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Adsorption of a Silicone-Based Surfactant on Polyethylene and Polypropylene Surfaces and Its Tribologic Performance

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ABSTRACT: Aqueous silicone-based surfactants are widely used in the processing of synthetic fibers in textile industries since they enhance a number of functional and processing properties. In this paper the interactions between silicone-based surfactants and textile-relevant surfaces (polyethylene and polypropylene) were investigated by quartz crystal microbalance with dissipation and the tribologic performance was evaluated by lateral force microscopy. Our results showed that the more hydrophobic polypropylene surface had higher affinity with silicone-based lubricants than polyethylene surface. These adsorbed layers provided lubricity in textile materials when subject to shear forces and offered protection to wear and abrasion. This is explained by the fact that the hydrophobic groups in the surfactant molecules interact more effectively with the polypropylene surface via hydrophobic forces. This information will ultimately help to further our understanding on lubrication phenomena in fiber processing. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40838.

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INTRODUCTION

Recently, silicone-based surfactants have received increasing attention for their superior properties, such as low surface tension, no irritation, and superwetting.¹ They are now commonly used in many manufacture processes, including foaming, coating, permeation control membrane and sensing membrane, surfactants, household/personal care products, and textile.¹⁻¹² For example, in the semiconductor area, silicone-based surfactants have been used as an antireflection coating in superluminescent diodes (SLEDs) to realize high power of SLEDs;^{5–7} while in textile processing, silicone-based surfactants are also important components in fiber and machinery lubrication, wetting, softening, and other surface treatments. Surface and bulk characteristics of fibers and fabrics such as softness (surface or inner), bounciness, tear strength, dry feel, wet feel, hydrophobicity, hydrophilicity, and several other fabric properties can be enhanced significantly by modifying silicones for desired transport and interfacial properties. Particularly, silicon-based textile lubricants perform better, last longer and most importantly, compared to organic lubricants. They are also extremely cost-effective.

Siloxanes, the polymerization product of silanols, have exceptional thermal and oxidative stability in addition to large viscosity

indices.¹³ Silanols are derived from the controlled hydrolysis of dialkylchlorosilanes.¹³ Siloxanes are also water repellent and have low surface tension that allows them to spread evenly on surfaces than most hydrocarbons; they are amenable to several different branch architectures.¹³ Silicone-based surfactants consist of a permethylated siloxane hydrophobic group coupled with one or more polar groups, such as nonionic groups of polyexyethylene (pEO) and polyoxypropylene (pPO), to allow them soluble in water.¹⁴ In recent years, silicone-based surfactants have been extensively investigated for their different applications.^{1–12} In the previous work, the properties of the surfactant solution and interfacial and wetting behaviors and have been mostly studied.^{2-4,14-19} However, the study on adsorption behaviors of silicone surfactants on solid surfaces, especially relevant to textile processing, are limited.²⁰⁻²² Zhu et al.²² exploited the spreading properties of several silicone surfactants with different molecular structures on hydrophobic surfaces. Wang et al.^{20,21} measured the interaction forces between silicone surfactants and solid surfaces immersed in the media of alcohol using atomic force microscopy. They discovered that silicone-based surfactants self-assembled and were adsorbed onto hydrophobic surfaces through the hydrophobic moieties on surfactant molecular chains. The hydrodynamic thickness of the adsorbed layer increased with the increase of the chain length

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Figure 1. Chemical formula of main component of silicone surfactant used in this investigation. R=H, CH3, or OAc.

of the hydrophilic moiety. Another interesting but important finding is that the adsorbed surfactant layer of silicone-based surfactants was more stable against alcohols and other organic solvents. Because the silicone surfactant could provide steric repulsion at an ethanol concentration as high as 80% in solution, in a comparison that polyalkylene glycol-based surfactants lose surface activity at approximately 40% ethanol. It is implied that silicone surfactants can be applied in aqueous as well as in nonaqueous media. This is not a common property in surfactant chemistries. In most conditions, the addition of short-chained alcohols in surfactant solutions usually results in a decrease of aggregation number and even disappearance of micelles in the solutions. Dixit et al.²³ studied the adsorption of a protein on silicone oil coated surfaces as a function of protein concentration, pH and ionic strength using quartz crystal microbalance (QCM).

Since silicone-based lubricants are extensively used in fiber processing, it is essential to find the relationship between the adsorption of silicone-based lubricants on various synthetic fibers with different hydrophobicity and their tribologic performance. 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 and the dynamics of adsorption. Our measurements were performed mainly using a 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) followed by a Milli-Q[®] Gradient unit (resistivity >18 M Ω). Gold QCM sensors (Q-sense, Sweden) were used as substrates which were coated with polymeric thin films.

The silicone-based lubricant used in the study was supplied by Goulston Inc. (Monroe, NC). It was a commercial product under a trade name, LN336-100I. The primary chemical component was polyalkylene oxide-modified polydimethylsiloxane, a surface-active block copolymer. Its chemical structure is present in Figure 1. The lubricant was used without any further purification or modification. A diluted solution of the lubricant was prepared with milli-Q water for surface tension measurement and adsorption measurement.

Methods

Preparation of Model Thin Films. Initially, QCM sensor were modified with polyethylene and polypropylene thin films. The procedures of model film preparation and film characterization were addressed in detail somewhere²⁴ but briefly here. Gold QCM sensors were cleaned using a solution consisting of H_2SO_4 and H_2O_2 $(V_{H_2SO_4(98\%)} : V_{H_2O_2(30\%)} = 7 : 3)$ for 1 h at room temperature, and then subjected to UV-ozone treatment for 10 min, immediately before spin-coating using a Laurell spin coater (North Wales, PA) with model WS-400A-6NPP. The preparation of PP and PE thin films involved dissolution of the precursor polymer in xylene (0.2% solution). In a typical protocol 20 mg of PP (or PE) and 10 ml xylene were placed in a small flask with a condenser (running water as cooling medium). The mixture was heated to boiling point and stirred for more than 2 h to dissolve the polymer. A wafer (or QCM sensor) was then placed on the rotor head of the coater while the infrared lamp (250 W) was used to keep the surface above 85°C (as measured by an infrared thermometer gun). 50-100 μ L of hot PP (or PE) solution was immediately spin coated onto the modified substrates at 3000 rpm for 20 s. The coated substrate was then removed from the coater and transferred to an oven pre-heated at 80°C for 2 h. Clean sensors were spincoated with a uniform and ultrathin PP or PE film. The thickness of the PP and PE films were measured in the range of 20 -50 nm using an atomic force microscopy.

Adsorption Experiments with the QCM-D Technique. A QCM Q-300 model (Q-sense, Inc.) was used in the study. Principles of QCM were addressed in detail somewhere.^{25–28} QCM was run in a continuous mode in this investigation. Milli-Q water was used to dilute pure silicon surfactant and no salt was added, resulting 0.0001 to 1% (w/v) surfactant aqueous solutions. Polymer-coated sensors were mounted in the QCM chamber initially.

Typical procedures in the QCM adsorption experiments consisted of the following sequential steps: (1) milli-Q water was injected through the QCM chamber to obtain a baseline; (2) when a constant stable baseline was obtained, a surfactant solution with a given concentration was passed through; (3) QCM frequency was then monitored until an adsorption equilibrium was reached, and (4) When a stable equilibrium was obtained, a large amount of milli-Q water was injected to remove loosely bound surfactants and excess surfactant in the bulk solution. As a consequence of the water injection, the frequency at new equilibrium was reached. Typical adsorption curves monitored by QCM are shown in Figure 2.

Frequency and dissipation values for the third, five and seventh overtones were usually recorded for further analysis on the adsorption dynamics of the surfactant. However, the adsorbed mass is typically very small in our experiments, resulting little difference among the overtones. The calculations in the study were simplified with the use of third overtone frequency and the Sauerbrey Equation.²⁵ Temperature has significant impact on the adsorption experiments using the QCM because it has correlation





Figure 2. Surface tension of the silicone lubricant used in this investigation.

with the density of fluid in QCM chamber. In this study, the temperature was held constant at $25\pm0.02^{\circ}$ C in all of our experiments. The flow rate was kept constant at 0.1 mL·min⁻¹.

Surface Tension Measurement. Surface tension was measured using 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 positioned horizontally by a 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 a film of the liquid in which it is immersed. The maximum pull force exerted on the ring by the liquid surface is measured and translated to the unit of surface tension, $mN \cdot m^{-1}$.

Contact Angle Measurement. The hydrophobicities of the PP and PE thin films coated on the QCM sensors were characterized by water contact angles, using a manual Rame-Hart goniometer. A droplet of Mini-Q water (10 μ L) was placed on the surface. After 1 min an optical magnifier recorded the outline of the droplet. 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. The results indicated that contact angles for the PP and PE coating were 102.9 ± 1.7°, and 95.1 ± 0.7°, respectively.

Friction Measured by LFM. A Scanning Probe Microscopy (NTEGRA Prima, NT-MDT) was employed to measure friction forces on polymeric thin films. The friction force measurements were conducted on a silicon wafer coated with PE. Scans were performed in air (air-test), and in the presence of a silicone lubricant solution with a concentration of 1% by weight. A tapping mode probe (MikroMasch, USA) with a force constant of 0.35 N·m⁻¹, and a resonance frequency of 145 Hz was used in all the measurements. The scanning velocity was 1 Hz and the scanning size was 1 μ m.

RESULTS AND DISCUSSION

Silicone lubricant is polyalkylene oxide-modified polydimethylsiloxane, which is a surface-active block copolymer.



Figure 3. 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. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polydimethylsiloxanes are very strong nonpolar molecules which produce an important lowering in surface tension. It is illustrated by the surface tension measurements in the tested range of concentrations as shown in Figure 2. It is 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 decreases slowly with the further increase of the concentration, resulting the lowest surface tension of 32 mN·m at the maximum concentration, 1% w/v. This value is not as low as stated in literature due to other components present in the mixture.^{29,30} Critical micelle concentration determined by the surface tension measurements is approximately 4×10^{-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 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

Surfactant adsorption was measured using the QCM, as explained in the methods section. Typical adsorption curves are shown in Figure 3 for the cases of PP and PE surfaces passed by a 0.1% (w/v) lubricant solution. The change of QCM frequency over time (solid line), which is a function of adsorbed mass, is shown on the left axis. 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. DI water was first injected continuously in the QCM's sampling loop until a stable baseline was obtained. The flat baseline is shown at the first 10 min in Figure 3. In all cases fluid injection was performed at low shear rates, with typical volumetric flow rate of only 0.1 mL·min. The silicone lubricant solution was introduced after 10 min, resulting sharp changes in frequency and dissipation as illustrated in Figure 3. These changes indicated lubricant adsorption on the sensor's surface.³¹ After the surfactant



injection has gone for about 10 min, the adsorption process reached an equilibrium indicated by stable frequency and dissipation profiles. Data acquisition in these stable conditions was continued for more than 1h to ensure that the adsorption equilibrium was indeed achieved. Then, this equilibrium condition was challenged by a new injection of pure solvent (DI water), which is a step of rinsing. As a result of the rinsing, the sharp changes in frequency and dissipation were observed again. The increase in frequency indicated that loosely-bound lubricant molecules were removed and then a thinner and less dissipative adsorbed lubricant layer remained on the surface.^{28,31}

After the rinsing has gone for about 35 min, a second equilibrium state was attained, resulting a significantly higher frequency and lower dissipation compared to the frequency and dissipation at the first equilibrium measured in the surfactant adsorption process. The difference between the two equilibrium conditions could be explained by a hypothesis that the first equilibrium is established at the interface between the adsorbed layer and a solution containing lubricant molecules, while in the second equilibrium is built at the interface between the adsorbed layer and a lubricant-free solvent.³¹ Based on the difference in lubricant's chemical potential the adsorbed mass can be classified into two categories, namely, reversible and irreversible adsorbed mass, corresponding to the first and the second equilibrium stages, respectively.

The lubricant adsorption was studied using the PP surface as well as the PE surface. When the same lubricant concentration was used, the frequency change measured on the PP surface was larger than that measured on the PE film, both in regard to the 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). It indicated that more lubricant molecules were adsorbed on the PP surface than on the PE surface, which implied that a higher affinity of silicone lubricant with PP than that with PE. As addressed in the section of contact angle measurement, PP is more hydrophilic than PE. Therefore, it might be due to the fact that the predominant driving force for the adsorption of silicone lubricant onto the PP and PE surfaces is the hydrophobicity.32 In addition, the irreversible adsorption was roughly half of the reversible adsorption on both PP and PE surfaces, suggesting that about 50% lubricant molecules were loosely bound on the polymeric surface and then were removed by DI water. It is worth noting that the QCM not only measures the adsorbed mass, but also the coupled water or any additional mass that is loosely attached to solid surfaces.

On the other hand, the change in energy dissipation measured the adsorbed silicone on PP indicates a "softer", more dissipative layer than that on the PE substrate.³¹ 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 dissipation is very low and no significant difference between the behavior of lubricants adsorbed on PP and PE was observed.

Friction Measured by LFM

When an AFM tip in lateral force microscopy (LFM) is sliding on a surface, lateral forces are measured both in air (no



Figure 4. Friction of PE film measured by LFM in air and after treatment of LN336-100I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lubricant applied) and in lubricant solution. Figure 4 displays a line scan across a PE surface tested both in air and in the commercial silicone lubricant solution. A static friction force is observed at the beginning of the measurement. It is known that there is a static friction force on the tip when a tip starts to move forward on a solid surface.^{33–35} The static friction force is evident in the force profile imaged in air during the forward and the backward scanning. However, when the tip is sliding on a surface coated with the lubricant solution, the large force corresponding to the static friction disappeared and it is replaced by a regularly oscillating force curve. The amplitude of force curve in the solution is much smaller than that in air, suggesting that the friction is reduced significantly by a boundary silicon lubricant layer on the polymeric surface. It is in a good agreement that the silicon lubricant shows excellent performance on fiber surface in textile processing.

Lubrication molecules adsorb on a surface to self-assemble a protective layer with a well-defined configuration.³⁶ The thickness of the adsorbed lubricant layer and the molecular structure of the adsorbed layer are crucial to the performance of lubrication.³⁷ A similar trend was also observed in the case of PP surface, even a slightly better lubrication performance on PP material than on PE material for the same silicone lubricant formulae.

Adsorption Isotherms of the Silicone Lubricant

Five silicone lubricant concentrations (in the range 0.001%–10%) were used in the QCM experiments. Figure 5 illustrates the adsorbed lubricant mass on PP and PE surfaces before and after rinsing as a function of the lubricant concentration. In the figure the change in frequency registered in the QCM was converted to effective adsorbed mass using the Sauerbrey equation.²⁵ The changes in the reversible adsorption were dependent linearly with the lubricant bulk concentration. On the other hand, a saturation or plateau state was observed in the irreversibly adsorbed mass with the increase of concentration. The saturation corresponded to an adsorbed monolayer which could be modeled roughly by a Langmuir-type isotherm.³⁸ Langmuir isotherms for the irreversible adsorbed mass on PP and PE surfaces





Figure 5. Adsorption isotherms of the silicone lubricant on PP (square) and PE (circle) surfaces. The solid and open symbols represent the adsorption mass before and after rinsing, respectively. The solid and dashed lines are the best fits to a Langmurian type isotherm. The adsorbed mass was calculated from the measured QCM frequency change by using the Sauerbrey equation.

are shown in Figure 5. 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.

Generally, the nonionic silicone lubricant adsorption on the PP and PE surfaces is a physical attachment in nature due to no reaction between the lubricant and the surfaces. Therefore, attraction forces are van de Waals forces, and an important contribution from hydrophobic forces.

The nature of the hydrophobic forces is still awaiting detailed elucidation from the surface science community. Such forces were described by Israelachvili and Pashley^{39–41} 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 is found that the experimentally measured forces are more attractive than those predicted by classic DLVO theory. This extra attractive force, termed by the authors as hydrophobic force ($F_{\rm h}$), is represented by a single exponential function as below:

$$F_h/R = C_0 \exp\left(-H/D_0\right) \tag{1}$$

where *R* is the mean radius of curvature of the interacting bodies, *H* the closest separation between the two curved surfaces, C_0 is a pre-exponential factor, and D_0 is known as the decay length. Hydrophobic forces may be classified into short-, medium-, or long- range forces, depending on the magnitude of the decay lengths. 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 as long-range force. Yoon and Ravishankar^{42–44} proclaimed that the decay length depends on the hydrophobicity of solid surfaces. When the solid surface has a water contact angle that is lower than 90° , the hydrophobic force is short-ranged and otherwise it is long-ranged.

Even though the previous knowledge originates from the studies for the inter- solid-surfaces, our recent research on the adsorption of nonionic polymer on hydrophobic surfaces indicated that it also applied to the interaction between a solid surface and a polymer.^{32,38} The water contact angle (WCA) of the PP and PE films is measured with results of 103° and 95°, respectively. The differences in WCA can be explained by the presence of $-CH_2-$ groups in PE while PP also contains lower surface energy $-CH_3$ groups. All in all, it is hypothesized that in the QCM measurements, a larger contribution to the irreversible adsorption comes from the hydrophobic forces while the van de Waals forces are predominant in the reversible adsorption.

In textile processing it is known that silicone nonpolar group provides the molecules with better performance, compared with typical hydrocarbon surfactants.^{45–47} This group of surfactants also leads to superior affinity to hydrophobic surfaces, typical in some textile polymers. In our case, water repellent segments of polydimethylsiloxane provide superior affinity to PP and PE surfaces. And the affinity is related to hydrophobic interactions between the polydimethylsiloxane segments with substrates. Since the hydrophobicity of PP is higher than that of PE. It is reasonable that the adsorbed silicone-based lubricant on PP surface is more than that on PE surface. This finding is also consistent with our previous reports.^{32,37,48}

Physisorption as a dominant effect in our experimental observations is 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.

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 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.

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