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Friction and Wear of Surface-Immobilized C_{60} Monolayers

Lorraine M. Lander and William J. Brittain*

Department of Polymer Science
The University of Akron
Akron, Ohio 44325-3909

Vito A. DePalma* and Sharon R. Girolmo

Manufacturing Research and
Engineering Organization
Eastman Kodak Company
Rochester, New York 14650-2158

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Introduction

We report the tribological properties of surface-immobilized monolayers of buckminsterfullerene. The isolation and characterization of fullerenes, particularly buckminsterfullerene (C_{60}),[1] have prompted considerable interest in the properties and reactivity of this unusual class of molecules.[2] Thin films of fullerenes have been studied using Langmuir−Blodgett techniques[3] and electrochemical studies of vapor deposited C_{60}.[4] Monomolecular films of C_{60} have been prepared by covalent attachment to inorganic surfaces. For example, C_{60} was tethered to a silicate surface via a C_{60}−OsO_4/pyridine coordination complex.[5] Mirkin and co-workers[6] attached C_{60} to an amine-functionalized silicate substrate. More recently, Mirkin and co-workers[7] have prepared C_{60} layers by chemisorption of thiol functionalized C_{60} to gold surfaces.

We used a similar approach by exploiting the reaction of C_{60} with an azide-functionalized self-assembled monolayer (SAM).[8] We characterized the structure of the surface immobilized C_{60} by water contact angles, X-ray photoelectron spectroscopy, UV−vis spectroscopy, and atomic force microscopy (AFM). AFM results were consistent with a 1 nm thick, monomolecular layer of C_{60}. The fullerenes were firmly attached to the surface in an ordered lattice of C_{60} molecules corresponding to the expected molecular pattern for the $\{h00\}$ faces of a face-centered cubic unit cell. Interestingly, Mirkin and co-workers[7] observed hexagonal packing using AFM. We account for this difference by the nature of attachment; Mirkin tethered functionalized C_{60} to gold, while we used a preformed a SAM as the template for native C_{60}. We have also studied the blood contact properties of these surface immobilized fullerenes.[9]

In this report, we continue our study of C_{60} monolayers by examining the friction and wear properties of these unique films. DePalma and Tillman[10] have investigated the boundary lubrication properties of SAMs formed on silicon substrates. However, investigations into the friction and wear properties of fullerene films have been limited. Sublimed and vapor deposited films of C_{60} have been examined and comparisons made to more traditional lubrication materials such as MoS_2 and graphite.[11,12] The feasibility of C_{60} and its derivatives for use as lubricating additives has also been investigated.[13] Here, we have studied the friction and wear properties of covalently bound monolayer films of C_{60} (C_{60}-SAMs), in sharp contrast to other reports on C_{60} films prepared by physisorption.

Experimental Section

Materials. All reagents were obtained from Aldrich or Fisher Scientific unless otherwise noted. Silicon substrates were type N, two-side polished silicon rectangles (1.5 cm × 4.0 cm × 5−6 mil) with (100) orientation (Semiconductor Processing Co.). Methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) were anhydrous.

Substrate Preparation. Silicon substrates were cut in half using a diamond-tipped glass cutter to measure 1.5 cm × 2.0 cm × 5−6 mil. Cut substrates were immersed in a soap solution (pH 9−10, Alconox) and hot water and then were scrubbed using a soft camel hair brush for approximately 30 s per side. Substrates were rinsed with large amounts of warm water followed by rinsing with distilled water. Substrates were then placed in freshly made "piranha" solution (70:30 v/v, concentrated sulfuric acid:30% hydrogen peroxide) for 1 h at 60−80 °C. The "piranha" solution was decanted, and the substrates were rinsed with large amounts of distilled water and dried under an argon stream. Cleaned substrates were used immediately.

Bromo-Terminated SAMs. Bromo-terminated SAMs were prepared by a previously established procedure.[8] Before rinsing with chloroform, rinsing was done by pipet with an additional 20 mL of CH_2Cl_2. SAMs were then soaked in CH_2Cl_2 overnight. After soaking, the SAMs were rinsed with acetone, scrubbed with a soft camel hair brush in hot distilled water, and again rinsed with acetone. The SAMs were then treated by 15 min sonication in chloroform followed by wiping with a chloroform saturated cotton swab (wiping in one direction only). The bromo-terminated SAMs were then allowed to air-dry.

Azide-Terminated SAMs. Bromo-terminated SAMs were placed in a 10% (w/v) solution of NaN_3 in DMF. After 24 h, the SAMs were rinsed with distilled water, scrubbed with a soft camel hair brush in hot distilled water, rinsed with acetone, and finally rinsed with chloroform. Azide-terminated SAMs were then wiped with a chloroform soaked cotton swab and allowed to air dry.

C_{60}-SAMs. C_{60}-SAMs were prepared by a previously established procedure from azide-terminated SAMs.[8] After rinsing with benzene and chloroform, C_{60}-SAMs were sonicated for 30−60 s in chloroform before being wiped with a chloroform soaked cotton swab and air dried.

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Scheme 1

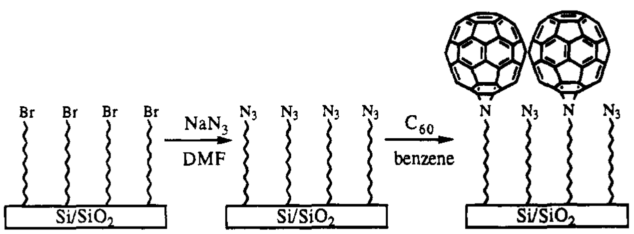

Table 1. Water Contact Angles for Br-, N_3-, and C_{60}-SAMs[a]

	this work		lit	
surface	θ_a, (deg)	θ_r, (deg)	θ_a, (deg)	θ_r, (deg)
Br	88 ± 2	74 ± 2	82 ± 1[b]	77 ± 2[b]
N_3	89 ± 2	71 ± 2	77 ± 2[b]	71 ± 2[b]
C_{60}	69 ± 2	50 ± 2	72[c]	

[a] θ_a = advancing water contact angle, θ_r = receding water contact angle. [b] Taken from ref 15. [c] Taken from ref 6.

All samples were given a final cleaning before storage by wiping with a chloroform soaked cotton swab. SAMs were stored between sheets of lint-free paper in Fluoroware containers.

Contact Angle Measurements. Contact angles were measured by the tilting stage method[14] using a Ramè-Hart NRL-100 goniometer equipped with an environmental chamber and tilting base. Humidity was kept at 100% by filling the wells of the environmental chamber with distilled water. The test solution used was 0.9% sodium chloride solution (Abbott Laboratories). Throughout this text, reported water contact angles refer to contact angles measured with this test solution. Contact angles reported are averages of three measurements per drop with 2–4 drops/plate.

Friction Measurements. The friction and wear measurements were done using WEAR III,[10] a pin-on-disk friction apparatus. All work was done in a clean air hood at ambient conditions (typically 24 °C and 50% RH). Friction measurements were made with a 3.6 mm diameter (nonrotating) glass sphere (with root-mean square roughness of 3.3 nm) moving at a relative velocity of 0.028 cm/s on the sample. A new glass sphere (slider) was used for each sample and load. Before using a slider, it was sonicated in acetone for several seconds, air-dried, and mounted in a collet. The top surface of the slider was rubbed on a clean room wipe (Absorbond) and examined at 50 and 200× to ensure it was free of defects and particulate material. Only defect and particle free sliders were used in this work. Two tracks were investigated at each load. The slider was cleaned between tracks by rubbing it on Absorbond.

The normal loads (F_n) on the slider were nominally 10, 30, 50, and 80 g. Data were recorded over a 30 s period using an A/D board and computer which analyzes the friction force (F_t) every 0.1 s. It uses the values at each 0.1 s and F_n to calculate a kinetic friction coefficient (μ_k). An average μ_k is computed for the final 27 s of sliding contact. The accuracy of measuring F_t is approximately ±0.25 g, and the accuracy in the F_n is ±0.001 g.

Results and Discussion

A method for the preparation of C_{60}-SAMs has been described previously.[8] The precursors to C_{60}-SAMs are the bromo- and azide-SAMs which were also studied in this friction and wear investigation (Scheme 1).

Water contact angle values for the samples used in this study and the corresponding literature values are shown in Table 1. Contact angles acquired for the bromo-SAMs and azide-SAMs are slightly higher than literature values but comparable. Samples used for contact angle measurements were not utilized for friction measurements due to possible contamination by the saline solution. Samples for friction measurements were handled with more care than in previous work; especially in the cleaning of the substrates and handling of the SAMs after formation and in situ reactions. Thorough cleaning and rinsing were done to ensure complete removal of any particulate material from the surface which could influence friction and wear results. Samples were examined at 200× to ensure the absence of particulate contaminants prior to measurement.

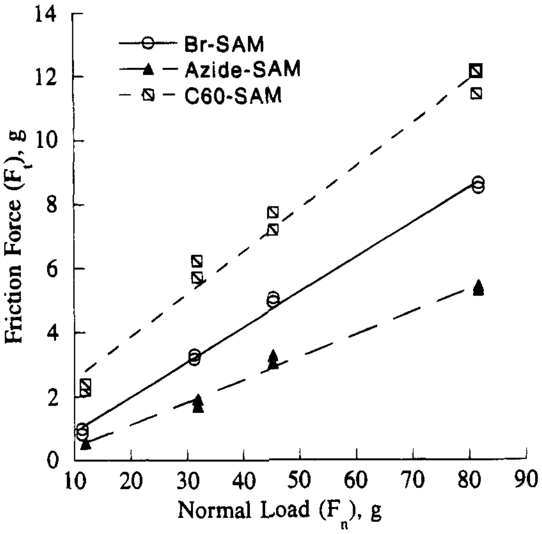

Figure 1. Friction force (F_t) vs normal load (F_n) for C_{60} (open squares), Br (open circles), and azide (filled triangles) SAMs. Linear regression lines are drawn in. Correlation coefficients were all >0.99.

Table 2. Friction and Wear of SAMs

SAM surface	kinetic friction coefficient, μ_k	evidence of wear[a]
$-(CH_2)_{11}-C_{60}$	0.13 ± 0.01	none
$-(CH_2)_{11}-N_3$	0.07 ± 0.01	none
$-(CH_2)_{11}-Br$	0.11 ± 0.01	sheetlike material
$-(CH_2)_{17}-CH_3$	0.07 ± 0.01[b]	none
$-(CH_2)_9-CH{=}CH_2$	0.09 ± 0.01[b]	none
$-(CH_2)_2-(CF_2)_6-CF_3$	0.16 ± 0.02[b]	significant
uncoated silicon wafer	≈1.2	very significant

[a] See text for discussion of wear. [b] Taken from ref 8.

Two runs were performed at each normal load (F_n = 10, 30, 50, and 80 g). Results are presented in Figure 1 as a plot of F_t vs F_n. The combined coefficient of kinetic friction coefficient, μ_k, for each SAM over the loads of interest is obtained from the slope of a linear least squares fit through the data. The samples were found to have different μ_k values for loads ranging from 11.4 to 81.5 g. The C_{60}-SAMs were found to possess the highest value of μ_k, while the azide-terminated SAMs gave the lowest. The SAMs in this study were ranked by μ_k value as follows: C_{60} > Br > N_3 (see Table 2). Values for the bromo- and azide-terminated SAMs were consistent with those obtained for other SAM systems using the same apparatus. DePalma and Tillman[10] investigated the friction and wear characteristics of OTS (octadecyltrichlorosilane), UTS (*n*-undecyltrichlorosilane), FTS ((tridecafluoro-1,1,2,2-tetrahydrooct-1-yl)-trichlorosilane), and bare silicon. Results indicated that OTS provided the best boundary lubrication followed by UTS. Information on surface wear was obtained indi-

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rectly by examination of deposits left on the slider after measurement. The presence of deposits as well as the amount was qualitatively assessed.

For both OTS and UTS, little or no deposits were found on the slider which is indicative of low wear. Also, no wear tracks were observed for these layers. The small amount of deposit left on the slider from the UTS surface came from contaminants on the layer surface. Using only μ_k values, FTS could also have been considered a good lubricant. However, DePalma and Tillman observed large amounts of deposits on the slider after measurement of the FTS layers. It was proposed that the monolayer was being destroyed and the slider was actually contacting the silicon substrate. This could possibly have been due to loose packing of the chains resulting in a large volume available for chain motion. This would permit the slider to push the chains aside, thus contacting the silicon surface. Looking at both friction and wear characteristics, FTS failed as a boundary lubricant.

In this study, μ_k results obtained for the azide-terminated SAMs were similar to OTS. Bromo-terminated SAMs gave μ_k values closer to those of UTS. Wear analysis of the bromo-SAMs revealed sheetlike deposits on the slider. No deposits were observed from the azide- or C_{60}-SAMs. The deposits from the bromo-SAMs may be due to contaminants on the SAM surface and not due to destruction of the SAM itself. The contaminants would contribute to an artificially high coefficient of friction. We speculate that another possible explanation for the deposits is a chemical reaction between the bromo-SAM and the glass slider (especially if the slider is basic) with transfer of material to the slider.

On the basis of both μ_k and wear, the bromo- and azide-SAMs were good boundary lubricants with the higher coefficient of friction for the bromo-SAMs being due to the presence of a contaminant. Results for the C_{60}-SAMs fell on the high end of the range found for the other SAMs.

Direct comparisons of friction values obtained using different experimental protocols are not possible. Despite this caveat, the results for the C_{60}-SAMs fell on the low end of the range reported for sublimed and vapor deposited films of C_{60} (0.12–0.18).[11,12] Bhushan and co-workers[11] found that the lowest observed μ_k for sublimed C_{60} films occurred when using a 1 N load. Higher values were obtained with 0.1 and 10 N loads. The same general trend of decreasing μ_k with increasing load was also observed for the C_{60}-SAMs. However, the range of F_n was not sufficient (0.11–0.80 N) to determine if μ_k continues to increase as F_n is increased above 1 N. It has been proposed that C_{60} may act as "molecular ball bearings" in lubricating additives by rolling or sliding between two surfaces in contact. However, this lubricating mechanism would only be applicable to surfaces which have a roughness less than the diameter of C_{60}. A more significant issue may be the deformation of the surface or C_{60}. A covalently bound film of C_{60} may provide greater separation of the surfaces and thus reduce adhesion for a lower friction force.

An important property for comparison of bound and free C_{60} is wear. Analysis of the wear characteristics of the physisorbed C_{60} monolayers revealed considerable amounts of debris left on the steel ball slider.[10] This "transfer film" of C_{60} debris on the slider was cited as being responsible for the low friction observed. This is in sharp contrast to the lack of debris found for the C_{60} SAMs in this study. Lack of debris indicates that the friction characteristics of C_{60} SAMs were not a result of a poorly organized monolayer (as was the case for the FTS monolayers) or a physisorbed, easily removed film. Instead they were due to the nature of the C_{60}-SAMs themselves. Because there is less deposit observed with the bound film of C_{60}, it can be concluded that it gives less wear than physisorbed C_{60}.

The significance of this work involving the use of covalently bound C_{60} as a lubricant relates to its low wear. For the conditions that we examined, the covalently bound C_{60} performed extremely well on a relative basis considering the high load that was used. Although C_{60}-SAMs do not have significantly different friction values than the other SAMs studied, the C_{60} layer may have the potential to entrain other molecules, such as hexadecane, within the interstices between the end groups. In this configuration, the layer would act like a brush to supply a source of lubrication while under pressure. We are currently studying this aspect of these unique monolayers.

Conclusions

The friction and wear properties of C_{60} monolayers have been studied using a pin-on-disk friction apparatus in which a glass sphere makes contact with the monolayers. The C_{60} monolayers were prepared by reaction of C_{60} with azide-terminated SAMs to produce a covalently bound layer of C_{60}. The coefficient of kinetic friction coefficient (μ_k) for the C_{60} monolayer was 0.13 ± 0.01, a value which is similar to literature reports of vapor deposited C_{60} films. However, there was little or no wear observed for the C_{60} monolayer, whereas significant transfer of C_{60} to the slider was reported for vapor deposited films. The friction and wear properties of C_{60} monolayers are comparable to other SAMs which, in general, are all good boundary lubricants. Values of μ_k for other SAMs range from 0.07 (azide- and methyl-terminated SAMs) to 0.16 (tridecafluoro-1,1,2,2-tetrahydrooctyl SAM).

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