formation of homogeneous polymer layer at this thickness without developed microdomain structure.

Figure 33 shows topographical and phase images for SEBS film with \( t/d \geq 0.3 \). The microdomain morphology is observed for all samples. The bright circular and cylindrical PS domains are distributed in the dark PEB matrix. For thicker films, the density of the microdomain packing increases (compare Figures 33b and 33d). The RMSD variation confirms conclusions made from the observation of AFM images. Indeed, for \( t > 8 \text{ nm} \), RMSD rises dramatically indicating the formation of highly heterogeneous microstructure (microdomains). With increasing film thickness (and time of the grafting) RMSD decreases gradually (Figure 34). This decrease indicates the formation of more mechanically homogeneous layer for thicker films.

![Figure 34. Root mean square deviation (RMSD) of phase shift versus the thickness. “Hard” tapping. Lines are guide for eyes.](image-url)
Figure 35a presents phase image (high forces or “hard” tapping) of spin-coated SEBS film with the thickness of 100 nm ($t/d = 3$). The film is annealed under vacuum at 110 °C for 1 week to reach equilibrium morphology. The phase image shows that the film has cylindrical structure as is anticipated for the bulk SEBS material with the given composition.\cite{120, 121} The characteristic spacing of microdomain structure determined from the 2D Fourier-transformation, is $32 \pm 2$ nm. This value is slightly higher than the one reported for SBS block copolymers with close composition ($d = 27-30$ nm).\cite{105}

![Figure 35. AFM phase images of the annealed SEBS films. (a) spin-coated film 100 nm thick. (b) grafted film 8.4 nm thick. Vertical scale is 20 degree. Bright parts correspond to higher phase shifts. “Hard” tapping.](image)

Figure 35b shows the phase image of the grafted SEBS film ($t = 8.4$ nm) after the annealing. The microdomain structure of the grafted film after the thermal treatment is virtually unchanged, and represents mixture of circular and cylindrical domains unlike thick SEBS film (compare Figures 35a and 35b). Apparently, in thin film, the chemical grafting of
rubber block to surface prevents the formation of well-developed cylindrical structure with microdomain spacing much larger than film thickness.

**Morphology development in SEBS monolayers**

Here, we summarize our observations of SEBS film microstructures. We observe several different morphologies of the grafted SEBS monolayer with different thicknesses. When the grafted film has thickness of 1.35 nm \((t/d = 0.05)\), rubbery blocks of SEBS are predominantly located close to the substrate surface and the topmost layer is mostly occupied by PS chains (Figure 36a). As the thickness reaches 1.8 nm \((t/d = 0.07)\), the uppermost layer consists mainly of PEB chains (Figure 36b). PS chains are distributed randomly within the SEBS layer.

For the film 2.6 nm thick \((t/d = 0.1)\), the first evidence of the microphase separation within SEBS film is detected. We observe circular PS domains covered by PEB layer as shown in Figure 36c. When the SEBS film reaches \(t = 8.4\) nm \((t/d = 0.3)\), the film displays the microsegregated structure. PS phase forms the microdomain network crosslinking the elastomeric matrix (Figure 33d). The array of circular and cylindrical PS domains is distributed in the PEB matrix tethered to epoxy-terminated SAM. The PS microdomains have shape of compressed spheres and cylinders.

**Thermal properties of the grafted SEBS monolayers**

The fundamental property of the thermoplastic elastomer materials is their ability to form thermally reversible cross-linking by glassy domains.\(^{122, 123}\) The material behaves as vulcanized rubber in many respects, while the domains soften when heated above the PS glass transition temperature, \(T_g\). We investigate the structure of the grafted SEBS film of 8.4 nm thickness from the room temperature to 125°C. From DSC measurements, we detected \(T_g\) of the PS blocks in bulk SEBS to be about 75°C, what is close to \(T_g\) observed for bulk PS with the similar molecular weight.\(^{124}\)
Figure 36. Schematic representation of the SEBS films showing the morphology development at different grafting density and film thicknesses.
Figure 37b presents the microstructure of the SEBS film at 105°C. The phase image shows PS microdomains at this temperature identical to the microstructure at room temperature (Figures 37a and 37b). At 110°C, PS microdomains can be still detected by AFM; however, the edges of the domains become fuzzy (Figure 37c). When temperature reaches 115°C, only isolated domains can be found (Figure 37d). Figure 37e shows that at 125°C the PS microdomains are not detected and film looks completely homogeneous. Observed changes are completely reversible (Figure 37f). Obtained results reveal that at the temperature well above \( T_g \) the PS chains are still segregated into microdomain structure within the grafted film. The microdomains become undetectable only when the temperature of the film reaches temperature close to the temperature of order-disorder transition measured for similar tri-block copolymer.\(^{125}\)

We measured the thermal expansion of the grafted SEBS film (\( t = 8.4 \) nm) by monitoring the temperature variation of the film thickness by ellipsometry. We conducted the comparative measurements for thin (11 nm) and thick (100 nm) spin-coated SEBS films as well (Figure 38). For the thermal expansion of the films, two limits can be identified. The expansion in all three possible directions (XYZ expansion) is possible for unrestricted film. When macromolecules are attached to the surface, the expansion in X and Y directions (in plane) is restricted. Therefore, the film can expand only in the vertical direction (Z expansion). Solid and dashed lines in Figure 38 correspond to thickness variation in these two cases. These plots are calculated from the temperature dependence of the SEBS density, which was estimated via additive molar contributions.\(^{108}\) Excellent agreement is observed between experimental data for the film of 100 nm thick and XYZ expansion (Figure 38). This behavior is anticipated, since the majority of chains of the thick polymer film is not in the contact with the surface and, consequently, has no limitations for their expansion in Y and X directions.
Figure 37. AFM phase images of SEBS grafted film (8.4 nm thick) recorded at different temperatures. (a) 25°C; (b) 105°C; (c) 110°C, (d) 115°C; (e) 125°C; and (f) AFM phase image of SEBS grafted film (8.4 nm thick) after thermal treatment at 150°C for 7 hours. Bright parts correspond to higher phase shifts. Vertical scale is 10 degree. "Hard" tapping.
Figure 38. Thermal expansion of the thickness of various SEBS films.

The chemically grafted film expands only in the vertical direction, as clearly seen in Figure 38. However, the observed expansion is somewhat higher than the calculated one from the dependence of SEBS density on temperature. The rate of thermal expansion of the thin spin-coated film (11 nm) lies between those for the grafted and thick (100 nm) films. Taking into account the SEBS radius of gyration (6.3 nm) (eq. (4)-(5)) we can presume that practically all chains in this film are in the contact with the surface that restrains, to some extent, in plane expansion.
Finally, we tested thermal stability of grafted films at high temperature. The grafted film with $t = 8.4$ nm was annealed for 7 hours in a vacuum oven at $150^\circ$C. After cooling, the PS microdomain structure is completely restored, since we clearly observed the PS
microdomain structure for the annealed film (Figure 37f). We compared the topography of the annealed grafted film and the film (t=11nm) spin-coated on bare silicon after identical treatment (150°C, 7 hours). The roughness of the grafted film slightly increased from 0.3 to 0.45 nm (Figures 39a and 36c). On the other hand, spin-coated film showed significant surface corrugations. Highly heterogeneous surface morphology with large corrugations was developed with microroughness increasing to 1 nm (Figures 39b and 39d).

4.1.2. Microtribological behavior of tethered reinforced polymer monolayers

In this section, we varied the thickness of grafted block-polymer films from 1.35 nm (disordered polymer layer) to 9 nm (well defined nanophase structure) and tested their friction, adhesion, shear and wearing properties on a microscale with scanning probe microscopy. Figure 40 shows friction coefficients, obtained from this analysis for SEBS films with various thicknesses. The friction coefficient for the bare silicon is about 0.1 that is within the range typically obtained for a silicon surface with silicon nitride tips (0.08-0.25). The friction coefficient drops to values close to 0.02 - 0.03 for films with 8 - 9 nm thickness. Significant reduction of the friction coefficient is observed for SEBS films with the developed microdomain morphology (at t > 2.5 nm). This is in a sharp contrast with a relatively high friction coefficient observed for tethered PS films of the same thickness.

Adhesive forces increase after the tethering a very thin SEBS film to the silicon surface (Figure 40). Significant increase of adhesive forces is observed for films with thickness less than 3 nm. At higher film thicknesses, adhesion drops to a lower level, which is close but still higher than that for the bare silicon surface. The adhesive forces for SEBS films are higher than ones for tethered PS layers of comparable thickness. Initial increase of the adhesive forces can be related to the presence of polar and reactive chemical groups of loosely grafted rubber fragments. Higher grafting density reduces the concentration of free reactive groups on the surface (more groups are tethered to the epoxy-terminated SAM) that should result in reduced adhesive forces. However, even for thicker SEBS films, the presence of the reactive surface groups manifests itself in somewhat higher adhesive forces.
as compared to the non-polar surface of PS films (Figure 40). Additional contribution comes from significant increase of the contact area between the AFM tip and compliant polymer films. The contact adhesion of rubber phase is much higher than for glassy polymer surfaces as was demonstrated for PS/PB blends.\textsuperscript{130}

![Figure 40. Friction coefficient and adhesive forces for SEBS films with different thickness in comparison with PS films and silicon oxide surface. Line is the guide for eyes.](image)

We recorded shear and friction properties of SEBS films under a nanometer lateral displacement by moving the AFM tip back and forth laterally for a small lateral distance (5 - 50 nm). In this regime, we can detect initial sharp increase in friction forces due to the shearing deformation of the surface and the threshold force required for the transition from
static state to sliding motion. Corresponding parameters are determined from the experimental data as a slope in the vicinity of zero displacement, $\Delta F/\Delta x$, and as onset, $\Delta F_0$, as demonstrated in Figure 41. Usually, the lateral displacement of 1 - 3 nm is required to initiate tip sliding motion. Significant fluctuation of the friction signal at this scale results in large uncertainty in the determined values, which can reach 20-30%. However, even within this accuracy, a clear tendency is observed for the set of SEBS films with various thicknesses (Figure 41). The bare silicon surface shows the highest $\Delta F/\Delta x$ and $\Delta F_0$ values, far exceeding any SEBS film value. Consistent reduction of both parameters is observed for SEBS films with the final value approaching 10-20% of the level for the silicon surface. SEBS films are very slippery despite their higher adhesion in comparison with both silicon and PS surfaces with the same thickness (PS films display twice as high $\Delta F_0$). Therefore, initial forces required to induce sliding motion are dramatically reduced for SEBS coated surfaces as compared to silicon and PS surfaces.

![Graph](image)

Figure 41. Variation of lateral forces at the nanometer displacement for several selected samples.
Apparently, the grafting of SEBS layers on the silicon surface significantly reduces shear stresses on the interface. From the experimental data, we try to make estimation of the shear strength of the tip-surface interface, $G_{int}$, from the initial slope $\Delta F/\Delta x$ and the known relationship: $\Delta F/\Delta x = 8G_{int}R$, where $R$ is the radius of the contact area.\textsuperscript{132} Obviously, not all parameters for such a complicated system as hard tip-ultrathin layer-hard substrate can be readily available and some assumptions are required to make even very crude estimation. We assumed the Hertzian elastic contact and elastic modulus of film-substrate system in the range from the typical value for pure polymer (6 MPa for SEBS)\textsuperscript{133} to some intermediate value between film and substrate (e.g., 10 GPa for SEBS film-silicon).\textsuperscript{131} For the range on normal loads from 10 to 100 nN, the Hertzian model gives the contact radius from unrealistic 50 nm (for tip radius 20 nm) for the first assumption to 2 nm for the latest assumption. In such a case, the shear strength of the tip-SEBS interface is estimated as ranging from 0.15 to 1.5 GPa. This range looks reasonable considering that the rubber phase is reinforced by glassy nanodomains, is densely packed, and chemically attached to the surface. If this scheme is applied to all SEBS films with different thicknesses, we observe consistent decrease of the shear strength from the value close to the bare silicon at very small thicknesses (1.3 - 1.7 nm) to the lower value for “thick” films (Figure 42).

To check if these estimations makes sense, we repeated these calculations for the data collected for other interfaces under similar assumptions. As a result, we obtained the shear strength for the tip-silicon contact in the range 10 – 30 GPa and for the tip-PS film contact in the range 2 – 8 GPa. These numbers are not out of line with expected ones, taking into account that the shear strength of silicon oxide is close to 20 GPa and the PS shear strength in glassy state is close to 1 GPa.\textsuperscript{134, 132, 135} Therefore, we can conclude that our crude evaluation gives a reasonable value of the shear strength of tethered SEBS layers.
Figure 42. (a) Variation of the slope, $\Delta F/\Delta x$ (1), a mid-point of the shear strength of the contact (2) and onset, $\Delta F_0$, (3) for SEBS films with different thicknesses. 4- the onset for PS films with different thicknesses. Line is a guide for eyes. (b) Figure 42. The average depth of the worn area as a function of applied normal load (expressed as a set point, 1 V corresponds approximately to 100 nN) for chemically attached (Δ) and spin-coated (□) SEBS films.
Finally, we used scanning at high normal forces within selected areas to test the wear stability. We repeated this test, under identical conditions, for chemically tethered SEBS films and spin-coated (physically deposited) SEBS films. The thickness of these films was chosen to be comparable with tethered films (8 - 11 nm) and to assure the developed microdomain structure. Wearing process of SEBS films is described by a plot in Figure 42 that characterizes the amount of material (= the depth of the worn area) removed from the scanned area at a particular normal load. Figure 43 displays surface morphology of the spin-coated and tethered SEBS films after scanning at different normal loads including the highest possible load. Obviously, the chemically tethered SEBS film remains intact under loading conditions that lead to a complete destruction of the conventional SEBS film with the same chemical composition and microstructure. Both tethered and spin-coated PS films are completely destroyed under identical load conditions similarly to alkylsilane LB and SAM studied earlier.\textsuperscript{136,137}

4.2. Conclusions

We fabricated robust molecular lubrication layers from the functionalized tri-block copolymer, SEBS. This polymer was chemically attached to the silicon oxide surface via the interfacial epoxy-terminated monolayer. We optimized the grafting density and the thickness of the SEBS films to assure the development of organized microphase structure within the molecular thick (<10 nm) films. Key components of this microstructure, which, we believe, are critical for obtaining superior interfacial properties, are 2D net of interconnected glassy PS nanodomain reinforcing the rubber matrix and dense chemical grafting of the rubber matrix to the substrate. These SEBS films with optimal microstructure show microtribological properties far exceeding those for other molecular coatings and self-assembled monolayers. They possess very low friction coefficient, modest adhesion, low stiction, and superior wear stability as compared to other, non-structured, non-tethered, or non-reinforced organic molecular lubrication coatings.
Figure 43. AFM images of the worn area of chemically attached ((a), (c), (e)) and spin-coated ((b), (d), (f)) SEBS films after identical wearing experiments: (a) and (b) initial films, (c) and (d) scan with moderate normal load, (e) and (f) scan with high normal load.
In chapter 5, we discuss bilayered nanocomposite coatings composed of a hard polymer layer placed on top of an elastomeric layer (Figure 44). The primary layer of SEBS (chapter 4) was attached to the surface by melt grafting to a chemically reactive silicon surface functionalized with epoxy-terminated SAM (chapter 3). The SEBS layer served as the compliant interlayer in the bilayered polymer coating. The topmost hard layer was a high performance polymer made of epoxy resin (EP) and an amino functionalized poly(phenylene) (PPP). The purpose of this study is to reveal the elastic response of the hard polymer layer affected by the underlying elastomeric layer. We expected that the SEBS layer serve as a compliant interlayer potentially capable of dissipating the interfacial stresses originating from dissimilarities in the physical properties between the polymer coating and inorganic substrate.

Figure 44. Microstructure of sandwiched nanocomposite coating grafted to silicon surface. The primary layer is SEBS thermoplastic elastomer and the topmost layer is EP/PPP composites.
5.1. Results and Discussion

5.1.1. EP/PPP layer: deposition and morphology

We built bilayered coating by deposition of the EP/PPP layer on the top of grafted SEBS layer. First of all it was checked if the SEBS layer could be washed out after the spincoating of the upper layer. Figure 45 shows the morphology of SEBS layer after the uncured EP/PPP film was removed by rinsing with THF. Both topography and phase images show that the elastic SEBS layer practically did not change as result of spincoating. We again observed the phase separated structure typical for the grafted SEBS layer (Compare Figures 33a and 33b Chapter 4 and Figure 45).

![AFM topographical (a) and phase (b) images of SEBS film after the spincoated EP/PPP mixture was washed out. Vertical scale is 7.0 nm and 20 degree for topography and phase images, respectively. Bright parts correspond to higher features and phase shifts.](image)

Different concentrations (0.15% - 0.7%) of EP/PPP solution were used to produce top layers with thicknesses from 4 nm to 22 nm. For some EP/PPP films, spincoated from the
concentrated solutions, a small fraction of aggregates was observed on the surface. We believe that the aggregates formed in the solution by the reaction between EP and PPP and then deposited on the surface. Generally, the films were complete on a microscopic level, except the thinnest one (image not shown). The thinnest film produced from the 0.15% solution (ellipsometry thickness 4 nm) did not form a uniform layer. We found droplets of the EP/PPP mixture randomly distributed on the top of the SEBS layer. Conversely, the EP/PPP mixture deposited from the 0.15% solution on the bare silicon wafer gave a continuous film. The instability of the thinnest film on the top of SEBS layer during the spincoating could be connected with the low surface energy of the SEBS layer (water contact angle 100° for SEBS against 5° for the silicon wafer). For the films produced from 0.3 - 0.5 % solution (ellipsometry thickness 9, 13 and 16 nm) we observed the formation of small holes (images not shown). The hole formation indicates that the very first stage of dewetting occurred during the deposition of the EP/PPP mixture on the low energy surface of SEBS layer.\textsuperscript{138} The amount of the holes decreases when the thickness of the EP/PPP layer reached 19 nm. Only several tiny holes per scanned area (10x10 \( \mu \text{m} \)) were observed for the films produced from 0.6 - 0.7 % solution (thickness 19 - 22 nm).

To reach optimal properties, bulk EP/PPP mixture was cured at the temperature well above 100 °C for 5-10 hours (see experimental part). The same regime was used for the solidification of the thin film. Initially homogeneous, the film completely dewetted the SEBS surface when heated above 100 °C. There are two concurrent processes during the top layer solidification at high temperature: crosslinking and decrease of viscosity. The crosslinking reaction should prevent the dewetting. However, the rate of dewetting is inversely proportional to the viscosity.\textsuperscript{139} Decrease of the viscosity provokes the dewetting processes before the film could be stabilized by the network formation. Consequently, in the next experiment, curing of the EP/PPP layer began at 45 °C for 15 hours. The films were annealed at 55 °C, 75 °C, and 90 °C for 15 hours. The solidification was completed at 110 °C (15 hours). We chose this procedure to initiate the crosslinking before the viscosity of EP/PPP mixture became too low and the dewetting occurred. After each annealing step, the
morphology of the films was examined by AFM. The results indicated that the morphology remained almost unchanged during annealing due to chemical crosslinking (Figure 46).

Figure 46. AFM topographical images of EP/PPP films with a thickness of 16 nm (a) and 19 nm (b) after curing. Vertical scale is 50 nm (a) and 20 nm (b) Bright parts correspond to higher features.

Figure 47 shows the higher magnification AFM topographical and phase images of EP/PPP film (thickness 21 nm) deposited on the top of SEBS film. Similar morphology was observed for the films with different thicknesses. The EP/PPP layers were smooth and uniform on the microscopic level (Figure 47a). The AFM microroughness of the films within 1 μm x 1 μm area was 0.35 nm. Phase imaging showed that the surface areas with slightly variable adhesion were randomly distributed (Figure 47b). Consequently, there was no phase segregation of EP and PPP during the curing. Thus, EP/PPP material, forming the topmost layer of the bilayered film, was homogeneous on the microscopic level.
Figure 47. AFM topographical (a) and phase (b) images of EP/PPP layer (21 nm) after the solidification. Vertical scale is 15 nm and 20 degree for topography and phase images, respectively. Bright parts correspond to higher features and phase shifts.

Selected annealed films were washed by multiple rinsing with THF and DMSO including the washing in an ultrasonic bath. The surface morphology of the film after the washing is presented in Figure 48. The film morphology showed little change as a result of the washing. Moreover, the ellipsometric thickness of the film was the same before and after the solvent treatment. The obtained results showed that the curing of the film was complete and the EP/PPP layer was strongly attached to the SEBS layer.

It was important to prove that the EP/PPP mixture did not penetrate inside the SEBS layer at elevated temperatures and the segregated bilayered structure was, indeed, obtained. To answer this question, we cured the incomplete EP/PPP film obtained by spincoating from the 0.15% solution. When the sample was annealed at 45-55 °C (15 hours), the droplets formed during the spincoating partially spread on the surface and the dewetted morphology shown in Figure 49a was formed. The phase-separated structure typical for the grafted SEBS layer was clearly observed underneath of the incomplete film (Figure 49b). Then, the film was annealed from 75 °C to 110 °C for 15 hours.
Figure 48. AFM topographical (a) and phase (b) images of cured EP/PPP layer (21 nm) after the washing with THF and DMSO. Vertical scale is 8 nm and 7 degree for topography and phase images, respectively. Bright parts correspond to higher features and phase shifts.

Figure 49c shows the structure of the film after the curing. The film morphology did not change in the course of the solidification. We measured the thickness of the EP/PPP layer annealed at different temperatures by AFM. No change was observed in the thickness during the curing of the EP/PPP layer. The results unambiguously showed that the EP/PPP layer did not penetrate inside the elastic primary layer during the solidification at the elevated temperatures. Thus, we fabricated the truly layered film ((EP/PPP)/SEBS/Si) consisting of the primary elastic and top hard layers.
Figure 49. AFM topographical ((a) and (c)) and phase (b) images of EP/PPP films produced from 0.15 % solution. Annealed at 55 °C ((a) and (b)) and 110 °C (c). Vertical scale is 60 nm and 20 degree for topography and phase images, respectively.

5.1.2. Micromechanical properties of the bilayered film

Force-distance curves were recorded for (EP/PPP)/SEBS/Si (Figure 50(a)) to determine if the compliant rubbery layer underneath the high modulus layer influenced the mechanical properties of the bilayered coatings. For the sake of comparison, measurements were also taken for the EP/PPP films deposited on the bare silicon ((EP/PPP)/Si) (Figure 50(b)) cured under the same conditions as (EP/PPP)/SEBS/Si. The slope of the force-distance curve was determined at the same tip deflection (3 nm) or identical applied force. Lower slope corresponds to a more compliant film. The values of the FDC slope versus the thickness of the EP/PPP layer are shown in Figure 50(c). The data presented in the figure were averaged over 12-20 measurements from different surface locations. When the thickness of the film was about 20 nm, the FDC slope was close for both (EP/PPP)/SEBS/Si and (EP/PPP)/Si. The slope observed for the films is lower than the one detected for bare silicon wafer. Hence, the AFM tip indented into the layer and caused the elastic surface deformation before the stress was transferred to the silicon substrate.
(EP/PPP)/Si

(EP/PPP)/SEBS/Si

Figure 50. Microstructure of (EP/PPP)/SEBS/Si (a) and (EP/PPP)/Si (b). (c) The slope of force-distance curve for (EP/PPP)/SEBS/Si and (EP/PPP)/Si versus the thickness of EP/PPP layer. 1.0 corresponds absolutely stiff surface for indent conditions.

However, there was no noticeable influence of SEBS elastomeric interlayer on the micromechanical behavior of the film with the thickness >16 nm. When the thickness decreased, pronounced differences in the mechanical behavior between (EP/PPP)/Si and
(EP/PPP)/SEBS/Si was observed. The FDC slope for (EP/PPP)/Si increased and became close to the one obtained for the bare silicon wafer. Thus, the (EP/PPP)/Si layer was not detected by AFM force-distance measurements. The stress applied to the film was transferred through the ultrathin EP/PPP layer to the silicon substrate. On the other hand, the slope for (EP/PPP)/SEBS/Si decreased. The underlying SEBS layer clearly affected the mechanical properties of the bilayered film. The bilayered (EP/PPP)/SEBS/Si film sustained much higher elastic deformations if compare with the (EP/PPP)/Si film of analogous thickness. Thus, the rubbery SEBS layer absorbed some of the applied stress and served as a compliant interlayer capable of reducing the stress originating from dissimilarity in physical properties between the polymer coating and the inorganic substrate.

5.2. Conclusions

We fabricated bilayered nanocomposite coatings with total thickness of 10-30 nm consisting of hard polymer layer placed on the top of an elastomeric layer. The primary SEBS layer was attached to the surface by melt grafting to a chemically reactive silicon surface functionalized with an epoxy-terminated SAM. The SEBS layer behaved as a rubbery material and could serve as a compliant interlayer in thin polymer film. We synthesized the bilayered film by the deposition of the EP/PPP layer on the top of the grafted SEBS layer by spincoating. The solidification of the topmost layer was initiated at low temperatures (40 – 50 °C) to avoid the dewetting. The curing of the film was finished at 110 °C (15 hours). The EP/PPP layer was strongly attached to SEBS layer. It was found that the EP/PPP did not penetrate in the elastic primary layer during the solidification.

The elastic response of the hard polymer layer on a normal external load was affected by the underlying elastomeric layer. Indeed, the SEBS layer served as a compliant interlayer capable of damping interfacial stresses originated from dissimilarity in the physical properties between the polymer coating and inorganic substrate. The influence of the bilayered structure on the ultimate microtribological properties of bilayered nanocomposite coatings is a focus of further investigation.
CHAPTER 6

OIL ENHANCED LAYERS

In a previous chapter, we reported the fabrication of a robust molecular lubrication layers from SEBS tri-block copolymers tethered to a solid surface.\textsuperscript{140} A functionalized block-copolymer was chemically grafted to a silicon oxide surface and possessed lower adhesion and friction. In this chapter, the tribological performance of this tri-block copolymer coating was enhanced by adding a minute amount of alkyl-chain paraffinic oil (Figure 51). We chose four alkyl-chain molecules with a number of carbon atoms from 15 to 24 and studied the swelling rate, evaporation kinetics, and diffusion processes of oil enhanced layer. We focused on the friction response and the wear stability of the nanoscale polymer gel layer using a combination of micro- and nanotribology studies with Auger electron spectroscopy (AES) that allows quantitative surface chemical analysis.\textsuperscript{141}

Figure 51: Microstructure of grafted SEBS layer grafted to epoxy-terminated surface. Hard blocks are presented by gray spheres and the soft rubber matrix contains anchoring groups shown by black dots. The paraffinic molecules entrapped in the rubber matrix of the SEBS layer are shown by light gray curves.
6.1. Results and Discussions

6.1.1. Enrichment of polymer layers with paraffinic oils

Figure 52 shows the swelling ratio $Y = \frac{W_t}{W_0}$ ($W_0$ is the initial weight of the dry polymer specimen and $W_t$ is the polymer weight at a certain time after immersion in oil) of bulk SEBS material as a function of time for the bulk polymer immersed in different oils at 60°C. We observed that bulk polymer specimens immersed in the short chain paraffinic oils ($C_{15}H_{32}$ and $C_{18}H_{36}$) reached equilibrium after 4 hours. For the longer chain oils ($C_{20}H_{42}$ and $C_{24}H_{50}$), the bulk polymer reached equilibrium after 15 hours. The diffusion coefficient, $D$, of paraffinic molecules within the bulk polymer at 60°C was calculated from the measurement of the swelling ratio as a function of time according to known approach (Table 3). For all oils, the swelling rate was very high at the early stage and became slower before the final equilibrium reached. The diffusion coefficient of paraffinic molecules within the bulk polymer was calculated from the measurement of swelling as a function of time according to:

$$\frac{W_t}{W_\infty} = \frac{2[D\times t / \pi I^2]^{1/2}}{1}$$ (10)

where $W_\infty$ is the sample weight at equilibrium, $D$ is the diffusion coefficient, and $I$ is the thickness of the sample. As expected, the diffusion coefficient for longer-chain molecules is about one order of magnitude lower than that of short-chain molecules. The highest oil uptake in the polymer was observed for $C_{24}H_{50}$ with more than 5 times mass increase. These results lend support to the original hypothesis that paraffinic oils are compatible to the rubber block of SEBS, which results in the polymer gel formation.
Figure 52. Top: time dependence of the polymer swelling ratio for bulk SEBS polymer submerged in oil, $W_t/W_0$. The dash line is a guide for an eye. Bottom: the effective oil layer thickness $d(t)$ obtained from ellipsometry measurement for the grafted polymer gel layer after removing from oils data.
Table 3. The diffusion coefficients of different paraffinic oils in polymer layer at 60 °C and the rate of oil evaporation from the grafted polymer layers at different stages.

<table>
<thead>
<tr>
<th>Paraffinic oil</th>
<th>Diffusion Coefficients (cm² / s)</th>
<th>Evaporation Rate (g/m² s) I</th>
<th>Evaporation Rate (g/m² s) II</th>
<th>Evaporation Rate (g/m² s) III</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₅H₃₂</td>
<td>1.01E-3</td>
<td>5.2E-6</td>
<td>3.4E-6</td>
<td>4.3E-7</td>
</tr>
<tr>
<td>C₁₈H₃₈</td>
<td>8.71E-4</td>
<td>1.8E-6</td>
<td>1.6E-6</td>
<td>8.0E-7</td>
</tr>
<tr>
<td>C₂₀H₄₂</td>
<td>7.15E-4</td>
<td>6.0E-7</td>
<td>4.0E-7</td>
<td>2.0E-7</td>
</tr>
<tr>
<td>C₂₄H₅₀</td>
<td>5.42E-4</td>
<td>5.0E-7</td>
<td>4.0E-8</td>
<td>2.0E-9</td>
</tr>
</tbody>
</table>

Another important property was the evaporation rate. The kinetics of oil evaporation from the grafted polymer gel layer as measured by ellipsometry is shown in Figure 52. From the measurements of effective oil content expressed in the terms of effective oil layer thickness, we determined the residual oil weight, \( \Gamma \) (g/m²), within the polymer film from the relationship:

\[
\Gamma(t) = d(t) \times \rho
\]  

(11)

where \( \rho \) was the density of the oil phase. The kinetic of oil evaporation was determined from \( \Gamma(t) \) by using an exponential approximation, thus:

\[
\Gamma(t) = A + B \exp(-kt)
\]  

(12)

where 'A' and 'B' represent the residual and volatile oil, thus providing A + B for the entire oil amount; and k represents the evaporation rate constant. This relationship describes the
overall evaporation behavior except near to the initial state. Here, the residual oil weight is analysed using a linear regression equation as follows:

$$\Gamma(t) = A_0 - B_0 t$$  \hspace{1cm} (13)$$

where $A_0$ is the constant and $B_0$ represents the evaporation rate at the initial stage. The diffusion coefficient of oil, $D$, within the grafted polymer gel film was obtained from the slope of $\Gamma(t)$ as a function of $\sqrt{t}$ and concentration $C_0$ according to the relationship

$$\Gamma(t) = 2C_0[D\pi / \pi ]^{1/2}$$  \hspace{1cm} (14)$$

The evaporation rate of oil from polymer layer was determined from the slope of the residual oil weight, $\Gamma(t)$, according to the equation (13). The overall kinetic curve of oil evaporation was divided into three different stages. During the initial, fast stage, the evaporation kinetic displayed a linear relationship as described by equation (13). We suggest that the process on this stage was governed mainly by the evaporation of the oil layer situated at the polymer surface and oil phase concentrated mainly within the topmost surface layer of the polymer gel layer. We can speculate that, to great extend, this is caused by the necessity of surface diffusion of alkyl molecules through swollen polymer matrix.

During the second stage for the effective oil thickness below 5 nm, a further decrease of the evaporation rate was observed. This can be related to mobility constraints imposed by the underlying polymer surface due to strong favorable interactions between alkyl chains of the oil phase and the alkyl-enriched surface. Under these conditions, the molecules are structured into discrete layers whose properties are "quantified" with the number of layers. Depending upon molecule-surface interactions, up to 10 molecular layers of long-chain molecules can be organized in this way that gives an overall thickness of the confined film of 5 nm. Such surface layers within the liquid phase behave more like a solid with extremely limited diffusion mobility of the confined molecules. At the final stage of evaporation, we
observed a very slow process, which was, obviously, limited by the diffusion of residual alkyl molecules from inside the grafted polymer gel layer to its surface.

Table 3 shows the rate of oil evaporation from the grafted polymer layer at different stages: (i) surface diffusion, (ii) swollen polymer matrix diffusion, and (iii) diffusion of residual alkyl molecules inside the grafted polymer gel layer. It appears that the short-chain paraffinic oil, C15, gradually evaporated from the polymer film with only some residual effective oil layer less than 1 nm left in the films. The overall evaporation rate is much lower for longer-chain molecules (Table 3). E.g., for C24 molecules, the rate of evaporation was $4.0 \times 10^{-9}$ g/m$^2$ s this value is over three orders of magnitude lower than that for C15 ($3.0 \times 10^{-6}$ g/m$^2$ s) and a free oil surface ($6.7 \times 10^{-5}$ g/m$^2$ s).\(^{148}\) This indicated that the mobility of the alkyl molecules was severely restricted when they were trapped within the rubber matrix grafted to the silicon substrate.

6.1.2. Surface microstructure and chemical composition of polymer gel layer

The grafted polymer films possess uniform, smooth, and homogeneous surface with only a few aggregates observed over surface areas of tens micrometers across as illustrated in Figure 53. Microroughness of 0.2-0.4 nm was measured within 1 square micron area for all polymer layers. For polymer layers exposed to long-chain oils, globular aggregates were detected. The highest surface concentration of aggregates was observed for the highest molecular weight paraffinic oil, C24. The lateral size of surface aggregates is within 400-500 nm. Larger aggregates, up to several microns across were observed on SEM images (Figure 54a). Obviously that this is related to the crystallization process of paraffinic oil with higher melting points during cooling from 60°C to room temperature that results in the formation of paraffinic crystals on the film surface. Indeed, optical microscopical analysis of similar paraffins (m.p. 48-49°C) in crossed polarizers show many fine "crystals" with random orientation after crystallization from melt.\(^{149}\) These crystals are usually composed of many overlapping thin prismatic lamellae with lateral sizes from several hundred nanometers to several microns.
Figure 53. (a) AFM topographical images of the dry polymer layers. (b), (c), and (d) presented polymer gel layer saturated with C15, C20, and C24 oils respectively. Scan size is 10×10 μm, height scale is 30 nm, light tapping mode.

As AES demonstrated the polymer layer was predominantly composed of carbon atoms (main component of polystyrene, rubber blocks, and paraffinic oil) with detected tracks of oxygen (MA groups, epoxy groups, and silicon dioxide layer) and silicon
The depth profile of the different elements within polymer gel layers exposed to different paraffinic oils are presented in Figure 55. The polymer gel layers exposed to C20 molecules shows higher carbon contain. There were no significant differences in the depth profiles of all elements in the polymer layers exposed to other oils. The layer thickness roughly estimated from AES data calibrated against silicon was about 8 nm that was close to 9 nm value obtained from ellipsometry. These findings imply that their initial microstructures are similar for all polymer gel layers.

6.1.3. Friction behavior and wear stability of the polymer layers

SEM image of polymer gel layer with CI8 oil exposed to rubbing with a steel ball at 0.3 N normal load shows a weak-wearing track (Figure 54(a)). An increase of silicon and oxygen elements was detected by AES for these partially worn areas (Figure 54b). This implied that the polymer gel layer might be partially oxidized and compressed. Indeed, depth profiling of various elements shows decreasing content of carbon and a sharp increase of oxygen (Figure 56). This confirms that the increase of oxygen content within the worn topmost surface layer was caused by the oxidation of the metal surfaces, oxidation and decomposition of the organic molecules from the surface lubricant layer. In addition, sputtering time was much shorter for the worn layer, which indicated its highly compressed state with a thickness not exceeding 4 nm. There were differences in the depth profile of oxygen and carbon elements among the polymer gel layers of the worn surfaces. For example, the polymer gel layer with C18 displayed higher carbon content than the polymer gel layers with C15, C20, and C24 and layer with C20 shows much higher oxygen concentration (Figure 56). These variations can due to occasional presence of surface aggregates and exposed silicon dioxide surface or debris.
Figure 54. (a) SEM image of polymer gel layer with C18 oil with a wearing trace under a low load (0.3 N). Boxes mark the surface areas for AES analysis performed for original (1) and partially worn (2) areas. (b) AES spectra of the original and worn surfaces areas.
AES analysis of the polymer gel layer saturated with C18 exposed to a high normal load showed that iron, silicon, and oxygen became dominant elements within the worn area (Figure 54b). Apparently, iron was present on the silicon surface due to material transfer from the counterpart steel ball to the worn surface during ultimate local damage of the silicon substrate and these AES data are entirely consistent with previously published data for the similar film studied in Ref 152.

![Graph showing depth profiles of different chemical elements for various polymer gel layers.](image)

**Figure 55.** AES results for the depth profiles of difference chemical elements for various polymer gel layers.
Figure 56. AES results for the depth profiles of different chemical elements for partially worn surfaces of various polymer gel layers.

Microtribometer was used to characterize the frictional characteristics of the polymer gel layers. The 3 mm diameter steel ball with a smooth surface (microroughness less than 10 nm) is mounted in a carrier head and oscillated against a stationary planar specimen with an applied load of 0.3 N and 1.8 N. Figure 57 shows the coefficient of friction calculated as a ratio of the lateral forces to the normal load as a function of the number of sliding cycles. At a low normal load of 0.3 N, the grafted polymer gel layers exposed to oils showed a performance much better than the uncoated silicon and the dry polymer film. The polymer gel layers did not show a failure or significant deterioration up to 20,000 cycles (the maximum number of cycles tested here) whereas the silicon and the dry polymer layer failed within 200 cycles and 2,700 cycles, respectively (both values were averaged over three independent measurements).
Figure 57. The coefficient of friction as a function of a number of sliding cycles for the bare silicon, dry polymer layer, annealed polymer layer, and polymer gel layers at the normal load of 0.3 N (a) and 1.8 N (b).
The polymer gel layers with short chain (C15) paraffinic oil showed the lowest friction coefficient among the layers (~0.05). The friction coefficient increased with the increasing molecular weight of paraffinic oils to 0.11-0.12 for the polymer gel layer with C24. The friction coefficient value reached the highest value of 0.13-0.17 for the dry polymer layer and a bare silicon substrate (Figure 57). The effect of paraffinic oil on the frictional behavior of the polymer layer became more significant for longer runs when the dry polymer layer finally started to deteriorate. At a higher normal load of 1.8 N, the dry polymer failed only after 250 cycles while the polymer gel layers were stable up to 500-700 cycles (C20-C24) and 900-1000 cycles (C15 and C18).

It is worth noting that additional annealing of the polymer layer at 60°C for 24 hours also resulted in significant improvement of wear resistance, especially under high normal load (Figure 57). Obviously that additional annealing of the polymer layer allowed MA functional groups of the rubbery block poly (ethylene-co-butylene) to react with the epoxy groups of the supporting surface, thus, resulting in a stronger adhered layer. However, the presence of alkyl-chain molecules is still more important factor in enhanced wear resistance at low normal loads (Figure 57a).

Finally, the nanotribological properties were characterized with friction force microscopy (Figure 58). Loading curves were obtained for a bare silicon substrate, annealed polymer layer, and the oil-exposed polymer layers under identical conditions (identical probe, scanning velocity, scanning size, and the range of normal loads). The friction coefficients calculated as a slope of a linear approximation were determined to be the lowest for polymer layers with C15 and C18 oils. The friction coefficient for their layers decreased to 0.02, which was much lower than that for the silicon substrate (0.07 – 0.1). Despite the fact than the absolute values of the friction coefficient calculated from AFM data were systematically lower than those determined with the microtribotester general trends were very consistent. Hence, we can conclude that the polymer gel layer treated with C15 and C18 paraffinic molecules showed the best tribological performance.
Figure 58. Friction forces vs. normal loads as measured for the bare silicon, dry polymer layer, annealed polymer layer, and polymer gel layers with paraffinic oil (C15-C24).

6.2. Conclusions

We report the friction response and the wear stability of the uniform, smooth, and homogeneous polymer gel layer grafted on a silicon surface and saturated with paraffinic molecules with different lengths of alkyl chains (15-24 carbon atoms). We observed that the presence of shorter chain paraffinic molecules (C\textsubscript{15}H\textsubscript{32} and C\textsubscript{18}H\textsubscript{38}) resulted in a lower value of the friction coefficient and higher wear-resistance as compared to a dry polymer layer and a polymer gel layer saturated with longer chain paraffinic oil (C\textsubscript{20}H\textsubscript{42} and C\textsubscript{24}H\textsubscript{50}).
Hence, we can conclude that shorter chain molecules improve the lubrication properties of the tethered polymer layers, resulting in the lowest value of the friction coefficient. This phenomenon can be understood considering known theories, which relate a quality of solvent and resulting osmotic pressure. As was demonstrated, higher osmotic pressure between grafted polymer chains shows up in the good solvent, which allows supporting a larger normal load. In addition, the frictional forces between compressed, rubbing solid surface may be dramatically reduced while shorter chain paraffinic molecules retaining a fluid interfacial layer, preventing significant interpenetrate and reducing lateral forces requiring to slide them. The coupling between the large normal compression sustained and a fluid interfacial region is the origin of the good lubrication properties of grafted polymer layers solvated by a good solvent. Using a better solvent for a given polymer layer reduces the friction coefficient relative to a less good solvent. The Flory-Rehner theory defines the best solvent as the one with the closest solubility parameter. Since the shorter chain paraffinic oils possess solubility parameters close to PEB segments, they are expected to be better solvents than the longer chain molecules.

These results may have some important technological applications since the durability of the organic ultrathin polymer surface films has been concerned. The most common case, low molecular weight lubricant is removed and evaporates from the protective layers, result to wear off when operated under high pressure. Thus, it may be possible to make ultrathin interfacial polymer layers (less than 10 nm) with ability to adsorb and held short-chain paraffinic molecules and support large pressures while operated under high-pressure conditions.
In this chapter, we discuss the permanent grafting of a dense and homogeneous polymer layer from melt onto a modified silicon surface. We focus on the nanomechanical and surface properties of the polymer brush layer by using the AFM techniques. In this study, we have chosen two polymers, carboxylic acid terminated polystyrene (PS) and polybutylacrylate (PBA), demonstrating a wide range of soft-adhesive to stiff polymer brush. The brushes were formed by a grafting from melt (chapter 2). The epoxysilane SAM deposited on a silicon wafer was used as an anchoring surface (chapter 3). We previously showed that the epoxy-SAM is homogeneous with terminal epoxy groups mainly located at the SAM surface.

7.1. Results and Discussions

7.1.1. Polystyrene homopolymer brush

The kinetics of the formation and morphology of PS brush layer

Figure 59 shows the kinetics of formation of the grafted layers for PS-COOH with different molecular weights from 4,500 to 672,000. For all polymers studied, 18 h of grafting time is enough to approach a virtually constant thickness of a grafted layer. Only statistically insignificant differences were observed for samples with grafting times between 18 and 48 h. The layer heights obtained independently by ellipsometry and AFM are close to each other (within 5-10% error range, Figure 59). This indicates that the polymer is densely packed in the film with a refractive index (and density) very close to the known value for bulk material.
Figure 59. Layer height as measured by ellipsometry and AFM versus time of the grafting for the different molecular weights for PS brush.
Figure 60 presents topographical images of the polymer layers at different deposition times for two selected molecular weights (low and high). Because the polymers are in a bad solvent (air) and are tethered to the surface, the chains are collapsed to a dense layer and do not dewet. For short deposition times, the low- and high-molecular-weight polymer layers display very different morphologies. The lower molecular weight polymers form densely packed nanometer-scale clusters distributed homogeneously and completely covering the substrate. When the layers are formed from high-molecular-weight polymer at short deposition times, the larger clusters are irregularly distributed on the surface, displaying the pattern of a partially dewetted film (Figure 60c). However, for all polymers, after 18-48 h of grafting time, the layer homogeneously covers the substrate and possesses very fine surface texture (Figure 60b,d).

Figure 61a shows the layer height and AFM roughness versus the degree of polymerization (N) for the polymer layers at 18 h of deposition. Microroughness is 0.24 ± 0.06 nm within a 1 × 1 μm² area for all polymer layers after 18 h of deposition time. The microroughness is very close to the roughness of the supporting epoxysilane monolayer and much lower than that of the height of the layers. After 18 h of the deposition, the grafted layers practically reach a constant thickness and therefore represent the maximum possible grafting at the given conditions. These observations allow us to translate the film thickness into a surface coverage (Γ), grafting density (Σ), and distance between grafting sites (D) using eqs 1-3 (see chapter 1).

The layer height and surface coverage initially increase for the range 43 < N < 440, passes through a maximum at N = 440, and then decreases (Figure 61a,b). The maximum is close to the critical entanglement molecular weight of PS, Mc, which is 31 200 g/mol (NC = 300). The same behavior is observed for the layer height scaled with 2Rg (Figure 61c), where Rg is the radius of gyration for the PS-COOH macromolecules, Rg = a(N/6)½, where a is the statistical segment length (a ≈ 0.6 nm for PS). The h/2Rg ratio can be considered as a measure of chain stretching within the layer. The grafted layers are somewhat squashed along the surface normal at all molecular weights except M ~ Mc (Figure 61c). It
reveals that at intermediate molecular weights close to $M_C$ the polymer chains constituting the layer have the highest degree of the stretching, which is the unperturbed coil dimension. Figure 61c also shows how the distance between the grafting sites ($D$) reduced to $2R_g$ varies with the degree of polymerization of the grafted polymer. The dependence shows a minimum at the intermediate molecular masses, which confirms the highest grafting density at $M_n \approx M_C$.

Figure 60. AFM topographical images of PS layers (a) and (c) after 2 and (b) and (d) 48 h of deposition for PS-COOH with (a) and (b) $M_n = 16\,900$ g/mol and (c) and (d) $M_n = 672\,000$ g/mol. The vertical scale is 10 nm.
Figure 61. (a) Layer height and roughness, (b) surface coverage $\Gamma$(mg/m$^2$), and (c) layer height and distance between grafting sites ($D$) reduced to $2R_g$ versus the degree of polymerization ($N$). Grafting time is 18 h.
A significant decrease of grafting density is observed for two polymers with the highest molecular weights. This can be connected to a very low rate of the interfacial reaction for high-molecular-weight polymers due to slow diffusion of entangled chains. For such polymers, the reactive ends become kinetically trapped within the limited distance from the surface. Indeed, it was shown\textsuperscript{163, 164} that for the polymer interfacial reaction, the effective reaction rate constant $k$ is proportional to $1/(\ln N)$ and $1/N \ln N$ below and above $M_C$, respectively. Thus, the rate constants for entangled polymer decreases by several orders of magnitude at $M_n > M_C$, which prevents dense grafting within the time interval studied (<48 h).

The theory for polymer brushes predicts that the thickness of the end-grafted polymer layer $h$ scales as $h \propto N\sigma$ in a poor solvent where $\sigma = (a/D)^2$ is the dimensionless grafting density.\textsuperscript{165} Figure 62a shows that the prediction holds for the grafted polymer layers obtained in this work. For such systems, the grafting process as a first approximation can be considered as the sequential adsorption of disks with diameter $2R_g$ onto the surface. This approach predicts a linear dependence $D \propto N^{1/2}$ and, consequently, $1/N$. The anticipated linear increase of the distance with the chain dimension is demonstrated in Figure 62b for various $D/R_g$ ratios. However, as can be seen from the Figure 62b, experimental data do not follow this relationship, and data points are scattered around the different lines. Consequently, the grafting density also does not follow $\Sigma \propto 1/N$ law.

It was proposed by Norton et al.\textsuperscript{166} that $\Sigma$ vary as $1/N$. This kind of behavior was confirmed for grafted PS layers on epoxy-terminated substrates.\textsuperscript{166} We replotted these data in Figure 63a along with the linear approximation used in the comparison with our data. From this consideration, we excluded the highest molecular weight polymer due to the fact that it shows underestimated grafting density because of its nonequilibrium state. Obviously, a simple linear regression falls short of describing all experimental results, because it predicts the stopover of the grafting at the degree of polymerization close to 2000 (Figure 63a). However, in the experiment, the grafting was determined for these and higher molecular weights. As we observed, fitting of experimental data by nonlinear functions of the type $\Sigma \propto$
$N^{-\delta}$ gives a more reasonable description of the experimental data that shows a minute variation of grafting density for high molecular weight. The parameter $\delta$ is in the range 0.4-0.6 for data combined from our experiments and those of Norton et al (Figure 63a).\textsuperscript{166}

Figure 62. Plots of (a) grafted layer height versus $N*\sigma$ and (b) distance between grafting sites ($D$) versus $N^{1/2}$.
Here, we discuss a simple geometrical model that adequately describes observed experimental behavior (see definition of end-grafted polymer brush and the radius of gyration, $R_g$ in Figure 6 chapter 1). Of course, the model discussed below is too simplistic to provide comprehensive representation of our system but, nevertheless, provides a valuable insight in possible nature of steric constrains during the grafting process. A major assumption of this model is that steric constrains between two grafted chains prevent grafting of an additional chain end, which reaches the surface at a later time. In the course of the grafting, the distance between the anchored chains decreases to the level that the segments with the restricted mobility overlap. The mobility of these segments is limited, because they or their neighbors are chemically connected to the surface. At such a critical distance, the surface became screened and there is no enough free volume in vicinity of interface for another segment to access a binding site. We suggest that the limiting free volume can be characterized by the distance between the surface and the intersection point of neighboring overlapped grafted macromolecules, $d$, in their unperturbed state (Figure 6(a)). Indeed, chains adopt random coil conformation during the grafting process from melt despite the fact that they are "squashed" in their final "dry" state.

In the framework of this geometrical model, an increase of the degree of overlapping (decrease of $D$) effectively leads to an increased "screening" of the surrounding surface. From geometrical consideration, one can obtain the relationship:

$$D^2 = 4d (2R_g) - 4d^2$$

(11)

which is valid for $R_g > 2d$. Thus, for this model,

$$D \propto R_g^{1/2} \text{ and } D \propto N^{1/4}$$

(12)
Figure 63. Plots of (a) grafting density $\Sigma$(chains/nm$^2$) versus $N$ and (b) distance between grafting sites ($D$) versus chain dimension. Grafting time was 18 h for our experimental data. Filled squares are data from Norton et al., and the linear fit is done for data points from Norton et al. Power fit includes all data points from both this study and that of Norton et al.
with a slope equal to $4d$. By plotting $D^2$ versus $2R_g$, we can estimate the critical distance $d$. For the evaluation, we included only data for the polymers with molecular weight close to and lower than $M_C$, because they certainly approach equilibrium grafting. The $D^2$ versus $2R_g$ dependence indeed shows a virtually linear relationship (Figure 63b). The slope of a linear fit corresponds to $d = 0.23$ nm, which is close to the length of the PS monomeric unit (0.25 nm). This dimension is reasonably close to the suggested meaning of the parameter $d$ as the low limiting size of the polymer chain, which can be placed onto the surface between two previously grafted chains (Figure 6(a) chapter 1). From the eq 12, simple arguments lead to a scaling law:

$$\Sigma \propto N^{-1/2}$$  \hspace{1cm} (13)

In fact, experimental data obtained here and those from Norton et al.\textsuperscript{166} lie between two limiting cases: a linear decrease as discussed in Norton et al. and the $N^{1/2}$ relationship (eq 13) derived here from steric arguments. However, eq 13 follows the experimental behavior at high molecular weights. It is interesting to notice that the same scaling prediction was found for the polymer-polymer coupling reaction at the polymer/polymer interface.\textsuperscript{163} It was pointed that the effective reaction rate constant becomes negligibly small when the area per chain drops below $N^{1/2}$.

**Micromechanical and surface properties of PS brush layer**

The surface distribution of the mechanical response for the PS brush layer was studied with pixel-by-pixel mapping of micrometer-sized surface areas. An example of the 3x3 $\mu$m image of topography, elasticity, and adhesion of grafted PS layers is presented in Figure 64. We observed that the shear response of PS layers is extremely homogeneous, as revealed by friction force microscopy (see Tsukruk et al.\textsuperscript{167}). Then, we tested the distribution of adhesive forces and elastic response of PS layer by doing force volume testing (Figure 64). This technique allows pixel-by-pixel probing of surface properties by collection of force-distance curves over selected surface area.\textsuperscript{168} We selected an area around the intentionally
damaged area (hole) produced by the AFM tip to emphasis the properties of the surrounding untouched polymer layer. We collected the data in a 32 × 32 array and extracted adhesive force values (pull-off forces as defined by the force-distance curve\textsuperscript{169}) and elastic compression moduli.\textsuperscript{170}

![Image](image_url)

(a) (b) (c)

Figure 64 (a) Topography (Z range is 40 nm), (b) elasticity (Z range is 100 GPa), and (c) adhesion (Z range is 950 nN) for PS layer of 8 nm thick with the worn area in the center. Collected for 32 × 32 pixels, lateral size is 3 × 3 μm.

As can be seen from topographical data (top of Figure 64), the worn area within PS layer is surrounded by polymer debris accumulated during "digging" procedure. Elastic moduli and adhesive forces are much lower along the debris area, but they are very homogeneous on the PS layer surface far from the damaged area. From the analysis of elastic modulus depth profiles according to Chizhik et al.,\textsuperscript{170} we concluded that the AFM tip indents and compresses very thin polymer layers and probes the underlying solid substrate. However, after tip retraction, the initial surface morphology (thickness, roughness, homogeneity) is completely restored without any trace of high local compression. This behavior indicates that the tethered polymer layer can sustain very high local mechanical distortions without compromising its integrity. It worth noting that physically adsorbed PS layers are completely destroyed under comparable probing conditions.\textsuperscript{168}
7.1.2. Polybutylacrylate homopolymer brush

The kinetics of the formation and morphology of polymer brush layer

Figure 65 shows the kinetics of formation of the grafted PBA-COOH layers. For this particular polymer, three hours of the grafting time is enough to approach a virtually constant thickness of the grafted layer. Only statistically insignificant differences were observed for samples with grafting times between 3 and 18 hours. The layer heights, $h$, obtained independently by ellipsometry and AFM measurements, are close to each other (within 5-10% error range). This indicates that the polymer is densely packed in the film with a refractive index (and density) being close to the known value for bulk material.

![Figure 65. Thickness of PBA brush layer versus time of the grafting as measured by ellipsometry and AFM.](image)
Figure 66 and Table 4 show the amount of grafted polymer, grafting density and the AFM surface roughness versus the grafting time of PBA chains. Increase of grafting time resulted in a gradual increase of the amount of grafted polymer within first four hours of grafting. After 18 hours of the deposition, the grafted layers practically reach a constant thickness and therefore represent the maximum possible grafting density. The amount of grafted polymer reached 3.5 mg/m$^2$ that is typical for the "grafted to" technique (1-10 mg/m$^2$). Accordingly, grafting density gradually increase to 0.32 chains/nm$^2$ that is higher than typical grafting densities achievable with grafting to from solution.

Figure 66. Grafting amount, grafting density, and microroughness of PBA brush layer versus time of the grafting.
Table 4. Characteristics of PBA polymer brush morphology.

<table>
<thead>
<tr>
<th>Grafting Time</th>
<th>Film Thickness (nm)</th>
<th>RMS Roughness (nm)</th>
<th>Grafting amount, $\Gamma$ (mg/m$^2$)</th>
<th>Grafting Density, $\Sigma$ (chain/nm$^2$)</th>
<th>Interchain Distance, $D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>1.3</td>
<td>0.20</td>
<td>1.30</td>
<td>0.12</td>
<td>3.25</td>
</tr>
<tr>
<td>1 hr</td>
<td>2.5</td>
<td>0.19</td>
<td>2.58</td>
<td>0.24</td>
<td>2.31</td>
</tr>
<tr>
<td>3 hrs</td>
<td>3.2</td>
<td>0.19</td>
<td>3.41</td>
<td>0.32</td>
<td>2.00</td>
</tr>
<tr>
<td>10 hrs</td>
<td>3.2</td>
<td>0.18</td>
<td>3.42</td>
<td>0.32</td>
<td>2.00</td>
</tr>
<tr>
<td>18 hrs</td>
<td>3.3</td>
<td>0.17</td>
<td>3.44</td>
<td>0.32</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Figure 67 presents AFM topographical images of the grafted PBA polymer layers at different grafting density. Comparable images were obtained for different regions in the same sample, and no structural differences were observed among different samples of the same molecular weight with the same grafting density. Comparison of the images revealed that the films obtained from different grafting densities have very different surface morphologies. At low grafting density ($\Sigma \sim 0.1$ chain/nm$^2$), a surface covered with densely packed islands, a characteristic of dimpled lateral structured predicted and observed for intermediate grafting densities in air and in a good solvent.\textsuperscript{172,173} This type of morphology is similar was related to the formation of isolated “mushroom” of grafted polymers in a poor solvent.\textsuperscript{174} At higher grafting densities, the formation of clusters with diameter of 40-50 nm and about 2-3 nm high is observed. A higher grafting density ($\Sigma > 0.2$ chain/nm$^2$) resulted in a higher level of overlapping of macromolecular chains and the formation of a truly uniform surface morphology as expected for high grafting densities. A lower value of surface roughness, below 0.17 nm, is observed for these grafted layers (Figure 66).

The thickness of the dry PBA layer at maximum grafting density reaches $3.0 \pm 0.2$ nm. This thickness corresponds well to the theoretical estimation, $h = 3.2$ nm, for the polymer brush layer in a poor solvent from $h \approx N\sigma = N (a/D)^2$ taking $a \approx 0.6$ typical for flexible polymer chains.\textsuperscript{175,176} On the other hand, the PBA thickness in a good solvent
(toluene) as measured by the AFM is much higher and reaches $9.5 \pm 0.5$ nm. This thickness is lower than the theoretical predictions calculated from the scaling law $h \approx N^{1/3}$ proposed for a brush layer in a stretched conformation.\textsuperscript{177} On the other hand, force balance measurements of the thickness of the polymer brushes demonstrated that the thickness of the layer in the good solvent varies according to $h \approx N^{0.6}$.\textsuperscript{178,179} The evaluation of expected brush layer thickness in a good solvent according to this equation gives a value of 8.9 nm that is fairly close to the experimental value observed here.

Figure 67. AFM topographical images (1x1 μm) of PBA brush layers fabricated at (a) 15 min, (b) 1 hour, (c) 3 hours and (d) 18 hours grafting time. The vertical scale is 10 nm.
Elastic mechanical properties of polymer brush layer

The surface distribution of the mechanical response for the brush layers was obtained with pixel-by-pixel micromapping of randomly selected surface areas. An example of histograms of surface distribution of elastic modulus within the 2x2 μm area for both PS and PBA brush layers is presented in Figure 68. The average value of the elastic modulus is about 1.1 GPa for the PS layer with the highest molecular weight tested but decreases to 600 MPa for the layers fabricated from low molar weight PS (Table 5). These values are within a range of values measured for glassy polymers of different molecular weights with AFM probing. In contrast, the PBA layer possesses the elastic modulus of 40 MPa, typical for rubbery polymer phases (Table 5). Under identical normal load, the elastic, reversible indentation of the AFM tip is much higher (3-5 times) for the rubbery PBA layer (Figure 68). Typically, the maximum indentation depth under the normal load of 40 nN was within 3 nm for the rubbery PBA brush layer but stays well below 1 nm for the PS brush layer. The pull-off force normalized to the tip radius R, \( \Delta F/R \), could be considered as a measure of adhesive energy required separating the AFM tip and a polymer surface. Strong adhesion is observed for the PBA brush layer as expected for rubbery polar polymers (Table 5). The PS brush layer shows consistently smaller adhesion forces as expected for stiffer polymer surfaces with lower surface tension (Table 5).

Table 5. Surface properties of PS and PBA polymer brush layers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>( M_n ) (g/mol)</th>
<th>Thickness (nm)</th>
<th>Grafting Density, ( \Sigma ) (chain/nm(^2))</th>
<th>Young’s modulus (GPa)</th>
<th>Adhesion (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>4500</td>
<td>2.3</td>
<td>0.32</td>
<td>0.6 ± 0.1</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>PS</td>
<td>16900</td>
<td>5.0</td>
<td>0.19</td>
<td>0.9 ± 0.1</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>PS</td>
<td>28500</td>
<td>6.7</td>
<td>0.15</td>
<td>1.1</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>PBA</td>
<td>6500</td>
<td>3.3</td>
<td>0.32</td>
<td>0.03-0.08</td>
<td>37 ± 3</td>
</tr>
</tbody>
</table>
Figure 68. Histograms of the surface distribution of the micromechanical responses for PBA and PS layers (a) and examples of penetration–load curves for these layers showing very different elastic response on mechanical load (b).
The elastic modulus of the PS brush layer increases with the layer thickness or the molecular weight of the grafted polymers (Table 5, Figure 69). This trend is continued consistently if additional data points for "grafted from" brush layer from high molecular PS discussed elsewhere. This relationship is reminiscent of the known molecular weight dependence of mechanical parameters such as tensile strength or elastic modulus or thermal parameters such as glass transition temperature. The increase of mechanical parameters and glass transition temperatures was related to the variation of free volume caused by decreasing concentration of end groups of polymer chains. Additional contribution comes from the constraints imposed by a denser physical entanglement network whose formation being intensified when molecular weight exceeds a critical segment weight, \( M_c \). For bulk polymers, thermomechanical parameters are a linear function of inverse molecular weight in the form: \( A-B(M + M_c)^{-1} \) where the parameter A gives an expected value for the polymer with infinite molecular weight.

In fact, the experimental data of elastic modulus for grafted polymers with different molecular weights follow this law with a value of \( M_c \) of 18,000 known for bulk PS as can be seen from Figure 6b. Reasonable linear fit could be obtained for a whole set of data. Similar relationships between physical mechanical parameters and molecular weight characteristics in the grafted and bulk polymers indicate that the process of the formation of the physical network within polymer melt of chains tethering to a solid substrate is similar to that occurring in unconstrained polymer melt. Extrapolation of the linear fit to infinite molecular weight gives an ultimate value of 1.4 GPa for the highest reachable elastic modulus that is close but a bit lower than usual values of 2.5-3 GPa measured for bulk PS. This difference might indicate that level of ordering in grafted polymer chains is somewhat lower than in the bulk state and additional disturbance due to the presence of spatial constraints leads to weaker compression resistance of ultrathin polymer layers.
Figure 69. (a) The elastic modulus versus the molecular weight ($M_n$) for PS brush layers studied in this work and brush layer from higher molecular weight polymer from Ref. 186 (a). The linear regression fit of the elastic modulus as a function of $(M_n + M_c)^{-1}$. 
Under these conditions, three PS brush layers studied here represent very different cases of chains without entanglements for $M<<M_c$ as well as chains with one or two entanglements for brushes with $M\geq M_c$ (Table 5). This transition between these two states shows itself in dramatic reduction of the compliance reflected in two-fold increase in the elastic modulus for grafted layers with $M\geq M_c$. These dramatic changes of the elastic properties of polymer brushes are observed in the range of molecular weights close to the critical segment length. However, it seems that spatial constrains imposed by tethered chain ends will only modestly influence the formation of chain entanglements in thicker brush layer. Our results indicate that modest lowering of “limiting” elastic modulus can be expected for thicker brushes.

7.2. Conclusions

In conclusion, we fabricated dense and homogeneous PS and PBA polymer layers permanently grafted to the epoxy-modified surface of silicon wafers. These layers did not dewet from the modified silicon surface and did not desorb in a good solvent under ultrasonic treatment. We proposed that the grafting from the melt is controlled by steric constrains through the limiting free volume between the grafted macromolecules that can be accessed by the late-arriving polymer chain. The reactive SAM surface becomes inaccessible for the reactive chain ends if the characteristic dimension $d$ becomes less than the size of a monomeric unit. At high molecular weight, the grafting density is limited by the very low rate of the interfacial diffusion. Grafted polymer layers obtained here possess laterally homogeneous morphology and very evenly distributed adhesive, shear, and elastic properties. They are very firmly tethered to the surface and can sustain significant shear stresses that far exceed those needed to damage physically absorbed polymer films.

Micromapping of the surface mechanical properties revealed that the average values of the elastic moduli are about 1.1 GPa for the PS layer, which contrasts sharply with 40 MPa for the PBA layer. The elastic modulus of PS polymer brush layers dramatically depends upon molecular weight and follows the inverse law with segment molecular weight, $M_c$ of
18,000 known for bulk PS. This result indicates that the process of the formation of the physical network within polymer melt of chains tethered to a solid substrate is similar to that occurring in unconstrained polymer melt. Under these conditions, three PS brush layers studied in this work represent very different cases of chains without entanglements for $M << M_c$ as well as chains with one or two entanglements for brushes with $M \geq M_c$. This transition shows itself in dramatic reduction of the compliance reflected in two-fold increase in elastic modulus. Our estimation predicts that modest lowering of "limiting" elastic modulus of 1.4 GPa can be expected for thicker polymer brushes.
CHAPTER 8

GENERAL DISCUSSION AND CONCLUSIONS

The rapid growth of MEMS field has generated significant interest in the implementation of microdevices in various commercial applications. During the early stage of this novel technology, the main emphasis was on the manufacturing of microsensors that can accurately sense the operating environment of macrodevices. As micromachined devices have begun transition from laboratory environment to commercial products, several challenging issues have to be resolved for further progress. In particular, understanding and control of surface phenomena is of paramount importance to the design of reliable and robust MEMS devices.

Since silicon micromachining is a well-established technology, the most logical (and cost-effective) solution would be retain silicon and it fabrication methodology, but develop methods to reduce the friction and wear of the MEMS by surface engineering. In conventional lubrication, low friction substrate (solid or liquid) is applied to a system by external means, which cannot be adopted in MEMS devices due to very small dimensions. For example, liquid lubricants may introduce capillary and viscous shear stresses, which may lead to stiction due to excessive viscous drag forces. Thus, ultrathin liquid films deposited at micromachine interfaces prior to the release-drying process are the ideal lubrications for this technology.

New organic and polymeric coatings shield electromagnetic field in microelectronic packaging, selectively reflect light in antireflective coatings, change hydrophobic/hydrophilic surface balance in antifogging layers, and reduce friction/adhesion on microdevice surfaces. These recent developments explore new ways of how active, “built-in”, functionally of molecular materials can be exploited for the functional molecular coating. In this thesis, we focus on the development in the field of molecularly assembled interfaces for nanotribological applications. These nanointerfacial assemblies can be designed to serve as a sophisticated
buffer that controls molecular-scale mechanical and energetic interactions between nanoscale-size mating surface features.

8.1 General Summary

In the framework of our approach, we first fabricated homogeneous and molecularly smooth epoxysilane SAMs on silicon substrates as a binding interfacial layer. Epoxysilane molecules form chemically grafted monolayers of 0.85 nm thickness predominantly oriented along the surface normal and are in their extended conformation. Terminal epoxy groups are mainly located at the surface of the SAMs. In addition, the complete monolayers are tightly packed with density close to the known value for bulk packing. The presence of epoxy groups at the SAM surface promotes high adhesive forces despite a lower contribution of capillary forces, which is indicative of the strong reactivity of the functional SAMs. These surfaces should be suitable for derivation with appropriate polymers for a long time after fabrication.

Then, we fabricated ultrathin elastomer (SEES) films by melt/solution grafting to a chemically reactive silicon surface functionalized with epoxy-terminated SAM. We optimized the grafting density and the thickness of these SEES films to assure the development of organized microphase structure within the molecular thick (<10 nm) films. Key components of this microstructure, which we believe are critical for obtaining superior interfacial properties, are 2D net of interconnected glassy PS nanodomain reinforcing the rubber matrix and dense chemical grafting of the rubber matrix to the substrate. These SEES films with optimal segregated microstructure show microtribological properties far exceeding those for other polymer coatings and self-assembled monolayers. They possess very low friction coefficient, low stiction, and better wear stability as compared to other, non-structured, non-tethered, or non-reinforced organic molecular lubrication coatings. However, there are two major undesirable characteristics of the SEBS lubrication layers: high surface adhesion and too low surface stiffness. To enhance the performance of these coatings, we proposed to exploit either bilayer design with capping layer or its saturation with low molar weight lubricant.
Thus, we fabricated bilayered nanocomposite coatings, with total thickness of 10-30 nm, consisting of a topmost hard polymer layer placed on the top of an elastomeric layer. The SEBS layer behaved as a rubbery material and could serve as a compliant interlayer in a bilayered polymer film. We synthesized the bilayered film by the deposition of the stiff EP/PPP layer on the top of the grafted SEBS elastomer layer. The EP/PPP layer was strongly attached to the SEBS interlayers through entanglements. We demonstrated that the SEBS layer served as a compliant interlayer capable of damping interfacial stresses originated from dissimilarity in the physical properties between the polymer coating and the inorganic substrate. On the other hand, topmost layer served as a protection coating, which prevents the penetration of solid asperities through the compliant layer.

Enhancement of surface properties of the elastomeric layer was also achieved by an adding paraffinic oil component to assure the presence of highly mobile oligomeric molecules inside of the elastomeric phase. SEBS tri-block copolymers adsorb significant (~300-600 %) equilibrium amount of oil. This oily fraction can be a source of an instant supply of mobile lubricant to a contact area, thus providing potential self-lubrication and self-healing mechanisms for surface areas affected by exceeding deformation. A 10 nm thick SEBS layer was saturated with paraffinic molecules with different lengths of alkyl chains (15-24 carbon atoms, molecular weight M = 212-338). We observed that the presence of shorter chain paraffinic oil (C_{15}H_{32} and C_{18}H_{38}) resulted in a lower value of the friction coefficient and higher wear-resistance as compared to a dry polymer layer and a polymer gel layer with longer chain paraffinic oil (C_{20}H_{42} and C_{24}H_{50}). This is the result of the coupling between the large normal compression sustained and a fluid interfacial region is the origin of the good lubrication properties of grafted polymer layers solvated by a good solvent. Using a better solvent for a given polymer layer reduces the friction coefficient relative to a less good solvent. Since the shorter chain paraffinic oils possess solubility parameters close to PEB segments, they are expected to be better solvents than the longer chain molecules.

Finally, we tested an alternative approach of the film of polymer brush layer. Carboxylic acid terminated polystyrene and polybutylacrylate were grafted from melt onto a
functionalized silicon substrate. The tethered layers fabricated from polymers of different molecular weights are smooth, uniform, mechanically stable, and cover homogeneously the modified silicon surface. We observed that for the PS layers with the thickness higher than 7 nm, the average value of the elastic moduli reach 1.1 GPa that is close but still lower one expected for bulk polymer. The elastic modulus of PS brush layers dramatically depends upon molecular weight and follows the inverse law known for bulk polymers. The value of a critical segment molecular weight, \( M_c \), is fairly close to \( M_c = 18,000 \) known for bulk PS. This result indicates that the process of the formation of the physical network within polymer melt of lengthening chains tethered to a solid substrate is similar to that occurring in unconstrained polymer melt. Under these conditions, three PS brush layers studied in this work represent very different cases of chains without entanglements for \( M<<M_c \) as well as chains with one or two entanglements for brushes with \( M>M_c \). This transition shows itself in dramatic reduction of the compliance reflected in two-fold increase in elastic modulus. Our estimation predicts that modest lowering of “limiting” elastic modulus can be expected for thicker brushes.

8.2. General Discussion

Nanotribology can be defined as the arts and sciences necessary to control adhesion, friction, stiction, and wear of the surface coming into contact at the micro/nano-scale. The hydrophilic surfaces of silicon leads to complete surface wetting under normal air/fluid conditions, and to the formation of very strong capillary forces, high surface adhesion and high friction force, resulting in the relatively poor tribological properties of a bare silicon. It is well known that the low surface energy of an organic film can dramatically reduce capillary and adhesion forces of silicon surfaces, resulting in lower friction coefficient and enhanced wear-resistance.

To qualify these differences, figure 70(a) shows that grafted polymer, such as bilayer and oil enhanced layer, on silicon surfaces significantly reduces the adhesion of the modified surface. These molecular coatings provide low surface energies, reduce capillary interaction
and increase hydrophobicity of the silicon surface, comparable with completely hydrophobic OTS SAM, which is one of the best approaches of current molecular lubrication. In addition, interfacial shear strength of modified surfaces decreases significantly due to the presence of a thin molecular layer with low shear strength. As a result, the greatly reduced friction coefficient is observed for coatings designed here as shown in Figure 70(b).

The number of cycles to failure was used to rank the wear-resistance for different coatings (Figure 70(c)). The bare silicon surface cannot perform well without molecular lubrication layer, and fails immediately after the test commences. Oil enhanced layer (~3,300 cycles under high load) performs the best as compared to bilayer (~500 cycles) and OTS SAM (~250 cycles). For the oil-enhanced layer, the mobility of lubricant molecules inside the elastomeric layers is an important parameter that governs the lubricant effectiveness. They perform much better than the completely bonded lubricant layers.\textsuperscript{11} When the lubricant molecules are bonded, there was no self-repair mechanism, hence, limited durability results as can be seen in the cases of bilayer and OTS SAM. The bilayers are observed to be superior protective coating as well with two times higher wear-life than the conventional OTS SAM while showing similar friction coefficient and adhesion.

As for molecular lubrication films, oil enhanced layers show the best tribological performance with lowest adhesion, friction coefficient (down to ~0.025) and the longest possible wear-life under ambient condition as compared to all other designs. This molecular design with self-healing mechanisms for extremely high wear resistance can be used for a variety of surfaces. Unlike the known conventional liquid lubrications, reversible mechanism of oil trapping within the oil-enriched layer makes it possible for applying of these coatings on textured surface with periodic, structured, and rough surfaces.
Figure 70. Surface tribological characteristics of bare silicon, OTS SAM, bilayer, and oil-enhanced layer. (a) adhesion force, (b) friction coefficient, and (c) wear life.
The conventional liquid lubrication cannot work on this surface structure since liquid lubrications flow down from the sharp cutoff wall of the texture surfaces to the flat areas with time. Oil enhanced layers developed in this work demonstrate the great sophistication and versatility of molecular protective coatings. They are truly multifunctional coatings, which may serve several purposes simultaneously, reducing adhesion and friction, incorporating hydrophobicity to the silicon surface, and allow controlling mechanisms for the variation of surface properties.

8.3. Prospectives

Epoxysilane SAMs on silicon substrates open exciting new possibilities of engineering smooth surfaces with their chemical properties fine-tuned at the molecular level. These novel systems exhibit a rich variety of packing and ordering phenomena with the angstrom-level control of the film thickness. In trying to assess the future potential of epoxysilane SAMs, we should consider both the advantages and disadvantages. The advantages of this monolayer are clear. First and foremost, this is the strong chemisorption to the silicon surface via Si-O bonds and intra-interlayer bonding through the formation of chemical network. Second and vital, this is the ability to form smooth and homogeneous monolayers for chemical tethering of functionalized polymers. Third important property is the chemical and thermal stability of these SAMs. The disadvantages, on the other hand, are not conceptual, but rather practical. The coating process is somewhat cumbersome in that the SAM solution must be freshly made and appropriately conditioned immediately before deposition. This is due to the sensitivity of the solution to ambient humidity and the tendency of the alkylsilane to polymerize. As a consequence, great care and control are needed for the coating process to be reliable.

Oil-enhanced polymer layers show the best tribological performance with lowest friction coefficient (down to ~0.025) and the longest possible wear life under ambient condition as compared to reinforced rubber (SEBS), bilayer (EP/PPP), bare silicon and OTS SAM. This molecular design provides the re-supply mechanism by surface diffusion from
surrounding regions that cannot be employed by the conventional lubricants that are removed and evaporated from the protective layer. This molecular design can be considered as a new generation of molecular lubricants with thickness less than 5-10 nm with ability to adsorb and held lubricant molecules and support large pressures while operated under high-load conditions. However, an unsolved problem of oil-enhanced layer is the evaporation of the paraffinic oil molecule from layer at high temperature. We suggest that paraffinic oil with strong polar groups can enhance their attachment and trap oil molecules within the layer through the strong cumbic interaction of the polar group with the rubber matrix and limit lubricant evaporation.

At the high normal stresses and elevated temperature conditions, the surface stiffness and thermal stability define stability of the protective coatings. Consequently, bilayer nanocomposite can provide the necessary high surface stiffness to prevent complete asperity penetration and direct surface contact. This unique composite molecular design with thickness less than 30 nm demonstrates that the formation of bilayer coating with low shear strength/high surface hardness combination results in significant reduction of dissipation of energy. This nanocomposite layer can be the promising candidate for the wear-resistant hardcoating with maximum wear-life under high normal stresses. However, an important problem to be considered for this molecular design is high surface adhesion, which is caused by epoxy and amino groups of the topmost layer. Our recommended approached to regulate surface adhesion is to overcoat the epoxy nanocomposite layer with 1-2 nm thick perfluoropolyether lubricant with polar end groups that enhance their attachment to the surface. High wear resistibility along with the low friction/stiction of bilayer nanocomposite with perfluoropolyether lubricant can make these molecular coatings very promising as a new generation of molecular lubricants and anti-wear coating.

PS and PBA brush layer were permanently grafted on silicon surface with control morphology and microstructure. They represent the initial step of understanding of fundamental principles of local molecular and supramolecular organization at nanostructured surface/interfaces and their adaptive/responsive behavior in different environment such as
pH, temperature, and solvent quality. These polymer brush can be used for important applications of colloid stabilization, drug delivery and biomimetic materials, chemical gates, and tuning lubrication, friction, adhesion, and wettability for tailored polymeric surfaces. In addition, the basic principle of self-organization of homopolymer brush layer can be useful for the next step of understanding of the more complex and sophisticated binary brush layer. In the case of binary brush layers, the variety of surface morphologies possible greatly increases depending upon the composition used. If the two polymers are incompatible, each chain will interact very differently with the surroundings, resulting in the change of surface morphologies due to switching of phase segregations.

In conclusion, we demonstrated that by applying sophisticated principles of molecular design and self-assembly, multifunctional nanoscale, composite coatings can be fabricated from functionalized organic and polymer molecules. These coatings, chemically grafted to silicon surfaces, demonstrate superior microtribologically performance with dramatically reduced friction and adhesion and many-fold increase of wear resistance.
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PREPRINTS AND ABSTRACTS


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