ADHESION, FRICTION AND MECHANICAL PROPERTIES OF CF₃- and CH₃-TERMINATED ALKANETHIOL MONOLAYERS: A COMPARATIVE STUDY

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Self-assembled monolayers (SAMs) have received considerable recent attention as molecular-level lubricants in, for example, micro-electro-mechanical systems (MEMS).[1] Of particular interest as tribological films have been SAMs terminated by fluorocarbon groups, because of their inert nature and enhanced thermal stability. Surprisingly however, fluorocarbon films were shown to actually produce higher coefficients of friction (relative to CH₃-terminated films) in atomic force microscopy (AFM) studies. Subsequent work has concluded that the increased van der Waals radius of the fluorine groups (~45%) causes a steric disruption of the order of the molecular surface giving rise to an increased friction.[2] We present results from a direct comparison of the adhesive, mechanical and frictional properties of SAMs terminated by CF₃ and CH₃ groups using both Interfacial Force Microscopy[3] (IFM) and the AFM. IFM results are shown for a two micron tungsten tip interacting with C₁₆ alkylthiol molecules assembled on Au(111) single-crystal surfaces. AFM results involve a ~20 nm tip interacting with the same two molecules assembled on Au films deposited on mica surfaces. A direct AFM comparison is accomplished by using a “nanografting technique”. [4]

Figure 1 shows the IFM results for friction force vs. normal force, again, indicating a higher value for the CF₃-terminated film. The looping behavior is suggestive of a friction force dependence on the contact area between the tip and film. However, the difference in behavior results almost entirely from the rapid friction rise in the attractive, light-contact region, although in both cases, there is significant friction in the true non-contact region. Figure 2 shows a direct comparison of the normal force vs. relative interfacial separation behavior for the two films, along with a fit to the long-range, non-contact behavior according to the van der Waals relation,[5]

\[
\frac{F}{R} = \frac{A}{6(d - d₀)^2},
\]

where R is the tip radius, A the Hamaker constant, d the relative separation and d₀ is the point of tip/film contact. This fit shows that at the longer ranges the force closely follows that the van der Waals relationship, deviating when the film begins to react to the presence of the metal tip. The fits also reveal that the van der Waals strength, indicated by the value of the Hamaker constants, is almost 4.5 times larger for the CF₃-terminate film relative to the film terminated by CH₃. This increased interaction is due to the Debye or dipole, induced dipole component of the van der Waals force and results from the strong dipole moment of the highly polar CF₃ groups.[5]
It can be seen, however, that the mechanical behavior of the two films is virtually identical in the contact region and only differs in the light and non-contact areas. Figure 3 shows the corresponding AFM comparison, indicating a linear friction behavior, commonly seen in AFM results, and a surprising twist. The CH₃ friction has two distinct slopes, the higher one having a value only slightly smaller than that for the CF₃ film. This two-slope behavior was seen, although not discussed and not observed consistently, in the older AFM results. The AFM friction results are linear because it is a very high-strain technique, utilizing a tip 100 times smaller then the IFM. As was earlier discovered by the Salmeron group,[6] the two-slope behavior results from a dramatic change in film structure as the strain increases at the higher loads, giving rise to higher friction. At light loads, the tip essentially rides on the surface of the film and the friction is affected by the near-surface structure, i.e., by the end-group size. However in the CF₃ case, the additional adhesive force is strong enough to cause the tip to penetrate the film surface and inter the high-friction region. The increased adhesive force shows up in the CF₃ IFM data as a significant film disturbance in the non-contact region, as well as an appreciable friction component resulting from film disturbance outside the actual area of contact in the light-contact region. As a result, the CF₃ behavior of Fig. 1 cannot be characterized, for example, by a JKR-type model for the contact area variation, as has been successfully demonstrated for other systems.[7]

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REFERENCES


