Density Dependent Friction of Lipid Monolayers†

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We measure frictional properties of liquid-expanded and liquid-condensed phases of lipid Langmuir−Blodgett monolayers by interfacial force microscopy. We find that over a reasonably broad surface-density range, the friction shear strength of the lipid monolayer film is proportional to the surface area (42−74 $Å^2$/ molecule) occupied by each molecule. The increase in frictional force (i.e., friction shear strength with molecular area can be attributed to the increased conformational freedom and the resulting increase in the number of available modes for energy dissipation.

Introduction

Thin films have long been studied as boundary lubricants between two solid surfaces. Recent studies have focused on self-assembled monolayers (SAMs) due to their importance as model systems and their applications as boundary lubricants for microscale and nanoscale devices, e.g., micro- or nanoelectromechanical systems (MEMS or NEMS).[1,2] Tribological properties of alkanethiol and alkylsiloxane SAMs have been extensively studied by force microscopies to address the dependences of frictional properties on molecular chain length,[3−6] end group chemistry,[3,7] tip scan velocity,[8] contact area,[9] and anisotropy of crystallographic directions.[10] These SAMs are usually characterized by crystalline order and close packing. In fact, deviation from a well-ordered molecular lattice is believed to be the main reason for increased friction in SAMs, due to the increased freedom of motions for the adsorbed molecules and, thus, more energy dissipation during lateral motion.[11]

In contrast to strongly adsorbed SAMs, much less is known about frictional properties of weakly adsorbed molecular films, e.g., Langmuir−Blodgett (LB) monolayers that lack the crystalline order of SAMs. In biological systems, weakly adsorbed phospholipid monolayers are believed to be common in biolubrication.[12,13] Weakly adsorbed perfluoroalkyl fatty acid monolayers are also critical to the development of the most successful MEMS product on the market today.[14] From a mechanistic perspective, the LB monolayer is an attractive model system for obtaining a molecular level understanding of friction because it allows us to vary molecular density over a much broader range than is possible in SAM systems. Here we report an experimental study, using interfacial force microscopy (IFM),[15,16] of the tribological properties of lipid monolayers over a reasonably broad density range prepared via the LB technique. We show that the normal and friction-force profiles in the compression region can be well-described by the Johnson−Kendall−Roberts (JKR) contact-mechanics model[17] and that the frictional force and friction shear strength scale inversely with the molecular density of the lipid layer.

Experimental Section

We investigate the two lipid molecules shown in Figure 1, 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC) and 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) (Avanti Polar Lipids, Inc. Alabaster, AL). Isotherms show that DLPC exists in the liquid-expanded (LE) phase over the entire pressure range studied here, conversely DSPC remains in the liquid-condensed (LC) phase over the entire pressure range studied (Figure 1). We use oxide-terminated silicon wafers as substrates for the lipid LB monolayers. The silicon surface is freshly cleaned in boiling Piranha (3:1 concentrated H_2SO_4/30% H_2O_2) (***Caution!*** Piranha solution is a strong oxidant and reacts violently with organic substances) for 1 h and thoroughly rinsed with 18 MΩ• cm H_2O. Pressure−area isotherms and LB depositions in increments of 10 mN/m were performed using a commercial LB trough (Nima Model 612D, UK) until film collapse. Freshly prepared lipid monolayers are characterized by IFM at room temperature and a relative humidity of ∼15%. We record normal and lateral force profiles as previously described[18] using a W tip (radius 1.3 μm, determined from Scanning Electron Microscopy). We obtain the lateral force simultaneously with the normal force by driving the sensor laterally with a ∼2 nm peak-to-peak dither at 100 Hz and synchronously detecting the force signal with a lock-in amplifier. Force profiles are repeated 3 times in 3 separate spots, allowing for averaging of 9 independent force profiles per monolayer. The dissipative component of the lateral force signal in quadrature with the drive is used as the friction signal.

Results and Discussion

Figure 2 shows a typical normal (A) and friction-force (B) profile for the LB monolayers (DLPC @ 40 mN/m). The fits are to the JKR contact mechanics model, which describes the contact area and deformation as a function of normal force.[17] To determine which, if any, contact mechanics models are appropriate, we use the α parameter of Carpick et al.[19] and fit friction as a function of normal force, Figure 2B. We find that fits to all the lipid monolayers yield an α parameter[19] of 0.9−

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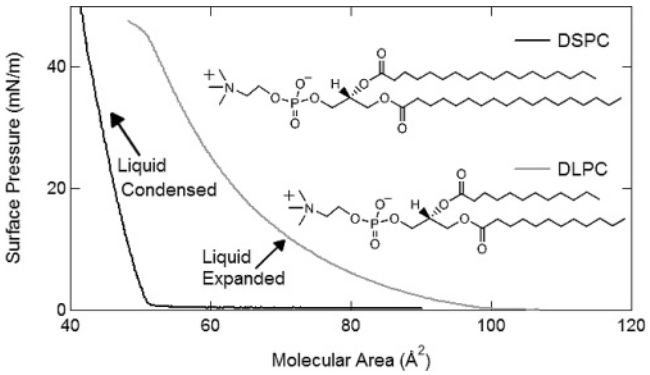

Figure 1. Isotherms showing surface pressure vs molecular area for DLPC (gray line) and DSPC (black line) monolayers on oxide terminated silicon. Molecular Structure of DLPC and DSPC are also shown.

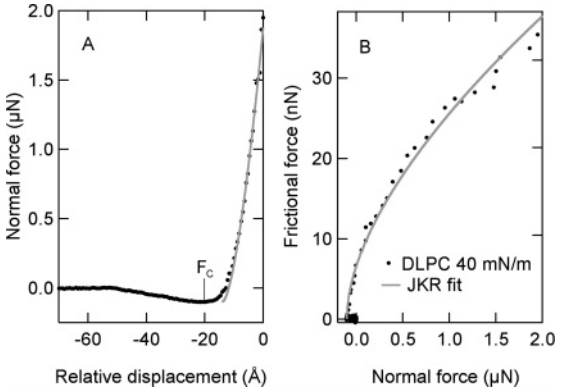

Figure 2. Normal force profile (A) and frictional force vs normal force (B) for a DLPC monolayer deposited on a native oxide terminated Si surface via the LB technique at a surface pressure of 40 mN/m. Fits are to the JKR contact mechanics model.

1.1, indicating that the JKR model ($\alpha = 1$) is most appropriate. This is in contrast to a previous AFM study showing that force measurements on LB films could not be adequately described by contact mechanics models.[20]

Most contact mechanics models, such as JKR, are derived from the Hertz theory.[21] These models are only strictly valid for linearly elastic materials, a condition not likely met over the full range of forces probed for the phospholipid monolayers. However, in this case, we find that the JKR model accurately describes the nature of contact after a small initial compression of the LB film. This can be seen in Figure 2A in the analysis of the location of F_c, the experimental critical force (maximum adhesion), a good indication of tip/film contact. The location of the critical force is ~5 Å before the contact predicted by the JKR model and ~10 Å before the fit begins to accurately describe the experimental data. This offset results from the fact that JKR theory assumes adhesive forces are very short-ranged, effectively acting only when contact occurs. These normal force features are characteristic of all lipid monolayer samples investigated. In Figure 2A we observe the normal force after contact slowly rises for ~6 Å and then rises sharply to meet the JKR model. The composite modulus values obtained from JKR fits for the compressed lipid monolayers in the tip/film/substrate combination are 33 ± 4 GPa for DLPC and 49 ± 6 GPa for DSPC; these values are, within experimental uncertainty, independent of surface pressure (10−50 mN/m) used in LB deposition and are much larger than the expected value of ≤1 GPa for the lipid monolayer itself.[22] Using the JKR model, we can estimate an effective modulus of the lipid film by fitting the first 10 Å of compression, which is dominated by response of the relatively soft LB film. The fit gives an effective modulus of ~1 GPa for each lipid film, which is also observed to be independent of deposition surface pressure. Upon further compression, the composite modulus of the contact increases, and the force profile is well described by JKR theory (gray curve in Figure 2A). We have also measured the mechanical properties of the control interface with no LB film; this measurement provided a composite modulus of 110 GPa, much higher than those obtained for the tip/film/substrate combination.

We conclude that the film is confined within the contact junction during compression, i.e., not squeezed out. The repeatability of our experiment in a single spot reveals that the lipid monolayer completely recovers during the time scale (~1 min) between force profiles. Note that we observe no evidence of discontinuity in force profiles corresponding to lipid membrane rupture, as seen in a previous AFM study.[20] This can be attributed to size differences of the tips used in measurements. In the previous AFM experiment, the tip radius of curvature was a few nanometers, more than 2 orders of magnitude smaller than that used in our IFM experiment. The maximum normal stress of ~10 MPa in IFM measurement is much smaller than the value for membrane rapture of 250 MPa estimated from AFM experiments.[23]

Note that the attractive region of the normal force may include contributions from van der Waals, electrostatic, and capillary forces. A further complication is that weakly adsorbed lipid molecules may respond dynamically and reorient under attractive forces. However, we do not observe out of contact friction in the adhesive region. Due to these complications, we do not attempt to quantitatively analyze the force profiles in the attractive region.

Having addressed the normal force profile, we turn to the frictional force, Figure 2B. The nonlinear behavior of the friction vs normal force plot and excellent agreement with JKR theory suggests a true single asperity contact.[9] Bowden and Tabor (BT)[1] showed that friction force is related to contact area through $F_f = \tau A$, where A is the contact area and τ is the friction shear strength. The contact area is a function of normal force as described by the JKR model.[19] We find that the experimental data in Figure 2B is well described by the BT equation with a small friction force offset, Δ_f ($|\Delta_f| \leq 4$ nN). The offset produces a better fit (gray curve in Figure 2B) than the BT equation alone. Δ_f is negative for DLPC and positive for DSPC monolayers. Though, the meaning of this small offset is unclear, it suggests that the combination of fits (BT and JKR) overestimate the friction (contact area) for the LE phase of the DLPC monolayer and underestimates that for the LC phase of the DSPC film. Further work is required to elucidate the origin of this offset by expanding the range of experimental conditions. After a small initial compression, the excellent fit in Figure 2B indicates that friction shear strength is pressure independent.[24] Using the above fitting method, we obtain the friction shear strength for the tip/film/substrate combination of each DLPC and DSPC deposition. This allows us to compare shear strength vs monolayer surface pressure (and thus, molecular area).

Figure 3 shows a plot of friction shear strength as a function of molecular area for both phospholipid monolayers. Here, the molecular area is the surface area per lipid molecule taken from the isotherms shown in Figure 1. Unlike the composite modulus for the compressed tip/film/substrate interface, we find a nearly linear relationship between friction shear strength and molecular area. Currently, we do not attempt to justify why this relationship is linear, which may only be an empirical result. This trend is more obvious for the LE phase DLPC monolayer than the LC

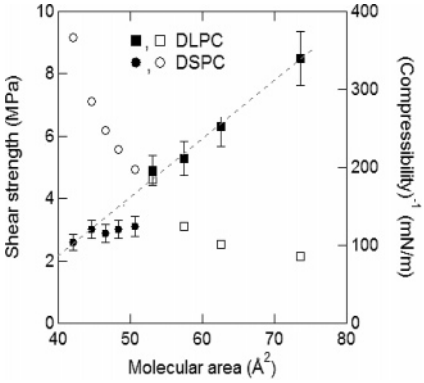

Figure 3. Friction shear strength (filled symbols) and compressibility^{-1} (open symbols) vs molecular area for DLPC (squares) and DSPC (circles) monolayers on oxide terminated silicon. The dashed line is a guide to the eye for the trend in friction shear strength.

phase DSPC monolayer, due to the much larger variation in molecular area of the former.

We now discuss the molecular origins for this observation. Surface sensitive spectroscopic measurements and computational simulations have revealed the major frictional dissipation mechanisms in the wear-less regime for monolayers confined between two sliding interfaces. These include intramolecular vibrations, molecular tilting, and other conformational changes.[11,25−27] For a nearly close-packed SAM, friction has been found to correlate closely with disorder. Deviation from two-dimensional crystalline-order due to shorter molecular backbones or bulkier terminal groups is believed to result in more conformational freedom for the adsorbed molecules and, thus, more channels for energy dissipation (i.e., higher friction) during sliding motion. The results in Figure 3 shows the influence of conformational freedom on friction in nearly close-packed SAMs can be extended to a much broader coverage range for LB lipid monolayers, with surface molecule density varying by nearly a factor of 2. Note that each lipid molecule consists of two alkyl chains (18 or 12 carbon each for DSPC or DLPC, respectively). At the smallest molecular area achievable in our LB monolayers, the area per DSPC molecule (two alkyl chains) is 42 Å.[2] This alkyl packing density is close to that in a typical alkanethiol SAM on Au.[11] Similar relationships between packing density and friction of a boundary lubricant have been observed numerous times, though previous experiments have been limited to strongly bound monolayer films.[3−6,28]

The friction shear strength for the close-packed, LC phase DSPC monolayer is much lower than that of the LE phase DLPC monolayer. This effect can be explained by both the aforementioned larger variation in packing density of LE phase film and the dramatic increase in ordering between the different phases of LB films. Previous sum frequency generation experiments have shown that the first-order transition between LE and LC phase films produces a "strong reorientation" of the alkyl chains of the surfactants.[29,30] The disorder in the LE films influences the ability to create internal conformational defects and changing molecular tilts, which is strongly opposed in well ordered films.[25]

A semiquantitative way of expressing conformational freedom, and ease of ordering the surfactant film, is compressibility. The compressibility (C), a uniquely measurable quantity of Langmuir films, is defined as $C = -(1/A)(\mathrm{d}A/\mathrm{d}\pi)$, where A is the average area per molecule and π is the surface pressure.[31,32] C^{-1} is the effective 2-D compressive modulus of the monolayer. The compressive modulus describes how much 2-D strain per unit of 2-D stress is needed to pack surfactant molecules closer together at the air/water interface. We have converted isotherms (π vs A) of each lipid monolayer to the compressive modulus vs A, shown in Figure 3. Assuming that LB transfer preserves the trends in compressibility, the compressive modulus increases with decreasing molecular area, indicating an inverse relationship between friction shear strength and compressive modulus.

Conclusions

We successfully use LB monolayers of lipids as model systems to establish the relationship between molecular density and frictional force for a weakly adsorbed boundary lubricant. We have found that both normal and friction forces are well described by the JKR and BT models, suggesting a single asperity contact with constant friction shear strength is formed in our experiments. The friction shear strength of the monolayer film is proportional to the surface area (42−74 Å^2/ molecule) occupied by each molecule over a relatively broad range. The increase in frictional force or shear strength with increasing molecular area can be attributed to the increased conformational freedom of the molecules, and the resulting number of energy-loss modes available.

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