Solvent-dependent friction response of poly(ethyleneimine)-graft-poly(ethylene glycol) brushes investigated by atomic force microscopy

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ABSTRACT: Lateral and normal forces between a surface-bound, brush-like copolymer, poly(ethyleneimine)-graft-poly(ethylene glycol) (PEI-g-PEG), and a silica colloidal probe were investigated with atomic force microscopy (AFM), and related to the relative mass of the solvent adsorbed within the polymer as measured with the quartz crystal microbalance (QCM). PEI-g-PEG was adsorbed onto an oxide passivated silicon wafer by exposure to the polymer solution created using a physiological buffer (HEPES). Frictional forces were measured between the colloidal probe and substrate by AFM as the polarity of the solvent was systematically varied (HEPES, methanol, ethanol, 2-propanol). Higher friction forces were encountered under solvents of lower polarity. Also, the effective thickness of the adsorbed polymer was observed to be greater under HEPES as compared to the alcohols. Higher solvent uptake from QCM measurements identified the origin of decreased friction and increased thickness under solvents of higher polarity as a stretched or extended conformation of the brush-like copolymer. The lateral and normal forces detected between the colloidal probe and this surface-bound copolymer were compared to those found between the colloidal probe and a surface-bound, brush-like copolymer of differing molecular architecture, poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG). Finally, friction forces were monitored under both symmetric and asymmetric PEI-g-PEG-coated interfaces to study conformational and bridging effects as the polarity of solvent was systematically varied.

1. Introduction

The lubrication of surfaces in shear is currently achieved mostly through the use of hydrocarbon oils. As friction is a form of energy loss to heat in all objects with moving components, its reduction is crucial to the efficient performance of nearly all devices that are used or could be developed for use in today’s society. While the use of hydrocarbon
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oils is not problematic in many instances, alternative forms of lubrication must be developed for more technologically-specific applications such as bio-microelectromechanical (bioMEMS) devices and joint lubrication in the human body where biomedical implants must mimic the lubricious behavior of articular cartilage, as in the knee. Vapor and solid phase lubrication are being actively researched for applications in many industrial processes and MEMS devices that will be used in space vehicles. Liquid phase lubrication, however, is clearly more appropriate for biomedical environments such as those listed above. Of particular interest for lubrication in the human body is the use of water-based lubrication for the purposes of biocompatibility and chemical inertness. One beneficial side-effect of water-based lubrication is its environmentally-benign nature; such forms of lubrication could potentially be used in many industrial processes where the disposal of hydrocarbon oils is harmful to the environment. The adsorption of polymer brushes onto surfaces in sliding motion has been shown to result in very low friction forces and coefficients of kinetic friction, especially in good solvents, through experimental studies employing atomic force microscopy (AFM), as well as the surface forces apparatus (SFA),\(^1\)\(^-\)\(^8\) and through theoretical work\(^9\)\(^-\)\(^12\). It has also been demonstrated, through the use of AFM, SFA, optical waveguide lightmode spectroscopy (OWLS), fluorescence microscopy, X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS), that the presence of polymer brushes on a surface increases the protein resistance of the surface\(^13\)\(^-\)\(^17\) by modifying steric-repulsion forces experienced by an approaching surface through the expanded structure of the brush in good solvents.\(^16\)\(^,\)\(^17\) In this work, the solvent-dependent modification of normal and frictional forces by the adsorption of a polymer brush at an oxide interface was studied through considerations of brush stretching as a function of amount of adsorbed solvent within the brush.

Poly(ethyleneimine)-*graft*-poly(ethylene glycol) (PEI-g-PEG) is a polycationic copolymer that physisorbs onto negatively-charged surfaces through coulombic and non-coulombic interactions.\(^18\)\(^,\)\(^19\) At physiological pH (7.4), the PEI backbone becomes positively-charged through protonation of amine groups, and the SiO\(_2\) surface is negatively-charged as the pH exceeds its isoelectric point. Recent work has made use of this adsorption behavior to increase the protein resistance of a surface, with implications
in many biotechnological applications.\textsuperscript{18-20} The adsorption of PEI-g-PEG onto SiO\textsubscript{2} also provides the opportunity to significantly reduce the interfacial kinetic friction in aqueous environments. Extensive work on the low friction detected at interfaces modified with poly(L-lysine)-graft-poly(ethylene glycol) as a function of solvent and molecular architecture\textsuperscript{21-25} and similarities between PLL-g-PEG and PEI-g-PEG in adsorption characteristics and stretch-collapse brush mechanisms due to solvent uptake have led to the study of the solvent-dependent tribological properties of PEI-g-PEG for the purpose of developing aqueous biomimetic lubrication with a copolymer brush structure alternative to PLL-g-PEG. While PLL-g-PEG takes on a rod-like backbone structure when adsorbed onto oxide surfaces, PEI-g-PEG has a more globular adsorbate structure, as shown in Figure 1, allowing for the study of a lubricious copolymer with different molecular architecture.
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**Figure 1.** (a) Structure of PEI-g-PEG, based on the branched PEI structure reported previously.\(^{26}\) Note that the PEI molecular weight, PEG molecular weight, and grafting ratio are represented qualitatively. (b) Schematic displaying the adsorption of PEI-g-PEG on SiO\(_2\)\(^{27}\) surfaces at pH values greater than 2 through the electrostatic attraction between the negatively-charged surface and positively-charged amine groups in the PEI backbone. Highlighted is the core/shell globular-like conformation of the copolymer when adsorbed onto the SiO\(_2\) surface.

Hartung *et al* conducted an analogous study in which the tribological properties of PLL-g-PEG and PAAm-g-PEG, with differing backbone architectures, were compared.\(^{28}\) The structure of PEI-g-PEG consists of a PEI backbone and PEG side chains that are grafted at the amine groups of PEI. The specific copolymer used in this study has a PEI molecular weight of 25 kDa, grafting ratio of 3.5 ethyleneimine units per PEG side chain, and PEG molecular weight of 4 kDa.

In this study, interfacial kinetic friction and normal force-displacement measurements have been conducted as a function of solvent for a PEI-g-PEG-modified silica microsphere-SiO\(_2\) interface using AFM. The amount of solvent adsorbed within the
PEI-g-PEG brush as a function of solvent polarity was detected using the quartz crystal microbalance (QCM) and related to the friction and normal force behavior. This work has demonstrated that, like PLL-g-PEG, PEI-g-PEG exhibits extremely lubricious behavior under good solvent due to the stretched conformation of the brush in such an environment, and that the friction is greatly reduced for a symmetrically-modified interface as compared to an asymmetric PEI-g-PEG-modified interface.

Introduction
References
2. Experimental Section

2.1. PEI-g-PEG Synthesis. PEI(25)-g[3.5]-PEG(4) was synthesized by SurfaceSolutionS GmbH (Zurich, Switzerland) following a modified procedure for the synthesis of PLL-g-PEG, producing brush-like copolymers with a PEI molecular weight of 25 kDa, grafting ratio of 3.5 ethyleneimine units/PEG side chain, and PEG molecular weight of 4 kDa.

2.2. Preparation of PEI-g-PEG-Coated SiO₂ Substrate. Silicon (100) wafers were cleaved to appropriate size (approximately 0.3 cm x 0.3 cm) for use as substrates. Before deposition of PEI-g-PEG onto the substrate, the wafers were treated by the following cleaning procedure: sonicated in acetone for 5 min and 2-propanol for 5 min, copiously rinsed with ultrapure water (18.2 Ω·cm⁻¹) (Barnstead International, Dubuque, IA), submerged in fresh PIRANHA solution (30% H₂O₂/70% H₂SO₄) at 80 °C for 10 min, copiously rinsed with ultrapure water, dried in a nitrogen flow, and exposed to an O₂/H₂O₂ plasma PDC-32G (Harrick Scientific Corp., Ossining, NY) for 2 min. The oxidized substrate was immediately submerged in a 0.25 mg/mL solution of PEI-g-PEG in 10 mM HEPES buffer solution (4-[2-hydroxyethyl]piperazine-1-[2-ethanesulfonic acid], pH 7.4) for 60 min. AFM experiments immediately followed deposition of the polymer on the substrate to eliminate time-dependent material transfer in HEPES buffer solution. The polymer-coated substrates were removed from solution, rinsed with HEPES buffer solution to remove unbound and multilayered PEI-g-PEG, and dried under a nitrogen flow.
2.3. PEI-g-PEG-Coated AFM Tips. Sodium borosilicate microspheres of 5.1 µm diameter were attached at the end of AFM cantilevers (Figure 2) with 0.58 N/m spring constant (Novascan Technologies, Inc., Ames, IA) for use as sliding counterfaces. For normal and friction force measurements with bare oxide counterfaces, the AFM tips were rinsed in 0.1 M HCl (pH 1.0), ultrapure water, exposed to O2/H2O2 plasma for 15 s, and submerged in HEPES buffer solution immediately prior to the experiments. For polymer-coated counterfaces, the tips were cleaned by the same method as the bare oxide tips, with immersion in 0.25 mg/mL solutions of PEI-g-PEG in 10 mM HEPES buffer solutions for 60 min following the plasma treatment. Upon withdrawal from polymer solution, the tips were rinsed with HEPES buffer solution to remove unbound and multilayered PEI-g-PEG and dried under a nitrogen flow prior to use in AFM measurements.

2.4. Normal and Friction Force Measurements Using AFM. Normal and frictional forces were monitored by AFM at the interface of the polymer-modified SiO2 substrate and the bare oxide or polymer-modified sodium borosilicate microsphere under liquid environments, made possible with the use of a liquid cell tip holder (Digital Instruments, Santa Barbara, CA). The AFM was controlled by AFM100/STM100 electronics and SPM32 software (RHK Technology, Inc., Troy, MI). Movement of the
substrate relative to the fixed AFM tip in the x, y, and z directions is due to the implementation of a single-tube piezoelectric scanner. Normal and lateral tip deflections are detected by the motion of a laser beam that is reflected off the back of the cantilever onto a four-quadrant photodiode. This AFM assembly has been discussed in more detail previously.\textsuperscript{2,3}

Kinetic friction was measured between the AFM tip counterface and modified substrate through the torsional deflection of the cantilever due to the sliding of the tip on the substrate during loading and unloading cycles. Both normal and frictional forces were recorded concurrently as the tip was rastered in a line scan mode while being ramped up and down to make contact with the substrate. The half difference between the forward and reverse traces of the friction loop was calculated to provide the friction force response as a function of tip/substrate separation. In this work, a scan rate of approximately 2000 nm/s was used over a distance of 200 nm.

Normal forces were detected as a function of separation of the two interfaces by monitoring the deflection of the cantilever in the direction normal to the surface. Starting at a distance of 200 nm from the substrate, the tip was brought into contact with the substrate and retracted to the original position. This approach/retract cycle allows for measurement of contact distance, comparative contact stiffness, and adhesion forces. In both friction and force-distance measurements, the normal load did not exceed 25 nN to preclude the possibility of tip and substrate damage or wear.

In this study, five friction and force-distance measurements were made at various locations on the substrate. The locations were at the corners and center of a square with side length of 100 nm. Therefore, all of the offset tip positions lie within an area of 10,000 nm\textsuperscript{2}. The offsets allow for representative friction force response data to be chosen based on the average and standard deviation of the coefficients of friction calculated in the five location-specific measurements. Solvents were exchanged in the liquid cell in the order of HEPES, methanol, ethanol, 2-propanol, and HEPES by transferring sufficient volume using two 5 mL syringes. Normal and friction force measurements were conducted under each solvent, with 30 min before the first measurement after injection of each solvent.
The same cantilever/tip assembly was used in solvent-dependent experiments in which the friction and normal force response was compared under the different solvents. With knowledge of the nominal spring constant of the cantilever ($k = 0.58 \text{ N/m}$), normal loads were found based on the known substrate displacement. Friction forces were calibrated by sliding a tip of nominal radius 20 nm, attached to the same cantilever assembly used in experiments, at selected normal force set-points on a silicon grating of known well depth and slope (TGF11, MikroMasch, Spain), allowing for the measured friction force response in mV to be expressed as a friction force in nN. The calibration was performed 3 times with different cantilever/tip assemblies of the same spring constant and radius to generate calibration sensitivity factor data with an average and standard deviation. This calibration method has been discussed in greater detail elsewhere.\(^4\)

**2.5. QCM Measurements.** The quartz crystal microbalance used in this work for relative solvent mass uptake measurements consisted of a SA250B-1 Network Analyzer and test fixture (Saunders & Associates, Inc., Phoenix, AZ), a liquid flow cell (Maxtek, Inc., Beaverton, OR), and QTZ control software (Resonant Probes GmbBH, Germany). The resonators used in QCM experiments were AT-cut quartz crystals (Maxtek) with silica-sputtered gold electrodes and a 5 MHz fundamental resonance frequency.

Prior to measurement, QCM crystals were cleaned with the following procedure: sonicated in acetone, 2-propanol, and ultrapure water for 5 min each with ultrapure water rinse in between each sonication; dried under a nitrogen flow; plasma cleaned in an $\text{O}_2/\text{H}_2\text{O}_2$ environment for 1 min. Immediately after plasma cleaning the crystal, the liquid flow cell was cleaned with 2-propanol and dried under a nitrogen flow, and the quartz crystal was placed in the flow cell. Measurements were made the following day to allow time for the stress relaxation of the Viton O-ring seal in the liquid flow cell. Data were recorded in air for the first 60 min to ensure stabilization of the QCM assembly. Solvents were injected into the liquid flow cell in the following order: methanol, ethanol, 2-propanol, and HEPES. This series of solvents represents the “blank” data to which solvent mass uptake measurements on the polymer-coated quartz crystal were compared. The deposition of PEI-g-PEG was performed *in situ* as the 0.25 mg/mL PEI-g-PEG solution was injected into the liquid flow cell and allowed to adsorb to the silica surface.
for 10 min, followed by a HEPES rinse to remove unbound and multilayered PEI-g-PEG. The solvent injection series (methanol, ethanol, 2-propanol, and HEPES) was then repeated, as before, on the polymer-coated quartz crystal for the purpose of comparison to the solvent mass present on the “blank” quartz crystal. Throughout the experiment, solvents were exchanged in 10 min intervals during which data were collected. Frequency and bandwidth shift values were calculated by averaging the data over 5 min intervals when the system was in equilibrium. The change in resonance frequency was related to the adsorbed mass by the Sauerbrey equation:

$$m_{\text{wet(Sauerbrey)}} = -C \frac{\Delta f}{n}$$

where $$m_{\text{wet(Sauerbrey)}}$$ is the adsorbed solvent mass, $$C$$ is a constant, $$\Delta f$$ is the change in frequency, and $$n$$ is the wavenumber.

### 3. Results and Discussion

The solvent-dependent tribological properties of a PEI-g-PEG interface have been investigated through friction force measurements with the use of AFM and related to the polymer brush stretching through AFM normal force measurements and adsorbed solvent mass within the brush through QCM measurements. The solvent was systematically varied from good solvent (HEPES buffer solution) to progressively worse solvent as the polarity of the alcohol molecule decreased (methanol, ethanol, and 2-propanol). SiO₂ was chosen as the material for both the substrate and counterface due to the electrostatically-driven adsorption of cationic copolymers such as PEI-g-PEG and PLL-g-PEG. A 5.1-μm diameter sphere was chosen as the counterface because it allows for small contact pressures on the soft polymer thin film. Typical AFM tips, with radii less than 100 nm, would have much larger contact pressures and could damage the soft thin film upon contact. In the following sections the effect of solvent on the frictional and normal forces for a PEI-g-PEG-modified interface, comparison of the tribological properties of PEI-g-PEG- and PLL-g-PEG-modified interfaces, adsorption of PEI-g-PEG on SiO₂ surface, adsorption of solvent within the PEI-g-PEG copolymer brush as a function of solvent
quality, and comparison of the tribological properties of symmetric and asymmetric PEI-g-PEG-modified interfaces will be discussed.

3.1. Effect of Solvent on the Frictional Forces at Polymer Brush-Modified Oxide Interfaces. Sliding of the SiO$_2$ substrate and silica colloidal microsphere while in contact allowed for the detection of interfacial kinetic friction, with the procedure already mentioned in the Experimental Section. In the study of the solvent-dependent tribological properties of the polymer-modified SiO$_2$/silica microsphere interface, both surfaces were coated with graft copolymers, of equal grafting ratio and component molecular weight, from aqueous HEPES buffer solutions to preclude material transfer from one surface to the other. The AFM cantilever/tip assembly remained consistent throughout these experiments. Measurements began 30 minutes after the injection of each solvent to remove any kinetically-driven differences in frictional and normal forces due to differences in solvation of the adsorbed copolymer brush.

(a)

![Graph showing friction response vs. normal load](image)

(b)
Figure 3. (a) Interfacial friction measured as a function of increasing load between a silica colloidal probe and SiO$_2$ surface, both modified by the adsorption of PEI(25)-g[3.5]-PEG(4). The solvents displayed in the legend are those under which the friction measurement was obtained, 30 minutes prior to injection. The measurements were all performed using the same AFM cantilever/tip assembly. (b) The inset provides interfacial friction measured as a function of increasing load between the probe and surface, both modified by PEI(25)-g[3.5]-PEG(4) in one experiment and PLL(20)-g[3.2]-PEG(5) in another. Both measurements were performed in HEPES buffer solution (pH 7.4) with the same AFM cantilever/tip assembly.

In Figure 3(a), interfacial kinetic friction is plotted as a function of increasing normal load for the symmetric contact of PEI(25)-g[3.5]-PEG(4)-modified tip and substrate. It is evident in the plot that the change in friction as a function of increasing normal load is the least for HEPES buffer solution and increases progressively for methanol, ethanol, and 2-propanol, i.e. the kinetic coefficient of friction $\mu_k$ is vanishingly low for the copolymer interface when solvated in HEPES and increases as the solvent progresses in the order methanol, ethanol, and 2-propanol. The nearly constant friction force magnitude at normal loads approximately less than 5 nN for all solvents can be attributed to the boundary layer of solvated PEI-g-PEG, as solvent molecules are not
“squeezed out” until loads are sufficiently high. The trend seen in the coefficient of kinetic friction as a function of solvent is due to differences in solvent polarity. At pH 7.4, HEPES buffer solution is dominantly comprised of water. Therefore, the polarity varies for the solvent series as follows: HEPES buffer solution > methanol > ethanol > 2-propanol. In HEPES buffer solution, the PEG side chains form hydrogen bonds with nearby water molecules. Since PEG is a polar molecule, it can be expected that the interaction between PEG side chains and nearby solvent molecules decreases with decreasing solvent polarity. For more polar solvents, then, the amount of trapped solvent in the brush-like structure of PEI-g-PEG is greater than for less polar solvents. The lubricity increases (friction decreases) for a good solvent such as HEPES in which the copolymer takes on a swollen brush-like structure. For a poor solvent such as 2-propanol, the lubricity decreases as a result of a more collapsed brush conformation due to decreased solvent uptake in the copolymer. Previous studies have shown similar results of low friction for polymer brush-modified interfaces in good solvents, specifically for the case of swollen polystyrene brushes in toluene, measured with both the surface forces apparatus (SFA) and AFM.

Previous work in our laboratory and those of collaborators on the tribological behavior of polymer brush-modified interfaces has primarily focused on PLL-g-PEG-coated SiO₂ surfaces. Comparison of the tribological behavior of PEI-g-PEG- and PLL-g-PEG-modified interfaces allows for the investigation of biomimetic material alternative to previously studied PLL-g-PEG. While the backbone (PLL) in PLL-g-PEG is an unbranched, linear polymer, the “backbone” (PEI) in PEI-g-PEG used in this study is branched; it is therefore of interest to compare the tribological properties of two graft copolymer brushes with differing molecular architecture and possible adsorption properties, which will be discussed below. Shown in Figure 3(b) is a plot of the friction as a function of increasing normal load for symmetric (both substrate and microsphere tip have adlayers) PEI(25)-g[3.5]-PEG(4)- and PLL(20)-g[3.2]-PEG(5)-coated interfaces in HEPES buffer solution, measured with the same AFM cantilever/tip assembly. Vanishingly low friction was observed for all ranges of measured increasing normal loads for both types of interfaces. Previous studies also found very lubricious behavior of PLL-g-PEG-coated interfaces in buffer solution (or water) and attributed it to a similar brush-like structure, as seen in Figure 3(b).
swelling mechanism in good solvent.\textsuperscript{11,13} Although the molecular architecture of these two copolymer systems are distinct, they share a similar mechanism of swelling in good solvents and very low friction in such solvents. It should be noted that the plots presented in Figure 3 all pass through the origin, meaning that any adhesion between the copolymer-coated surfaces is of negligible magnitude.

3.2. Effect of Solvent on the Normal Forces at PEI-g-PEG-Modified Oxide Interfaces. Contact between the SiO\textsubscript{2} substrate and silica colloidal microsphere AFM tip allowed for the normal forces at such an interface to be monitored as a function of substrate displacement from its original position (as the displacement increases, the substrate-tip separation distance decreases), as described previously in the Experimental Section. A symmetric interface was formed by coating both substrate and tip with PEI(25)-g[3.5]-PEG(4) from HEPES buffer solution. The effect of solvent on the normal forces detected at this interface was probed by obtaining force-distance curves 30 minutes after the \textit{in situ} injection of methanol, ethanol, 2-propanol, and HEPES. The AFM cantilever/tip assembly remained constant throughout these force-distance measurements. It should be noted that for comparative purposes minor shifts were made to the curves so that they share a common point for their maximum normal load.

(a)

(b)
Figure 4. Normal load detected as a function of the $z$ displacement of the piezoelectric tube scanner, upon which the sample rests, for the contact between a PEI-g-PEG coated silica colloidal probe and SiO$_2$ surface under various solvents. For zero $z$ displacement, the tip-sample separation is maximized. (a) The approach curve represents increasing load while (b) the retract curve represents decreasing load.

Presented in Figure 4 are the approach (increasing normal load) and retract (decreasing normal load) load-displacement curves for the symmetric PEI-g-PEG-modified interface that was described above. In both curves it is clearly evident that a solvent-dependence exists for the load-displacement behavior. When solvated by HEPES, the contact point of the two modified surfaces occurs at a displacement of approximately 100 nm for increasing load; contact is made at a displacement of approximately 150 nm in the alcohols. This difference in contact point suggests that the PEI-g-PEG brush is in a more stretched conformation under HEPES than under the alcohols. In a qualitative sense, it is also evident that there is a softer contact between the surfaces under HEPES than under the alcohols, as the normal load increases less rapidly as a function of displacement under HEPES as compared to the alcohols. Also depicted in Figure 4(a), there is a long-range repulsive interaction prior to contact when the brush is solvated with HEPES. While the normal load remains virtually zero until contact under the alcohols, it
gradually increases prior to contact under HEPES. This behavior can be attributed to steric-entropic repulsion effects of a more stretched conformation of the adsorbed copolymer, as discussed below. The decreasing normal load-versus-piezoelectric displacement curves displayed in Figure 4(b) show similar solvent-dependence to the increasing load curves in Figure 4(a). The retract curves for the alcohols show very little hysteresis when compared to the approach curves. Comparison of the approach and retract curves under HEPES, on the other hand, reveal the presence of hysteresis. This observation, along with a “pull-off” point at a separation that is 50 nm greater than for the contact point, suggest that there is adhesion between the two PEI-g-PEG-modified surfaces as they are separated (which will be discussed in greater detail below).

The solvent-dependent surface forces monitored at PEI-g-PEG-modified interfaces are a measure of the ability of this copolymer to adopt collapsed and extended conformations under solvents of varying polarity. The more stretched conformation observed under HEPES can be attributed to entrapment of water molecules within the PEG brush structure. PEG forms hydrogen bonds with nearby water molecules, causing the grafted PEG chains to expand when solvated with a buffer solution that is comprised mainly of water. It is important to note, however, that hydrogen bonding is not the only form of interaction between polar solvents and PEG. As PEG is a polar molecule due to the ether group in the \([-C-C-O-]\) \(_n\) repeat unit, van der Waals’ interactions will be present in both water and the alcohols. Dipole-dipole interactions, as well as hydrogen bonding, will cause association between PEG and polar solvents. Due to the \(-\text{OH}\) group in the alcohols, hydrogen bonding will exist between these solvent molecules and the PEG chains; however, the alcohols show weaker attractions to PEG as the forces of hydrogen bonding and dipole-dipole interactions decrease as solvent polarity decreases. As the solvent molecule becomes progressively less polar (methanol > ethanol > 2-propanol) hydrophobic dispersion interactions between the hydrophobic tail of the alcohol and the hydrophobic portion of the PEG repeat unit become more important, and the polar interactions become less dominant. When the solvated brush is compressed as the two surfaces approach and make contact, de Gennes scaling theory predicts that there will be a strong repulsive force due to osmotic pressure of the solvent within the brush and a weak attractive elastic restoring force due to extension of the polymer chains.
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osmotic pressure within the brush will act to squeeze the solvent out of the brush as it is compressed. Since the PEG-water interaction is stronger than the PEG-alcohol interaction, more alcohol will be forced out of the brush than will water. Therefore, as solvent quality (polarity in this case) decreases, the PEG-solvent interaction decreases and PEG-PEG interaction increases as the PEG brush is compressed. This phenomena can explain both the softer contact and lower friction observed between compressed brush-modified surfaces under HEPES buffer solution.

The normal interfacial forces observed as the tip approaches the substrate can be represented by a combination of electrostatic and steric-entropic repulsion forces. Electrostatic forces could be caused both by the presence of surface charges and ions in buffer solution (HEPES). It is unlikely that similar surface charges would generate electrostatic forces between the two surfaces because no long-range repulsion is observed in the increasing normal load-displacement curves in alcohol. In HEPES, on the other hand, electrostatic interactions could contribute to the long-range repulsive forces that are observed in Figure 4(a). Charged ionic salts in buffer solution that are adsorbed in each polymer brush layer could cause electrostatic repulsion as the two layers approach each other. It is likely that another contributor to the long-range repulsive forces seen in HEPES is polymer brush steric-entropic forces. Since the brush is most expanded under HEPES from osmotic pressure, the grafted brush may interact more repulsively with an approaching particle (brush-modified microsphere, in this case) than for the alcohols due to steric and entropic repulsions associated with an increase in PEG-PEG interactions and decrease in PEG-solvent interactions. It should be noted that compression of the underlying PEI layer is also possible as contact is made between the two surfaces.

The hysteresis observed between the increasing and decreasing normal load-displacement curves in Figure 4 is due to adhesion that is often characteristic of either bridging or entanglement of polymer chains between the AFM tip and substrate. Although the interface studied in this case is symmetric with polymer adsorbed on both surfaces, it is still possible that some bridging of polymer chains between the two surfaces occurs. In the case of an asymmetric interface this idea would be more important as the bare silica microsphere, for example, adheres to the polymer chains tethered to the substrate through coulombic interactions (in the pH environment used in
this study PEI is positively-charged and silica is negatively-charged). The small adhesive force shown in Figure 4(b) for HEPES can also be attributed to physical entanglement of polymer chains as the substrate is pulled away from the tip. The lack of adhesion when the brush is solvated with the alcohols can be explained by a collapsed brush structure, in which bridging and entanglement of chains is precluded by their decreased stretching from the surface as compared with HEPES-solvated PEI-g-PEG; this decreased stretching is evident in Figure 4(b), where separation of the two surfaces occurs at a distance that is approximately 100 nm greater for HEPES than for the alcohols. The difference in contact point between the approach and retract curves for HEPES further suggests that adhesion occurs under HEPES, while the contact point remains approximately constant between approach and retract curves for the alcohols. The jagged pattern of the adhesion is due to the detachment of individual polymer chains from the other polymer-coated surface.

Previous work on PLL-g-PEG has shown that the adhesion forces for a symmetric interface are negligibly small.\textsuperscript{11,12} While it has been shown that PLL-g-PEG exhibits a rod-like conformation with extended PEG brushes when adsorbed onto oxide interfaces\textsuperscript{10-13}, the difference in magnitude of adhesion forces suggests that these two lubricious systems have distinct conformational structures when adsorbed onto such interfaces.

3.3. Adsorption of PEI-g-PEG on Oxide Surfaces and Solvent Within the Brush as a Function of Solvent Quality. Detection of changes in mass and dissipation of energy by QCM resulted in the study of adsorption of PEI-g-PEG on SiO_2-coated QCM crystals and the adsorption of solvent molecules within the copolymer brush. Adsorption of the copolymer was allowed to occur \textit{in situ} over a period of 10 minutes, and the relative masses of solvents before and after polymer adsorption were compared to arrive at values for solvent mass uptake as a function of solvent quality. Changes in dissipation measured the differences in energy loss of the resonating crystal for different solvents.

PEI-g-PEG physisorbs onto negatively-charged oxide surfaces through both coulombic and non-coulombic interactions. This copolymer consists of the weak PEI polybase and PEG chains that are grafted at some of the amine groups of the PEI backbone. For pH values less than 9, PEI is positively-charged due to protonation of the amine groups present.\textsuperscript{17-19} Coulombic attraction between the PEI backbone of PEI-g-PEG
and the SiO₂ substrate used in this study occurs because the substrate becomes negatively-charged at pHs above its isoelectric point (IEP) of approximately 2.0.\textsuperscript{13,20,21} Claesson \textit{et al} have shown that there are approximately 2.5 amine groups of the PEI chain adsorbed at each negatively-charged surface site on mica.\textsuperscript{19} Assuming similar characteristics for adsorption on SiO₂, the adsorption of the copolymer then causes a transition of the effective surface charge from negative to positive. Aside from the coulombic component, there also exists a noncoulombic component to the attraction between the PEI backbone and negatively-charged substrates\textsuperscript{22}, including van der Waals’ attractions and hydrogen bonding between the –OH termination of the plasma-treated SiO₂ substrate and amine groups in PEI. Consistent with our findings, desorption of PEI-g-PEG from negatively-charged surfaces does not occur upon rinsing with solvents.\textsuperscript{23} While PEI has been shown to adsorb onto negatively-charged surfaces in the form of a flat adlayer\textsuperscript{19}, PEI-g-PEG adsorbents exhibit a more globular conformation.\textsuperscript{17} This adlayer conformation differs from that of PLL-g-PEG, in which the PLL backbone takes on a more rod-like structure with the PEG chains extending away from the surface.\textsuperscript{10-13} However, we observed, through the use of QCM, that the adsorption of these two graft copolymers is very similar kinetically (data not shown) as the greatest mass uptake occurs within the first several minutes of exposure of a SiO₂ substrate to the copolymer solution at pH 7.4. In each case the adsorption is largely associated with electrostatic interactions, suggesting that the kinetic nature of the adsorption process is due to electrostatic repulsive (and steric) barriers as the coverage of the adsorbed layer is increased.\textsuperscript{22}
Table 1. The wet mass of PEI(25-g[3.5]-PEG(4)) adsorbate on SiO$_2$-coated QCM crystals as a function of solvent. Each value represents the difference in mass between combined viscous and adsorbate loading and solely viscous loading of the solvent. The combined loading is under the respective solvent following adsorption of the copolymer, while only viscous loading is due to only that of the corresponding solvent baseline before copolymer adsorption. The series of injections following copolymer adsorption was as follows: HEPES, methanol, ethanol, 2-propanol, and HEPES. Therefore, HEPES (first rinse) represents the comparison of the first HEPES injection following adsorption to its pre-adsorption baseline, while HEPES (second rinse) compares the second HEPES injection after adsorption to the baseline.

Depicted in Table 1 is the wet mass of the PEI-g-PEG brush as a function of solvent. The wet mass is a measure of the mass of adsorbed copolymer as well as that of solvent molecules adsorbed within the brush. The viscous loading of each solvent can be neglected because the wet mass is calculated by taking the difference between the mass following adsorption for each solvent and the “baseline” mass of each solvent prior to adsorption. The data provided clearly show a direct correlation between solvent quality and the mass of solvent absorbed within the brush. The adsorbed mass increases significantly as the polarity of solvent increases in the following manner: 2-propanol < ethanol < methanol < HEPES. This relationship follows from the increased interactions between PEG chains and solvent molecules as the polarity of the solvent increases, as
discussed previously. The rise in mass uptake in HEPES from the first to the second rinse can be rationalized in terms of solvent trapping within the brush, caused by incomplete solvent exchange upon injection of the next solvent. Injection of the alcohols likely does not remove all of the water molecules trapped within the brush after the HEPES injection. The change in energy dissipation in the QCM resonator, related to the bandwidth shift, was greatest when PEI-g-PEG was solvated with HEPES and decreased as the solvent polarity decreased. In HEPES, where the adsorbed polymer mass is greatest due to maximized solvation of the brush, the increased viscoelastic damping of the piezoelectric resonator originates from the highest mass loading condition of the crystal. This QCM data thereby corroborates the lubricious behavior and brush expansion observed, through AFM measurements, in polar solvents by displaying the direct relationship between adsorbed solvent within the brush and solvent quality.

3.4. Comparison of the Tribological Properties of Symmetric and Asymmetric PEI-g-PEG-Modified Interfaces. Frictional forces were measured using AFM as a function of increasing normal load for the contact between the PEI(25)-g[3.5]-PEG(4)-modified SiO$_2$ substrate and both bare and PEI(25)-g[3.5]-PEG(4)-modified counterfaces. The effect of symmetry on the tribological properties was studied under various solvents as the series of injections was as follows: HEPES, methanol, ethanol, 2-propanol, HEPES.
Figure 5. Interfacial friction recorded as a function of increasing normal load. (a) Asymmetric interface in which only the SiO$_2$ substrate is coated with PEI-g-PEG (the silica tip is uncoated). (b) Symmetric interface in which both the silica tip and SiO$_2$ substrate are coated with PEI-g-PEG. In both cases, the series of injection was as follows: HEPES, methanol, ethanol, 2-propanol, and HEPES. The two measurements performed under HEPES are thereby distinguished based on relative order in the legend.
Figure 5 displays friction-load behavior in each solvent for the (a) asymmetric and (b) symmetric PEI-g-PEG-modified interface. Both the coefficient of kinetic friction $\mu_k$ and magnitude of friction force (note the respective friction force scale bars) for a particular normal load are significantly greater for the asymmetric interface for each solvent. The symmetric interface exhibits more lubricious behavior because there are greater repulsions for this case than for the asymmetric interface as the substrate approaches the microsphere. These repulsions are steric in nature and characteristic of polymer brush structures, as explained previously. For the symmetric interface the PEG chains tethered to each surface repel one another due to unfavorable increases in entropy and decreases in free volume as they are compressed. In the asymmetric case, there is only one “layer” of tethered PEG chains causing repulsions at the interface since the opposing surface is an uncoated silica microsphere. Increased polymer-polymer repulsions lead to greater normal loads required to achieve equal compression of the copolymer for the symmetric interface than for the asymmetric interface. Qualitative evidence of distinctions in compression of the interface can be seen in comparing the change in friction force over the range of normal load 0-5 nN for both cases in Figure 5. The friction begins increasing immediately for the asymmetric interface, while the friction remains constant for loads up to approximately 5 nN for the symmetric interface. As described earlier, the friction is independent of load in this low-load regime for the symmetric interface due to inability to force solvent molecules out of the brush. Thus the brush at the asymmetric interface is more compressed at low normal loads than that of the symmetric interface. Representing a “softer” brush-like interface, the symmetrically-coated surfaces experience lower shear forces as they slide relative to one another due to increased polymer-polymer repulsions. Therefore, differences in steric-entropic repulsions cause the symmetric interface to display lower friction than the asymmetric interface for all solvents, originating from brush-brush as opposed to silica-brush interactions, respectively.

While the trends in friction-load behavior as a function of solvent are in accordance for both interfaces under the second HEPES injection and the alcohols, there exists hysteresis in the behavior between the two HEPES solvations for the asymmetric interface. Although it is imaginable that material transfer from the coated substrate to the
negatively-charged bare tip could cause the friction to be significantly lower after the transfer event due to effective sliding of a polymer-polymer interface, it was found that this mechanism was not responsible for the observed hysteresis. Friction-load behavior was measured under HEPES and ethanol for an asymmetric PEI-g-PEG-modified interface, followed by measurement again under HEPES after cleaning the AFM tip by soaking in 0.1 M HCl and ultra-pure, de-ionized water and exposure to an H$_2$O$_2$/O$_2$ plasma for 15 s. The friction was unchanged between the two HEPES solvations and dropped substantially after subsequent modification of the tip with PEI-g-PEG, excluding the possible material transfer mechanism (data not shown). The authors believe that the mechanism responsible for the observed hysteresis is bridging of amine groups in the PEI backbone with the bare silica microsphere. Amine groups not utilized in PEG grafting are positively-charged at pH 7.4, while the microsphere is negatively-charged at this pH. Upon adsorption of PEI-g-PEG on the SiO$_2$ substrate, it is conceivable that not all of the available charged amine groups are attracted to the substrate due to the globular adsorption structure of this copolymer.$^{17}$ As the bare, negatively-charged microsphere approaches the substrate during friction measurements, these freely-moving portions of the PEI backbone would adhere to the probe through electrostatic attractions; thus causing increased friction due to adhesion between the two surfaces. Upon solvation in the alcohols, the collapse of the brush due to decreased polymer-solvent interactions may effectively cause these free amine groups to electrostatically bind to the substrate in regions of local negative surface charge. When the brush is again solvated with HEPES the entrapped water molecules would give rise to an extended brush conformation, but the once-free amine groups would remain adhered to the substrate as adhesion of the copolymer was observed to be irreversible in the solvents used in this work. The burying of positively-charged amine groups of the PEI backbone then explains the transition from high to vanishingly low friction in HEPES buffer solution.
4. Conclusion

The tribological properties of a surface-bound, brush-like copolymer (PEI-g-PEG) have been studied as a means to decrease the normal and shear forces experienced between a silica colloidal probe and oxide surface. PEI-g-PEG was adsorbed from solution onto oxide passivated silicon surfaces through both coulombic and non-coulombic interactions to form molecularly thin films, making AFM appropriate for this study. Lateral force measurements detected vanishingly low friction in HEPES buffer solution, a good solvent, while friction was found to increase for the alcohols as the solvent polarity decreased (methanol, ethanol, 2-propanol). The solvent-dependent friction response observed in AFM experiments was corroborated by solvent mass uptake studies using QCM. Greater mass uptake in the PEI-g-PEG brush was seen under HEPES buffer solution versus the alcohols. Normal force-displacement relationships monitored using AFM revealed an increased film thickness for the PEI-g-PEG brush under HEPES buffer solution as the separation distance of the “contact point” for the colloidal probe/substrate interface was greater for HEPES than the alcohols. Increased solvent mass uptake and film thickness under solvents of greater polarity associated the lubricious behavior with an expanded or stretched PEI-g-PEG brush conformation.

Friction force measurements of symmetric (PEI-g-PEG-coated substrate and probe) and asymmetric (PEI-g-PEG-coated substrate and unmodified probe) interfaces demonstrated differences in the solvent-dependent friction response due to bridging effects present between the brush and unmodified probe in the asymmetric interface. Comparison of the friction response of PEI-g-PEG and PLL-g-PEG brushes under HEPES buffer solution revealed vanishingly low friction forces in good solvent for both systems, even though there are significant differences in molecular architecture. The similar tribological behavior of these two brushes allows for the use of PEI-g-PEG as an alternative to PLL-g-PEG in aqueous biomimetic lubrication.
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