ABSTRACT

SONG, JUNLONG. Adsorption of Amphoteric and Nonionic Polymers on Model Thin Films. (Under the direction of Prof. Orlando J. Rojas).

Understanding the adsorption behaviors of polymers from solution is critical in applications such as fiber processing, specifically in the development of fiber bonding and lubrication. Therefore, in situ and real time Quartz Crystal Microbalance and Surface Plasmon Resonance were employed to monitor the adsorption of hydrosoluble polymers (including amphoteric and nonionic macromolecules) on ultrathin films of cellulose, polypropylene, polyethylene, nylon and polyethylene terephthalate.

The extent of adsorption of amphoteric polymers on cellulose (and also on silica) depended on the charge density of the polymer, the substrates and pH of the medium. More importantly, the adsorbed amount exceeded that found in the case of simple polyelectrolytes. We hypothesized that this extensive adsorption is the result of a polarization effect produced by the charged substrate, which also determined the characteristics (thickness and viscoelasticity) of the adsorbed layers as well as bonding abilities.

Surface active polymers including diblock polyalkylene glycols and triblock polymers (based on ethylene- and propylene- oxide) as well as silicone surfactants were used to study the formation of boundary layers that are relevant in fiber lubrication. Adsorption isotherms for the nonionic polymers followed a Langmuirian behavior in which the hydrophobic effect was a major driving mechanism. It was concluded that surface-active molecules form robust self assembled (lubricant) layers that withstand high shear forces and are able to control friction and abrasion due to the unique molecular structures they form at the interface.
Adsorption of Amphoteric and Nonionic Polymers on Model Thin Films

by

Junlong Song

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APPROVED BY:

Dr. Orlando J. Rojas
Committee Chair

Dr. Martin A. Hubbe

Dr. Dimitris S. Argyropoulos

Dr. Kirill Efimenko
BIOGRAPHY

The author was born on May 6, 1974 in Yongchuan, Chongqing, People’s Republic of China. He grew up in his hometown until Fall 1994 when he joined Beijing Forestry University, Beijing. He obtained a Bachelor degree in Chemical Engineering in 1998 and a Masters degree in Pulp and Paper Science in 2001, from the same institution and department. After graduation, he worked as a process engineer for China International Engineering Co. Ltd (China BCEL) for three years. In July, 2004, he came to Raleigh to join the Ph.D. program in the Department of Wood and Paper Science in North Carolina State University. He married Hongyan Li in 2004 and they have a one year old daughter, Cindy.
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Chapter 1

Background
INTRODUCTION

Surfaces and interfaces play important roles in defining the interactions between “objects” in everyday life. The term “surface” refers to an interface between an object and its environment (e.g., air). Recent developments in science and technology have demonstrated the importance of interfaces in materials science, including applications involving microelectronics, coatings, colloids, and surfactants. In these applications, the interfacial properties can be more important than the bulk ones and in fact define the molecular characteristics of the system.

The “thickness” of a boundary between two phases, if possible to define, is expected to be extremely narrow. For example, the interface between two crystals can be only few atoms; on the other hand, a thick polymer interface entails a soft contact. The scale we, in polymer science, are interested in is much thicker than that in the case of crystals, usually in the range of one or few polymer layers. Using polymers to modify the interface offers some advantages due to the possibility to tune their properties, including the molar mass, architecture, and monomer composition, etc. However, in order to effectively modify the interfacial properties of a surface, the polymer has to be bound to the respective interface. The process whereby a polymer binds to the surface is called “polymer adsorption”. Therefore, polymer adsorption is fundamental in many important applications involving for example, adhesives, motor oils, colloidal stabilizers and coatings, to name only a few.

Adsorption is a consequence of the balance of the surface energy and the nature of the polymer. In the bulk, the conformation of a polymer depends on the chain composition and architecture. At an interface, the conformation is perturbed by the attraction of polymer segments
towards the surface (see Figure 1.1). The attraction may involve chemical or physical attraction. In this respect, adsorption can be classified into chemisorption and physisorption, respectively.

![Figure 1.1. Polymer adsorption onto surfaces from solution. D is the thickness of adsorbed polymer layer.](image)

Polymers or macromolecules possess a broad diversity of properties that are often related to their dissociation ability in aqueous solution. As such they are classified into ionic (so called polyelectrolytes) and nonionic polymers. Ionic polymers are also sub-classified into simple polyelectrolytes, with either positive or negative charged groups, and polyampholytes, which contain both positive and negative charged groups. As can be expected, the interaction between a polymer and a surface is different for these different types of polymers.

Polymer adsorption has been studied for many years from theoretical and experimental approaches. In this research, we focused on the adsorption of polyampholytes and nonionic polymers on solid surfaces. In the next sections, a review on polyampholytes in papermaking and nonionic lubricants in boundary lubricant will be given. At the end of this chapter, a brief account on the techniques used to study polymer adsorption will be also presented.
POLYAMPHOLYTES IN PAPERMAKING

Polyampholytes are charged macromolecules carrying both acidic and basic groups. Under appropriate conditions the acidic and basic groups in polyampholytes dissociate in aqueous solution producing ionic groups and the respective counterions. If the ionic groups on the polymer chain are weak acids or bases, the net charge of the polyampholytes can be changed by varying the pH of the aqueous medium. At the isoelectric point (IEP) the number of positive and negative charges on the polyion is the same, giving a net charge of zero. In the vicinity of the isoelectric pH, the polymers are nearly charge-balanced and exhibit the unusual properties of polyampholytes. At conditions of high charge asymmetry (far above or below the isoelectric pH), these polymers exhibit a simple polyelectrolyte-like behavior.

Recent reports indicate that polyampholytes could be used in colloid stabilization, wetting, lubrication, adhesion waste water treatment and papermaking. In the case of papermaking, for example, as more recycled fibers are used, more interesting and new molecular architectures have been proposed to improve product strength. Every time a fiber is recycled, it loses some of its strength: especially tensile and burst strengths. After being reused several times, recycled fibers in the absence of chemical additives, may not be any longer useful for papermaking. One possible alternative to overcome this challenge caused by fiber recycling is the addition of polyampholyte additives, which are expected to enhance the wet and dry strength of the paper product.

To our knowledge, the first report on the application of polyampholytes to enhance strength of paper was published in 1977 by Carr, Hofreiter et al. Starch-based polyampholytes were
prepared by xanthating cationic cornstarch derivatives, which had either tertiary amino
\([-\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]\) or quaternary ammonium \([-\text{CH}_2\text{CHOHCH}_2\text{N}^+\text{(CH}_3)_3]\) groups attached
through linkages. Anionic xanthate groups were introduced into the cationic starch amines. The
substitution degree of the obtained derivatives ranged from 0.023 to 0.33 for the amine cation and
0.005 to 0.165 for the xanthate anion. This work demonstrated that wet-end additions of a starch
polyampholyte was effective in providing both wet and dry strengths, exceeding those given by
either cationic or anionic starch polyelectrolytes. For a given amine degree of substitution (DS),
there was a charge ratio of \(A\) (amine, positive)/\(X\) (xanthate, negative) at which each polyampholyte
gave a well-defined maximum wet strength. This \(A/X\) ratio was about 1 for tertiary amine with a
low DS (DS of 0.023, 0.035, and 0.06) but was about 2 to 3 for tertiary amines with a high DS of
0.33 (see Figure 1.2). The authors also found that polyampholytes with quaternary amines
substitution were slightly more effective than those with tertiary amines.

More recently fully synthetic polyampholytes were systematically introduced to enhance
paper strength by our labs \(^9, 22-27\). The employed polyampholytes were prepared by free-radical
polymerization of cationic monomer N-[3-(N’,N’-dimethylamino)propyl]acrylamide (DMAPAA),
a tertiary amine, anionic monomer methylene butanedioic acid (known as itaconic acid, IA) and
neutral acrylamide (AM) monomer. The advantages of synthetic polyampholytes over
natural-based ones include the higher charge density that can be achieved; simple control of the
molecular weight and charge ratio of cationic and anionic groups; uniform molecular weight
distribution (lower degree of dispersity), etc. Superior dry strength of polyampholytes over simple
polyelectrolytes was reported in several publications \(^9, 22-27\) from which an illustrative figure is
used here (see Figure 1.3). Under the experimental conditions used, polyampholytes were applied at 1% addition level on bleached hardwood kraft fibers. Paper’s breaking length increased 20-50% compared with control experiments. An interesting phenomenon reported was that the strength increased with the charge density and reached the maximum for polyampholytes of intermediate charge density (PAm4 and PAm8, see Chapter 3 from detailed nomenclature) and then the strength fell with highly charged polyampholytes. A near neutral pH was found to be optimum condition for strength performance. This could be explained by the fact that under this condition, which is close to the iso-electric point (IEP) of the polyampholytes, a maximum efficiency for adsorption is achieved and bonding between fibers is promoted.

![Figure 1.2. Wet strength of paper treated with xanthated starch amine (XSA) having various tertiary amine and xanthate degrees of substitution (DS). The paper samples were prepared from unbleached kraft furnish treated with 3% XSA, oven dry pulp basis, at pH 7.0. Figure redrawn from reference 32.](image)

Not only can polyampholytes enhance paper strength, but also they may be used as retention/drainage/formation aids. They can also be used to treat coated broke where the white
pitch or stickies and pigments are fixed to the long fibers and fiber fines and, finally, in process water clarification to settle or float the solids from the white water for solids removal \(^{26, 32, 33}\).

Despite the fact that a number of theoretical and computational efforts has been reported \(^{13, 14, 17, 18, 21, 28, 34-36}\), there is a lack of experimental data to advance our knowledge in this field. The previous account and ensuing citations is only an example of some of the few reports available in this area. Therefore there is a need for understanding the adsorption phenomena, especially in the case of polyampholytes, that will lead to new functional additives and improved performance.

In this study we carried out adsorption experiments with a series of polyampholytes having increased total charge densities at a constant ratio of cationic to anionic monomeric groups and molecular mass. The principal aim of our efforts in polyampholyte research (Chapter 5) is to clarify the relationship between the charge nature of these polymers and the adsorption and

![Graph](image-url)
conformation of the respective adsorbed layers.

**LUBRICATION AND TRIBOLOGY IN TEXTILE PROCESSING**

The science of friction, lubrication and wear, also called tribology, has long been of both technical and practical interest, since the functioning of many mechanical systems depends on these phenomena \(^{37}\). This field has received increased attention as the incommensurable waste of resources resulting from unwanted high friction and wear has become evident. In fact, according to some estimations, proper attention to tribology could lead to economic savings of 1.3% to 1.6% of the Gross National Product (GNP) \(^{38}\).

In textile processing, fibers, threads and yarns go through many different stages, including pretreatment, dyeing, printing and finishing until they are weaved into end products. Machinery and equipment are inevitably involved in handling fibers at high shear rates. Fiber materials are subjected to destructive abrasive forces that can be the result of both mutual abrasion between strands and/or between the strands and equipment surfaces. In order to control friction and reduce wear between fibers and between fibers and metal surfaces (and other materials such as ceramics, etc.), the use of lubricants is indicated. Fiber lubricants are commonly used during the production of many different fiber grades, including fiberglass and synthetic fibers such as polyesters, polyolefins, polyacrylics, polyamides, etc. \(^{39}\). A myriad of different lubricant formulations exists depending on the intended use and operation conditions. We worked closely with industry to identify model fiber lubricant systems. An advisory team provided us with input and shared their industrial expertise. Four general classes of boundary lubricants for low energy polymer surfaces were identified:
(1) High molecular weight, water dispersible products - significantly reduce abrasion damage to fibers in aggressive textile processes and seem to function most effectively in dynamic, higher speed situations;

(2) Waxy materials - traditional boundary lubricants that function in both low speed (fiber to fiber) and high speed (fiber to metal, fiber to ceramic) applications;

(3) Low molecular weight polymers that have high affinity for the polymer surface and tend to structure themselves on the surface and,

(4) Silicone based materials - tend to have high affinity for the surface of many of the polymers that are used in fibers.

Our focus in this research involved nonionic surface-active polymers and silicone surfactants. With the technological development in fiber processing, there is a major trend in textile operation towards higher speed, higher productivity and better quality. Therefore, the motivation of our research rested on the need to develop better quality lubricants to meet the requirements of fiber processing. This prompted us to understand the structure-property relations of lubricants that would eventually lead to the design of systems that better meet textile demands.

**Lubrication phenomena**

Lubrication phenomena are involved when substances such as grease or oil (so-called lubricants) are applied to moving objects to reduce friction. Amonton's law, one of the best known theories concerning lubrication and friction, was proposed in the 17th century in order to describe sliding friction analytically, at the macroscopic scale:  

\[ \mu = \frac{F_f}{N} \]  

(Equation 1.1)
where $\mu$ is the coefficient of friction, which is a dimensionless scalar value that describes the ratio of the force of friction between two bodies, $F_f$, and the force pressing them together and the normal force applied, $N$. From a macroscopic view, $\mu$ is a constant, which is related to the nature of both contacting objects; here the frictional force ($F_f$) is independent of the apparent contact surface. This equation can be applied in many cases, at the macroscopic scale and for sliding objects directly in contact. However, simple experimental observation shows that frictional forces do depend on the contact area, the surface roughness as well as the chemical nature of the sliding substances.

When dealing with fluid lubricants, it is found that the situation becomes even more complicated since the gap between the two moving objects may vary. The friction coefficient may depend on the gap between the sliding surfaces as well as the sliding speeds or shear rates. According to Hamrock $^{40}$, four different regimes of fluid film lubrication can be defined, i.e., boundary, mixed, elasto-hydrodynamic and hydrodynamic regimes, depending on the film parameter $A$. A profile of friction coefficient as a function of $A$ is illustrated by the Stribeck curve (Figure 1.4). The film parameter, $A$, represents the minimum film thickness separating the two surfaces and can be quantified by using Equation 1.2:

$$
\Lambda = \frac{V \times \eta_b}{P}
$$

(Equation 1.2)

where $V$ is the threadline speed in the case of textile processing; $\eta_b$ is the bulk viscosity of the lubricant (or textile finish) and $P$ is the pressure applied between the two sliding surfaces.
In full-film lubrication (i.e. the so-called hydrodynamic lubrication), the surfaces are separated by a thick lubricant film. Ideally, there is no wear of the solid surfaces, and the friction is determined by the rheology, surface chemistry, and intermolecular forces of the lubricant. In boundary lubrication the performance essentially depends on the boundary film since in this boundary regime the load is carried by the surface asperities and the lubricant film. In the intermediate, mixed region both the bulk lubricant and the boundary film play key roles. Therefore under these conditions the properties of the adsorbed components of the lubricant, and the chemistry and dynamics of the interfacial region between the tribosurfaces are of utmost importance.

In the Stribeck curve, the bulk viscosity $\eta_b$ applies to all the cases considered, from wide to narrow gaps between the sliding surfaces. However, in reality, the local or microscopic effective viscosity $\eta_{\text{eff}}$ may be quite different from the bulk viscosity $\eta_b$, especially in the case of very
confined systems of ultra narrow gaps. Discontinuous transitions between different dynamic states (e.g. solid-to-solid or static-to-kinetic sliding transitions) not considered in the Strubeck theory often occur in thin films (produced by the lubricant molecules specifically adsorbed on the surfaces). In addition, the ordering and frictional behaviors of the confined molecules are found to switch at some critical load, velocity or temperature (which is different from the melting point of the bulk fluid). Therefore, Luengo, Israelahvili and Granick proposed a set of improved Strubeck-type curves that are based on experimental data typical in engineering conditions. They used three individual figures, shown as Figure 1.5, 1.6 and 1.7, to illustrate how friction changes against with shear rate, sliding velocity and load. In Figure 1.5, three main classes of fluid behaviors can be distinguished: (1) Thick film, elasto-hydrodynamic sliding: At zero load (L=0), $\eta_{\text{eff}}$ is independent of the shear rate except that shear–thinning may be displayed when shear rate is sufficiently large. (2) Boundary layer film, intermediate regime: A Newtonian regime is observed at low loads and low shear rates, but $\eta_{\text{eff}}$ is much higher that the bulk value, $\eta_b$. As the shear rate increases beyond $\dot{\gamma}_{\text{min}}$, these systems reach a point where the effective viscosity starts to drop with a power-law dependence on the shear rate. As the shear rate increase still more, beyond $\dot{\gamma}_{\text{max}}$, a second Newtonian plateau is again encountered. (3) Boundary layer films, high load: The $\eta_{\text{eff}}$ continues to grow with load and the behavior is Newtonian provided that the shear rate is sufficiently low. Transition to sliding at high velocity is discontinuous and usually of the stick-slip type.
The corresponding generalized map of friction force plotted against sliding velocity in various tribological regimes is shown in Figure 1.6. In this figure, with increasing load, the Newtonian flow in the elasto-hydrodynamic (EHD) regimes crosses into the boundary regime of lubrication. Note that at the highest velocities, even elasto-hydrodynamic (EHD) lubrication lowers the shear stress response. At the highest loads ($L$) and smallest film thickness ($D$), the friction force passes through a maximum (the static friction, $F_s$), followed by a regime where the friction coefficient ($\mu$) is roughly constant with increasing velocity (i.e. the kinetic friction, $F_k$, is roughly constant). Non-Newtonian shear-thinning is observed at somewhat smaller load and larger film thickness; the friction force passes through a maximum at the point where $De \sim 1$ ($De$, the Deborah number, is the point at which the applied shear rate exceeds the natural relaxation time of the boundary layer film). The velocity axis from $10^{-10}$ to $10^{10}$ (arbitrary units) indicates a large span. The corresponding $F-L$ map is shown in Figure 1.7. With an increasing velocity ($V$), $F$ increases at
first moderately, then more rapidly, with increasing $V$. A discontinuous transition to $F$ independent of $L$ is eventually expected.

![Friction Force vs Sliding Velocity Diagram](image)

**Figure 1.6.** Proposed generalized friction map friction force plotted against sliding velocity. Figure redrawn from reference \(^{42}\).

Friction curves illustrate the phenomena and trends on how friction or friction coefficient varies with operational parameters at a macroscopic scale. However, several issues are still unexplained, for example, what is the origin of friction and why does friction change in the fashion presented in these figures? To answer these questions we have to resort to studies at the nano or molecular levels. This is the so called molecular tribology, which focuses on the lubricant films’ formation and structure.
While this thesis covers the general topic of boundary lubrication, only a few parameters were studied. Our focus lay in the chemistry and adsorbed layer state of nonionic and silicone surfactants. Issues related to roughness, asperities and others are not considered here.

**Thin film lubrication**

**Lubrication in textile processing**

Within the boundary lubrication regime, the load is carried by the lubricant thin film. A typical lubricant film is very thin, usually 100 nm or lower, i.e., only several to hundreds of molecules thick \(^{43-45}\). Studying the structure of lubricant thin films and how the molecules organize during the lubrication process is of utmost importance. Here physisorption (as opposed to chemisorption) is a dominant effect since in textile processing the lubricant film is not always

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Figure 1.7. Proposed generalized friction map of friction force plotted against load. Figure redrawn from reference \(^{42}\).
intended to be retained onto the surface of the fibers, specially if the lubricant on fiber surfaces would interfere with successive processes, such as finishing and dyeing. However, the robustness or strength of adsorbed layer in textile processing is an issue that hasn’t been addressed systematically.

Property changes and transitions in thin films

The properties of lubricant thin films change depending on their distance from the surface. When the thickness of the adsorbed film is comparable to the dimensions of the lubricant molecules themselves, the properties of the thin film is quite different than that of the bulk medium. As shown in Figure 1.8, the effective viscosity, elasticity and relaxation time grow with diminishing thickness and diverges when the film thickness is sufficiently small. In this case, classical continuum considerations, which apply to the bulk phase, do not apply to thin films.

![Figure 1.8. Schematic diagram of how the effective viscosity, elasticity and relaxation change with thickness of a lubricant film. Figure redrawn from reference 41.](image)

The diffusion coefficient of lubricant molecules in thin films also diverges when compared with that in the bulk. Mukhopadhyay et al. 46 found that the molecular diffusion coefficient
decreases exponentially from the edges towards the center in systems under Hertzian contact.
Hertzian contact is an ideal model to describe deformation and lubrication. In this model, only
small deformation occurs in contact areas, contacting bodies are elastic and therefore only vertical
forces are considered. Granick et al. \(^{47, 48}\) studied the influence of shear behavior on polymer
interfacial diffusion. According to their results, shear did not modify substantially the Brownian
diffusion.

Phase behaviors of lubricants may change in confinement conditions. This may be one of
the reasons why properties of thin films differ from the bulk. Confinement-induced phase states of
lubricant layers could change from liquid-like to an amorphous state and then to a solid-like state \(^{49}\).
Low friction is exhibited by solid-like and liquid-like layers; high friction is exhibited by
amorphous layers. A change of some factors, such as temperature and humidity generally can shift
the phase status from the solid-like towards the amorphous or liquid-like states.
Confinement-induced solidity of lubricant was observed by Denirel and Granick \(^{50}\) by placing
octamethyl cyclotetrasiloxane (OMCTS) liquids between two rigid mica plates when spacing was
decreased below \textit{ca.} 10 molecular dimensions. This phenomena was also observed by Israelachvili
and coworkers \(^{51, 52}\) by shearing polybutadiene (PBD) of 7000 molecular weight . They found that
at low shear rates, PBD exhibited bulk-like properties in films thicker than about 200 nm. In
thinner films (200-20 nm), the shear viscosity \(\eta_{\text{eff}}\) and moduli \(G'\) and \(G''\) became quite different
from those of the bulk. On entering the tribology regime (film thickness <30 nm) PBD exhibited
highly nonlinear behavior and yield points, indicative of phase transitions to "glassy" or
"solid-like" states. Klein et al \(^{53}\) discovered that the transition between liquid-like behavior and a
solid-like phase of the liquids under progressive confinement take place abruptly at a distance around six molecular layers. The films that are thinner than six molecular layers behaved in a solid-like fashion, in the sense that they required a critical stress in order to shear them.

**Structure of lubricant films**

Why can lubricants reduce friction, i.e. how do lubricants work and how do the lubricant molecules behave under shear? This question is being investigated by several groups. Lubricant molecules organize themselves under shear as illustrated in Figure 1.9 by Yoshizawa et al. A critical velocity $V_{c}^{*}$ exists; if the sliding velocity of two surfaces are below it, a polymeric lubricant film exhibits amorphous structure and chains of polymer interplay and entangle with each other. In this case high friction is produced (static-kinetic sliding). This phenomenon supports that chain interdigitation is an important molecular mechanism that gives rise to “boundary” friction and adhesion hysteresis of monolayer-coated surfaces. If the sliding velocity of two surfaces is above the critical velocity, polymer chains will be aligned or “combed” by shear into an ordered conformation and therefore will result in very low friction (superkinetic sliding).

![Figure 1.9. Lubricant molecules organized by shear. Figure redrawn from reference 49](image)

Shear–induced alignment of lubricant molecules was supported by a number of
experiments. Frantz and co-workers \(^5^4\) adsorbed polyisoprene onto a single solid surface and found that the backbone of the polymer oriented in the direction of flow. They also found that the extent of orientation increased with increasing molecular weight. The structure of the lubricant, such as chain length \(^5^4\), packing densities \(^5^5,^5^6\), and nature of the polymer (brush-like \(^1^1\) or grafted polymer \(^5^7\) and chain ends \(^5^8\)) influenced its alignment under shear.

Within these investigations, the work of Urbakh et al \(^5^7\) is very significant. They used grafted polyelectrolytes, hyaluronan and hylan, to mimic cartilage lubrication. These polysaccharides (outermost cartilage layer) were not expected to be the responsible molecule for the great lubricity of cartilage; however, the authors found that they may contribute to the load bearing and wear protection in these surfaces. Their study showed that a low coefficient of friction is not a requirement for, or necessarily a measure of, wear protection. This gives us much inspiration to think about the design and formulation of lubricants and their layer structure for wear protection.

**Techniques to study thin films and lubrication phenomena**

It is well known that the function of thin films in boundary lubrication and mixed lubrication regimes is to offer friction reduction and wear protection. Therefore, thin film lubrication is a phenomenon that exists universally in conventional tribological systems. A better understanding of thin film lubrication will improve our knowledge of how lubricants work, and will result in the development of superior lubricant formulations for use in industry, and also will improve our capabilities to predict tribological failures.

In the last few decades, rapid advancements in analytical instruments and techniques and
the expansion in computer power offered an unprecedented opportunity to unveil how lubricant polymers behave under boundary lubrication conditions (at the atomic/molecular or nano levels). Atomic force microscope (AFM) with lateral force capabilities measures the friction between a substrate and a few to several hundred atoms on a sharp tip. The lateral resolution can be less than an atomic spacing 59, 60. On the other hand the surface force apparatus (SFA) can measure the forces between atomically flat surfaces as their separation is varied with Ångstrom level resolution. The friction and adhesion can be studied as a function of the chemistry and thickness of the material between the surfaces 11, 61-65. Computer simulation has played an important role in interpreting and explaining the findings from these experimental methods. Computer simulations and theoretical investigations have shed much light on the molecular details underlying both structural and dynamic behavior of liquids in the highly confined regime 66, 67.

From the molecular view, lubrication molecules adsorb on a metal or organic surface with ordered or oriented chains. As mentioned before, the interactions of solid surfaces and lubricant films could be physical adsorption, or chemical reactions 68. The thickness or the adsorption mass and structure of the adsorbed layer are crucial to the performance of lubrication 69-72. SPR and QCM both are well-established noninvasive techniques capable of providing a wealth of information about interfacial phenomena in situ, in real time and in fluid media 3, 8, 73-87. The resolution of surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) are in the Ångstrom/nano scale. Even though friction cannot actually be measured with QCM and SPR, they can help find a relationship between adsorbed mass (or thickness) and lubrication phenomena. Ellipsometry is another powerful technique which can be applied to measure the thickness of
adsorbed layers. The advantages of QCM are that it can provide some intrinsic properties of the adsorbed film, such as its viscoelasticity (QCM with dissipation monitoring) and coupled water (if results from the QCM are compared with those from SPR or ellipsometry).

The ability to evaluate dynamic behaviors is quite similar with both systems from a technical point of view, but when it comes to sensitivity they differ. Table 1.1 compares the QCM-D and SPR techniques. QCM-D systems are more sensitive to water-rich and extended layers, while the SPR system is favored for compact and dense layers. The reason to this difference is due to the different physical principles by which the coupled mass is measured. The mass-uptake estimated from SPR data is based on the difference in refractive index between the adsorbed materials and water displaced upon adsorption. Therefore, water associated with the adsorbed materials, e.g. the hydration water, is essentially not included in the mass determination. In contrast, changes in frequency acquired with QCM-D are affected by the coupled water arising from hydration, the viscous drag and/or entrapment in cavities in the adsorbed film. This means that the SPR response is proportional to the "dry mass", while in QCM-D measurements the layer is essentially sensed as "hydrogel" composed of the macromolecules and coupled water. While SPR measures one parameter only, the additional information contained in energy dissipation measurements when using QCM-D increases the base for a detailed interpretation. Changes in the dissipation are related to the shear viscous losses induced by the adsorbed layers, and thus provide information that has the potential to identify structural differences between different adsorbed systems, or structural changes in the same type of molecule during the adsorption process through D-F profile.
To reveal the intricacies of boundary lubrication, techniques to probe adsorption, friction, topography accompanied by molecular dynamics simulation, were used in our lab. In this chapter, we discuss the principles of SPR and QCM and their applications to boundary lubrication. In the next sections and also in Chapter 6 to 8, we focus our attention in the measurement of adsorption of lubricants in textile processing by SPR and QCM. Finally, we will also introduce briefly the measurement of friction via lateral force microscopy (LMF) and molecular dynamic simulation (MDS), last chapter of this thesis.

Table 1.1. Comparison between QCM and SPR techniques (*).

<table>
<thead>
<tr>
<th>Instrument</th>
<th>QCM-D</th>
<th>SPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principles</td>
<td>Piezoelectric/electromechanical</td>
<td>Optical</td>
</tr>
<tr>
<td>Resolution</td>
<td>3 ng/cm² (QCM-E4) in water</td>
<td>10 ng/cm² in water</td>
</tr>
<tr>
<td>Limitation</td>
<td>N/A</td>
<td>Small molecules with Mw&lt;1000 give very small response</td>
</tr>
<tr>
<td>Detection range</td>
<td>The detection range varies from nanometers to micrometers, depending on the viscoelasticity of the adsorbed film. In pure water it is approximately 250 nm.</td>
<td>~300 nm</td>
</tr>
<tr>
<td>Information provided</td>
<td>- Adsorbed mass - Adsorption kinetics - Dissipation</td>
<td>- Total adsorbed mass - Adsorption kinetics - Reflective index adjacent to metal surface</td>
</tr>
</tbody>
</table>

(*) Source: QCM and SPR manuals and manufacturer websites.

Methods used in this research

Principles of SPR and QCM

*Surface Plasmon Resonance (SPR)*

A surface plasmon is a charge density wave occurring at the interface between a metal (gold is the most used in SPR) and a dielectricum. Surface plasma are excited when the energy of
the photon electrical field is just right so that it can interact with the free electron constellations in the gold surface. The photon energy is then transferred to the charge density wave. This phenomenon can be observed as a sharp dip in the reflected light intensity. The angle where the sharp dip happens is called “SPR angle”. Outside the metal surface there is an evanescent electric field, which decays exponentially. This evanescent field interacts with the close vicinity of the metal. Changes in the optical properties of this region will therefore make the (SPR) angle shift. This is the principle basis of SPR. A schematic of SPS is shown in Figure 1.10.

![Figure 1.10. Schematics of surface plasmon resonance, from Ref. 89.](image)

The position of the SPR angle depends on the refractive index of the substance with a low-refractive index close to the sensing surface. The refractive index near the sensor surface changes because of the binding of polymers to the surface. As a result, the SPR angle will change according to the amount of bound polymers. The thickness of the adlayer can be estimated from Equation 1.3, which assumes that the thickness of the dielectric film is much less than the
wavelength of the probing laser:

\[ d_f = \frac{n\lambda}{2\pi} \sqrt{-\varepsilon_m \varepsilon_s (\varepsilon_s - \varepsilon_m)} \frac{\varepsilon_f}{(\varepsilon_f - \varepsilon_s)(\varepsilon_f - \varepsilon_m)} \frac{\varepsilon_m + \varepsilon_s}{\varepsilon_m \varepsilon_s} \Delta (\sin \theta_c) \]  \hspace{1cm} (Equation 1.3)

where \( d_f \) is the thickness of adlayer; \( n \) is the solvent refractive index; \( \lambda \) is the wavelength of the incident laser; \( \varepsilon_f \) is the dielectric constant of the film; \( \varepsilon_s \) is the dielectric constant of the solvent; \( \varepsilon_m \) is the real part of the dielectric constant of the metal; and \( \theta_c \) is the critical resonant angle on the plasmon resonance curve. So for a given system with known solvent and metal, \( \theta_c \) is the only variable. Equation 1.3 can be simplified as:

\[ d_f = k \Delta (\sin \theta_c) \]  \hspace{1cm} (Equation 1.4)

where \( k \) is a factor that can be obtained after a calibration. In most case, \( \theta_c \) is very small and there is a linear relationship between the amount of bound material and the shift of the SPR angle \(^{79, 83}\). SPR response values are usually expressed in resonance units, RU (1 RU = 0.0001°) or refractive index units, RIU (1 RU = 0.001 RIU = 1 \( \mu \)RIU). For most proteins and polymers, changing of 1 RU is roughly equivalent to a change in concentration of about 1 pg/mm² and changing of 10 \( \mu \)RIU is roughly equivalent to a change in concentration of about 1 ng/cm² on the sensor surface. The exact conversion factor between RU and surface concentration depends on properties of the sensor surface and the nature of the molecule responsible for the concentration change.

One limitation of SPR technique is that for those compounds with molecular weights smaller than 100 - 200 Daltons can’t be detected because the change in refractive index for small molecule binding is too low to be detected directly. On the other side, since the penetration depth of the evanescent wave’s limitation, for those particles larger than this range cannot be measured.
totally. However, both situations are not relevant in most cases and linear relationships hold\textsuperscript{90}. The reader is referred to a number of excellent review papers\textsuperscript{79,83} and internet resources\textsuperscript{90} that discuss SPR and its principles of operation.

Quartz Crystal Microbalance with Dissipation, QCM-D

A QCM crystal consists of a thin quartz disc sandwiched between a pair of electrodes (cf. Figure 1.11a). Due to the piezoelectric properties of quartz, it is possible to excite the crystal to oscillation by applying an AC voltage across its electrodes (cf. Figure 1.11b).

![Figure 1.11. QCM sensor (a) and schematic principle of QCM](image)

The resonant frequency ($f$) of the crystal depends on the total oscillating mass, including water coupled to the resonator. When a thin film is attached to the sensor crystal the frequency decreases. If the film is thin and rigid, no or minimum energy dissipation occurs, the decrease in frequency is proportional to the mass of the film. This is Sauerbrey relation\textsuperscript{91}:

$$\Delta m = -\frac{\rho_q f_0 \Delta f}{n f_0} = -\frac{\rho_q v_q \Delta f}{2nf_0^2} = -\frac{c\Delta f}{n}$$

(Equation 1.5)

$C = 17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ for a 5 MHz quartz crystal.

$n = 1,3,5,7$ is the overtone number.

Since the change in frequency can be detected very accurately the QCM operates as a very
sensitive balance. The quartz crystal microbalance (QCM) was first used to monitor thin film deposition in vacuum or gas atmospheres at first. More recently, it was shown that the QCM may be used in the liquid phase, thus the number of applications for the QCM increased dramatically. The Sauerbrey relation was initially developed for adsorption from gas phase, it is now extended to liquid media where it holds in most cases. In order to describe soft adlayers of polymer adsorbing from liquid media, the dissipation value was introduced. Rodahl et al. 80 extended the use of the QCM technique and introduced the measurement of the dissipation factor simultaneously with the resonance frequency by switching on and off of the voltage applied onto the quartz. The measured change in dissipation is due to changes in the coupling between the oscillating sensor and the surroundings. It is affected by any energy dissipating process and thus influenced by the layer viscoelasticity and slip of the adsorbed layer on the surface. The dissipation factor $D$, is the inverse of the so-called $Q$ factor and defined by:

$$D = \frac{1}{Q} = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$  \hspace{1cm} (Equation 1.6)

where $E_{\text{dissipated}}$ is the energy dissipated during one period of oscillation and $E_{\text{stored}}$ is the energy stored in the oscillating system. The resonance frequency is measured when the oscillator is on and when it is turned off the amplitude of oscillation, $A$, can be determined in it decay as an exponentially damped sinusoidal function:

$$A(t) = A_0 e^{-t/\tau} \sin(\omega t + \phi) + c$$  \hspace{1cm} (Equation 1.7)

where $\tau$ is the decay time, $\omega$ is the angular frequency at resonance, $\phi$ is the phase angle and the constant, $c$, is the offset. The dissipation factor is related to the decay time through Equation
1.8.

\[ D = \frac{1}{\pi f \tau} \]  
(Equation 1.8)

Combining Equations 1-5 and 1-8, the dissipation changes can be expressed as Equation 1.9.

Dissipation changes not only with the properties of the adsorbed layer but also with the density and viscosity of the solution \(^{81}\):

\[ \Delta D = \sqrt{n} \frac{1}{\rho f} \sqrt{\frac{\eta f}{2\pi f}} \]  
(Equation 1.9)

Generally, soft adlayers dissipate more energy and thus are of higher dissipation value. From this point of view, dissipation value is an indicator of the conformation of the adlayers. This is the fundamental basis of QCM-D technique.

A practical QCM-D system records the signals of fundamental frequency (5 MHz) and overtones (e.g., 15, 25 and 35 MHz and even high frequencies for newly developed systems). Each overtone has its own detecting range in thickness. This enables its abilities to measure non-uniform adlayer. Theoretical work was done by Voinova and coworkers \(^{92}\). A general equation was derived to describing the dynamics of two-layer viscoelastic polymer materials of arbitrary thickness deposited on solid (quartz) surfaces in a fluid environment.

\[ \Delta f \approx -\frac{1}{\pi \rho_0 h_0} \left\{ \eta_3 + \sum_{j=1,2} \left[ h_j \rho_j \omega - 2h_j \left( \frac{\eta_3}{\delta_3} \right)^2 \frac{\eta_j \omega^2}{\mu_j^2 + \omega^2 \eta_j^2} \right] \right\} \]  
(Equation 1.10)

\[ \Delta D \approx \frac{1}{2\pi f \rho_0 h_0} \left\{ \eta_3 + \sum_{j=1,2} \left[ 2h_j \left( \frac{\eta_3}{\delta_3} \right)^2 \frac{\mu_j \omega}{\mu_j^2 + \omega^2 \eta_j^2} \right] \right\} \]  
(Equation 1.11)
where ρ stands for density; h stands for thickness; η stands for viscosity and δ stands for the viscous penetration depth (δ = \sqrt{\frac{2\eta}{\rho\omega}} ). The subscript 0, 1, 2 and 3 denote quartz crystal, layer 1, layer 2 and bulk solution respectively. From this model, the shift of the quartz resonance frequency and the shift of the dissipation factor strongly depend on the viscous loading of the adsorbed layers and on the shear storage and loss moduli of the overlayers. These results can readily be applied to quartz crystal acoustical measurements of the viscoelasticity of polymers which conserve their shape under the shear deformations and do not flow, and layered structures such as protein films adsorbed from solution onto the surface of self-assembled monolayers. By measuring at multiple frequencies and applying this model, which has been incorporated in Q-Sense software QTools™, the adhering film can be characterized in detail: viscosity, elasticity and correct thickness may be extracted even for soft films when certain assumptions are made.

In summary, QCM technique with dissipation monitoring has the advantage that it can measure the adsorbed amount via Δf and conformation via ΔD, simultaneously in situ and in real time. Furthermore, some adlayer properties, such as viscosity, elasticity and effective thickness can also be extracted from a set of measurements, as will be illustrated later in the respective chapters.

**Applications of SPR and QCM to Study Lubricant Films**

**Monitoring adsorption and desorption of lubricants**

The basic application of SPR and QCM is to monitor the adsorption and desorption of macromolecules on surfaces. They can be used in various ways to study lubrication: Firstly, they
are useful to find out if a lubricant has affinity or not with a given organic/polymeric substrate. Secondly, they enable elucidation of how strong the affinity is and, thirdly, QCM and SPR can measure the actual kinetics of adsorption and desorption.

Typical adsorption curves can be seen in other chapters of this thesis. If we take Figure 8.2 as a reference, it can be succinctly explained here that we compared the affinity difference for a commercial silicone-based lubricant onto polyethylene (PE) and polypropylene (PP) surfaces. The experiment started with a baseline, and then silicone lubricant solution was injected in the loop. Correspondingly, a sharp frequency drop and dissipation raise were observed (see Figure 8.2) since the lubricant adsorbed on the surface. When both frequency and energy dissipation reached their equilibrium state, large amount of pure water was injected to rinse. A sharp rise in frequency and a sharp drop in dissipation could then be observed. This behavior indicated that lubricant molecules in bulk as well as molecules loosely bonded on the surface were removed by rinsing. During the experimental process, the injection speed of the sample was kept constant at 0.1ml/min. Comparing the adsorption curves of PP with those of PE, the frequency change for PP film was observed to be larger than that for PE film, either on the basis of total adsorption (-22.5 Hz vs -18.4 Hz) or adsorption after rinsing (-10.2 Hz vs -8.6 Hz). This indicates that the affinity of silicone lubricant with PP is much higher that that with PE surface. We note that energy dissipation values didn’t change significantly. This indicated that the adsorbed layers on PP and PE had similar viscoelasticities (related to thickness, composition and conformation).
Lubricant degradation can also be measured by the QCM technique. In order to monitor the degrading process of lubricants at high temperature, Wang et al. 93 developed a QCM system which could endure high temperatures (more than 200 °C). They evaluated the thermal stability of polyol ester lubricants in the QCM chamber. Figure 1.12 provides an example that demonstrates how different lubricants showed different sensitivities to temperature. Here the lubricants were held in a T-controlled chamber. The lubricants degraded gradually when they were heated to very high temperature leaving solid residues on the tested QCM crystal surfaces. Two commercial-grade pentaerythritol tetrapelargonate based lubricants, EM, AF (codes for two commercial lubricant compositions), are shown in this figure. During the first nine hours, both EM and AF didn’t change too much with the temperature treatment which indicated that both lubricants were stable. However, after exposure to high temperatures for nine hours the frequency of AF decreased rapidly while EM barely changed. This indicated that EM was much more stable.
than AF at the tested temperature of 200 °C. The results from QCM can thus provide an integral picture of the thermal stability of lubricants from the quantitative, real-time, in situ information it generates during the thermal decomposition of the lubricants.

**Kinetics of adsorption and desorption**

![Image of QCM data with theoretical Langmuir fit](image)

Figure 1.13. Change in frequency for 5 MHz Si crystals upon injection of OTS (10 mM). The arrow indicates injection time. Insert is an enlargement of the region indicated by the box, to show the stability level. Figures from reference 7.

The time-dependent signals (changes in frequency and refractive index in QCM and SPR, respectively) can be used to study the adsorption kinetics. The Langmuir isotherm, an often used model, is a simple equation that relates adsorption and concentration. For such a mechanism, the adsorption rate can be written as represented in Equation 1.12:

$$\phi(t) = \frac{\beta}{\alpha} [1 - \exp(-\alpha t)]$$  \hspace{1cm} (Equation 1.12)

where $\phi$ is the fraction of free active sites on the surface, $\alpha = C_b k_{af} + k_{ar}$ and $\beta = C_b k_{af}$. $C_b$ is the concentration of lubricant, while $k_{af}$ and $k_{ar}$ represent the constants of adsorption and desorption, respectively. The parameters $\alpha$ and $\beta$ can be obtained by fitting the frequency to Equation 1.12. An example of QCM data with its theoretical Langmuir fit is shown in Figure 1.13 7. From the relation
between $\alpha$ and $C_b$, the values of $k_{ar}$ and $k_{af}$ can be determined. The results of the adsorption rate calculations, the equilibrium constant ($K_{eq} = k_{af}/k_{ar}$), and free energy of adsorption were also determined by Equation 1.13:

$$\Delta G = -RT \ln K_{eq}$$  \hspace{1cm} (Equation 1.13)

**Conformation of lubricant films revealed by the QCM-D**

As described before, the conformation of adsorbed lubricant layers can be derived from QCM data. For rigid, ultrathin, and evenly distributed adsorbed layers, the Sauerbrey equation \(^{91}\) describes successfully the proportional relationship between the adsorbed mass ($m$) and the shift of the QCM crystals’ resonance frequency ($f'$). Under these conditions, the dissipation value is a constant. It doesn’t change with time or with increased adsorbed mass. On the other hand, if the adsorbed material exhibits a viscoelastic behavior, such as for layers of proteins, substantial deviations from the Sauerbrey equation can occur. Using $\Delta D - \Delta f$ plots one can eliminate time as an explicit parameter and as concluded in previous studies \(^{6, 81, 88, 94}\), the absolute slopes and their changes provide information about the kinetic regimes and conformational changes \(^{88}\). These slope values indicate the conformation of adsorbed layer: The lower value indicates a softer layer. If more than one slope exists, it can be concluded that more than one conformation states of the adsorbed layer are present during the adsorption process. Figure 1.14 shows the relation between dissipation change and frequency change for low and high charge density polyampholytes. From these slope values one can draw meaningful conclusions including the fact that the low charge density polyampholytes tend to form a uniform layer. For high charge density polyampholytes, the adsorbed layer is no longer uniform since the slope changes and the inner layer is more compact.
compared with the outer layer, which exhibits a flat slope.

Figure 1.14. $\Delta D-Df$ profiles for polyampholyte adsorption on silica surfaces. The low charge density polyampholite (PAmp4) consisted of 5% cationic and 4% anionic groups while the high charge density polyampholyte (PAmp16) contained 20% of cationic and 16% anionic groups. The “cationic” polymer had a charge density of 5% (cationic groups).

Nonionic lubricants, on the other hand, show different conformation than that those of typical polyampholytes. Figure 1.15 shows $\Delta D-Df$ curves for two Pluronic nonionic polymers. One can see that the polymer with longer hydrophilic chains (E76P29E76) form a thicker adsorbed layer than that with shorter hydrophilic chains (E37P65E37).
Figure 1.15. $\Delta D$-$\Delta f$ profile of nonionic lubricants E76P29E76 and E37P65E37 as they adsorb onto PET surfaces before rinsing.

**Coupling QCM and SPR**

As explained before SPR and QCM are often used to monitor ultrathin-film deposition and dissociation; however, each has its own specific strengths, weaknesses, and assumptions inherent in data collection and analysis. By combining these two techniques in performing *in-situ* measurements, we are able to take advantage of the strengths of each.

By using SPR and QCM independently to monitor interfacial processes, we are able to obtain two measures of a process that rely on fundamentally different principles of physics, namely optical and electromechanical, respectively. Figure 1.16 is an example to demonstrate how QCM and SPR data can be combined to study the kinetics of adsorption of a thin organic film.

In this case both curves agree with each other very well.
Figure 1.16. Comparison of adsorption kinetics of a perfluoropolyether lubricant (Fomblin ZDOL) on silver surfaces as measured by SPR and QCM. Figure from reference 84.

Any differences between the signals in QCM and SPR, indicate that the film is viscoelastic or there is some coupled water in the adsorbed layer. By carefully considering the nature of each measurement, one is able to decouple the viscoelastic property and the contribution of coupled water in the film. Below we present more detailed explanation about the role of coupled water and how to determine it.

Water is one of the most important “lubricants” and can be applied to boundary, elasto-hydrodynamic and hydrodynamic conditions. Water can be used as a boundary lubricant due to the fluidity of hydration layers nanoconfined between two surfaces is totally different from the water in bulk 95-98. The coupled water with lubricant polymers has the same function to protect the contact surfaces to minimize abrasion. To measure the coupled water is not an easy task since it is difficult to distinguish the coupled from the bulk water. In addition to the comparing QCM and SPR signal to get some insight about water contribution, we explain below two alternative ways to decoupled water from the bulk.
The first approach is to substitute water with D₂O, as reported by Hook and others. D₂O substitution increases the density and shear viscosity of the bulk liquid and coupled water by ~10% and ~25% respectively but doesn’t change any kinetic and equilibrium state. Therefore, from the slight difference in frequency from experiments conducted in normal and heavy water, the coupled water fraction can be obtained through Equation 1.14.

\[
S_{\text{fraction}} = \frac{\Delta f_s - \Delta f_d}{\Delta f_s (1 - \frac{\rho_d}{\rho_p}) - \Delta f_d (1 - \frac{\rho_s}{\rho_p})}
\]

(Equation 1.14)

Subscript s, d, p represents solvent, deuterated water and polymer respectively. In some cases where \( \rho_p = \rho_s \), Equation 1.14 can be simplified to Equation 1.15.

\[
S_{\text{fraction}} = \frac{\Delta f_s - \Delta f_d}{\Delta f_s (1 - \frac{\rho_d}{\rho_p})}
\]

(Equation 1.15)

Since the difference is pretty small, only polymers adsorbing in large quantities or carrying large amounts of coupled water can be analyzed with this approach.

The other way to decouple hydration water is by combining QCM and optical methods, for example SPR or ellipsometry. The change in resonant frequency \( f \) of the QCM crystal depends on the total oscillating mass, including water coupled to the oscillation. While for SPR or ellipsometry, water coupled with adsorbed molecules doesn’t affect the refractive index. In other words SPR and ellipsometry are blind to water coupled with the adsorbing species. Therefore by subtracting the mass determined from SPR or ellipsometry from that from QCM the contribution of coupled water is revealed. Figure 1.17 is an example used here to demonstrate the combination of QCM and SPR techniques. The polymer tested was a cationic polyamide.
cationic groups), with molecular weight ca. 3 millions. The surface used in this experiment was negatively charged silica surface. The results showed that there was around 25\% of water in the adsorbed polymer layer. The same system was studied by using the deuterated water method. Unfortunately, the results showed a much lower coupled water value, around 4\% water content. This may have been caused by the small adsorption amount and low fraction of water in the adlayer, therefore the difference between $\Delta f_s$ and $\Delta f_d$ was relatively small, which was affected by experimental errors significantly.

![Graph](image)

Figure 1.17. Decoupling water content through the combination of QCM and SPR measurements. The polymer used in this experiment is a cationic polyamide, with molecular weight of ca. 3 millions. Coupled water determined by this method was found to be 25\%.

**Lateral force microscopy and molecular dynamic simulation**

In the previous section, we focused on the principles and applications of SPR and QCM. Both instruments allow measurement of adsorption. In this section, we will briefly address
friction measurements and molecular dynamics simulation.

Lateral Force Microscopy (LFM) is a technique that can measure actual friction by lateral forces and so it is able to evaluate lubricants’ performance on specific surfaces. Molecular Dynamic simulation (MDS), on the other hand is a tool to simulate and quantify the interaction between lubricant molecules and with the surfaces. MDS can be used to understand further how lubricants interact with the surface and how lubrication properties are produced through self assembly using theoretical predictions. Both LFM and MDS, were used with SPR and QCM techniques, to unveil a more comprehensive understanding of lubrication phenomena.

**Lateral Force Microscopy (LFM)**

LFM is a technique based on scanning probe microscopy, and is one of the few experimental methods capable of assessing forces at the single contact or atomic level. LFM is a special atomic force microscopy (AFM). They share the same principles. A typical AFM comprises three main components: laser source, cantilever and photo-detector (see Figure 1.18).

When an atomic force microscopy (AFM) tip slides on a surface, it is deformed both in the vertical and the horizontal directions (Figure 1.18). The force $F_n$, which is normal to the surface of the sample, results in vertical bending of the free end of the cantilever. By contrast, the force $F_l$, which is parallel to the probed surface and is in the opposite direction to the sliding direction, leads the cantilever into a twisting motion. A typical AFM measures only the normal force, $F_n$. What distinguishes LFM form AFM, just like the name indicates, is that it measures both $F_n$ and $F_l$.

In order to precisely detect the forces between the tip and the surface, a laser beam is reflected off the back of the cantilever onto a quadrant photodiode detector. The output of the
quadrant detector is used to determine the degrees of bending and twisting of the cantilever. The laser beam method is the most commonly used monitoring technique as it can achieve a resolution comparable to that of an interferometer while it is also inexpensive and easy to use. The availability of lateral force microscopy (LFM) has made it possible to explore friction and wear at the molecular level and to examine the effectiveness of a finishing treatment in modifying a specific behavior of the textile substrate. LFM has been used extensively to study molecular lubrication phenomena on hard surfaces, such as mica, silica, and graphite. Studies on polymer surfaces, relevant to textile applications, however, have been limited, primarily due to the fact that polymer surfaces deform easily, which adds complexity to the experiment and to the interpretation of the data.

![Diagram of lateral force microscopy](image)

Figure 1.18. Schematic of lateral force microscopy and twisting and bending motions acting on the cantilever.

Lateral force acting on cantilever usually arises from two sources: changes in surface friction and changes in slope, as illustrated in Figure 1.19. In the first case, since the different
materials provides different friction, the cantilever can experience different twisting extent even though the surface being measured is topographically smooth. In the second case, the cantilever may twist when it encounters a steep slope. In order to eliminate the roughness effect caused by the second case in lubrication, two scans on the same line (back and forth) are performed on the substrate in order to measure the net effect.

Figure 1.19. Lateral deflection of the cantilever from changes in surface friction (top) and from changes in slope (bottom). (Source http://mechmat.caltech.edu/~kaushik/park/1-4-0.htm).

When a tip in lateral force microscopy is sliding on a surface, lateral force profiles can be measured both in air (no lubricant applied) or in solution. Figure 1.20 shows lateral force profiles for a cellulose surface imaged in air and while immersed in a solution with one of the Pluronic
lubricants we used in this thesis. During these experiments, the lubricant was dissolved in ethanol aqueous solutions at various levels of ethanol concentration (22, 38, 52, 66, and 87%). It was observed that the friction forces measured in air were significantly larger than those in the respective solutions, confirming the lubrication characteristics of the lubricant. However, the force profiles in the five solutions were undistinguishable, making the effect of ethanol concentration unimportant.

![Graph](image)

Figure 1.20. One line scanning profiles for the cellulose coated surface both in a Pluronic lubricant (E19P29E19, see Chapter 3 for detail) solutions and in air. P65 is the symbol of lubricant E19P29E19, which is a triblock copolymer with 19 EO groups at both ends and 29 PO groups in the middle. P65-1~P65-5 represent a series of ethanol solutions with the increase of ethanol concentration. Data contributed by project member Yan (Vivian) Li, from Cornell University.

**Molecular Dynamic Simulation**

For the ultra-thin films used in this work it is very difficult to determine the boundary conditions and fluid properties by experimental measurements. In these thin films the expected shear rates can be very high and beyond the values that can be studied in laboratories. Molecular
dynamics simulation (MDS), however, has proved to be an efficient method for investigating these complex systems at high shear rates and under extreme conditions.\(^{101-106}\) Modeling and simulation methods have been around for long time. But only in recent two decades it has gained rapid progress due to the advances in computer hardware and algorithms developed to study polymers. Molecular dynamic simulation is able to describe dynamic behaviors at the atomic and mesoscopic levels for polymer mixtures and surfaces. In the case of our project, a commercial Amorphous Cell\(^\text{\textregistered}\) module of Materials Studio\(^\text{\textregistered}\) platform was employed to explore the interaction energy between lubricant molecules and specific surfaces. It was also used to obtain the properties of lubricant film under confinement and when subject to shear. The Amorphous Cell\(^\text{\textregistered}\) module allowed us to construct and characterize models of isolated chains or bulk polymers, either crystalline or amorphous, and predict key properties, including miscibility and blending, mechanical behavior, diffusion, cohesion and wetting, and adhesion at surfaces.

![Figure 1.21. Sandwich-like layer to study the effect of shear in MDS. Top and bottom layers are Fe. Lubricant used was octane, C8H18, which can be seen between the two surfaces. The shear velocity for the two solid surfaces was set to 5 m/s. MDS results contributed by project member Hongyi Liu, from NC State.](image)

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Figure 1.21 shows an illustrative MDS snapshot involving a lubricant molecular during shearing. A sandwich-like layer with top and bottom solid walls (Fe) and lubricant liquid layer in the middle was build. The protocol worked by imposing a user-defined velocity of 5 m/s on the walls. The two walls were sheared with an equal but opposite velocity in the x direction and they are held in a fixed position in the z direction relative to one another by harmonic springs.

Figure 1.22 demonstrates the shear process by a series of consecutive pictures or frames. Lubricants close to the surfaces bind to the surface while shearing can be observed.

The properties of lubricants under confinement can be simulated with the Amorphous Cell. In Figure 1.23a, the distribution of molecular center of lubricant fluid shows a peculiar small peak that is neighbor to the first peak nearest to the solid wall. To understand the alignment of liquid molecules in the solid-like structure near the solid surface, we also can study the velocity profile (Figure 1.23b). The flow observed in Figure 1.23b is quite similar to the Couette flow, which is expected in a macroscopic sense, although the velocity gradient is slightly decreased at a point close to the solid surface, which is resulting from increase of liquid viscosity due to the solid-like liquid structure. On the other hand, anomalous energy distribution is observed in Figure 1.23b. In the layers of liquid and solid molecules that are neighbor to each other, i.e., the contacting layers, it is obvious that kinetic energy is not distributed equally. Between the solid walls, octane exhibits two states: solid-like close to the solid wall and liquid-like in the middle of the layer, with a linear velocity profile.
Figure 1.22. Animation of shear process for lubricant octane confined between two Fe surfaces. Shear velocity applied on both solid surfaces was 5 m/s. MDS results contributed by project member Hongyi Liu, from NC State.
Figure 1.23. Average density distribution (a) and velocity profile (b) of octane between two Fe surfaces. Shear velocity applied at both solid surfaces was set to 5 m/s. MDS results contributed by project member Hongyi Liu, from NC State.

The temperature also can be monitored by calculating the average kinetic energy of the system through the equipartition principle (Figure 1.24). The temperature shows thermal energy that is distributed to rotational motion of molecules and each degree of freedom of translational motion of molecules. At the middle of the liquid layer, there is a temperature maximum peak. This can be explained by the rotation movement from the animation. These liquid molecules in the middle of the layer were orientated strongly by the shear of solid walls and these solid-like molecules. The orientation produced the viscosity heat which can be displayed by the temperature increase. With the results of the temperature profile, the maximum temperature reaches to 417K, which is expected to occur at the interface in the presence of a polymeric lubricant.
Finally, MDS was also useful to calculate the interaction energy at the octane-Fe interface by using:

\[
E_{\text{interaction}} = E_{\text{total}} - (E_{\text{wall}} + E_{\text{fluid}})
\]

\[
=-229684.686052-(-226856.183644-304.817203)
\]

\[
=-2523.685178 \text{ kcal/mol· Å}^2
\]

\[
= -3.071578 \text{ kcal/mol· Å}^2
\]

\[
= -0.255 \text{ cal/m}^2
\]

The interaction energy of octane-Fe interface (see Figures 1.21-1.23) was negative, which indicated that attractive forces took place in this system. Similar approaches were used in the case of the several lubricants and surfaces investigated in this thesis, a subject that will be discussed in later chapters.
**SUMMARY**

SPR and QCM are well-established, noninvasive techniques that are able to provide a wealth of information about interfacial phenomena (*in situ*, in real time and in the presence of a fluid) with extremely high resolution (at the nano scale levels). In this thesis we applied QCM to monitor the adsorption of polyampholytes and simple polyelectrolytes on charged silica and cellulose surfaces, and applied both SPR and QCM to monitor the adsorption of nonionic lubricants on textile materials. Information was obtained from measurements with both instruments and their combination. This approach allowed the determination of (1) the affinity of lubricants to the substrate, (2) the conformation of adsorbed lubricant layer, (3) the kinetics of adsorption and desorption, and (4) the thickness of the adsorbed layer as well as the amount of coupled water in adsorbed film.

Based on information provided by SPR and QCM, we can deepen our knowledge on how the polymers and lubricants behave in the presence of natural and synthetic surfaces. By studying the relationship of lubricants’ structure with the performance of lubrication, novel lubricants with superior performance can be designed. In return one can significantly improve the efficiency of cellulose fiber and textile processing and improve the quality of products being manufactured.

LFM was used to measure actual friction, which can verify our results obtained from adsorption: It is also instrumental to understand the effect of the extent of adsorption and the conformation of adsorbed layers on friction. MDS, on the other hand, was used to understand how lubricant molecules interact with the surfaces and provided a theoretical platform to compare our experimental results. Adsorption, friction and simulation results can help to unveil a more
complete understanding about boundary lubrication. In the following chapters we explain in
details some of our observations.
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Chapter 2

Polymer Systems Studied and

General Hypotheses
Interfacial phenomena involving polymers are strongly affected by their interactions with the surface and in the case of net attraction we refer to polymer adsorption. The adsorbed amount, conformation and adsorption kinetics for polymer depend on the molecular composition and architecture, and also the surface properties. In general, there are three types of adsorption conformation of polymers\textsuperscript{1}. For homopolymers, if each segment is similarly attracted to the surface the resulting conformation consist of segments tails, loops and trains, as depicted in Figure 2.1(a). End-functionalized homopolymers, which have special functional groups grafted to the substrate tend to arrange on the substrate as shown in Figure 2.1(b). A third type of polymer such as diblock or multi-block polymers (see Figure 2.1(c)), with attractive and repulsive (or neutral) blocks, also self-assemble on surfaces via their attractive segments and entangle with their neutral or repulsive segments in the bulk. One potential advantage of block copolymers is that the attraction of a block can be amplified by simply increasing the number of attractive block segments.

In general, driving forces for adsorption may include chemical bonds, electrostatic, hydrophobic and van de Waal forces, among others. Chemical bonds contribute to chemisorption; since the chemical bonds are not easy to break, this is an irreversible process. The electrostatic forces are strong and long-ranged. The electrostatic interaction between a charged polymer and a charged surface usually dominates over other non-electrostatic ones. However electrostatic forces are strongly affected by the medium pH and ionic strength. One of the weakest driving forces is the van de Waals interaction, which is related to the dielectric properties of the interacting species. It usually contributes to reversible adsorption. However, for multi-point
attachments the sum of van de Waals interactions can account to an appreciable force.

Hydrophobic forces are more complicated compared to other forces, since to date there is no full understanding of its origins \(^2\text{–}^4\). Depending on the hydrophobicity of the surface, the hydrophobic effect may be classified into short-, medium- or long- range forces.

Figure 2.1. Conformation of adsorbed polymers at interfaces for (a) homopolymers, (b) end-functionalized homopolymers, (c) Block polymers, and (d) polyampholytes.

Based on the principles addressed above, the hypotheses leading to our research efforts are applied to two cases, namely the adsorption of charged and uncharged polymers. The case of charged polymers was studied by using polyampholytes, which are macromolecules that have found increased use in papermaking, as paper strength aid. On the other hand, the case of nonionic polymers was of interest in applications involving lubrication control in fiber processing.
For the charged polymers we focused on polyampholytes (or amphoteric polymers) adsorbing on charged surfaces. Electrostatic forces are in this case the predominant driving mechanism for the adsorption of amphoteric polymers as long as net charges exist. On the other hand physical adsorption is the dominant effect at the isoelectric point condition for the tested amphoteric polymers. Our polyampholyte samples were random polymers and the conformation of the adsorbed species is expected to differ for the cases addressed above (Figure 2.1a-c). Opposite charged groups are expected to be attracted and adsorbed onto the surface while remaining charged groups in the polymer chain can be enriched in the outlayer. Due the steric barrier, there is not a complete segregation of the charge and uncharged segments. Therefore the enriched outlayer with net charges can adsorb polymers in solution to form multilayers. The conformation of polyampholytes is therefore hypothesized to be as depicted as Fig 2.1d. Steric barrier could influence the adsorption process especially for high charge density polymers. The dynamics to reach equilibrium thereby enriching charged groups at the interface and outlayers can be a long process.

In order to evaluate the hypotheses above, experiments were designed as follows:

In the case of polyampholytes, variables including charge of surfaces, charge ratio of the polyampholytes and pH of the solution were tested, since they affect the electrostatic forces between polyampholytes and surfaces. In our plan, four polyampholyte samples with same charge ratio of acidic to basic groups but different charge density and one cationic and one anionic polyelectrolytes were be investigated. The employed surfaces included silica and cellulose. Silica could be a very good model surface for cellulose since it carries negative
charges in the range of pH from 4 to 10. However, silica carries more charges than cellulose at the same pH. This gives us an opportunity to investigate how the charge density of the surfaces affects the adsorption of polyampholytes and how the conformation of adsorbed layer varies with the balance of charge. The solution pH was varied between pH 4, 7 and 10, representing acidic, neutral and basic conditions, respectively.

In the case of nonionic polymers, no chemical reaction is expected and no electrostatics is involved. Therefore only van de Waal forces and hydrophobic forces can be factored in. Physisorption may be dominant in the case of adsorption of nonionic polymers, while the hydrophobic forces may be the main contribution for irreversible adsorption. The affinity of nonionic polymers to a surface in an aqueous medium depends mainly on the hydrophobic part in the macromolecule chain. Polymers with higher molecular weight are expected to have higher adsorption affinity due to more prominent role of van der Waal forces. Conformation of adsorbed diblock or triblock polymers should be as shown in Figure 2.1c. Also, hydration may play an important role in boundary lubrication.

The nonionic polymers tested are typically used as lubricants in fiber processing, and therefore the surfaces chosen were typical ones used in textile and paper manufacture. In order to test the statements made above, experiments were designed as follows:

Various surfaces with different surface energies were investigated, including polypropylene (PP), polyethylene (PE), polyester (PET), nylon and cellulose. Within these surfaces, cellulose is hydrophilic, PP is the most hydrophobic and PE posses a slight lower hydrophobicity. The hydrophobicity of PET and nylon is between that of cellulose and PP.
Nonionic polymers with different chemical structure were tested. These include diblock or triblock structures with different length of the hydrophobic and hydrophilic chains, as well as different molecular masses. All these variables were investigated in this thesis and the results presented in the next chapters.
REFERENCES


Chapter 3

Development and Characterization of

Polymer Films Relevant to Fiber Surfaces
ABSTRACT

In order to use quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) sensors to monitor the adsorption behavior of lubricants onto solid surfaces, typical textile material were deposited an ultra thin film on metal surfaces by using the spin coating technique. Dilute solution of cellulose, polypropylene, polyethylene, nylon and polyester were spun-coated on SPR and QCM gold sensors as well as on silicon wafers. The optimum spinning conditions were achieved and the produced ultrathin films were characterized by atomic force microscopy (AFM) for morphology, ellipsometry for thickness and water contact angle for surface energy. X-ray photoelectron spectrometry was also used to determine the surface composition of the produced films. Results showed that the films were manufactured reproducibly, they were uniform and smooth and their thicknesses was very small, lower than 50 nanometers (which make them suitable for precise QCM and SPR sensing). The manufacture ultrathin model films facilitated the studies on adsorption of polymers on flat films at the nano scale, in situ and in real time.
INTRODUCTION

Our work involved the use of quartz crystal microbalance (QCM), ellipsometry, surface plasmon resonance (SPR) and atomic force microscopy (AFM) as methods that were applied to monitor the adsorption of polymers onto surfaces relevant to fiber technologies. Most of the tools available (including the cited techniques) demand the use of flat, well defined surfaces and therefore use of actual fibers is usually prevented. To this end surfaces that mimic those present in textile and paper processes were needed. Metallic sensors are primary platforms in QCM (gold and silica resonators) and SPR (gold wafers) techniques. Therefore, in order to employ both techniques to monitoring the adsorption of polymers onto (model) textile and fiber surfaces, the QCM and SPR sensors required coating in the form of thin films of organic materials that could represent those in actual fiber operations. Films of cellulose, polypropylene (PP), polyethylene (PE), nylon and polyester (polyethylene terephthalate, PET) were obvious candidates of choice since these are leading materials in most common fiber formulations. As such, ultrathin films of these (natural and synthetic) polymers were developed and applied in a number of studies in our laboratories.

Surprisingly, to our knowledge there are no reports available concerning studies of surface phenomena on textile-relevant model films, especially in the case of synthetic polymers. Consequently, no standards were available for the production of reproducible, robust model films of these materials which could be used in research concerning the molecular mechanisms involved in adsorption, friction and wear.
For the preparation of polymer films, doctor-blading techniques \(^1\) can be applied if the target layer thickness is in the mm range. Chemical vapor deposition \(^2\) is typically used when organic materials to be deposited on substrates are of low boiling points. In contrast, in the case of ultrathin films of organic molecules Langmuir-Blodgett \(^3\)\(^,\)\(^6\) and spin coating \(^7\)\(^-\)\(^10\) techniques are two of the most frequently used methods. In Langmuir-Blodgett deposition monomolecular layers can be built on the substrate and by using multiple deposition, multilayers can also be obtained, with controlled surface density and multilayer thickness. An advantage of these techniques is the excellent control in layer density and the fact that very small roughness and complete coverage can be attained. The limitation of the Langmuir-Blodgett technique, however, is the demand for relatively complex instrumentation, laborious protocols and time consuming. In this investigation we used spin-coating since it is very simple for implementation and involve simple operation. The films obtained by spin coating albeit not as smooth as in the case of Langmuir-Blodgett films were found suitable for our purposes. In spin coating the thickness, coverage and roughness are affected by factors such as molecular weight and concentration of the film-forming compound, solvent type (viscosity, density and surface energy), rotation speed of the rotor and temperature \(^8\). Through carefully control these parameters, optimum results (roughness and thickness) can be obtained.
EXPERIMENTAL

Materials

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) followed treatment in a Milli-Q® Gradient unit for water with a resultant resistivity of greater than 18 MΩ.

Cellulose used was Avicel® PH-101 (Fluka Chemical Corporation) micro-crystalline cellulose (MCC). Medium density polyethylene (PE) (received as a powder), polypropylene (PP) (syndiotactic and with Mn and Mw of 54000 and 127000, respectively) and nylon 6 (with a Tg of 62.5°C and particle size of 3 mm) were all purchased from Sigma-Aldrich. Poly (ethylene terephthalate) (PET) was provided by Goulston Inc. (Monroe, NC). Polyvinylamine (PVAm) from BASF Corporation.

Solvents such as xylenes (HPLC grade), hexafluoroisopropanol (HFIP, 99.5+%) and 50% N-Methylmorpholine-N-Oxide (NMMO) were purchased from Fisher Scientific.

In our experiments we used silica wafers (cut into smaller pieces of 1.5x1.5cm, from Wafer World Inc., FL), silica or gold QCM sensors (Q-Sense Inc., Sweden) and gold SPR sensors (Reichert Inc. NY).

Methods

All substrates except silica QCM sensors were cleaned before use with Piranha™ solution (70% H₂SO₄+30% H₂O₂ (30%)) for one hour without heat and then subject to by
UVO radiation (28 mW/cm² at 254 nm) for 10 minutes, immediately before spin-coating. Silica QCM sensors were cleaned by sodium dodecyl surfate (SDS, 2% aqueous solution). Since the preparation of the films, especially those concerning the synthetic polymers, involved newly developed methods, a detailed description of their preparation is given below.

**Preparation of cellulose films**

Cellulose thin films were prepared on silica wafer or gold QCM resonators according to a procedure reported elsewhere and modified slightly as follows. Cellulose solution was first prepared by dissolving micro-crystalline Avicel cellulose (MCC) in 50%wt water/N-Methylmorpholine-N-Oxide (NMMO) at 115 °C. DMSO was added to adjust the concentration (0.05%) and viscosity of the cellulose suspension. Polyvinylamine (PVAm, BASF) was used as anchoring polymer to attach cellulose film on the silica/gold surface. The silica/gold surfaces were immersed in PVAm for 20 min followed by washing with milli-Q water and drying with gentle nitrogen jet. The cellulose solution was then used in the spin coater (Laurell Technologies model WS-400A-6NPP) by depositing one or two drops on the substrates and spun at 5000 rpm for 40 seconds. We found these conditions as optimal for obtaining robust, smooth films. The cellulose-coated substrate was removed from the coater and then immersed in milli-Q water for more than four hours and then placed in an oven for two hours at 80 °C. The cellulose-coated substrates were then washed thoroughly with milli-Q water, dried with nitrogen jet and stored at room temperature in a clean chamber for further use.
Preparation of PP and PE films

Thin polyethylene (PE) film prepared by spin coating was first reported by Bartczak and Argon et al.\textsuperscript{12}. An inconvenience of their method was that an oven was required adjacent to the spin coater to reduce the transfer time between spin coater and the oven, which was used to prevent a drop in the temperature of the coated surfaces (and keep a high temperature for annealing). In our modified method, an infrared lamp was employed instead to heat the substrates. Other modifications, mainly processing conditions, were implemented in order to obtain ultrathin and uniform films. The same methodology was used in the case of PP films (explained below). The preparation of PP and PE thin films involved dissolution of the polymer in xylenes (0.2% solution): In a typical protocol 20mg PP/PE and 10ml xylenes were placed in a small flask with a condenser (running water as cooling medium). The solution was heated and stirred for more than 2h to dissolve the polymer. A wafer was then placed on the coater rotor head (Laurell Technologies model WS-400A-6NPP) while an infrared lamp (250 Watts) was used to keep the surface above 85 °C (as measured by an infrared thermometer gun). One or two drops of hot PP or PE solution was then immediately transferred on the substrates and rotated at 3000 rpm for 20 seconds. The coated substrate was then removed from the coater and then transferred to an oven where the coated substrate was kept at 80 °C for 2h. This temperature and time was found to be sufficient to remove all residual solvent (see XPS measurements in later section). Once cooled the coated substrate was then stored at room temperature in a clean chamber until use.
Preparation of Nylon and PET films

Nylon and polyester (PET) are very difficult to dissolve in common solvents. m-cresol at 100°C has been the solvent of choice. In recent years, scientists found fluorine-containing polymers to have excellent solving for nylon and PET, even at room temperatures. In our work, we found that hexafluoroisopropanol (HFIP) was an excellent solvent to dissolve both nylon and PET. Ultra thin films were prepared from 0.16% solution: 10 mg Nylon or PET and 6 g of HFIP were mixed in a small vial until complete dissolution. The time required for dissolution was typically several hours. Once fully dissolved, 1-2 drops of the solution were placed on the substrate which was sitting on the rotor head of the spin coater (Laurell Technologies model WS-400A-6NPP). As before, infrared light was used to keep the surface warm before placing the solution (at least tens seconds of IR radiation were needed). A spinning rate of 3000 rpm and 20 seconds time were used in the coating process. The coated substrate was then removed from the coater and transferred to an oven at 80°C for 2h to remove the residual solvent. The finished substrate was then stored at room temperature in a clean chamber for further use.

AFM

Film surface morphologies were investigated by atomic force microscope (AFM) (Q-Scope™ 250 from Quesant Instrument Corporation) with tapping mode under atmospheric conditions. For each sample, scans were acquired on a wide area varying from 1×1 to 20×20 µm. A planar background was subtracted from the data to compensate
for tilt of the sample relative to the scanning plane. The results were checked for reproducibility by imaging several regions of the same sample.

**Contact angle measurement**

The contact angle of untreated and polymer-coated PET surfaces against pure water was measured on a manual Rame-Hart goniometer. After 1 min of placing a droplet of Mini-Q water (10 µL) onto the surface the outline of the droplet was detected with an optical magnifier. The tangent line on the droplet in the three-phase zone was traced with a protractor within the optics and therefore provided a measurement of the contact angle.

**Film Thickness**

Two methods were used to measure the thicknesses of the films obtained by spin coating: namely, an ellipsometric and a piezoelectric method. We used a Rudolph Single Wavelength Ellipsometer to measure the change in polarization of elliptically polarized light when it is reflected on the sample surface. When a mineral substrate (silica wafer) is optically modified (for example, with an ultrathin organic layer), the associated change in polarization light can be measured and used to calculate the thickness of the coated layer. From the changes in the ellipsometric angles (Δ, Ψ), the refractive index, n, and the optical (ellipsometric) thickness, δe of the film can be obtained.

The QCM technique was also employed to measure the thickness of our model films. Here the film thickness was derived from an electro-mechanical measurement as opposed to the former optical measurement. In QCM measurements the resonant frequency (f) of the piezoelectric material (quartz crystal) was measured. This oscillation
frequency depends on the effective mass of the sensor-coating layer element \(^{15-17}\). As stated by the Sauerbrey equation \(^{18}\), if a thin and rigid film is adsorbed on the sensor the decrease in frequency (relative to the bare surface) is proportional to the mass added:

\[
\Delta m = -\frac{c\Delta f}{n}
\]

where \(C = 17.7 \text{ ng Hz}^{-1} \text{ cm}^2\) for a 5 MHz quartz crystal and \(n = 1,3,5,7\) is the overtone number. Knowing the density of the coating layer one can therefore calculate the respective layer thickness. In our investigation, only the QCM third overtone frequency was measured before and after spin coating in air at constant temperature of 25 °C. These values were used to calculate the “QCM” thickness of the layers obtained by spin coating.

**X-Ray Photoelectron Spectroscopy (XPS)**

A Riber XPS system was employed to provide chemical state information for the obtained model surfaces. In XPS the soft X-rays from the Al K\(\alpha\) source ionize electrons from the elements residing on the surface of the sample. The kinetic energy of the ejected photoelectrons was measured and the respective binding energies determined. The binding energy, being an intrinsic characteristic of the given electrons of the core orbital, was used to determine the composition of chemical species present in the top few atomic layers of the material. Here XPS was used to confirm the chemical composition of the model surfaces and therefore was useful to establish the identity (purity) of the organic layer.
RESULTS AND DISCUSSION

**AFM topography and RMS (roughness)**

Model films were produced according to the protocols described in previous sections. Film surface morphologies were investigated by atomic force microscope (AFM) with tapping mode under atmospheric conditions. Topographical images of the spin coated films of cellulose, PP, PE, nylon and PET were acquired by using AFM wave mode (with a scanning speed set to 1 Hz). Figure 3.1 shows AFM images for all the films generated. Cellulose films typically had granular features that were distributed evenly. Compared with PE films, PP films were smooth and no features were observed. However large granules and small indentations were observed in the case of nylon and PET films.

All the films were very flat and uniform at the macro scale. Root-mean-square roughness (RMS) obtained by AFM are shown in Table 3.1. Among these model films, PET had the lowest RMS, lower than 1 nm. PP and nylon film roughness ranged from 1 to 2 nm while the cellulose film had a higher roughness (RMS larger than 2 nm). The cellulose films produced by the spin coating technique were much rougher compared to cellulose films obtained by Langmuir-Blodgett deposition (RMS roughness is less than 1 nm as reported by\(^4\)). However, as explained previously, the advantage of spin coating is that the procedure is easy to implement, fast and more efficient for higher throughput work. Among all these samples, PE films presented the largest roughness, with RMS larger than 4 nm.
Contact angle

Contact angle is very sensitive to the surface energy of the material. If a liquid with well-known properties is used as probe, the resulting contact angle can be used to characterize the surface energy of the solid. The contact angle against pure water was measured on a manual Rame-hart goniometer after placing a droplet of Milli-Q water (10 µL). The procedure was addressed in detail in the experimental section.

The water contact angles (WCA) of our model films are shown in Table 3.1. PP film presented the highest WCA, up to 103º while PE rendered a WCA of ca. 95º. Since
both materials have only -CH2- or -CH3 groups, they were expected to exhibit very low surface energies. Nylon and PET produced similar WCA (61.9° and 64.8°, respectively) while cellulose, due to its hydrophilicity, showed the lowest WCA (28.6 ± 3.4 °). This value for cellulose agrees with the data from other reports (25-35 °)\textsuperscript{4,19}.

**Thickness**

In this investigation, both QCM and ellipsometry were employed to measure the thicknesses of our developed films. In the case of QCM, the frequency of the third overtone was measured before and after spin coating in air at constant 25°C. Since the model films were rigid Sauerbrey equation was taken as reliable in the calculation of thickness. The ellipsometric thickness was measured to confirm this assumption. In fact, the data obtained from ellipsometric measurements agreed with those from QCM quite well (see Table 3.1).

Table 3.1. Characterizations of model surfaces.

<table>
<thead>
<tr>
<th>Model film</th>
<th>Solvent</th>
<th>Precursor polymer solution Concentration (% w/w)</th>
<th>Thickness (nm)</th>
<th>RMS (nm)</th>
<th>WCA (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Xylenes</td>
<td>0.2</td>
<td>17-21</td>
<td>0.7-2.3</td>
<td>102.9 ± 1.7</td>
</tr>
<tr>
<td>PE</td>
<td>Xylenes</td>
<td>0.3</td>
<td>30-34</td>
<td>4-6</td>
<td>95.1 ± 0.7</td>
</tr>
<tr>
<td>Cellulose</td>
<td>NMMO/DMSO</td>
<td>0.3</td>
<td>10-15</td>
<td>2-2.5</td>
<td>28.6 ± 3.4</td>
</tr>
<tr>
<td>Nylon</td>
<td>HFIP</td>
<td>0.15</td>
<td>41-47</td>
<td>1.3-2.1</td>
<td>61.9 ± 1.0</td>
</tr>
<tr>
<td>PET</td>
<td>HFIP</td>
<td>0.15</td>
<td>33-38</td>
<td>0.3-1.1</td>
<td>64.8 ± 1.1</td>
</tr>
</tbody>
</table>

*Data acquired by ellipsometry. Remaining thicknesses were determined from QCM data.
Thicknesses of model films obtained after spin coating solutions with respective polymer concentrations is shown in Table 3.1. In the process of preparation of these model films, our ultimate goal was to modify surfaces of QCM and SPR sensors. Therefore, two factors had to be considered, namely, coverage of the film and sensor sensitivity. The surfaces of our sensors were required to be homogeneous in order to avoid effects of the underlying substrate (thus requiring thick films). On the other hand, if the films are excessively thick the sensitivity of SPR and QCM measurements is impaired. A compromise between coverage and sensitivity (that also takes into account the need for a low relative roughness), led the selection of film thickness of the order of 20-50 nm as optimum values for experiments involving adsorption measurements.

**X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of model surfaces and also to confirm the absence of residual solvent in the films. Xylenes, the solvent for PP and PE, with its aromatic ring allows a clear detection via XPS, from the respective binding energies. In fact, if there is any residual solvent on the film, $\pi-\pi^*$ bonding of carbons in the benzene ring would be observed at around 292 eV binding energy. As observed in the detailed XPS spectra for PP and PE (see insets in Figure 3.20, no peaks were detected in the region around this binding energy. Therefore, it was apparent that evaporation at high temperature spin coating and oven treatment were enough to fully evaporate the solvent. We noted that traces of oxygen at 527 eV were
detected in both PE and PP films. This small amount of oxygen was explained by partial oxidation of the polymer during the dissolution process which, as noted before, was carried out at elevated temperature. Since the time required to dissolve PE was longer than that of PP, a larger oxygen peak was expected and confirmed in the survey spectra for both films, as shown in Figure 3.2.
Figure 3.2. XPS survey spectra for bare PP (a) and PE (b) films. Detail spectra (inset) for C1s BE region are included in each figure.

Cellulose was dissolved in NMMO, which contains nitrogen. Therefore, any XPS
nitrogen peak in the spectrum (corresponding to a binding energy of 400 eV) would indicate the presence of residual solvent. As observed in Figure 3.3 no such peak was observed; therefore it can be concluded that the cellulose films were solvent-free.

We performed multiple XPS scans on several cellulose samples. In a given sample we also run XPS in different locations. We didn’t find evidence of sample degradation during the X-Rays exposure time (kept as short as possible). Unfortunately, the sampling depth of X-Rays is comparable to the film thickness. Since the roughness of the thin films of cellulose was up to 2.8 nm and the lateral resolution of the used unmonochromated XPS is in the nm range, some underlying areas are expected to contribute to the XPS signal. As a result, signals from the Au substrate or adhesive PVAm anchoring layer (1-2 nm ellipsometric thickness) were present in the spectra collected.

We note that full coverage (material distribution and topography) of cellulose on the sensor was confirmed from the AFM images while spatial distribution of material on the surface was difficult to judge from our XPS measurements.

Regarding the chemical composition of cellulose films we observed that the carbon emission of the XPS spectrum showed a larger contribution of the bonded carbons in the cellulose film than the Au and N peaks from inner layers (substrate or PVAm anchoring layer). The measured O/C ratio was 0.85, comparable to the theoretical value of 0.83. Also, the ratio of carbon with two bonds to oxygen to the carbon with one bond to oxygen (O–C–O/C–O or C3/C2) corresponded to a value close to the theoretical cellulose composition (0.22 versus 0.2). The differences with respect to the theoretical
values for these ratios were explained by the signal contribution from carbon atoms with shifted binding energies from the underlying PVAm. Also, possible oxidization of molecules after treatment of film in the oven can not be ruled out. We note that a C1 peak was detected. This peak was mainly due to adsorption of airborne contaminants during handling and XPS preparation. We consider that the obtained XPS spectra confirmed the presence of pure cellulose and were in agreement with spectra reported elsewhere. Survey and detailed C spectra are presented in Figure 3.3.

In order to minimize the risk of any uncovered cellulose areas, in our investigations on nonionic polymer adsorption we utilized cellulose solutions at a concentration of 0.5% (w/w) during the coating process of the sensor. This concentration was found as optimal to ensure a full coverage while the sensitivity in measurement was not diminished.

Nylon and PET were dissolved in HFIP, which is a solvent carrying six fluorine atoms per molecule. The presence of any residual solvent on the films could be detected by distinctive XPS fluorine peak at a binding energy of around 700 eV. As seen in Figure 3.4, no such a peak was detected in the case of nylon and PET films and therefore it can be concluded that they were solvent-free. Small peaks and shoulder structure could be observed in the detail spectra (insets) which covered the C1s region. These structures confirmed the carbonyl in nylon and benzene structure, as well as carbonyl and carboxyl groups in PET.
Figure 3.3. XPS spectra of cellulose model films (top). Detailed C1s spectra (bottom).
Figure 3.4. XPS spectra of model (a) Nylon and PET (b) films. Detailed C1s spectra are seen in the insets.
A summary of the main elemental composition obtained from XPS is listed in Table 3.2. The experimental data agreed with the theoretical values very well. Based on the evidence presented it can be concluded that the films were highly pure, homogeneous, flat and therefore are expected to be good models for textile and fiber surfaces.

Table 3.2. Comparison of the chemical composition from XPS and theoretical value

<table>
<thead>
<tr>
<th>Film</th>
<th>C (Atom %)</th>
<th>O (Atom %)</th>
<th>N (Atom %)</th>
<th>Au (Atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (Expt.)</td>
<td>99.28</td>
<td>0.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C3H6)n</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE (Expt.)</td>
<td>98.7</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C2H4)n</td>
<td>100</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose (Expt.)</td>
<td>52.93 (54.93)</td>
<td>45.64 (45.07)</td>
<td>1.43 (0)</td>
<td></td>
</tr>
<tr>
<td>(C6H10O5)n</td>
<td>54.55</td>
<td>45.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon (Expt.)</td>
<td>75.56</td>
<td>12.35</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>(C6H11O4N)n</td>
<td>75</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>PET (Expt.)</td>
<td>69.47</td>
<td>30.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C10H8O4)n</td>
<td>71.43</td>
<td>29.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Spin Coating as a Platform for the Manufacture of Model Films

Spin coating is one of most often used techniques to prepare thin organic films due to its efficiency and reproducibility. In the process of spin coating, an excess amount of a solution is placed on the substrate, which is then rotated at high speed (usually in thousands RPM) in order to spread the fluid by centrifugal force. Usually the applied solvent is volatile, therefore it evaporates simultaneously with rotation. Rotation is continued until the desired thickness of the film is achieved. Variables involved in the process of spin coating which influence the thickness and uniformity of the obtained film include viscosity, concentration, angular frequency of the rotating substrate and operation...
temperature \textsuperscript{7,9,20}. A model which is used to describe the final thickness in term of these factors is the Lawrence’s equation \textsuperscript{8}:

$$h_f \propto \frac{c_0 (\eta_0 D_0)^{1/4}}{\Omega^{1/2}}$$ (Equation 3.2)

where $c_0$ is initial polymer concentration; $\eta_0$, initial kinetic viscosity; $D_0$, the solute diffusivity and $\Omega$ is the spinning speed. From this relationship, which is confirmed by extensive experimental work \textsuperscript{7,19}, it is obvious the strong dependency between final thickness and initial polymer concentration. This relationship was also supported by our experiments: six PP films were made in sequence and then their thickness was measured by ellipsometry. A clear trend could be observed for the thickness of PP films which increased with preparation sequence. This preparation sequence is related to the time the solution is exposed to air before use in the spin coater: The larger the sequence numbers, the longer the time elapsed and therefore the higher the polymer concentration $c_0$ (as a result of solvent evaporation). Therefore, as the polymer in the container (flask) became more concentrated with time (sequence number), the thicker the produced film would be. Another reason which may contribute to the increased thickness of thin film is that the viscosity of solution. Polymer was oxidized at elevated temperature (this could be observed in the oxygen peak in XPS spectra increases with heating time). The viscosity of solution might increase with oxidation. Higher viscosity could lead to higher thickness of thin film. These observations mean that in order to prepare reproducible surfaces we must exercise care in the sequence and time of preparation in order to keep same operational conditions.
Note that if other thicknesses different than the targeted 20-30 nm are desired

Lawrence relationship can be used for related adjustment.

![Graph showing ellipsometric thicknesses of PP films](image)

Figure 3.5. Ellipsometric thicknesses of PP films obtained after different sequence times (larger sequence number indicates longer time and therefore larger $c_0$).

**Model surfaces as a platform for adsorption**

Modified sensors were mounted in the QCM chamber and a nonionic polymer solution was passed through to test their performance. The tested polymers was a pluronic surfactant, E37P56E37 or a tri-block polymer with 37 ethylene oxide (EO) groups at both ends and 56 propylene oxide (PO) groups in the middle. The adsorbed isotherms (adsorbed mass against lubricant concentrations) on different surfaces are shown in Figure 3.6. As demonstrated by this figure, PP surface showed the highest adsorbed polymeric surfactant mass, while cellulose was the lowest. Nylon and PET yield
intermediate adsorption masses. These results indicate that the protocols used in the preparation of ultrathin films are consistent with expected results. This together with the previous characterization indicated that suitable flat and uniform surfaces were produced and can be employed to study phenomena such as adsorption, friction, wear, etc.

Figure 3.6. Adsorption of a nonionic polymer (lubricant) (E37P56E37) on various model films. Adsorption isotherm was obtained by using the QCM-D technique.

**SUMMARY**

In summary, we reported on the methods to prepare model surfaces as substrate for studies relevant to fiber materials. Thin films of cellulose, PP, PE, Nylon and PET were manufactured by using spin coating and optimum conditions for such manufacture were proposed. Robust, uniform and fully covering thin films required when using surface-sensitive techniques, especially SPR, QCM, were presented. Among these films,
nylon and PET films were introduced for the first time. Finally, application of the protocols to modify QCM sensors and use as a platform to study adsorption was demonstrated in this chapter.
REFERENCES


Chapter 4

Bulk Properties of Amphoteric and Nonionic Polymers

Part content of this chapter was published in “Charge and the dry-strength performance of polyampholytes. Part 1: Handsheet properties and polymer solution viscosity”.

ABSTRACT

In this investigation the bulk properties of six ionic polymers (four polyampholytes and two simple polyelectrolytes) as well as seven nonionic lubricants are presented. Their structural information, chemical composition, molecular weight, and degree of polymerization, as well as surface tension, viscosity and viscosity change with ionic strength are described here. This information is useful to understand the nature of the samples to be used in future studies and to further help us to understand how the nature of the polymers influences the interfacial behavior upon adsorption onto different surfaces. The ultimate purpose is to help us to establish *structure* (of polyampholytes and nonionic polymers)-*properties* (strength-enhancing of polyampholytes and boundary lubrication of nonionic polymers) *relations* that can be used in designing new polymers in targeted applications.
INTRODUCTION

In our investigation, a number of chemicals were used. Key samples, including polyampholytes and nonionic lubricants are introduced in this chapter in order to allow a clear understanding of their chemical structure, degree of polymerization, molecular weight, etc. Bulk properties, such as viscosity of polyampholytes, surface tension of nonionic lubricant, are described as well. This is expected to be helpful in understanding the interfacial behavior and their applications and to produce relationships between the nature of chemicals and their functions.

EXPERIMENT

Materials

Polyampholytes

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) followed treatment in a Milli-Q® Gradient unit for water with a resultant resistivity of greater than 18MΩ. Inorganic chemicals (salt, acid and alkaline) all were of reagent grade. Polyampholyte and polyelectrolyte samples had been prepared by free-radical polymerization for a final content of charged monomers as indicated in Table 4.1. Synthesis work was conducted by T. Sezaki in Harima Chemical Corp. A representative structure of the amphoteric terpolymers used is shown in Figure 4.1. The cationic monomer was N-[3-(N’,N’-dimethylamino)propyl]acrylamide (DMAPAA), a tertiary amine. The anionic monomer was a
dicarboxylic acid, methylene butanedioic acid also known as itaconic acid (IA). In each case the balance amount of neutral acrylamide (AM) monomer was added to comprise 100% on a molar basis. A typical procedure of synthesis (see for example sample “An” in Table 1) was as follows: 174 g of 40% acrylamide aqueous solution were added to a reaction vessel, 3.25 g of 80% itaconic acid and 300 g of water that had been purified by ion exchange were placed into a four neck flask provided with a reflux condenser and the mixture was heated to 60 °C in a nitrogen atmosphere. Then 10 g of 1% ammonium persulfate aqueous solution were added to the reaction solution and allowed to react at 85 °C for one hour. After cooling, an anionic polyacrylamide solution (sample “An”) was obtained. The cationic and amphoteric variants were prepared using the monomer ratios shown in Table 1 (see Table 1 for molar composition). Methylenebisacrylamide was added at a 0.04 mole percent level to the reaction mixtures as a cross-linking agent in order to increase the average molecular masses. As shown, the mean weight-averaged molecular masses of the polyampholyte samples were within the range 2.85 to 2.93 x 10^6 Daltons, and the polyelectrolyte masses also were similar.

The polymer solution samples described above were first purified by two cycles of dissolution in water and precipitation in methanol; then the pure samples were collected by freeze-drying. NMR analysis was performed by Xingwu Wang and results confirmed the compositions reported in Table 4.1. Samples were prepared by making 2-3% polymer solution in D_2O. Crystals of CrK(SO_4)_2 were added at a concentration of 1.5 mM in order to reduce the spin-lattice relaxation times (T_1). The NMR experiments were performed in a Bruker 300MHz spectrometer equipped with a Quad dedicated probe at room temperature. The quantitative ^{13}C
spectra were acquired using an inverse gated proton decoupling sequence with a 90° pulse and a relaxation delay of 4.5 s, that was ~5 times of the longest T_1 measured for the samples. The \(^1\)H spectra were measured with 60° pulse and a pulse delay of 3 s. Note that in the case of polyampholytes the molar ratio of DMAPAA and IA is 5:2. Since IA is a dicarboxylic acid the effective content of anionic (carboxylic) groups is twice the value of the respective IA which is equivalent to a ratio between cationic (tertiary amine) and anionic (carboxylic) groups of 5:4.

Figure 4.1. Molecular composition of monomers in random polyampholytes prepared by free-radical polymerization (DMAPAA, IA and AM).
Table 4.1. Synthesis of acrylamide-based polyampholytes and simple copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer type</th>
<th>Basic group * (if any)</th>
<th>Acidic group * (if any)</th>
<th>Basic group molar content (%)</th>
<th>Carboxylic (acidic) group molar content (%)</th>
<th>Polydispersity ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PAmp2$</td>
<td>Amphoteric</td>
<td>DMAPAA</td>
<td>IA</td>
<td>2.5</td>
<td>2</td>
<td>3.7</td>
</tr>
<tr>
<td>$PAmp4$</td>
<td>-</td>
<td>-</td>
<td>IA</td>
<td>5</td>
<td>4</td>
<td>3.7</td>
</tr>
<tr>
<td>$PAmp8$</td>
<td>-</td>
<td>-</td>
<td>IA</td>
<td>10</td>
<td>8</td>
<td>3.6</td>
</tr>
<tr>
<td>$PAmp16$</td>
<td>-</td>
<td>-</td>
<td>IA</td>
<td>20</td>
<td>16</td>
<td>3.8</td>
</tr>
<tr>
<td>Cat</td>
<td>Cationic</td>
<td>DMAPAA</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>3.7</td>
</tr>
<tr>
<td>An</td>
<td>Anionic</td>
<td>-</td>
<td>IA</td>
<td>-</td>
<td>4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

DMAPAA = N-[3-(N',N'-dimethylamino)propyl]acrylamide; IA = itaconic acid

* measured at 25 °C and 100 s⁻¹.
** SEC-LALLS-VIS (TDA-302, Viscotek).

Nonionic lubricants

Nonionic lubricants used in this investigation included two sets of polymer with known structures, polyalkylene glycols (PAGs) from Dow Chemical Co. (Midland, MI), and triblock copolymers based on ethylene and propylene oxide (Pluronic) from BASF Corporation (Florham Park, NJ). General chemical structures of PAGs (Figure 4.2a) and Pluronics (Figure 4.2b) can be seen in Figure 4.2a and 4.2b respectively.

![Figure 4.2. Chemical structure of PAGs (a) and Pluronics (b).](image)

Lubricants with different $m$, $n$ are listed in Table 4.2. They have different chemical structures and different molecular weights. We intend to use these polymers as representatives of nonionic lubricant finishes in order to understand how the respective structures influences the assembly of lubrication layer (and thus boundary lubrication and friction).
Table 4.2. Structure information of PAGs and Pluronics

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Commercial name</th>
<th>MW</th>
<th>n (PO)</th>
<th>m (EO)</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>UCON 50-HB-400</td>
<td>1230</td>
<td>10</td>
<td>13</td>
<td>11.92</td>
</tr>
<tr>
<td>RP13E17</td>
<td>UCON 50-HB-660</td>
<td>1590</td>
<td>13</td>
<td>17</td>
<td>12.00</td>
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<tr>
<td>RP33E44</td>
<td>UCON 50-HB-5100</td>
<td>3930</td>
<td>33</td>
<td>44</td>
<td>8.51</td>
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<tr>
<td>E19P29E19</td>
<td>Pluronic P65</td>
<td>3400</td>
<td>29</td>
<td>19</td>
<td>21.67</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>Pluronic F68</td>
<td>8400</td>
<td>29</td>
<td>76</td>
<td>27.97</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>Pluronic P105</td>
<td>6500</td>
<td>56</td>
<td>37</td>
<td>17.34</td>
</tr>
</tbody>
</table>

* UCON polymers from Dow Co. and Pluronic polymers from BASF Co.
* HLB values were calculated by the method described by Guo et al. 1
* R stands for a butyl group, P stands for propylene oxide group and E stands for ethylene oxide group respectively in this table.

Silicone-based lubricant was supplied by Goulston Inc. (Monroe, NC) under trade name LN336-100I. It was a commercial product with main component silicone polymer and some additives. The main component is a surface-active block copolymer of polyalkylene oxide-modified polydimethylsiloxane.

**Methods**

**Viscosity of polyampholytes**

Viscosities were measured with an Ubbelohde viscometer in a thermostated water bath at 25.0 °C in 0.1% solids aqueous polymer solutions in the presence and absence of 0.01 M NaCl. The pH was adjusted with aqueous HCl or NaOH.

**Radius of gyration measurement**

A DAWN laser photometer and an OPTILAB interferometric refractrometer of Wyatt Technology Corporation were employed in this experiment. Only one sample PAmp4 with three conditions of pH (pH4, pH7, and pH10) representing acidic, neutral and basic condition was
investigated. Zimm plots were obtained with a static light scattering (SLS) data fitting program provided by Wyatt Technology Corporation.

**Surface tension measurement**

A Fisher Surface Tensiomat®, model 21 with a Du Noüy Ring was employed to measure the surface tension of lubricant solutions. In the Du Noüy method, a platinum-iridium ring of precisely known dimensions is suspended from a counter-balanced lever arm. The arm is held horizontal by torsion applied to a taut stainless steel wire, to which it is clamped. Increasing the torsion in the wire raises the arm and the ring, which carries with it a film of the liquid in which it is immersed. The maximum pull force exerted on the ring by the surface was measured and translated to units of surface tension, mN/m

**RESULTS AND DISCUSSION**

**Bulk properties of polyampholytes**

**Viscosity without salt**

A series of experiments were carried out to evaluate the bulk properties of solutions of polyampholyte $P_{Amp2}$ through simple polyelectrolyte $An$ in Table 4.1. As shown in Figure 4.3a, the relative viscosity of each of the polyampholyte solutions was strongly affected by changes in pH. In the case of the polyampholyte samples $P_{Amp2}$ through $P_{Amp16}$, a broad viscosity minimum was observed at close-to-neutral pH (about $6<pH<7$). The viscosity of the polyampholytes generally increased as the pH was changed from neutral to higher (or lower) pH. Viscosity maxima are observed at both sides of neutral pH but then they are reduced again at
extreme values pH, i.e., beyond ca. pH=3 and above ca. pH=11. The initial increase in viscosity with increasing difference of pH relative to the neutral region is consistent with an increase in net ionic charge of the polymers, noting that the degree of dissociation of both the acidic and the basic groups on the polyampholytes depends on the pH\textsuperscript{2,3}. An increase in net charge is expected to increase the degree of molecular expansion in solution\textsuperscript{4,5}. Once ionization is complete, addition of more acid or base simply increases the ionic strength of the solution. The subsequent decreases in viscosity of polyampholyte solutions at extreme values of pH are consistent with the increase in ionic strength of solution resulting from addition of large amounts of acid or base. In these cases the counterions screen the electrostatic and osmotic forces, collapsing the charged polymers.

Figure 4.3b illustrates the effect of polymer charge density on the relative viscosity in cases of net anionic or net cationic behavior. For comparison purposes the viscosities of simple polyelectrolytes are also presented.

![Graph showing viscosity changes against pH and % charged groups](image)

Figure 4.3. Viscosity of polyampholytes (a) and viscosity changes against % charged groups of polyampholytes and simple polyelectrolytes (b).
Results corresponding to simple polyelectrolyte samples *Cat* and *An* are also reported in Figure 4.4. Contrary to the observations made above for the case of amphoteric polymers, each of the simple polyelectrolytes showed one maximum viscosity with pH. pH titrations indicated a pKₐ for that the cationic polyelectrolyte *Cat* of 9.8, and a pKₐ for the anionic polyelectrolyte *An* of 4.1 and 6.8 for the two carboxyl groups \(^6\). Thus, one would expect the molecules in sample *Cat* to have a relatively expanded conformation at relatively low pH values corresponding to the charged, protonated form of the tertiary amine groups. Then, with increasing pH above a value of 8 it is reasonable to expect a drop in viscosity, consistent with a reduced molecular extension. Considerations in the case of the anionic polymer *An* are similar, except that decreasing the pH is expected to increase the proportion of protonated, uncharged carboxylic acid groups relative to charged carboxylate groups on the polymer.

Figure 4.4. Viscosity for simple polyelectrolytes *Cat* and *An* (see Table 4-1)
Viscosity of polyampholytes as a function of ionic strength

Results shown in Figure 4.5 for polymer solutions of 0.01M ionic strength to reduce the effect of electrostatic interactions, give additional insight on how net charges of backbone affect the extension of polyampholytes. In this figure lower values of relative viscosity are observed, consistent with screening of electrical charge interactions within the macromolecular chain. The general pattern of the results, however, was similar to what was observed in the absence of salt. One effect that becomes more evident in Figure 4.5 is the differentiation between $P\text{Amp}_2$, the lowest-charge polyampholyte, vs. those of higher density of ionic groups. Near to neutral pH, the solution viscosity of $P\text{Amp}_2$ was considerably higher than for the other samples. This observation suggests that at neutral pH (pH of 7) this macromolecule does not have a sufficient density of oppositely charged ionic groups in order for the molecule to contract to the same extent as the other polyampholyte solutions.

Figure 4.5. Relative viscosity of polyampholytes with salt (ionic strength = 0.01M)
Viscosity with addition of poly aluminum chlorohydrate (PAC)

Poly aluminum chlorohydrate (PAC), with a formula $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$, is often used in the pulp and paper industries as a size bonding agent and drainage aid. It was found that there was some synergistic effect to dry-strength enhancing of polyampholytes $^6-10$. In this investigation, the viscosity of polyampholytes with addition of PAC was studied. At pH of 4, 5 and 8.5, the relative viscosity of polyampholytes and simple polyelectrolytes change against dosage is presented in Figure 4.6. An obvious synergistic effect of viscosity for polyampholytes could be seen in Figure 4.6a and 4.6b at pH4 and pH5, respectively, while not presented at pH8.5 for simple polyelectrolytes.

![Figure 4.6. Relative viscosity of polyampholytes measured at pH 4 (a), pH 5 (b), and pH 8.5(c) after applying Poly aluminum chlorohydrate (PAC).](image)

As shown in Figure 4.7a, addition of a low level of PAC (0.01% in solution, on an as-received basis) consistently increased the relative viscosities of polyampholyte solutions in the absence of added salt, both at pH=4 and pH=5. The opposite was seen in the case of
polyelectrolytes. A higher level of PAC (0.1%) was no longer effective in increasing the relative viscosity of the polyampholyte solutions.

It is apparent, first of all, that there exists a specific interaction between PAC and the polyampholytes. It is proposed that the increase in viscosity upon addition of PAC at the 0.01% level is due to complexation between cationic aluminum ionic species and carboxylate groups on the polyampholytes. Since all of the results in Figure 4.7 pertain to pH values below the isoelectric points of the polyampholytes, such complexation would be expected to increase the net positive charge in each case, resulting in a more extended conformation. The reversal of the trend at higher PAC is again consistent with increasing ionic strength of the solution.

* A=PAmp2; B=PAmp4; C=PAmp8; D=PAmp16; F=Cat; G=An.

Figure 4.7. Effects of polyampholyte charge density and PAC addition on relative viscosities at (a) pH=4 and (b) pH=5.
Influence of pH on the radius of gyration

![Graph showing the radius of gyration (Rg) at different pH conditions (pH4, pH7, pH10).](image)

Figure 4.8. The radius of gyration of PAmP4 at different pH conditions.

The radius of gyration at different pH conditions were performed by using multi-angle light scattering. For example, the radius of gyration ($R_g$) of PAmP4 in aqueous medium at pH 7 was $69 \pm 7$ nm while at pH 4 and pH 10 $R_g$ increased up to $95 \pm 6$ and $182 \pm 36$ nm, respectively (see Figure 4.8). These data agree well with the viscosity results discussed above.

**Bulk properties of nonionic lubricants**

Surface tension, an important property for surfactants and amphophilic polymers must be taken into consideration when dealing with interfacial phenomena. Surface tension was measured to characterize the adsorption at the air/liquid interface. Also, the critical micelle concentrations (CMC) of all polymeric lubricants used in our research were determined. At the CMC, the interface between solution and air is saturated with the solute molecules. Before this
concentration, the surface tension changes rapidly with surfactant concentration. Any further addition of surfactants after CMC will lead to the formation of micelles, while the surface tension remains constant. The curves of surface tension against polymer concentration are presented in Figure 4.9a and 4.9b for PAG and Pluronic polymers, respectively. Figure 4.10 includes data for the silicone surfactant.

For those polymers with low MW, such as RP10E13 and RP13E17, the surface tension changes roughly linearly with concentration. Lubricants with higher MW, larger than 3000 Dalton such as RP33E44 and all Pluronic polymers, showed typical surface tension curves. The CMC was located within a concentration range around 0.0001%-0.001%.

The silicone surfactant used in this study was a surface-active block copolymer of polyalkylene oxide-modified polydimethylsiloxane. Polydimethylsiloxane is very strong nonpolar group which produces a lowering in surface tension. It can be observed that the surface tension dropped sharply from ca. 72 mN/m to ca. 35 mN/m as the lubricant concentration increased from $10^{-5}$ to $5\times10^{-3}$% (w/v). The surface tension then decreased slowly, down to 32 mN/m at 1% maximum concentration. This behavior is indicative of a surface active molecule with strong polar and nonpolar groups. Compared with PAGs and Pluronic polymers, the silicone lubricant showed a much lower surface tension but higher CMC. Silicone lubricant was found to have a greater surface activity than regular hydrocarbon surfactants, as expected.
At a given temperature, the adsorption of the surface active molecules at the air/liquid interface is related to the polymer concentration and surface tension. This relationship is described by Gibbs adsorption equation:

\[
\Gamma = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_T
\]

(Equation 4.1)
where $\Gamma$ is surface excess; $R$ is universal gas constant (8.3145 J/mol K); $T$ is Kelvin temperature. In our investigation, the temperature was kept at 297.15K. As the concentration increase, the interface gets saturated, where $\Gamma = \Gamma_m$. At the saturated state, all the molecules are packed at the air/liquid interface. We assumed that each molecule occupied equal spaces. Thus the area for each molecule $A_m$ at interface could be calculated by

$$A_m = \frac{1}{\Gamma_m \cdot L_0} \quad \text{(Equation 4.2)}$$

where $L_0$ is the Avogadro constant. Based on the data obtained from surface tension measurements, the surface excess and the maximum surface excess, as well as the area for each molecule were calculated. The calculated maximum surface excess and area for each molecule are presented in Table 4.3. There are no $\Gamma_m$ or $A_m$ data available for the silicone lubricant.

Table 4.3. The maximum surface excess and area for each molecule calculated from Gibbs adsorption isotherm.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\Gamma_m \times 10^7$ (mol·m$^2$)</th>
<th>$A_m$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>6.9</td>
<td>2.4</td>
</tr>
<tr>
<td>RP13E17</td>
<td>8.9</td>
<td>1.9</td>
</tr>
<tr>
<td>RP33E44</td>
<td>15.8</td>
<td>1.1</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>17.4</td>
<td>1.0</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>10.5</td>
<td>1.6</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>15.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

RP10E13 and RP13E17 don’t show as major surface activity as the other polymers. No CMC was observed, and low maximum adsorption amount $\Gamma_m$ and larger occupied area can be observed in these cases. This indicates that they are loosely aligned at the interface, rather than well-organized in the form of a compact layer at interface, as is the case of other surfactants.
E19P29E19 and E76P29E76 share the same hydrophobic part, but exhibit quite different occupied areas per molecule. This is obviously the result of the two longer hydrophobic chains in the case of E76P29E76. It can be concluded that there is no one part that can totally control the adsorption of the adsorbed polymer at the interface. Both hydrophobic and hydrophilic parts are very important in the formation of interfacial layers.

**CONCLUSIONS**

In this chapter, key samples, including polyampholytes and nonionic polymers which are used in our adsorption studies were introduced and characterized in term of their bulk properties. The nature of polymers, such as their chemical structures, degree of polymerization and molecular weight, and their properties, including viscosity of polyampholytes, surface tension of nonionic lubricant, were described in detail. The information compiled here can help to further understand the interfacial behavior during adsorption of amphoteric and nonionic polymers on different solid surfaces and to help to establish the relationship between the nature of chemicals and their functions.
REFERENCES


Chapter 5

Adsorption of Polyampholytes on Solid Surfaces

Measured by the QCM Technique
ABSTRACT

In this chapter we discuss the relation between polyampholyte bulk properties and adsorption on silica and cellulose surfaces. Four polyampholytes carrying different charge densities but with same ratio of positive to negative groups, and two structurally similar polyelectrolytes (one cationic and the other anionic) were studied by using a Quartz Crystal Microbalance (QCM). This technique allowed time-resolved measurements of changes in frequency ($\Delta f$) (c.f. mass) and energy dissipation ($\Delta D$) (c.f. rigidity or viscoelastic properties) of a sensor, which made it possible to investigate the dynamics and extent of adsorption, the viscoelastic properties and the conformation changes of the different adsorbed layers. Through this research, we determined that the charge properties of a solid surface play a crucial role in the adsorption behavior of polyampholytes. This is explained by the capability the surface has to polarize the adsorbed polyampholyte layers. In our experiment, silica surfaces adsorbed much more polyampholytes than cellulose surfaces, under the same experimental conditions. The polyampholytes with the higher charge density adsorbed more extensively on silica and also produced a softer adsorbed layer. We propose that this is due to the polarization effect of the highly-charged silica surfaces on the high charge density polyampholytes. In the case of cellulose surfaces we conclude that the effect of charge density is less important as compared to that of silica surfaces.
INTRODUCTION

Polyampholytes are charged macromolecules carrying both acidic and basic groups. Under appropriate conditions these groups dissociate in aqueous solution, producing ionic groups on the polymer chains and the respective counterions in solution. If the ionic groups on the polymer chain are weak acids or bases, then the net charge of the polyampholyte can be changed by varying the pH of the aqueous medium. At the isoelectric point the amounts of positive and negative charges on the polyion are the same, giving a net charge of zero. In the vicinity of the isoelectric pH, the polymers are nearly charge-balanced and exhibit the unusual properties of polyampholytes. At conditions of high charge asymmetry (far above or far below the isoelectric pH), these polymers behave similar to simple polyelectrolytes.

Due to the unique properties of polyampholytes they are promising in controlling wetting, lubrication, adhesion and other phenomena. Polyampholytes are currently used to control the colloidal stability of dispersions in such applications as waste water treatment. Recent reports indicate that polyampholytes provide superior strength improvements for paper manufacture, compared to the addition of simple polyelectrolytes.

There is a need for understanding the adsorption phenomena, especially in the case of polyampholytes, that will lead to new functional materials and performance. Despite the existence of few theoretical and computational reports on polyampholyte behaviors at solid interfaces, there is a lack of experimental data to confirm the proposed theories and to directly allow the elucidations of the complex polyampholyte adsorption phenomena.
In this study we carried out adsorption experiments with a series of polyampholytes having increasing total charge densities at a constant ratio of cationic to anionic monomeric groups and molecular mass.

There are several methods available to study polymer adsorption on planar surfaces. These include radio labeling 23, reflectance FTIR 24, *in situ* ellipsometry 25, 26, and surface plasmon resonance 27-32. However, the main technique employed in our experiments consisted of a Quartz Crystal Microbalance with Dissipation monitoring (QCM-D), which provided a unique way to investigate the adsorption behavior of polymers. In fact, the mechanical oscillatory nature of QCM resonators enabled the measurement of unique properties such as the viscoelasticity adsorbed polymer films in addition to the mass uptake 33-36.

In this research, silica and cellulose thin films were used as substrates to study polyampholyte adsorption. The main aim was to clarify the relationship between the charged nature of these polymers and the adsorption and conformation of adsorbed layer. Our results indicated that the largest adsorption gains were obtained at intermediate charge densities and under conditions of pH favoring instability of the aqueous polymer mixtures. This corroborated the relationship between the bulk and the surface behavior of polyampholytes as compared with neutral polymers as well as simple polyelectrolytes.

**EXPERIMENTAL**

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) followed by a Milli-Q® Gradient unit (resistivity >18MΩ). Inorganic chemicals all were of reagent grade.
Polyampholyte and polyelectrolyte samples were prepared by Dr. T. Sezaki (Harima Chemical Corp.) by free-radical polymerization for a final content of charged monomers as indicated in Table 5.1. A representative structure of the amphoteric terpolymers used is shown in Figure 5.1. The cationic monomer was N-[3-(N’,N’-dimethylamino)propyl]acrylamide (DMAPAA), a tertiary amine. The anionic monomer was a dicarboxylic acid, methylene butanedioic acid also known as itaconic acid (IA). In each case the balance amount of neutral acrylamide (AM) monomer was added to comprise 100% on a molar basis. A typical procedure of synthesis (see for example sample “An” in Table 1) was as follows: 174 g of 40% acrylamide aqueous solution were added to a reaction vessel, 3.25 g of 80% itaconic acid and 300 g of water that had been purified by ion exchange were placed into a four neck flack provided with a reflux condenser and the mixture was heated to 60 °C in a nitrogen atmosphere. Then 10 g of 1% ammonium persulfate aqueous solution were added to the reaction solution and allowed to react at 85 °C for one hour. After cooling, an anionic polyacrylamide solution (sample “An”) was obtained. The cationic and amphoteric variants were prepared using the monomer ratios shown in Table 1 (see Table 1 for molar composition). Methylenebisacrylamide was added at a 0.04 mole percent level to the reaction mixtures as a cross-linking agent in order to increase the average molecular masses. As shown, the mean weight-averaged molecular masses of the polyampholyte samples were within the range 2.85 to 2.93 x 10^6 Daltons, and the polyelectrolyte masses also were similar.

The polymer solution samples described above were first purified by two cycles of dissolution in water and precipitation in methanol; then the pure samples were collected by
freeze-drying. NMR analysis was conducted by project collaborator Dr. Xingwu Wang. Samples for NMR analysis reported in Table 5.1 were prepared by making 2-3% polymer solution in D$_2$O. Crystals of CrK(SO$_4$)$_2$ were added at a concentration of 1.5 mM in order to reduce the spin-lattice relaxation times ($T_1$). The NMR experiments were performed in a Bruker 300MHz spectrometer equipped with a Quad dedicated probe at room temperature. The quantitative $^{13}$C spectra were acquired using an inverse gated proton decoupling sequence with a 90$^\circ$ pulse and a relaxation delay of 4.5 s, which was ~5 times of the longest $T_1$ measured for the samples. The $^1$H spectra were measured with 60$^\circ$ pulse and a pulse delay of 3 s. Note that in the case of polyampholytes the molar ratio of DMAPAA and IA is 5:2. Since IA is a dicarboxylic acid the effective content of anionic (carboxylic) groups is twice the value of the respective IA which is equivalent to a ratio between cationic (tertiary amine) and anionic (carboxylic) groups of 5:4.

![Molecular composition of monomers in random polyampholytes prepared by free-radical polymerization (DMAPAA, IA and AM).](image)

Figure 5.1. Molecular composition of monomers in random polyampholytes prepared by free-radical polymerization (DMAPAA, IA and AM).
Table 5.1. Acrylamide-based polyampholytes (PAmp 2, 4, 8 and 16) and simple polyelectrolytes (Cat and An). Note that in the case of the polyampholytes the %mol ratio cationic:anionic groups was kept constant at 5:4 and the molecular weight was approximately the same for all polymer samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer type</th>
<th>Cationic groups (mol %)</th>
<th>Cationic groups, NMR (mol %)</th>
<th>Anionic groups (mol %)</th>
<th>Anionic groups, NMR (mol %)</th>
<th>Viscosity* (mPa⋅s)</th>
<th>Mw ** (10^6 Da)</th>
</tr>
</thead>
<tbody>
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<td>PAmp2</td>
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<td>2.6</td>
<td>2</td>
<td>2.4</td>
<td>5300</td>
<td>2.95</td>
</tr>
<tr>
<td>PAmp4</td>
<td>Amphoteric</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4.4</td>
<td>4900</td>
<td>2.85</td>
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<tr>
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<td>5</td>
<td>0</td>
<td>(1.2)</td>
<td>3600</td>
<td>2.98</td>
</tr>
<tr>
<td>An</td>
<td>Anionic</td>
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<td>0.5</td>
<td>4</td>
<td>3.6</td>
<td>5300</td>
<td>3.23</td>
</tr>
</tbody>
</table>

*measured at 25 ºC and 100 s⁻¹.

** SEC-LALLS-VIS (TDA-302, Viscotek).

Solution viscosities were obtained with a Brookfield Model B8L viscometer (Tokimec, Inc.) at approximately 15% solids at 25 ºC. Molecular weight was obtained via multiangle light scattering with a SEC-LALLS-VIS (TDA-302, Viscotek).

**Viscosity measurement**

Further viscosity measurements to be described was obtained with an Ubbelohde viscometer in a thermostated water bath at 25.0 ºC in 0.1% solids aqueous polymer solutions in the presence and absence of 0.01 M NaCl. The pH was adjusted with aqueous HCl or NaOH.

**Radius of gyration measurement**

A DAWN laser photometer and an OPTILAB interferometric refractormeter of Wyatt Technology Corporation were employed in these experiments. Only one sample, PAmp4 under three conditions of pH (4, 7, and 10) representing acidic, neutral and basic conditions was
investigated. Zimm plots were obtained with a static light scattering (SLS) data fitting program provided by Wyatt Technology Corporation.

**Cellulose thin films**

The protocol of cellulose films and the quality of films were addressed in detail in Chapter 3.

**QCM-D measurements**

Adsorption of polyampholyte and polyelectrolyte samples was conducted on a Quartz Crystal Microbalance with Dissipation mode, QCM-D Q300 model (Q-Sense, Gothenburg, Sweden). The principles of this technique could be referred in Chapter 1. Resonators consisting of gold-coated quartz AT-cut crystals with fundamental frequency of 5 MHz were used as sensors. Unless stated otherwise the sensors used in this investigation were coated with a silica layer on gold. SiO$_2$-coated crystals were cleaned by immersion in 2% sodium dodecyl sulfate solution (SDS) for at least 30 min, followed by double rinsing with Milli-Q grade water, drying with N$_2$. Just before use, SiO$_2$-coated crystals were exposure to UV-ozone treatment for 10 min to oxidize impurities and to regenerate SiO$_2$ on Surface.

These crystals provide a mass sensitivity of 17.7 ng cm$^{-2}$ Hz$^{-1}$ for rigid layers. During the measurement, the crystal was mounted in a thermostated liquid chamber, designed to provide a rapid, non-perturbing exchange of the liquid in contact with one side of the sensor. This system allows for the measurement of up to four harmonics. In this study, the frequency and dissipation responses were recorded at around 15, 25, and 35 MHz, corresponding to the third, fifth and
seventh overtones (n = 3, 5, and 7, respectively). For clarity, only the normalized frequency shifts, normalized $\Delta f$ ($\Delta f_n/n$), and the dissipation shifts, $\Delta D$, for the third overtone are presented. In a typical experiment, fresh polymer solutions were prepared with Milli-Q water, at a concentration of 0.1 µl/g with background ionic strength of buffer solution of 0.1mM. Before running the polymer solutions, the instrument was stabilized with the respective buffer solution. After running the QCM for ten min with the buffer solution a constant QCM baseline was obtained and thereafter 1 ml polymer solution was injected in the adsorption module at a low rate (0.12ml/min). The frequency and dissipation were monitored until equilibrium. Finally, 3 ml buffer solution was used to rinse the adsorbed layer (using the same injection rate). By using this rinsing procedure any loosely bound polymer was removed from the interface and the net adsorption was therefore accounted for.

RESULTS AND DISCUSSION

Polyampholyte adsorption on silica surfaces

Adsorption kinetics

Figures 5-2, 3 and 4 show the adsorption curves for the polyampholytes PAmp2, PAmp4, PAmp8 and PAmp16 as well as simple polyelectrolytes Cat and An at three different pH conditions of the buffer solution (pH 4, 7 and 10). The data plotted in the top panel of each figure represent the frequency change monitored with time, while those on the bottom frames represent the change in energy dissipation as recorded by QCM. In all cases the dynamics of polymer adsorption followed a similar pattern: At first, when polymers were injected into the adsorption
module, the molecules adsorbed rapidly on the silica surface, driven by electrostatic interactions. It is interesting to observe that in this initial step all the polymers exhibited similar adsorption rates (similar slope in the adsorption curves). Following this first step a slower adsorption dynamics was observed. The turning point from the fast to slow adsorption rate was related inversely with the charge density of polymer, in both acidic and basic conditions. Note that the polymer of higher charge density was more effective in neutralizing the solid surface charge. However, at around pH 7 (the isoelectric point for the different polyampholytes) a net charge of zero was expected and the coiled polyampholytes produced less distinctive effects.
Figure 5.2. Frequency (top) and Energy dissipation change (bottom) curves for polyampholytes *P*Am*p*2, *P*Am*p*4, *P*Am*p*8 and *P*Am*p*16 as well as simple polyelectrolytes *Cat* and *An* at pH 4.
Figure 5.3. Frequency (top) and Energy dissipation change (bottom) curves for polyampholytes PAm2, PAm4, PAm8 and PAm16 as well as simple polyelectrolytes Cat and An at pH 7.
Figure 5.4. Frequency (top) and Energy dissipation change (bottom) curves for polyampholytes PAmp2, PAmp4, PAmp8 and PAmp16 as well as simple polyelectrolytes Cat and An at pH 10.
Interestingly, the simple cationic polyelectrolyte Cat reached the turning point much faster than any of the other polymers. Furthermore, there was an obvious difference between low and high charge density polyampholytes: For the low charge density polymers an equilibrium adsorption was reached relatively fast (frequency changes are minimal after the turning point). However, for the highly charge polyampholytes, equilibrium was reached only after a longer time (frequency changes are slower). It is proposed that this phenomenon is caused by the conformational change of the polymers at the interface and also by the possible formation of multiple layers.

This process can be also observed from the change in dissipation values depicted on the bottom panels of Figure 5.2, 3 and 4. The energy dissipation for adsorbing polyampholytes PAmP8 and PAmP16 were much larger than for polyampholytes PAmP2 and PAmP4. They were also larger than for the simple polyelectrolytes. The dissipation value increased with the increasing charge density of the polymers. If one takes a larger dissipation value as indication of a softer layer, the dissipation results were therefore consistent with the formation of multiple layers, as proposed before.

Note that in all curves presented in Figures 5-2 to 4, a large amount of buffer was used to rinse excess (loosely adsorbed) polymer from the interface. A second equilibrium amount can be derived, i.e., the effective (or irreversible) adsorbed mass after rinsing.

In our cases, the dissipation value for all the polyampholytes or polyelectrolytes were very high. Therefore, the Sauerbrey approximation could not be applied for accurate calculation of the adsorbed mass. Therefore, we applied the Voigt model to calculate the thickness and mass
of the adsorbed layers (for both polyampholytes and polyelectrolytes). The procedure for fitting the experimental data to the Voigt model the principles was described in Chapter 1.

In Figure 5.5, the thickness of a low and a high charge density polyampholytes is presented to illustrate how the adsorption mechanism compares for extreme cases. In Figure 5.6, the solid lines stand for the thickness calculated by Sauerbrey equation, while the dashed lines stand for the thickness calculated by Voigt model. In our case, even a more rigid film such as that for PAmp2, the Sauerbrey value was only half of the Voigt thickness. For softer polymers, such as PAmp8, larger differences were noted; in this case the Sauerbrey thickness was one fourth of the Voigt thickness.

All three pH conditions in our adsorption experiments involved negatively-charged solid surface since the IEP for silica is close to pH 2. Thus it is expected that the cationic groups in the polyampholytes and simple polyelectrolytes are responsible for the adsorption on the oppositely-charged surface. In this situation, the negative groups in the macromolecule are expected to be enriched in the outer regions of the adsorbed layers. In turn, these negative groups located in the outside regions are expected to interact with available positive groups in neighboring polymers which drives the formation of multiple adsorbed layers. From these two figures, one can distinguish two different adsorption mechanisms for polyampholytes based on their charge density.

For the low charge density polyampholytes, such as PAmp2 and PAmp4, it is noted that their behavior was similar to that of cationic polyelectrolytes. Results on adsorption of PAmp2 are used here to illustrate this statement (see Figure 5.5(a)). The adsorption process underwent a
rapid initial kinetics and it then reached an equilibrium state. The adsorbed layer was found to be around 28 nm (Voigt). This indicates that the polymer was adsorbed forming long loops at the interface. It is expected that a polymer layer was adsorbed and the net charges were not high enough to facilitate electrostatic interactions with additional polymers (therefore, multiple adsorbed layers were unlikely to occur). Since no additional polymer was expected to adsorb, the process reached equilibrium very fast. For the high charge density polyampholytes, such as PAmp8 and PAmp16, the process explained above was different (see Figure 5.5(b)): They were suited to adsorb during the first stages but the polymer loops were much shorter or denser (ca. 10 nm) than those for adsorbed low charge density polyampholytes. Therefore, the adsorbed layers are expected to be much denser. Additionally, it is expected that due to excess charges they have the capacity to interact with other polyampholytes in solution, thereby forming multiple layers; a process that is much slower, in kinetic terms. In the case of PAmp8, for example, it took more than five hours to reach its adsorption equilibrium. For the highest charge density polymer, PAmp16, equilibrium was not reached even after more than one day, a striking difference compared to the adsorption kinetics of low charge density polymers. Back of envelope calculations suggest that in the case of PAmp8 the equivalent of 10 polymer layers are formed. Another reason that may contribute to the slow dynamics of frequency and dissipation change during the adsorption process was precipitation from solution. Within the IEP region, polyampholyte molecules tend to contract to form coils and therefore precipitate at surfaces; however this would not happen beyond the IEP region (e.g. pH 4 and pH 10). In our case, this
slow stage of mass accumulation (multilayer forming) occurs regardless the pH conditions. Therefore, the contribution from polymer precipitation is suggested to be negligible.

It is further very interesting to note in Figure 5.5(b) that after rinsing with buffer solution the proposed adsorbed multiple layer was dissolved and only a thin polymer layer remained. This is taken as an indication that the attraction forces between the irreversible adsorbed layer and any additional layers in the presence of polyampholyte in solution was too weak to stand rinsing (shear and dilution).

![Figure 5.5](image_url)

Figure 5.5. Comparison of thickness calculated by Sauerbrey and Voigt models for low (PAmp2, left) and high (PAmp8, right) charge density polyampholytes.

**Conformation of adsorbed layers and multiple layer mechanism**

For rigid, ultrathin, and evenly distributed adsorbed layers, the Sauerbrey equation describes successfully the proportional relationship between the adsorbed mass ($\Delta m$) and the shift of the QCM crystals’ resonance frequency ($\Delta f$). On the other hand, if the adsorbed material
exhibits a viscoelastic behavior, such as for layers of proteins or DNA, substantial deviations from the Sauerbrey equation can occur\textsuperscript{33, 35, 38, 39}. Our results fall in the latter category. If one observes the dissipation value for polyampholytes, values as high as $200 \times 10^{-6}$ were reached.

$\Delta D-\Delta f$ plots eliminate time as an explicit parameter and as concluded in previous studies\textsuperscript{33, 35, 38, 39}, the absolute slope and the changes in the slope in these plots provide information about the kinetic regimes and conformational changes. Figure 5.6 shows the relation between dissipation and frequency changes at pH 7 condition. It is noted that for the other conditions of adsorption at pH 4 or 10, the $\Delta D-\Delta f$ plot exhibited similar trends and are not shown here for brevity. At the beginning of adsorption, all polymers, including polyampholytes and polyelectrolytes, produced a $\Delta D-\Delta f$ profile that resembles a straight line (see inset of Figure 5.6). The slope is indicator of the conformation. An interesting phenomenon that was observed is that slope is in the order of charge density. PAmp2 had the steepest slope and thus had the softest conformation while the opposite applied to the case of PAmp16. The cationic polymer had similar slope to PAmp16, but the anionic polymer was just a “point” in this D-f profile because it did not adsorb. As the adsorbed mass increases, the changes in slopes differ for polyampholytes with low and high charge density. For polyampholytes with low charge density, for example, PAmp2 and PAmp4, as well as simple polyelectrolytes, the profile was a straight line and no change in slope was observed. Polyampholytes with high charge density, for example, PAmp8 and PAmp16, showed a change in slope (becoming steeper with increased $f$). This indicates that there was no major conformation change for low charge density polyampholytes and simple polyelectrolytes, but there was conformation change for high charge density polyampholytes. This observation agrees
with our earlier hypothesis that adsorption occurs as a single/simple layer for low charge density polyampholytes and simple polyelectrolytes, but multilayer, more complex polymer adsorption occurs for high charge density polyampholytes. Furthermore, the softness (viscoelasticity) of the adsorbed film was expected to increase as the adsorbing polymers were farther from the solid plane and probably with more loose segments and hydration water.

![Graph](image)

**Figure 5.6. ΔD-Δf profile during adsorption on silica of polyampholytes and polyelectrolytes.**

**Effect of Solution pH on polyampholyte adsorption**

The QCM frequency measured at adsorption equilibrium for different pH conditions is shown in Figure 5.7. If one takes a larger frequency as indication of a larger adsorbed amount it is clear that in all cases the extent of adsorption for polyampholytes is consistently larger than for those of simple polyelectrolytes. For the negatively charged polyelectrolyte, \( An \), no adsorption is observed. In the case of the polyampholytes, it is evident that as the charge density is increased, a
larger adsorption is measured. Changes in the pH of the polymer solution did not play a distinctive role in terms of the extent of polyampholyte adsorption. Dobrynin and Rubinstein\textsuperscript{40} demonstrated that polyampholytes was able to adsorb on both cationic and anionic surfaces, since they had both charge groups. These authors demonstrated that the adsorbed polymers could change conformation in solution to allow the opposite charge groups to interact more effectively with the oppositely charged surfaces.
Figure 5.7. Frequency change for different polyelectrolytes after reaching adsorption equilibrium.

An interesting phenomenon can be observed after inspection of Figure 5.7: In this figure it can be seen that the frequency change for adsorption at pH 4 and 10 was larger than that in pH
7. We attribute this observation to the fact that water couples to a larger extent with polymer at the extreme pH values. At pH4 and pH10, which are far from the IEP of the polyampholytes, the polymers tend to be extended, while at pH7, which is very close to their IEP, they trend to contract into coils therefore preventing water molecules to couple, as extensively as in the other cases, with the polymer segments. The polyampholytes’ conformation in solution (extension or contract according to media pH conditions) can be related to the viscosity and hydrodynamic radius results presented in Chapter 4.

Figure 5.8. Illustrative chart with the net charge of surfaces and polymers at different pH and indication of dominant electrostatic interactions between surfaces and polymers.

Figure 5.8 illustrates the electrostatic interaction between silica and the tested polymers. The silica surface is negatively charged in the pH range from 4 to 10, while the simple cationic and anionic polyelectrolytes are always positively and negatively charged, respectively. The polyampholytes carry net positive charges between pH4 and the respective IEP while a net negative charge is dominant between the respective IEP and pH10.
This model can be used to explain the extent of adsorption for the cationic and anionic polymers. However, rationalization of the adsorption of polyampholytes is more challenging. From this model, the polyampholytes carry zero or negative net charges at pH7 and pH10, respectively; therefore it is expected that no or little polyampholyte adsorption occurs at around these two pHs. This is in contrast with our experimental observations: There is a quite large adsorption at these pHs. It is hypothesized that hydrogen bonding between the polymers and the surfaces may contribute to some extent to this behavior. What is more evident, however, is that the polarization effect in the case of charged surfaces is a dominant driving mechanism for adsorption, as will be discussed in the next section.

**Adsorption of polyampholytes on cellulose surface**

Adsorption studies of polyampholytes onto cellulose surfaces were performed only in the pH 7 condition. Figure 5.9(a) and (b) show the change in QCM frequency and dissipation with adsorption time. The curves are quite different from those discussed before for silica surfaces. First, the extent of adsorption was much lower on cellulose compared to the case of silica surfaces. The second difference was that in the adsorption equilibrium state the dissipation values were much higher. Inspection of the frequency curves revealed that reorganization or maybe some desorption occurred in the case of polyampholytes PAmp8 and PAmp16. This reorganization phenomenon of polymers also can see in Figure 5.10.
Figure 5.9. Polymer adsorption isotherms for cellulose substrates as measured by frequency (top) and dissipation (b) changes with time.
Figure 5.10. $\Delta D - \Delta f$ profile during adsorption on cellulose of polyampholytes and polyelectrolytes.

Why does desorption occur in the case of cellulose surface but not onto silica surfaces? Dobrynin, Rubinstein and Joanny have recently proposed a new adsorption mechanism that is induced by the polarization of the chains in the electric field of the surface $^{40}$. In fact, one of the most interesting features of polyampholytes is their polarizability in external electric fields. The electric field pulls oppositely charged monomers in opposite directions, polarizing the chain. However, the redistribution of the charged monomers inside the polymer coil is opposed by the chain elasticity. As a result of these conflicting forces the polyampholyte chain is stretched into a “tug of war” configuration. It has recently been established that the polarization of polyampholyte chains is responsible for adsorption of these polymers on charged surfaces, resulting in formation of multiple protective polymer layers $^{11, 40-44}$. Even net neutral
polyampholytes with equal numbers of positively and negatively charged monomers are able to adsorb on a charged surface due to a polarization-induced attractive interaction as long as the surface charge is high enough \(^\text{11}\).

Although cellulose surfaces also bear negative charges, its charge density is much lower than that on the silica surfaces. According to Radtchenko et al. \(^\text{45-47}\), the charge density of cellulose in their case was 0.80 and 0.21 mC/m\(^2\) at pH 9.5 and pH 4, respectively. On the other hand, the charge density of silica surface in aqueous medium was 20 and 100 mC/m\(^2\) at pH 4 and 8, respectively \(^\text{47, 48}\). According to Dobrynin’s theory \(^\text{40}\), adsorbed polyampholytes films on cellulose would be of the a uniform multiple layer type, with stretched chains, while the adsorption of polyampholytes on silica would be multiple layers with self-similar stretched pseudo-brush in the inner layer and stretched chains in the outer layers. Our experimental data agrees this theory very well.

**CONCLUSIONS**

The adsorption onto charged surfaces for four polyampholytes with charge density ratios of 1:2:4:8 and two simple polyelectrolytes (anionic and cationic) were measured by using the QCM-D technique. It was found that the charge properties of both substrates and polymers were important in the adsorption mechanism (extent and confirmation). Adsorption in the case of high charge density surfaces and high charge density polyampholyte is driven by polarization mechanisms. Under this situation, the adsorbed polyampholytes tend to form multiple, dissipative layers. The further the layer is away from the substrate, the softer and looser it is. For surfaces of low charge density adsorbing low charge density polyampholytes, polarization is
unlikely to occur. Under this situation, simple, more compact layers are observed. Overall, the results presented in this chapter allow a better understanding of polyampholyte adsorption and reveals that the extension of adsorption and conformation of the adsorbed species is a result of a subtle balance of factors (including charge properties of surfaces, charge density of polyampholytes and pH of the aqueous medium).


Chapter 6

Adsorption of Lubricants on PET Surfaces
ABSTRACT:

The adsorption on polyester (PET) surfaces of nonionic polymer surfactants (poly alkyl glycols and pluronics with different structures) was studied by using the QCM and SPR techniques. The results indicate that the chain length of the hydrophobic group of the nonionic polymers strongly correlates with the polymer affinity to the surface. The polymer molecular weight also has a strong influence on the maximum adsorption density. Finally, it can be concluded that hydrophobic and van der Waals interactions are the predominant driving mechanism in the adsorption of nonionic polymers on PET surfaces.
INTRODUCTION

Lubrication is an important phenomenon that takes place when substances such as greases or oils (so called lubricants) are applied to moving objects to reduce friction. In paper and textile processing, fibers go through many different unit operations and stages under high shear forces. Moving machinery and equipment are heavily involved in paper and textile processing where demands for faster production rates are ever present. Therefore, better performance lubricants are to be applied to reduce friction and wear under extreme conditions. It can be concluded that lubrication is an extremely important phenomenon, especially in textile processing as it is critical to improve production and efficiency.

A typical lubricant film is very thin, usually several hundreds of molecules thick for thicknesses of about 100 nm or lower \(^1,^2\). Therefore, understanding the structure of lubricant thin film and the way the molecular components organize at the interface \(^3\) during the lubrication process is of utmost importance \(^4\).

Nonionic polymers are commonly used in textile finishes as a component of the formulation to work as lubricants and to facilitate the processing of synthetic fibers in various operations. In this chapter, the influence of the nature of nonionic polymers (including structure, molecular weigh, HLB and hydrophobic segments’ length) on the resultant adsorption behaviors will be discussed. The ultimate goal of this investigation is to find structure-property relations applicable to nonionic polymers and thus set the heuristic rules that will eventually help to optimize finish performance by the design of new lubricants.
Quartz Crystal Microbalance with Dissipation (QCM-D) was used to study the interaction between a series of nonionic lubricants and the cellulose and synthetic surfaces. QCM-D allowed the study of interfacial behaviors (including adsorption and desorption) in situ, in real time at the nano scale. It provided information on the adsorbed mass (from vibration frequency changes) and also energy dissipation (which is related to the conformation of the adsorbed species). Surface Plasmon Resonance (SPR) was also employed to study the adsorption of nonionic polymers on the model textile surface and to verify the determinations made with the QCM-D. In order to facilitate this study, gold QCM sensors were modified with ultrathin, flat films of nylon, polypropylene (PP), polyester (PET) and cellulose polymers, as surrogates of textile fibers. These films were obtained by spin coating polymer solutions, as was explained in previous chapters. However, in the present chapter, only the adsorption of nonionic lubricants onto PET surfaces is addressed. A discussion on the influence of the substrate on the adsorption of nonionic polymers is described in detail in a following chapter.

**EXPERIMENTAL**

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) which was further processed in a Milli-Q® Gradient unit to ensure ultrapure water with resistivity greater than 18MΩ.

The substrates used in this investigation were circular Q-Sense gold sensors (Q-sensor Co, diameter is 12 mm) and square (Rechaint Co, 12 × 12 mm) wafers suitable for QCM and SPR experiments, respectively.
The nonionic lubricants used in this investigation included two sets of polymers with known structures: polyalkylene glycols (PAGs) from Dow Chemical Co. (Midland, MI), and triblock copolymers based on ethylene oxide and propylene oxide (Pluronic) from BASF Corporation (Florham Park, NJ). Generic chemical structures of PAGs and Pluronics are shown in Figure 6.1.

\[
\text{CH}_3\quad \text{RO-}[\text{CH}_2\text{CHO}]_n[\text{CH}_2\text{CH}_2\text{O}]_m\text{-H}
\]

\[
\text{H-[CH}_2\text{CH}_2\text{O}]_m-[\text{CH}_2\text{CHO}]_n[\text{CH}_2\text{CH}_2\text{O}]_m\text{-H}
\]

Figure 6.1. Chemical structure of polyalkylene glycols (PAGs) (left) and Pluronics (right).

Table 6.1. Structural information of polyalkylene glycols (PAGs) and Pluronics

<table>
<thead>
<tr>
<th>Symbol used in this thesis</th>
<th>Commercial name</th>
<th>MW</th>
<th>(n) (PO)</th>
<th>(m) (EO)</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>UCON 50-HB-400</td>
<td>1,230</td>
<td>10</td>
<td>13</td>
<td>11.92</td>
</tr>
<tr>
<td>RP13E17</td>
<td>UCON 50-HB-660</td>
<td>1,590</td>
<td>13</td>
<td>17</td>
<td>12.0</td>
</tr>
<tr>
<td>RP33E44</td>
<td>UCON 50-HB-5100</td>
<td>3,930</td>
<td>33</td>
<td>44</td>
<td>8.51</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>Pluronic P65</td>
<td>3,400</td>
<td>29</td>
<td>19</td>
<td>21.67</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>Pluronic F68</td>
<td>8,400</td>
<td>29</td>
<td>76</td>
<td>27.97</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>Pluronic P105</td>
<td>6,500</td>
<td>56</td>
<td>37</td>
<td>17.34</td>
</tr>
</tbody>
</table>

* UCON polymers are from Dow Co. and Pluronic polymers are from BASF Co.
* HLB values were calculated by the method described by Guo et al.⁵
* \(R\), \(P\) and \(E\) stand for butyl, \(r\) propylene oxide and ethylene oxide groups, respectively.

PAGs and Pluronic lubricants with different structural parameters \(m\) and \(n\) (see Figure 6.1) used in this study are listed in Table 6.1. It is worth noting that the supplied samples not only had different monomer composition but also different molecular weights. The lack of a systematic variation in the molecular parameters was a limitation in our efforts; nevertheless, these polymers are comparatively purer and better defined than commercial nonionic mixtures commonly used in industry. Therefore they enabled us to understand better how polymer
structure and molecular weight affects the assembly of boundary layers (and thus influence lubrication and friction phenomena, to be discussed in later chapters).

**Methods**

**Preparation of model films**

All substrates (gold sensors and wafers) were cleaned with Piranha solution (70% H$_2$SO$_4$+30% H$_2$O$_2$ (30%)) for one hour and then subjected to Ultra-violet Ozone (UVO) radiation for 10 minutes immediately before spin-coating with PET solutions.

Polyester poly(ethylene terephthalate) (PET) is a thermoplastic polymer resin of the polyester family which is widely used in synthetic fibers; beverage, food and other liquid containers. PET is resistant to acid, base and most solvents and for the same reason it is not surprising that little or no report was available about PET dissolution in the manufacture of spin coated films. However, given the fact that hexafluoroisopropanol, (HFIP) was found to be an excellent solvent for nylon 6, even at room temperature, we developed a method to manufacture ultrathin films of PET from same (HFIP) solution. After experimental optimization, we found that proper amounts of PET and HFIP can form thin films (ca. 40 nm) by dissolving in small vials (3 h minimum dissolution time) and then by applying the solution (0.16 %) onto the gold substrate and spinning at 3000 rpm for 30 seconds. Detailed procedures and obtained PET film characterization can be found in Chapter 3.

**QCM-D technique**

A QCM-E4 (Q-sense Inc.) was used in this investigation to measure the adsorption of the nonionic polymers on PET films. The principle of the QCM technique involves the monitoring
of the resonant frequency ($f$) of a gold-coated piezoelectric material (quartz crystal) which depends on the total oscillating mass $7-9$. If the film is thin and rigid, the decrease in frequency is proportional to the mass of the film, as stated by Sauerbrey equation $^{10}$:

$$\Delta m = -\frac{n \Delta f}{C}$$

(Equation 6.1)

where $C = 17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ for a 5 MHz quartz crystal.

$n = 1,3,5,7$ is the overtone number.

Since frequency can be detected very accurately, the QCM operates as a very sensitive balance. Since the density of the given polymer film are easy to finding respective databases, the thickness can be obtained. In our investigation, only the third overtone frequency was measured before and after spin coating. The resonant frequency for the film in dry condition was obtained in air at constant temperature of 25 °C.

**Surface Plasma Resonance (SPR)**

A Reichert SR7000 Surface Plasmon Resonance Refractometer was used to conduct complementary adsorption studies of the nonionic lubricants on PET films. The resolution of SPR is about 10 ng/cm$^2$, comparable to that of the QCM. By conducting the experiments under the same set of conditions as those used in QCM experiments (lubricant concentration, temperature, flow rate, etc.) more meaningful conclusions can be reached regarding the adsorption behaviors. The use of two different physical principles (electromechanical and optical for QCM and SPR, respectively) allows us to obtain more information about adsorption, specially the role of coupled water.
Contact angle measurement

The contact angle of untreated and polymer-coated PET surfaces against pure water was measured on a manual Rame-Hart goniometer. After 1 min of placing a droplet of Mini-Q water (10 µL) onto the surface the outline of the droplet was detected with an optical magnifier. The tangent line on the droplet in the three-phase zone was traced with a protractor within the optics and therefore provided a measurement of the contact angle.

RESULTS AND DISCUSSION

Adsorption of Nonionic Lubricant Polymers

Adsorption experiments were conducted with the QCM-D as described above. Typical QCM profiles as a function of adsorption time are shown in Figure 6.2. This is an example of how the raw data is collected in a given experiment. Note that frequency and dissipation values of three overtones are recorded simultaneously and can be plotted in a single chart. Since the third overtone vibration reaches a larger area in the sensor (as compared to the other two overtones), we used the frequency and dissipation changes from the third overtone, unless specified otherwise.. The lubricant used in Figure 6.2 was E76P29E76 at a concentration of 0.0001%. Before any experiment, water was injected in the QCM’s sample loop continuously until a stable (frequency and dissipation) baseline was obtained. Then nonionic (lubricant) polymer of given concentration was injected in the loop. As a result of the introduction of the polymer solution in the QCM chamber a sharp drop in frequency and increase in dissipation
were observed, as seen in Figure 6.2. These changes are indicative of the adsorption of the lubricant on the sensor surface.

The adsorption of nonionic lubricants was found to be a very fast process, as required in demanding actual applications. Around 10 minutes after injection, both adsorption and dissipation curves reached a plateau. The experiment showed in Figure 6.2 was run for another 10 minutes to ensure that an equilibrium state was achieved. Thereafter, pure water was injected to rinse the system. As a result, a sharp increase in frequency and a sharp drop in dissipation were observed. These changes are indicative of the fact that loosely bound lubricant molecules as well as molecules in the bulk were removed by this rinsing step. After ca. 10 minutes, the second equilibrium state was observed with higher frequency and lower dissipation as compared with the initial values. Based on these observations, the adsorption mass on the sensor surface was divided into two categories: Total or reversible (first plateau) and irreversible (second plateau) adsorbed mass.

From the changes in dissipation it can be concluded that the adsorbed film was very thin and “rigid” (the difference of dissipation with and without lubricant film was no more than $1 \times 10^{-6}$ dissipation units). Note that the flow rate for fluid (with or without polymer sample) was always kept constant at 0.1 ml/min as produced with a peristaltic (QCM) or syringe pump (SPR).

Five polymer lubricant concentrations (ranging from 0.0001% to 1%) were run in all the adsorption experiments by QCM for at least three repetitions. The equilibrium adsorption mass before (total adsorption) and after rinsing (irreversible adsorption) was recorded as a function of
concentration, as can be seen in Figures 6-3(a) and 6-3(b), respectively. In these curves each data point was drafted from triplicate runs as those illustrated in Figure 6.2. The lubricant adsorbed amount was calculated from the frequency change by using the Sauerbrey equation. The total adsorption, i.e., adsorption before rinsing, changed roughly linearly with lubricant concentration. A clear trend is observed in the case of the lubricants with lower molecular weights which adsorbed less extensively. Similar observations apply to the irreversible adsorption. Furthermore, it is noted that the irreversible adsorption tend to reach a saturation at the highest concentrations used.

Figure 6.2. Typical QCM $f$ and $D$ curves for an adsorbing nonionic polymer. Polymer sample was E76P29E76 in 0.0001% aqueous solution. Frequency ($f$) change (left axis) and dissipation ($D$) change (right axis) for three overtones (3, 5, 7) were recorded simultaneously. Flow rate was constant 0.1 ml/min.
All samples also were studied by SPR experiments. Similar trends could be observed, as illustrated in Figure 6.4(a) and 6-4(b). One significant difference between the data acquired from QCM and SPR is that the calculated adsorbed mass determined from SPR was only around half of that calculated from QCM. This difference is explained by the different principles applied in both techniques and also by the presence of hydration water associated with ethylene oxide (EO) groups and coupled water in the adsorbed layer (QCM is sensitive to coupled water). It is expected that under boundary lubrication regimes, these bound water molecules contribute positively to lubrication.
Figure 6.3. Equilibrium adsorption isotherms for nonionic lubricants adsorbed on PET surfaces at 25 °C before (a) and after (b) rinsing measured by QCM. The flow rate was constant at 0.1 ml/min.
Figure 6.4. Equilibrium adsorption isotherms for nonionic lubricants adsorbed on PET surfaces at 25 °C before (a) and after (b) rinsing measured by SPR. The flow rate was kept constant at 0.1 ml/min.
Figure 6.5. Equilibrium adsorption isotherms for nonionic lubricants adsorbed on PET surfaces expressed by mol/m\(^2\). The data converted from Figure 6.3.

Another obvious trend observed is that the adsorption mass started to go saturate at high concentration. In order to compare with the maximum adsorbed mass at air/water which had been addressed in Chapter 4, adsorbed mass of ng/cm\(^2\) in Figure 3 was converted into the unit of mol/m\(^2\) as in Figure 6.5. The maximum adsorbed mass at air/water was in the range of 8-15 \(\times\) 10\(^{-7}\) mol/m\(^2\). The adsorbed mass on PET films before rinsing was larger than that range and kept increasing with concentration increase. This indicated that multilayers formed before rinsing. But after rinsing, the adsorbed mass for each nonionic polymer was close but slightly lower than the maximum adsorption mass obtained from air/water interface. It can be concluded that there is a monolayer strongly bound onto the surface. The reason why the values of maximum adsorption mass on PET are lower than those obtained from air/water interface may attribute to the hydrophobicity of PET is not high as that of air.

For rigid, ultrathin, and evenly distributed adsorbed layers, the Sauerbrey equation\(^\text{10}\) describes successfully the proportional relationship between the adsorbed mass (\(\Gamma\)) and the shift
of the QCM crystals’ resonance frequency ($\Delta f$). On the other hand, if the adsorbed material exhibits a viscoelastic behavior, (a condition that applies to many polymer and protein adsorption), substantial deviations from the Sauerbrey equation can occur. The $\Delta D-\Delta f$ plots eliminate time as an explicit parameter and as concluded in previous studies, the absolute slope and the changes in the slope in these plots provide information about the kinetic regimes and conformational changes. For the data we obtained from QCM, dissipation value $\Delta D$ was plotted against frequency change $\Delta f$ in Figure 6.5 for diblock and triblock polymers. The curves for RP10E13 and RP13E17 overlap and exhibit a steep slope. This means that for these two polymers with lowest molecular weight, the adsorbed film was very soft. Loops are seen in each curve, these loops are the result of the rinsing effect. For other polymers, two slopes are observed in the respective profiles. The first slope is flat while the second one is a steep one. Our explanation for this distinctive behavior is that the lubricant molecules first adsorb onto the surface as a compact layer (flat slope). As more molecules diffuse to the interface, multiple layers can be formed (steep slope with large dissipation). Since the binding between the multiple layers is expected to be weak compared with the molecules in the close vicinity to the surface, they can be easily removed by rinsing (loops). Furthermore, it is also observed that the conformation of the adsorbed layer for high molecular weight polymers is more compact than in the cases described before.
Figure 6.6. $\Delta D$ and $\Delta f$ curves to study the conformation of adsorbed nonionic diblock polyalkylene glycols (a) and triblock Pluronics (b) on PET surfaces.
Effect of Lubricant Type on Adsorption

In order to reveal the underlying phenomena involved in lubricant-surface interactions, we fitted the adsorption data to the Brunauer-Emmett-Teller (BET) and the Langmuir isotherms. It is concluded that in all cases the adsorbed mass can be accurately described with a Langmuir-type isotherm (see values of R-squared close to 1 in Table 6.2). On the other hand the BET equation failed to describe the experimental data (see low values of R-squared in Table 6.3). All the fitting work was conducted by freeware Isofit V1.2 (Free Software Foundation, Inc. Boston, MA) by minimizing the weighted sum of squared error between experimental data and corresponding isotherm-computed values. The Langmuir adsorption isotherm assumes a monomolecular adsorption layer with a maximum number of equivalent binding sites, each of which can be occupied by one molecule. The adsorbed mass \( \Gamma \) is assumed to be a function of the adsorbate concentration, \( C \); maximum adsorption density, \( Q_0 \) and the affinity between lubricant and surface, \( b \) (see Equation 6.2):

\[
\Gamma(X, C) = \frac{Q_0 b C_i}{1 + b C_i} \tag{Equation 6.2}
\]

The fitted parameters of the Langmuir equation for all adsorbed curves after rinsing are listed in Table 6.2.
Table 6.2. Langmuir fitting parameters for adsorption curves of nonionic lubricants on PET surface after rinsing (irreversible adsorption).

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>bQ₀</th>
<th>b</th>
<th>Q₀</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>3.08E+03</td>
<td>3.52E+01</td>
<td>8.75E+01</td>
<td>0.967</td>
</tr>
<tr>
<td>RP13E17</td>
<td>5.74E+03</td>
<td>3.22E+01</td>
<td>1.78E+02</td>
<td>0.93</td>
</tr>
<tr>
<td>RP33E44</td>
<td>2.21E+04</td>
<td>1.00E+02</td>
<td>2.21E+02</td>
<td>0.98</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>1.11E+04</td>
<td>1.00E+02</td>
<td>1.11E+02</td>
<td>0.967</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>1.70E+04</td>
<td>6.67E+01</td>
<td>2.55E+02</td>
<td>0.975</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>4.11E+04</td>
<td>1.00E+02</td>
<td>4.11E+02</td>
<td>0.919</td>
</tr>
</tbody>
</table>

Table 6.3. BET fitting parameters for adsorption curves of nonionic lubricants on PET surface after rinsing (irreversible adsorption).

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>bQ₀</th>
<th>b</th>
<th>Q₀</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>2.28E+03</td>
<td>1.00E+02</td>
<td>2.28E+01</td>
<td>0.713</td>
</tr>
<tr>
<td>RP13E17</td>
<td>5.15E+03</td>
<td>1.00E+02</td>
<td>5.15E+01</td>
<td>0.984</td>
</tr>
<tr>
<td>RP33E44</td>
<td>3.95E+04</td>
<td>1.00E+02</td>
<td>3.95E+02</td>
<td>0.477</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>4.45E+04</td>
<td>1.00E+02</td>
<td>4.45E+02</td>
<td>0.979</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>1.13E+05</td>
<td>1.00E+02</td>
<td>1.13E+03</td>
<td>0.59</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>2.69E+04</td>
<td>1.29E-03</td>
<td>2.09E+07</td>
<td>0.319</td>
</tr>
</tbody>
</table>

In Figure 6.7, the maximum adsorption density, Q₀ and affinity between lubricant and surface, b are plotted for the various lubricants. Lubricant RP10E13 showed the lowest maximum adsorption density, while E37P56E37 produced the highest. Regarding the affinity between the nonionic polymers and the PET surface, RP10E13 and RP13E17 showed the lowest b values while R33E44, E19P29E19 and E37P56E37 have the highest ones.
Figure 6.7. Fitted Langmuir parameters $b$ and $Q_0$ as a function of the lubricant type.

Since it is difficult to draw meaningful conclusions based on the obtained data as was presented before, we discussed in the following sections, more details about the effect of lubricant molecular weight and hydrophobic-hydrophilic balance on its adsorption ability.

**Effect of Nonionic Polymer Molecular Mass**

In Figure 6.8, the maximum adsorption density and Langmuir affinity constants between the tested lubricants and PET surface are plotted as a function of the molecular weight. A clear trend could be distinguished for the maximum adsorption density, regardless the structure (hydrophilic-lipophilic balance of the molecule). This is the reason why conformation of the adsorbed layer with high molecular weight polymer is “more compact” than that with lower molecular weight ones. On the other hand, there was no obvious trend for the fitted affinity constants as a function of the molecular weight.
Figure 6.8. Fitted Langmuir parameters change with molecular weight (MW). Highly dependency of maximum adsorption density on MW can be observed.

Effect of the HLB of the Lubricant on Adsorption on PET

The nonionic polymers presented in Table 6.1 are actually surface-active molecules (polymeric surfactants) since they carry hydrophilic (EO groups) and hydrophobic (PO groups and alkyl group) segments that provide amphophilic character to the molecule. Further, adsorption and association behaviors typical of monomeric surfactants are also displayed by these polymers. In fact, nonionic lubricants can assemble into layers to offer protection to friction and wear. The hydrophilic-lipophilic balance (HLB) of a surfactant, a widely used indicator of its partitioning tendency between oil and water phases, can also be applied to nonionic polymers. The maximum adsorption density and affinity number between the polymeric lubricants and PET surface are plotted against the HLB number in Figure 6.9. The HLB values
were calculated by the method of group contribution described by Guo et al.\textsuperscript{5}. Details about this calculation are provided in the next section. As can be observed in Figure 6.9, there is no clear trend regarding the effect of HLB on adsorption. However, it is expected that a lower polymer HLB will favor larger adsorption (and larger adsorption affinity constants) on hydrophobic PET surfaces since in this case hydrophobic interactions are dominant. Since the molecular weight is also an important factor independent on the surface energies of the system, it is the combination of HLB and molecular mass that explain the observed trends. Unfortunately, no series of polymers with same molecular mass and different HLB (or vice versa) were available for more detailed inquiries.

![Figure 6.9. Fitted Langmuir parameters as a function of polymer’s HLB values.](image-url)
Hydrophobic Numbers and Adsorption

Ever present van de Waals forces are a component of the total adsorption energy but it is not expected to be the main driving force for irreversible adsorption. In this section we will discuss the other, likely more important, contribution for irreversible adsorption of the tested surfactants on PET surfaces.

Since no reaction with surface takes place upon adsorption and since there are no charged groups in the nonionic surfactant chains, their adsorption is expected to obey physical processes and therefore the attractive forces are a combination of van de Waals and hydrophobic effects.

Explanations of the hydrophobics forces have been attempted relatively recently in classical discussions of surface science. It is hypothesized that the hydrophobic force depends on the hydrophobicity of the adsorbate and surface and it can be divided into short-, medium- and long-ranged forces. In our case, the water contact angle of PET is around 65° a somewhat hydrophobic material and therefore the involved hydrophobic forces may be of the short-range type.

HLB was used in the previous session as a way to determine the hydrophobicity (or hydrophilicity) balance of the molecule. However, it is not the only method to determine the hydrophobicity of the involved species. In fact, the group contribution and the effective chain length proposed by Guo et al inspired us to use an alternate way to characterize the hydrophobicity of the polymers.

In group contribution methods, it is assumed that a mixture does not consist of molecules, but of functional groups. By using thermodynamic fundamentals, it can be shown that the
required activity coefficients can be calculated when only the interaction parameters between the functional groups are known. The advantage of group contribution methods is that the number of functional groups is much smaller than the number of possible molecules\textsuperscript{19-21}.

In our case, the \( R \) and \( PO \) groups are relatively more hydrophobic than the \( EO \) groups (see Table 6.1) and therefore we will use a descriptor for these units based on what is known for a straight alkyl chain. A fully stretched lipophilic chain length is directly proportional to the number of \(-CH_2-\) groups. Here \( N_{CH_2,eff} \) is given by

\[
N_{CH_2,eff} = 0.965N_{CH_2} - 0.178
\]  
(Equation 6.4)

and \( N_{PO,eff} \) is given by

\[
N_{PO,eff} = 2.057N_{PO} + 9.06
\]  
(Equation 6.5)

Where \( N_{CH_2,eff} \) and \( N_{PO,eff} \) represent effective chain lengths for \(-CH_2-\) and \( PO \) groups, while \( N_{CH_2} \) and \( N_{PO} \) represent actual chain lengths for \(-CH_2-\) and \( PO \) groups, respectively.

In Equation 6.4 and 6.5 coefficients from group contribution calculation is used as pre-factor: 0.475 for \(-CH_2-\), and 0.15 for \( PO \)\textsuperscript{5}.

Thus the hydrophobic number of one molecule is the product of effective chain length and group contribution number. The calculated hydrophobic numbers for the polymers listed in Table 6.1 are shown in Table 6.4.

When the maximum adsorption density, \( Q_0 \) and affinity constant, \( b \) are plotted against the respective hydrophobic number an obvious trend emerges, as seen in Figure 6.10: The affinity strongly depends on the hydrophobic number. When the hydrophobic number is small, \(<8\), the
affinity constant is around 20; when hydrophobic number reaches up to 10, the affinity constant is doubled and when hydrophobic number is high, >13, the affinity reaches a maximum value of 100 and reaches a plateau. Therefore, it is concluded that the affinity is very sensitive (and strongly depends on) the hydrophobic number of the polymer.

Table 6.4. Calculated hydrophobic numbers for tested nonionic polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Hydrophobic number</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>6.19</td>
</tr>
<tr>
<td>RP13E17</td>
<td>7.15</td>
</tr>
<tr>
<td>RP33E44</td>
<td>13.37</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>10.40</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>10.28</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>18.61</td>
</tr>
</tbody>
</table>

Figure 6.10. Fitted Langmuir parameters change as a function of polymer’s hydrophobic number
The hydrophobic number of Guo$^5$ as used above incorporates both the effect of hydrophobicity of the group (pre-factor) and the molar mass (number of hydrophobic -CH$_2$- and PO groups) while it decouples the contribution of the EO (hydrophilic) components. Since the extent of adsorption depends more profoundly on the nature of the anchoring groups (the hydrophobic ones) it is therefore reasonable to expect that the hydrophobic number relates closely with the affinity constant. Interesting findings observed in Figure 6.10 for two samples, E19P29E19 and E76P29E76, is noted now: Both polymers have the same hydrophobic components, and therefore similar affinity constants were obtained from the Langmuir fitting, even thought the maximum adsorption density was quite different. This last observation is explained by the difference in the molecular mass for these two polymers. A maximum affinity achieved when hydrophobic number is over 14, this indicates a polymer with a hydrophobic number more than 14 will absorb onto PET surface, no matter how long its hydrophilic chain is.

**Contact angle-and surface assembly**

The contact angle is very sensitive to the surface energy of the material. Even a trace amount of adsorbed molecules can change the contact angle to a large extent. The change in contact angle for PET surfaces after treatment with nonionic polymeric lubricants is shown in Figure 6.11. Spin coated PET surfaces were immersed in 1% lubricant solution and allowed to equilibrate overnight. The surfaces were then rinsed extensively with milli-Q water and then dried via a nitrogen gas stream directed gently on the surfaces. The water contact angle was then measured.

As observed in Figure 6.11, P10E13, RP13E17 and E19P29E19 did not produce a
significant change in the water contact angle (WCA) compared with that for the bare PET surface. RP33E44 lowered the WCA and the WCA in the case of surface treated with E76P29E76 and E37P56E37 showed an extensive change (from 63 degree to 40 and 52 degrees, respectively). The contact angle change supports the observed fact that a layer of nonionic lubricant molecules forms during adsorption onto surface. As discussed in previous sections, the hydrophobic segments of the polymer are attracted by hydrophobic surface on the surface through hydrophobic forces, letting the hydrophilic segments to extend out, facing the water phase to form a brush-like layer as illustrated in Figure 6.12. Therefore, the polymer which has higher adsorption and long hydrophilic chains would lower the contact angle more significantly.

![Figure 6.11. Contact angle changes for PET surfaces before and after (overnight) treatment with 1% nonionic polymer solutions followed by rinsing with mini-Q water and drying with nitrogen.](image)

The WCA results also confirm that the adsorbed mass of E76P29E76 is lower than that of
E37P56E37. E76P29E76 has longer hydrophilic chains than E37P56E37 and therefore is expected to produce a larger WCA change, as observed.

![Figure 6.12. Proposed illustration for the adsorption of diblock and triblock nonionic polymers. Black segments represent the hydrophilic block of the polymer while the green segments represent the hydrophobic block of the polymer chains.](image)

All the nonionic polymers used in this investigation are amphiphiles with hydrophobic PO segments and hydrophilic EO segments. At the interface of PET and water, water doesn’t favor to hydrophobic PET surface. From a thermodynamics view, when amphiphilic nonionic polymers presence in the system, the hydrophobic segments of polymers are prone to bind to the PET surface while hydrophilic segments are drawn toward the water phase to reduce the surface energy. As a consequence, nonionic polymers reorient their configurations at the interface and self-assemble to form a compact layer. The new equilibrium state is more stable than the initial one therefore the surface is stabilized.

**CONCLUSIONS**

The adsorption of a nonionic lubricant onto a surface is a complex process where many different interactions are present. The adsorption behavior and dynamics were measured by both
QCM and SPR techniques. The formation of an adsorbed layer of nonionic polymer on PET surface was illustrated through Langmuir fitting. In this chapter, the nature of nonionic lubricants, such as molecular weight, HLB value and hydrophobic number was discussed. van de Waals and hydrophobic forces are expected to play an important role in reversible adsorption while the hydrophobic interactions drives the irreversible adsorption. Hydrophobic segments provide the affinity to anchor the lubricant polymers and higher molecular weight can provide maximum adsorption density. Furthermore, the nature of molecule assembly also was investigated through contact angle measurement and thermodynamic principles. The hydrophobic segments in an amphophilic nonionic polymer tend to adsorb onto hydrophobic surface and hydrophilic one tend to buoy in the solvent to reduce the interfacial energy between PET surface (hydrophobic surface) and solvent (water). Therefore, adsorbed nonionic copolymer can stabilize the surface.

To sum up, this chapter discussed the effects of the nature of nonionic polymers in molecular self-assembly. This is highly relevant to boundary lubrication. In next chapters, we will discuss how the surface influences the adsorption process.
REFERENCES


Chapter 7

Adsorption of Nonionic Polymers on Cellulose, Polypropylene, Nylon and PET Surfaces
ABSTRACT

In this chapter the adsorption of nonionic polymers on model surfaces (cellulose, polypropylene, nylon and polyester) were studied with the QCM and SPR techniques. The underlying driving force for adsorption of nonionic lubricants onto these surfaces is discussed and our experimental observations confirm expected behaviors: A greater affinity of the more hydrophobic polymer species with the hydrophobic surfaces and vice versa. Hydrophobic interactions are concluded as being a predominant factor in adsorption of PAGs and Pluronic polymers on textile-relevant surfaces.
INTRODUCTION

Polymer adsorption at the solid/liquid interface plays a crucial role in different technologies involving paintings, coatings, lubricant formulations, ceramics additives, and adhesives \(^1\). Textile fibers include synthetic polymers (polyester fiber, nylon/aramid fiber, olefins, acrylic/modacrylic fibers), as well as generated cellulose, and natural fibers (cotton, wool, and silk fibers), and some specialty fibers. In this investigation, cellulose, polypropylene (PP), nylon and polyester polyethylene terephthalate (PET) were used as representatives of most relevant paper and textile fibers.

Quartz crystal microbalance (QCM) and surface plasmon resonance (SPR), two noninvasive methods that have been used extensively by our group to monitor the adsorption of polymers and surfactants on differences surfaces, were used here to inquire on the adsorption on fiber-relevant surfaces. In most studies typical surfaces used involve metal, (e.g., gold, stainless steel, etc) and silica substrates. In order to employ both QCM and SPR techniques to investigate the adsorption of lubricant molecules on fiber surfaces, the QCM and SPR sensors needed to be modified by the respective ultrathin organic polymer. Therefore, ultrathin films of cellulose, PP, nylon and PET developed by our group (and reported in a previous chapter) were used in the present study. We have discussed already the influence of the type of polymer (hydrophilic-hydrophobic balance) on the adsorption of nonionic polymers. In this chapter, we will focus our attention on the influence of the nature of surface materials, especially their hydrophobicity, on the adsorption behavior of nonionic polymers.
EXPERIMENTAL

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) which was further processed in a Milli-Q® Gradient unit to ensure ultrapure water with resistivity greater than 18MΩ.

The substrates used in this investigation were circular Q-Sense gold sensors (Q-sensor Co, diameter is 12 mm) and square (Rechaint Co, 12 × 12 mm) wafers suitable for QCM and SPR experiments, respectively.

![Chemical structure of polyalkylene glycols (PAGs) and Pluronics](image)

Figure 7.1. Chemical structure of polyalkylene glycols (PAGs) (left) and Pluronics (right).

<table>
<thead>
<tr>
<th>Symbol used in this thesis</th>
<th>Commercial name</th>
<th>MW</th>
<th>n (PO)</th>
<th>m (EO)</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP10E13</td>
<td>UCON 50-HB-400</td>
<td>1,230</td>
<td>10</td>
<td>13</td>
<td>11.92</td>
</tr>
<tr>
<td>RP13E17</td>
<td>UCON 50-HB-660</td>
<td>1,590</td>
<td>13</td>
<td>17</td>
<td>12.0</td>
</tr>
<tr>
<td>RP33E44</td>
<td>UCON 50-HB-5100</td>
<td>3,930</td>
<td>33</td>
<td>44</td>
<td>8.51</td>
</tr>
<tr>
<td>E19P29E19</td>
<td>Pluronic P65</td>
<td>3,400</td>
<td>29</td>
<td>19</td>
<td>21.67</td>
</tr>
<tr>
<td>E76P29E76</td>
<td>Pluronic F68</td>
<td>8,400</td>
<td>29</td>
<td>76</td>
<td>27.97</td>
</tr>
<tr>
<td>E37P56E37</td>
<td>Pluronic P105</td>
<td>6,500</td>
<td>56</td>
<td>37</td>
<td>17.34</td>
</tr>
</tbody>
</table>

* UCON polymers are from Dow Co. and Pluronic polymers are from BASF Co.
* HLB values were calculated by the method described by Guo et al. ²
* R, P and E stand for butyl, r propylene oxide and ethylene oxide groups, respectively.

The nonionic lubricants used in this investigation included two sets of polymers with known structures: polyalkylene glycols (PAGs) from Dow Chemical Co. (Midland, MI), and triblock copolymers based on ethylene oxide and propylene oxide (Pluronics) from BASF.
Corporation (Florham Park, NJ). Generic chemical structures of PAGs and Pluronics are shown in Figure 7.1.

PAGs and Pluronic lubricants with different structural parameters $m$ and $n$ (see Figure 7.1) were used in this study, as listed in Table 7.1. It is worth noting that the supplied samples not only had different monomer composition but also different molecular weights. Nevertheless, these polymers are comparatively pure and better defined than commercial nonionic mixtures commonly used in industry.

**Methods**

**Preparation of model films**

All substrates (gold sensors and wafers) were cleaned with Piranha solution (70% H$_2$SO$_4$+30% H$_2$O$_2$ (30%)) for one hour and then subjected to Ultra-violet Ozone (UVO) radiation for 10 minutes immediately before spin-coating with PET solutions.

Fiber precursor materials were dissolved in diluted solution and then employed in the spin coater to cast a uniform ultrathin film onto the QCM sensors. Details on the development of cellulose and synthetic films can be found in a previous chapter.

**QCM-D and contact angle measurements**

A QCM-E4 (Q-sense Inc.) was used in this investigation to measure the adsorption of nonionic lubricants on model films. The principle of operation was described in detail in Chapters 1 and 6. Likewise, water contact angle (WCA) was described in Chapter 1 and 6.
RESULTS AND DISCUSSION

Adsorption experiments

In this investigation, nonionic polymers with five different concentrations (from 0.0001% to 1%) in aqueous media were used in the adsorption experiments with cellulose, polypropylene (PP), nylon, and polyester polyethylene terephthalate (PET). For cellulose surfaces, there was no noticeable change in either frequency or dissipation. Therefore, it was concluded that no adsorption of the studied nonionic polymers occurred on this hydrophilic surface. This was also confirmed by SPR experiments. For the rest of the model surfaces, the adsorption mass before (total adsorption) and after rinsing (irreversible adsorption) were plotted against concentration, as shown in Figures 7.2, 7.3 and 7.4, respectively for PP, nylon and PET surfaces.

An apparent trend in the Sauerbrey adsorbed mass can be observed, and was also noted in previous chapters, i.e., those lubricants with lower molecular weight adsorbed to a lesser extent compared to the polymers with higher molecular weight. The total adsorption was observed to increase with concentration and no apparent saturation was reached. However, for the irreversible adsorption a plateau with concentration was observed for nylon and PET surfaces.

In order to compare the adsorption data on solid surfaces with the maximum adsorbed mass at air/water which had been addressed in Chapter 4, adsorbed mass of ng/cm² in Figure 7.2 to Figure 7.4 was converted into the unit of mol/m² as presented in Figure 7.5 to 7.7 accordingly. The maximum adsorbed mass at air/water was in the range of $8-15 \times 10^{-7}$ mol/m². The same observation as in Chapter in 6 is the adsorbed mass on each film before rinsing at high
concentration was larger than the maximum adsorption mass at air/water interface. This indicates that multilayers are formed before rinsing for all the solid surfaces. But after rinsing, the adsorbed mass for each nonionic polymer exhibits different:

The values of adsorption mass after rinsing on PET and nylon surfaces were close but slightly less than the maximum adsorption mass obtained from air/water interface. It can be concluded that there is a monolayer strongly bound onto the surface. The reason why the values of maximum adsorption mass on PET and nylon are lower than those obtained from air/water interface may attribute to the hydrophobicity of PET and nylon is not as strong as that of air, resulting in a not so compact self-assembly layer.

For small molecules, RP10E13 and RP13E17, the values of adsorption mass after rinsing on PP surface are larger than the maximum adsorption mass obtained from air/water interface. It can be concluded that multilayers are formed at the interface of PP and water. This maybe attribute to the hydrophobicity of PP surface and its long-ranged hydrophobic forces. This will be address in the next section. But for the rest nonionic polymers which with large molecular size, their maximum adsorption mass on PP surface is very close to the value obtained from air/water interface. This means a compact self-assembly nonionic polymer layer is formed at the interface between PP surface and water for large nonionic polymers.
Figure 7.2. Adsorption isotherms for nonionic polymers adsorbed on polypropylene surfaces. The polymer solution flow rate was kept constant at 0.1 ml/min.

Figure 7.3. Adsorption isotherms for nonionic polymers adsorbed on nylon surfaces. The polymer solution flow rate was kept constant at 0.1 ml/min.
Figure 7.4. Adsorption isotherms for nonionic polymers adsorbed on PET surfaces. The polymer solution flow rate was kept constant at 0.1 ml/min.

Figure 7.5. Adsorption isotherms for nonionic polymers adsorbed on polypropylene surfaces expressed by mol/m². The data converted from Figure 7.2.
Effect of the nature of surfaces on polymer adsorption

In order to reveal the underlying adsorption phenomena, we fitted the QCM experimental data after rinsing (irreversible adsorption) with the Langmuir isotherms. It was demonstrated that the adsorbed mass could be described satisfactorily (correlation values of R-squared are high
in Table 7.2) with the Langmuir equation. The adsorption also was conducted on cellulose surfaces; however, no detectable signal was observed. The Langmuir adsorption isotherm assumes an adsorbed layer with a maximum number of equivalent binding sites, each of which can be occupied by one molecule. The adsorbed mass $\Gamma$ is a function of the polymer concentration, $C$, maximum adsorption density, $Q_0$ and affinity between adsorbate and the surface, $b$ as in Equation 7.2:

$$\Gamma(X, C_i) = \frac{Q_0 b C_i}{1 + b C_i}$$  \hspace{1cm} (Equation 7.2)

The fitted Langmuir parameters for all adsorption isotherms (irreversible adsorption) are listed in Table 7.2.
Table 7.2. Langmuir parameters for (irreversible) adsorption isotherms of nonionic polymers on PP, nylon and PET surfaces (no adsorption was observed on cellulose surfaces).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Lubricant</th>
<th>bQ0</th>
<th>b</th>
<th>Q0</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
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</tr>
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<tr>
<td></td>
<td>RP13E17</td>
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</tr>
<tr>
<td></td>
<td>RP33E44</td>
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<td>221.37</td>
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</tr>
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<td>E19P29E19</td>
<td>11118.58</td>
<td>100.00</td>
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</tr>
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In Figure 7.8, the maximum adsorption density, \( Q_0 \) and affinity between polymer and surface, \( b \) are displayed for the polymers for the three model surfaces. The three surfaces showed similar trends with respect to the maximum adsorption density: the maximum adsorption density increased with molecular weight of the lubricants. This was also discussed in detail in Chapter 6. Molecules with higher molecular weight carrying longer buoy chains favor the formation of denser adsorbed layers compared with the resultant layers from polymers carrying short buoy chains. By comparing the trends for all three surfaces, adsorption to the most hydrophobic PP surface was more obvious than for the other less hydrophobic surfaces. This implies that the hydrophobicity of the surfaces influences to a large extent the maximum adsorption density.
Regarding the binding or adsorption affinity between lubricants and surfaces, a clear trend was found: the more hydrophobic surfaces showed a higher affinity with the lubricants. The PP surface, which has a water contact angle of 103° (see Table 3.1 in Chapter 3), showed the highest affinity with most of the polymers tested, except for E76P29E76. Nylon and PET surfaces, which had similar contact angles (around 60-65°) showed a lower affinity with the polymers, as compared to the PP surface. Hydrophilic cellulose surface, which had the lowest contact angle, around 30°, showed the lowest affinity (there was in fact no detectable adsorption).

In previous chapter 6 the hydrophobic interactions were considered as a major driving mechanism for irreversible adsorption. Hydrophobic effects are indeed important when we deal with interaction between two surfaces within a narrow distance 4-6. This force might apply to the adsorption of the tested nonionic polymers. According to results reported by Yoon and Ravishankar 7-9 hydrophobic forces generally, depend on the hydrophobicity of the surfaces involved. The magnitude of the decay lengths (hydrophobic force vs. separation distance between surfaces), of these forces allows for a classification in terms of short-, medium- or long-ranges. Yoon and Ravishankar found that decay length depended on the hydrophobicity of surface, with a transition regime at \( \theta_b \) (WCA) = 90°, below of which the hydrophobic forces were short-ranged and above of which they become long-ranged.
Figure 7.8. (a) Maximum adsorption density for different polymer types adsorbing on model surfaces. (b) Affinity constant for different polymers and surfaces. The charts are plotted with increased order of polymer molecular weight and hydrophobic number, respectively. Note that the molecular weight and hydrophobic numbers are indicated in the respective charts.
Even thought the system they studied consisted on measuring inter-surface forces, our results imply that this theory could also hold to the interaction between a surface and a polymer. PP surface, of a contact angle around 103° may involve long-ranged hydrophobic forces; while nylon and PET films, with a contact angle around 60-65°, may exhibit short-ranged hydrophobic forces. The hydrophilic cellulose surface, on the other hand, is expected not to involve any noticeable hydrophobic forces (contact angle of cellulose is 30°). These conclusions are embodied in the affinity chart that shows PP with the highest affinity constants followed by nylon and PET. This theory can also give us an explain why nonionic polymers with small molecule size can form multilayer on PP surface but nonionic polymers with small molecule size form monolayer on PP surface and all nonionic polymers form monolayer on intermediate hydrophobic nylon and PET surfaces.

**Contact angle- and polymer assembly**

The water contact angle (WCA) was measured for different model surfaces after treatment with lubricant samples (with a concentration of 1% in aqueous solution) in order to provide further confirmation regarding the adsorption of the tested lubricants and to uncover how lubricant molecules self assemble at the interface. Water contact angle was measured for different model surfaces after treatment with 1% concentration polymer solutions.

PP, nylon and PET surfaces were immersed in 1% polymeric lubricant solution overnight and then rinsed with milli-Q water followed by gentle drying with a nitrogen jet. The measured WCA for PP, nylon and PET surfaces after treatment with the polymeric lubricants is shown in Figure 7.9. In all cases it is observed that the contact angle is reduced after treatment with the polymeric solution. This is explained by the fact that the hydrophobic surfaces are coated with a very thin lubricant layer where the molecules are oriented in such a way that their hydrophobic chains are close to the surface whereas the hydrophilic parts are extend out into the bulk solution.
As a consequence the surface energy is reduced and the surface is stabilized.

![Figure 7.9. Water contact angle for PP, nylon and PET surfaces before (CTRL) and after treatment with 1% lubricant solutions (adsorption allowed overnight at 25 °C).](image-url)

A well-defined adsorbed polymer layer might be formed so that it could provide boundary lubrication and also offer some protection against friction and wear. We note that the contact angle experiment agreed with the adsorption experiment very well. It is also apparent that contact angles strongly depend on the original contact angles for the bare surfaces. The adsorbed layer is soft and contains a lot of water molecules (see Chapter 6). The adsorbed layer may change their monolayer configuration and form some other patterns when it is dried to the high surface tension of water. Therefore, when the contact angle is measured, it does not test the contact angle with well-defined nonionic polymer layer, but the complex of substrate and polymer layer.
CONCLUSIONS

The adsorption of nonionic polymeric lubricants onto fiber-relevant surfaces can be described as a complex process. In this chapter the nature of the substrate, more specifically, its surface hydrophobicity was studied in terms of the adsorption behavior of non ionic polymers. From the obtained results it can be concluded that hydrophobic forces play an important role in irreversible adsorption:

a) The hydrophobic segments in the adsorbing molecule and the surface energy of the substrate are the most important factors to determine the extent and strength of adsorption. Longer hydrophobic segment in a nonionic lubricant molecule and higher hydrophobicity of the surface leads to higher affinities.

b) The molecular weight of the nonionic polymers is crucial in defining the maximum adsorbed amount. Higher molecular weight (longer polymer chains) is more likely to bind on the surface.
REFERENCES


Chapter 8

Adsorption of Silicone-based Surfactants
ABSTRACT

Aqueous silicone-based surfactants are widely used in the processing of synthetic fibers in textile industries. Silicone surfactants enhance a number of functional and processing properties while keeping cost-effectiveness. In this chapter we discuss the interactions between silicone-based surfactants and textile-relevant surfaces. This information will ultimately help to understand lubrication phenomena in fiber processing. Our results showed that the more hydrophobic polypropylene surfaces had higher affinity with silicone-based lubricants than polyethylene surfaces. This is explained by the fact that the hydrophobic groups in the surfactant molecule were interact more effectively with the PP surfaces via hydrophobic forces. Also, well-organized silicone lubricant films were observed at the interface. These adsorbed layers are expected to provide lubricity in textile materials when subject to shear forces and offer protection to wear and abrasion.
INTRODUCTION

Conventional ionic and nonionic surfactants, which are extensively used in many industrial applications, typically contain hydrocarbon groups in the hydrophobic chain. A class of surfactants that has received increasing attention is the silicone-based surfactants which contain polydimethylsiloxane groups in the hydrophobic chain.

In recent years, silicone-based surfactants have been extensively investigated regarding their applications\(^1\)\(^-\)\(^9\), properties of the solution and interfacial and wetting behaviors\(^4\),\(^7\),\(^8\),\(^10\)-\(^27\). One of their outstanding features is their ability to reduce the surface tension of water down to values as low as 20-25 mN/m. By comparison, typical organic surfactants reduce the aqueous solution surface tension down to the 30-45 mN/m range. An additional characteristic of silicone surfactants is their superior wetting abilities\(^2\). For example, they are effective in spreading and wetting such low energy surfaces as polyethylene therefore they are used as additive to help insecticide to spread on leaves. Interestingly, even fluorocarbon surfactants which have the lowest surface energies known, do not wet polyethylene surface as efficiently as silicone-based surfactants. Due the unique properties of silicone-based surfactants (including the named low surface tension, their activity in both aqueous and non-aqueous media, and their little skin irritation effects\(^28\)), silicone-based surfactants are a commercially important class of amphiphiles that find application in numerous processes, including the manufacture of polyurethane foams, coatings, household and personal care products, foam control and wetting additives, etc.\(^2\). Silicone-based lubricants are important components in many formulations used in textile processing; it is used in thread lubrication, surface treatment and others. Compared to organic
materials, silicon-based textile lubricants perform better, last longer and most importantly, they are also extremely cost-effective.

However, studies on the adsorption behavior of silicone surfactants on solid surfaces, especially those relevant to textile processing, are very limited \(^{28,29}\). Silicone-based surfactants can adsorb onto hydrophobic surfaces by self-assembly through their hydrophobic moieties. The hydrodynamic thickness of the adsorbed layer was found to increase with chain length of the hydrophilic moiety \(^{28,29}\). One interesting and also important property found for silicone-based surfactants was the fact that the adsorbed layer was more stable against alcohols and other organic solvents. That means that they can be applied in aqueous as well as in nonaqueous media. This is not a common property in surfactant chemistries since in most conditions addition of short-chained alcohols usually results in the decrease of the aggregation number and even the disappearance of micelles in solution, with a simultaneous loss in surface aggregation \(^{28,29}\). In their studies with silicon surfactants, Wang and coworkers found that silicone surfactant could provide steric repulsion up to 80% ethanol in solution, while the Pluronic-type of surfactants lost their surface activity at approximately 40% ethanol.

In the present study, we addressed the adsorption behavior of a commercial silicone surfactant and investigated the influence on adsorption of hydrophobicity of the substrates. Our measurements were performed mainly with the help of a quartz crystal microbalance (QCM). Our main objective was to reveal the molecular assembly mechanism of silicone surfactants, and their function in boundary lubrication in textile processing.
In order to facilitate the study of adsorption phenomena on surfaces relevant to textile processing, model thin films of typical polymers were deposited on QCM-D gold sensors. Films of polypropylene (PP) and polyethylene (PE) were used to investigate the interactions with the commercial silicone-based surfactant.

EXPERIMENTAL

Materials

All experiments were performed with deionized water from an ion-exchange system (Pureflow, Inc.) followed by a Milli-Q® Gradient unit (resistivity >18MΩ). Substrates used in this investigation consisted of gold QCM sensors (Q-sense, Sweden).

The studied silicone-based lubricant was supplied by Goulston Inc. (Monroe, NC) under trade name LN336-100I. It was a commercial product with main component a surface-active block copolymer of polyalkylene oxide-modified polydimethylsiloxane. Silicone lubricant sample was diluted with milli-Q water for surface tension measurement and adsorption measurement.

Methods

Gold QCM sensors were cleaned with solution consisting of 70 % H₂SO₄ and 30 % H₂O₂ (30%) for one hour without heat and then subject to UV-ozone treatment for 10 minutes, immediately before spin-coating. Clean sensors were modified by a uniform and ultrathin (20-50
nm) PP or PE film through spin coating technique. Procedures of model film preparation and film characterization can be found in Chapter 3.

**Adsorption experiments with the QCM-D technique**

A QCM Q-300 model (Q-sense, Inc.) was used in our experiments. Principles of QCM were addressed in detail in Chapter 1. QCM was run in a batch mode. Polymer-coated sensors were mounted in the QCM chamber and silicone surfactant solution was passed through with a known given concentration. The silicone surfactant was diluted with milli-Q water and no salt was added.

The typical procedure in the adsorption experiments consisted of the following sequential steps: (1) first milli-Q water was injected through the QCM system to obtain a baseline; (2) when a constant stable baseline was obtained, surfactant solution with a given concentration (ranging from 0.0001 to 1 (w/v%)) was passed through; (3) the QCM frequency was then monitored until adsorption equilibrium was reached, and (4) When a stable equilibrium was obtained, large amounts of milli-Q water were used to rinse the system in order to remove loosely bound surfactants and also excess surfactant in the bulk solution. As a consequence, a new equilibrium frequency was reached. Typical adsorption curves monitored by QCM are shown in Figure 8.2.

Usually, frequency and dissipation values for the third and seventh overtones were recorded and from these data, the dynamics of adsorption of polymers were characterized in detail. The film viscosity, elasticity and thickness were extracted from the experimental data by fitting with a Voigt model. However, since the adsorbed mass was typically very small and little
difference among the overtones were found, our calculations were simplified with the use of third overtone frequency and the Sauerbrey Equation. The temperature was found to be very critical in the adsorption experiments since it affected the density of fluid in the QCM module. Temperatures were held constant at \(25 \pm 0.02\, ^\circ\text{C}\) in all of our experiments.

**Surface tension measurement**

Surface tension was determined by a Fisher Surface Tensiomat®, model 21 with a Du Noüy Ring. In the Du Noüy method, a platinum-iridium ring of precisely known dimensions is suspended from a counter-balanced lever arm. The arm is held horizontal by torsion applied to a taut stainless steel wire, to which it is clamped. Increasing the torsion in the wire raises the arm and the ring, which carries with it a film of the liquid in which it is immersed. The maximum pull force exerted on the ring by the surface was measured and translated to units of surface tension, mN/m.

**Contact angle measurement**

The hydrophobicities of PP and PE surfaces were characterized by their water contact angles. The procedures of contact angle measurement were addressed in Chapter 6. The results indicated that contact angles for PP and PE were \(102.9 \pm 1.7^\circ\), and \(95.1 \pm 0.7^\circ\), respectively.

**Friction measured by LFM**

A Scanning Probe Microscopy (NTEGRA Prima, NT-MDT) was employed to measure friction forces. The test was conducted on a polyethylene modified silicone wafer. Scans were performed in air (air-test), and in the presence of silicone lubricant solution with a concentration of 1% by weight. In all the tests, the same tapping mode probe (MikroMasch AFM probe) with a
force constant of 0.35N/m, and a resonance frequency of 145Hz was used. All of the tests were performed with a scanning velocity of 1Hz and a scanning size of 1 micron.

RESULTS AND DISCUSSION

The silicone lubricant used in this study was a surface-active block copolymer of polyalkylene oxide-modified polydimethylsiloxane. Polydimethylsiloxanes are very strong nonpolar molecules which produces an important lowering in surface tension. In fact, the surface tension of the silicone lubricant was measured for the range of concentration as shown in Figure 8.1. It can be observed that the surface tension drops sharply from ca. 72 mN/m to ca. 35 mN/m as the lubricant concentration increases from $10^{-5}$ to $5 \times 10^{-3}$ % (w/v). The surface tension then decreased slowly with concentration, down to 32 mN/m at 1% maximum concentration. This value is not as low as stated in literature due to other components present in the mixture. Critical micelle concentration determined by this method was around $4 \times 10^{-3}$ % (w/v). This figure is indicative of a surface active molecule with strong polar and nonpolar groups. Similarly to the case of the air/liquid interface, it is expected that in the presence of a low energy solid surface the nonpolar groups of the dissolved molecules are attracted to the surface by means of hydrophobic forces. It is expected that the surfactant molecules arrange themselves by self assembly in the form of a well-defined lubricant layer that is effective in reducing wear and friction.
Adsorption of silicone surfactant on polymeric surfaces

Adsorption from solution was conducted with the QCM instrument, as explained in the methods section. Typical adsorption curves are shown in Figure 8.2 for PP and PE surfaces exposed to 0.1% (w/v) lubricant solution. The change of QCM frequency with time (solid line), which is related to the adsorbed mass, is shown on the left axis. While the change in the dissipation factor (dashed line), which is related to the viscoelasticity of the adsorbed thin film, is shown on the right axis. Before experiments, water was injected continuously in the QCM’s sampling loop until a stable baseline was obtained. Silicone lubricant solution was then injected in the sampling loop. In all cases fluid injection was performed at low shear rates, with typical volumetric flow rate of only 0.1 ml/min. As a result of silicone lubricant injection, sharp changes in frequency and dissipation were observed, as illustrated in Figure 8.2. These changes are
consistent with lubricant adsorption on the sensor’s surface. Around ten minutes after injection, the adsorption process reached equilibrium as judged by stable frequency and dissipation profiles. Data acquisition under these stable conditions was continued for more than 1h to ensure that adsorption equilibrium was indeed achieved. This equilibrium condition was then challenged by injection of pure solvent (water), as a rinsing step. As a result of this rinsing step, sharp changes in frequency and dissipation were observed. The increase in frequency indicated that loosely-bound lubricant molecules were removed and therefore a thinner, less dissipative adsorbed layer remained on the surface.

After 30-40 minutes from rinsing a second equilibrium state was attained with a distinctive higher frequency and lower dissipation compared to the equilibrium values measured in the first adsorption stage. The main difference between the two equilibrium conditions explained so far is that in the first stage equilibrium is established between the adsorbed layer and a solution containing lubricant molecules while in the second case equilibrium is established with lubricant-free solvent. Based on the difference in lubricant’s chemical potential the adsorbed mass can be classified into two categories, namely, reversible and irreversible adsorbed mass, for the initial and the final equilibrium stages, respectively.

We now turn our focus to the difference between the PP and PE substrates. Under the same lubricant concentration condition, the frequency change for the PP film was larger than that for PE film, both in regard to the total (reversible) adsorption (-22.5 Hz vs -18.4 Hz for PP and PE, respectively) and irreversible adsorption (-10.2 Hz vs -8.6 Hz for PP and PE, respectively). This indicates that the affinity of silicone lubricant with PP is much higher that that with PE.
Since PP is more hydrophilic than PE there is reason to believe that the predominant driving force for adsorption of silicone lubricant onto the hydrophobic surfaces is the hydrophobic effect.

In both cases (PP and PE) the irreversible adsorption was roughly half of the total (reversible) adsorption. On the other hand, the change in energy dissipation for the adsorbed silicone on PP indicates a “softer”, more dissipative layer than that on the PE substrate. This observation is rationalized in terms of the adsorbed mass and adsorbed layer thickness which is higher in the case of the PP substrate. For the irreversibly adsorbed layer (after rinsing conditions), the absolute frequency is very low and no significant difference between the behavior of lubricants adsorbed on PP and PE was observed.

Figure 8.2. Adsorption curves of silicone lubricant (0.1 % aqueous solution concentration) on polypropylene (black) and polyethylene (red) surfaces. The solid lines represent frequency change, while the dashed lines represent the change in dissipation factor.

**Adsorption isotherms of the silicone lubricant**

Five different silicone concentrations (in the range 0.001% - 10 %) were used in adsorption experiments. The adsorbed mass before and after rinsing was plotted as a function of
lubricant concentration, as seen in Figure 8.3. In this figure the change in frequency registered in
the QCM was converted to effective adsorbed mass by using the Sauerbrey equation. The
changes in the reversible (total) adsorption were seen to depend linearly with the lubricant bulk
concentration. It is worth noting that the QCM not only detects the adsorbed mass, but also the
coupled water or any additional mass that might be loosely attached to the adsorbed layer. In the
case of the irreversibly adsorbed mass it is clearly seen that a saturation or plateau state is
reached with increased concentration. It can be argued that this state corresponds to an adsorbed
monolayer which could be model by a Langmuir-type isotherm. The surface density $\Gamma$ of
adsorbed molecules can be expressed as a function of solute concentration in the aqueous phase,
c, with the Langmuir equation:

$$\Gamma(X, C_i) = \frac{Q_i b C_i}{1 + b C_i}$$  \hspace{1cm} (Equation 8-1)

Langmuir isotherms for irreversible adsorbed mass on PP and PE surfaces are shown in
Figure 8.3. When compared to the adsorption isotherm on PE, the adsorption on PP can be
described as occurring with a higher affinity and saturation adsorption. In other words, the
silicone lubricant interacts more strongly with the PP than with the PE surfaces.
Hydrophobic forces in lubricant adsorption

Since it is expected that no reaction occurs between the (PE or PP) surface and the (nonionic) silicone lubricant the observed adsorption is predicted to be physical in nature. Therefore, attraction forces are proposed to be of the van de Waals type with also an important contribution from hydrophobic effects.

The nature of the hydrophobic forces is still awaiting detailed elucidation from the surface science community. Such forces were described by Israelachvili and Pashley in their experiments on the interaction forces between two cylindrical mica sheets at separation.
distances less than 5 nm in $10^{-5}$ M cetyltrimethylammonium bromide (CTAB) solutions. At such small separation distances, it was found that the experimentally measured forces were more attractive than predicted by classic DLVO theory. This extra attractive force, termed by them as hydrophobic force (Fh), was represented by a single exponential function as follows:

$$F_h / R = C_0 \exp(-H / D_0)$$  \hspace{1cm} (Equation 8.2)

where R is the mean radius of curvature of the interacting bodies, H the closest separation between the two curved surfaces, C0 is a pre-exponential factor, and D0 is known as the decay length.

Generally, depending on the magnitude of the decay lengths, hydrophobic forces may be classified into short-, medium- or long- range forces. When the decay length lays in the range 1-2 nm, it is referred to as short-range hydrophobic force. If it is in the range 2-10 nm, it is referred to as medium-range; while for distances in excess of 10 nm the force is referred to as long-range force. Yoon and Ravishankar 33-35 also found that the decay length depended on the hydrophobicity of the surface: below a “transition” regime for surfaces with WCA (water contact angle) $\theta_a \approx 90^\circ$, the hydrophobic forces were short-ranged and above this contact angle they were described as long-ranged.

Even though, their findings are based on the inter-surface interactions, our previous research on adsorption of nonionic polymer on hydrophobic surfaces also indicated that it also applied to the interaction between surface and polymer. The water contact angle of the studied PP and PE films were 103° and 95°, respectively. The differences in WCA can be explained by the presence of -CH2- groups in PE while PP also contains lower surface energy -CH3 groups.
All in all, it is hypothesized that the larger contribution to the irreversible adsorption is from the hydrophobic forces while van de Waals interactions are predominant in the reversible adsorption.

Unfortunately, exact information regarding the nature and composition of the commercial silicone surfactant we used is not available. However, in textile processing it is known that silicone nonpolar group provides the molecules with better performance\textsuperscript{36-39}, compared with typical hydrocarbon surfactants. This group also leads to superior affinity to hydrophobic surfaces, typical in some textile polymers.

Physisorption as a dominant effect in our experimental observations is very relevant to textile processing. It is envisioned that typical lubricant molecules or finishes are not intended to remain adsorbed on the surface of the fibers. A strong interaction would lead to lubricant layers that would interfere with successive processes, including surface finishing and dyeing. While the evidence presented here indicates that a very thin layer remains irreversibly adsorbed on the surface of PE and PP other factors such as shear stress and the application of rinsing steps (with solutions of different composition and ionic strength) could lead to important variations in the surface chemistry of the treated surfaces. Such treatments should be a subject of future efforts.

**Friction measured by LFM**

When a tip in lateral force microscopy is sliding on a surface, lateral force profiles can be measured both in air (no lubricant applied) and in solution. Figure 8.4 displays a line scan across a polyethylene surface tested both in air and in the commercial silicone-based lubricant solution. A static friction force was seen in Figure 8.4. It was known that when a tip starts to move forward on a sample’s surface, there is a static friction force on the tip. The static friction force
was evident in the force profile imaged in air during the forward and the backward scanning. However, when the tip was sliding on a surface coated with the lubricant solution, the high force corresponding to the static friction disappeared and it was replaced by a regularly oscillating force curve. As expected, the amplitude of force curve in the solution was much smaller than that in air. That meant friction was reduced a large quantity by a boundary lubricant film of silicone molecules.

![Graph showing friction of PE film measured by LFM in air and after treatment of LN336-100I. Data courtesy of project member Yan (Vivian) Li, Cornell University.](image)

Lubrication molecules adsorb on a surface with a well-defined configuration to form a protective layer. The chemistry of the surface is changed. As we addressed in Chapter 1, the thickness or the adsorption mass and structure of the adsorbed layer are crucial to the performance of lubrication. In our case, it is expected that this silicone lubricant has better lubrication performance on PP material than on PE material.
CONCLUSIONS

Silicone surfactants are attracting attention in application such as textile processing due to their excellent surface activity, performance and low cost. In this study, the surface activity and adsorption behavior on two hydrophobic surfaces of a commercial silicone surfactant was investigated by using the QCM-D technique. Through this study, the following conclusions can be drawn: (1) Silicone surfactants are of superior surface activity, their surface tension can reach values of ca. 30 mN/m. (2) The hydrophobic moiety of the silicone surfactant interacts with the hydrophobic surface through hydrophobic forces, in such a way that high affinity isotherms are observed. (3) The adsorption affinity was found to be related to the hydrophobicity of the surface, the higher hydrophobicity of a surface, the higher the affinity with the silicone surfactants. (4) The self assembled surfactant layer is expected to reduce the friction and prevent wear to some extend in the condition of boundary lubrication.
REFERENCES


Chapter 9

Lubrication Studied by Lateral Force Microscopy and Molecular Dynamic Simulation

Yan Vivian Li and Hongyi Liu, from Cornell and NC State, respectively are acknowledged for their contribution in this chapter.
ABSTRACT

In this chapter, lateral force microscopy (LFM) and Molecular Dynamic Simulation (MDS) were employed to study boundary lubrication produced by the adsorption of the polymers discussed in previous chapters. Friction coefficient after treatment of nonionic polymers was measured on polypropylene (PP), polyethylene (PE) and cellulose surfaces. Results indicated that: (1) The friction coefficient is reduced after application of nonionic polymers on PP and PE surfaces, (2) The friction coefficients is reduced with increased normal force, but after a threshold force, it increases sharply due close physical contact. MDS results also confirmed that nonionic lubricants have a strong affinity to hydrophobic PP and PE surfaces, while little affinity was observed in the case of cellulose surface. These conclusions are in agreement with our adsorption data and confirm our hypotheses. Finally, lubricant molecules between hydrophobic surfaces under confinement were studied by using Molecular Dynamic Simulation (MDS). MDS results illustrated how the hydrophobic moieties in lubricant chains approach to the surface to eventually be adsorbed. Overall, LFM and MDS revealed the details about lubricant molecules behavior and self-assembly on the surface to form a protective films and change friction.
INTRODUCTION

Tribology in fiber processing cover issues related to friction during processing of fibers, conversion of fibers and wovens and nonwovens into products, and handling of paper and textile products. In all these cases boundary lubrication phenomena play important roles, even though usually they are usually overlooked. Lubrication is most relevant in the boundary regime when the amount of finish applied is low (~0.1 %) and, in most applications, the speed involved is small. In boundary lubrication, the finish, usually only several molecular layers in thickness, covers the fiber surface \textsuperscript{1,2}. Thus the interaction between two sliding surfaces is governed at least partially by the physicochemical properties of this adsorbed lubricant layer. Therefore, the interaction involved during a friction process occurs at the molecular level. Accordingly, in order to fully understand the boundary lubrication phenomena and determine the role of a finish composition, the interaction between finish and fiber surface must be explored at such a level.

In previous chapters, the relation between affinity of lubricants and surfaces and their chemical structure (mainly controlled by their hydrophobic length) was explored by quartz crystal microbalance (QCM) and surface plasmon resonance (SPR). In this chapter, we will discuss further the relation between lubrication performance and the involved chemical structures (surface and adsorbing species). Techniques used included lateral force microscopy (LFM), while the self-assembly of the layer of lubricants formed onto the surfaces were studied by molecular dynamic simulation (MDS).

Lateral force microscopy (LFM) makes it possible to explore friction and wear at the molecular level and to examine the effectiveness of a finishing treatment in modifying specific
behaviors on solid surfaces. LFM is based on scanning probe microscopy, and is one of the few experimental methods capable of assessing forces at the single contact or atomic level. LFM has been used extensively to study molecular lubrication phenomena on hard surfaces, such as mica, silica, and graphite\textsuperscript{3-5}. Studies on polymer surfaces, relevant to fiber applications, however, have been limited, primarily due to the fact that polymer surfaces deform easily, which adds complexity to the experiment and to the interpretation of the data.

In the boundary regime, it is very difficult to determine the boundary conditions and fluid properties by experimental measurement in the case of ultra-thin films. Furthermore, it is expected that shear rates can be very high, beyond the values that can be accessed in laboratories. Molecular dynamics simulation (MDS), however, have proved to be an indirect but efficient method to investigate these complex systems at high shear rates and under extreme conditions\textsuperscript{6,7}. MDS gained rapid progress in recent years due to the advances in computer hardware and algorithms developed to study polymers. MDS techniques include \textit{ab initio} atomic level simulation, mesoscopic treatment of polymers and polymer mixtures and macroscopic simulation. In our case, MDS was employed to explore the interaction energy between lubricant molecules and specific surfaces, and to study properties of lubricant films and their change under confinement and shear.

The experimental efforts in this part of our project were conducted by team members Yan Vivian Li and Hongyi Liu, from Cornell and NC State Universities. Some of their results are succinctly summarized here and put into the perspective of results of previous chapters.
EXPERIMENTAL

Adsorption measured by quartz crystal microbalance (QCM)

Adsorption experiments were conducted with the help of the quartz crystal microbalance (QCM), as presented in Chapters 6 and 7. Here we attempt to relate these results with LFM and MDS as follows.

Friction measured by Lateral Force Microscopy (LFM)

The principles of LFM were addressed in Chapter 1. In this investigation, a Scanning Probe Microscopy (NTegra Prima, NT-MDT) with lateral force was employed to characterize the performance of lubricant on three polymeric substrates (PP, PE and cellulose). All of the tests were performed with a scanning velocity of 1Hz and a scanning size of 1 micron. Both topography and phase images of the samples were collected simultaneously in the tapping mode AFM. In the case of topographic images, all images were 256×256 pixels size.

Molecular Dynamic Simulation

The program of Materials Studio® was used as a platform and the Amphous Cell model was employed to simulate the lubricants behavior in confined and shear conditions. General principles of these methodologies were addressed in Chapter 1. Furthermore, COMPASS 8 force-field was employed. Here the bonded terms of the potential energy function are quadratic terms that describe the bond length and valence angles. Also a three-term Fourier transform for torsion angles is used. For the non-bonded contributions, the van der Waals interactions were
calculated using a 9-12 Lennard-Jones function. Electrostatic interactions were accounted for through a classical Coulomb potential; the charge equilibration method was used to calculate charges for each atom. The cut-in and cutoff distances were fixed at 10 and 11 Å, respectively. The minimum image convention was imposed in order not to duplicate nonbonded calculations.

The minimization procedure used the conjugate gradient scheme with the convergence criterion of the root-mean-square of the atomic derivatives of 0.05 kcal mol\(^{-1}\)Å\(^{-1}\). Molecular dynamic calculations were based on the canonical NVT (constant Number of particles, Volume, and Temperature) ensemble. The equations of motion were solved using the velocity Verlet algorithm, with a time step of 1 fs.

**Protocol construction**

A sandwich-like layer with top and bottom solid walls (PP, PE, Cellulose) and lubricant liquid layer in the middle were set up.

The protocol worked by imposing a user-defined velocity of 5m/s on the walls. The two walls were sheared with an equal but opposite velocity in the x direction and they were held in a fixed position in the z direction relative to one another by harmonic springs.
RESULTS AND DISCUSSION

Friction Coefficients measured by LFM

Friction coefficients of four nonionic polymers, RP10E13, RP13E17, E26P40E26 and E133P50E133 on cellulose, PP and PE surfaces were measured by LFM and are reported in Figure 9.2 (a, b, c, respectively). The friction coefficients in air (dry state) and in water are also included in these figures. The friction coefficients in air always were the highest, since there was...
no interfacial fluid or lubricant present. When the surfaces were immersed in water, the friction coefficients were reduced sharply. This confirmed the lubricant effect of water. With addition of the nonionic polymers, the friction coefficients were reduced significantly, compared with water, in the case of PP and PE. Interestingly, in the case of cellulose surfaces such effect was not observed. This last fact can be explained by our adsorption data, discussed in Chapters 6 to 8. Here the underlying effect is the fact that the interfacial energy minimized by self assembly of amphiphilic polymers at interface. Since PP and PE are hydrophobic while cellulose is hydrophilic. Therefore, the hydrophobic segments of the amphiphilic polymers tend to bind to PP and PE surface while the hydrophilic segment(s) buoy in water. Likewise, the hydrophilic segment(s) in the amphiphilic polymer tend to bind to cellulose surface and while the hydrophobic segment(s) buoy in water. Since the process occurs in aqueous medium, this kind of hydrophilic-hydrophilic interaction is weak and shear sensitive (for example by rinsing with water). This agrees with the adsorption data. Little adsorption was observed after applying shear (rinsing with water), as shown in previous chapters i.e., no (irreversible) adsorption of nonionic lubricants was observed on cellulose surfaces.

Another trend observed is that, for all polymers under low normal forces the coefficient of friction decrease with the normal force. However, at high normal forces, the friction coefficients increase with the normal force. The threshold for this transition was around 30-40 nN. This can be explained by the fact that lubricant molecules self assemble onto the surface and form a layer under shear and normal forces. At higher shear rates or normal forces, the polymer aligns better and forms a compact structure with very low coefficient of friction. However, at
even higher pressures, the polymer film might be destroyed (molecules can be driven out from the interface) and the tip can make direct contact with the surface, thus showing a higher coefficient of friction. This is especially important in the case of sharp LFM tips where even a normal force of only 30-40 nN can produce a substantially high pressure.
Figure 9.2. The relationship of friction coefficient (COF) and normal force (F_n) on cellulose (a), polyethylene (b) and polypropylene (c) films in air, water and in the presence of four types of nonionic polymers. E: polyethylene oxide; P: polypropylene oxide; R: alkyl groups. Data from project collaborator Yan Vivian Li, Cornell University.

For the lubricants with different structures, unfortunately, no obvious trend can be observed. This would require more carefully or sophisticated examination in terms of lubrication performance and structure. However, the measured differences in friction coefficient for the different surface morphologies of PP, PE, and cellulose surfaces confirmed that molecular self-assembled structures were formed on the surface. These changes mainly depend on the chemical natures of the surface and the fluid composition. In boundary lubrication, it is confirmed that surface coatings of organized, molecular liquid films control friction and is expected to reduce wear and abrasion in fiber processing.
Interaction energy between lubricant and surface simulated by MDS

In this investigation, interaction energies between nonionic polymers and PP, PE and cellulose were calculated by MDS method. The interaction energies for propylene oxide (PO) and ethylene oxide (EO) groups with PP, PE and cellulose were calculated separately and the differences of interaction energies are given in Figure 9.3. Cellulose, PP and PE surfaces exhibit similar attractive energies to PO groups, but quite different interaction energy with EO groups. Therefore, the difference of interaction energy of PO and EO, which are key components of the nonionic lubricants tested in this investigation, can be considered as the interaction of nonionic lubricants to model surfaces. Cellulose showed negative attractive forces to nonionic lubricants, this is supported by the insignificant adsorption and limited friction reduction observed in QCM and LFM experiments, respectively. On the other hand, polypropylene and polyethylene showed attractive forces to nonionic lubricants. This is also supported by results from adsorption and friction experiments. It is noted that in Figure 9.3. PE had a slightly higher attractive interaction with nonionic lubricants than PP, which is opposite to our results from adsorption experiment presented Chapter 8.

MDS allowed us to model how a small lubricant in solution adsorbs on a surface. As an illustration we use the case of hydrophobic PP in contact with polymer RP6E8, a very small molecule, which has a hydrophobic head RP6 and a hydrophilic end E8. In this investigation, two PP surfaces were constructed and then 2000 water molecules added to fiveRP6E8 molecules. The temperature was set at 298K, and density of the solution assumed to be 1.0g/ml. The simulation time scale was 100 ps and the initial state is shown in Figure 9.4. Polymer molecules
were distributed randomly in between the two surfaces (initial state). The simulation results are shown in Figure 9.4b: It can be seen that the polymer molecules bind onto the two PP surfaces.

![Interaction energy graph](image)

Figure 9.3. Interaction energies of propylene oxide (PO) and ethylene oxide (EO) groups and the interaction energy difference. The surfaces used were cellulose, polypropylene (PP) and polyethylene (PE). Data from project collaborator Hongyi Liu, NC State University.

Also, in Figure 9.4c a detailed image shows how the hydrophobic butyl group is adsorbed on the hydrophobic PP surfaces. This agrees with our hypothesis that the hydrophobic forces are the main driving force for adsorption of nonionic lubricants and self assembly on the tested surfaces.
Figure 9.4. Simulation of adsorption behavior of RP6E8 molecules in water on PP surface. 2000 water molecules (red) and five RP6E8 molecules were placed in between the surfaces. The temperature was set at 298K, and the density of the solution assumed to be 1.0g/ml. The simulation time scale was 100 ps. Data from project collaborator Hongyi Liu, NC State University.

SUMMARY

In boundary lubrication, polymers and surfactants might form self-assembled molecular structures on the surfaces. This process is driven by the molecular interactions with the surface (of the fiber). These interactions appear to determine the alignment modes of the molecules of a lubricant and hence its lubrication efficiency. From our simulation results, it is believed that hydrophobic forces are the driving mechanism for adsorption. Lateral force microscopy was effectively used in this research to measure friction. Molecular assemblies are expected to control friction behavior of the lubricated surfaces. It is foreseen that understanding of the
molecular structure and conformation of the lubricant’s chemical compounds on a fiber surface will serve as a fundamental guide for the formulation of improved finishes and fiber additives.
REFERENCES


Chapter 10

Summary of Conclusions and

Proposed Future Work
To summarize, this dissertation focused on the adsorption behavior of two important classes of polymers: polyampholytes and nonionic copolymers. In both cases, we investigated the relationship of chemical structures of the polymer (charge density of polyampholytes and block size of the nonionic polymer) and their adsorption behavior by using the quartz crystal microbalance with dissipation monitoring (QCM-D), surface plasmon resonance (SPR), water contact angle (WCA), lateral force microscopy (LFM) and molecular dynamics simulation (MDS) techniques.

QCM and SPR are non-invasive techniques that were used to monitor polymer adsorption in situ and in real time. In order to employ QCM/SPR to monitor the adsorption behavior, we first developed ultrathin films of cellulose, polypropylene (PP), polyethylene (PE), nylon and polyester (PET) etc. typical paper and textile materials by using the spin coating technique. Optimum operation conditions, such as polymer concentration, spinning speed and temperature were documented, and the achieved model films were characterized by atomic force microscopy (AFM) for morphology, ellipsometry for thickness and contact angle for surface energy. Our results showed that films were reproducible, uniform, and smooth. Their thickness was tunable through the polymer concentration. The optimum thickness was found to be in the range of 20-50 nm in order to attain good surface coverage and sensor sensitivity. These ultrathin model films facilitated studies of adsorption and lubrication at the nano scale.

For the amphoteric polymers, the adsorption of four polyampholytes with charge density ratios of 1:2:4:8 and two simple polyelectrolytes were monitored with the QCM-D...
technique, both onto cellulose and silica surfaces. The silica surface carried much more negative charge compared with that of the cellulose surface, at a given pH condition. It was concluded that the charge properties of both substrates and polymers were dominant factors for adsorption. Since the polyampholytes carry both weak base and weak acid groups, their net charge depended on the solution pH conditions. At the iso-electric point (IEP), the polyampholytes contracted, while far off their IEP, they showed a more expanded conformation. The adsorption data revealed that:

(1) Polyampholytes adsorbed more extensively on silica and cellulose compared to simple polyelectrolytes.

(2) The Adsorption mechanism was considered to be the result of a polarization effect produced by the substrates, even for the polyampholytes at the IEP. The polarizing ability of substrates determined the conformation of adsorbed layer and also the adsorbed amount.

Polyampholytes tended to change their conformation, resulting in oppositely charged groups in polyampholyte chains enriched in the inner layer while the charged groups carrying the same charge type as the substrate was enriched in outer layers. This is due to the fact that polarization effect of the substrate decays exponentially in the fluid media. Therefore, for a low charge density surface and a low charge density polyampholyte, a simple layer of adsorbed polymer was produced. The combination of a high charge density surface and a high charge density polyampholyte enabled a stronger polarization effect. Under this situation, the conformation of adsorbed layer tended to form multiple
layers. Since the polarization effect of the substrate decayed exponentially in the fluid media, the conformation of the adsorbed multiple layers was much looser than that of inner ones. This was evidenced by the rapid change of dissipation values of adsorbing polyampholytes. The extension of adsorption and conformation of the adsorbed species depended on a subtle balance of factors including charge properties of surfaces, charge density of polyampholytes and pH of the aqueous medium.

Adsorption of nonionic polymers was investigated including diblock polyalkylene glycols (PAGs) and triblock Pluronic polymers and also a special silicone surfactant. Surfaces we investigated included hydrophilic cellulose, partially hydrophobic nylon and PET and hydrophobic PP films. Conclusions that were drawn from this investigation include:

1. All the adsorption isotherms of nonionic polymers (diblock, triblock and silicone polymer) were fitted successfully to a Langmuir isotherm. The strongly bonded self assembled lubricant layer was able to bear normal pressures and also shear which could align the adsorbed polymers into a well-defined structure to reduce the friction.

2. The adsorption of nonionic lubrication onto the surfaces with different hydrophobicity is controlled by the balance in surface energies. In an aqueous medium, the nonionic (and amphiphilic) polymer prefers to adsorb onto a hydrophobic surface via its hydrophobic moieties, leaving the hydrophilic groups extended into solution. This produced a reduction in the interfacial energy between the substrate and solution and thus made the system more stable. In aqueous condition, the amphiphilic polymers didn’t
adsorb tightly onto the hydrophilic surface due to the competition with water molecules.

(3) Hydrophobic forces were the dominant driving force for adsorption of nonionic polymers. These forces were determined by both the hydrophobicity of the substrate and hydrophobic moieties of the polymer. From our experiments it was evidenced that PP had the largest adsorption amount of nonionic polymers, and nylon and PET were next. On the other hand, no adsorption was observed on the cellulose surface.

(4) The molecular weight of the polymer is an important factor influencing adsorption of the nonionic polymers.

(5) Compare with hydrocarbon-containing hydrophobic surfactants, silicone based surfactants have a higher surface activity and have a higher affinity to hydrophobic surfaces. That is one of the reasons why silicone lubricants were of superior lubrication performance.

Future work can include but not limited to:

(1) To test the adsorption behavior and friction reduction performance at the nanoscale for more lubricants, such as fatty acid, mineral oils and small molecular ionic lubricants with different chemical structures.

(2) To study a more complicated lubricant system, which is composed of more than one key component, to see how the layer of polymer adsorbs, and to explore the optimum ratio of each component where the best performance is obtained.

(3) To test the stability of lubricant films to see the normal shear range where the
lubricant is able to provide protection to substrates.

(4) To test the stability of lubricant films in the presence of small molecules, such as alcohols and acids.

(5) To uncover the function of water molecules in boundary lubrication.

(6) To relate friction at nanoscale or micro-scale to the actual macro-scale friction. This requires evaluation in an actual friction experiment involving fiber/fiber and fiber/metal or ceramic at the macro-scale.