

Solid Lubricant Properties of the Supramolecular Assembled Films of Fullerene C₆₀

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The ultra-thin films of fullerene C₆₀ were prepared and their nanotribological behavior has been investigated. The fullerene C₆₀ formed three-dimensional aggregates on the ultrapure water. On the other hand, the fullerene C₆₀ spreads as a quasi two-dimensional film on the aqueous solution in the presence of the water-soluble hosts. UV-VIS absorption spectra showed that the amphiphilic supermolecule of fullerene C₆₀ and host molecule was formed at the air-water interface. The supramolecular assembled films on the silicon wafer exhibited a lower frictional force than bare silicon surface. The lowered friction and high wear-resistance propose that the supramolecular assembled film acts as a lubricant. The low frictional force could be attributed to the rotational motion of fullerene C₆₀, even if the fullerene C₆₀ makes a complex with host molecule.

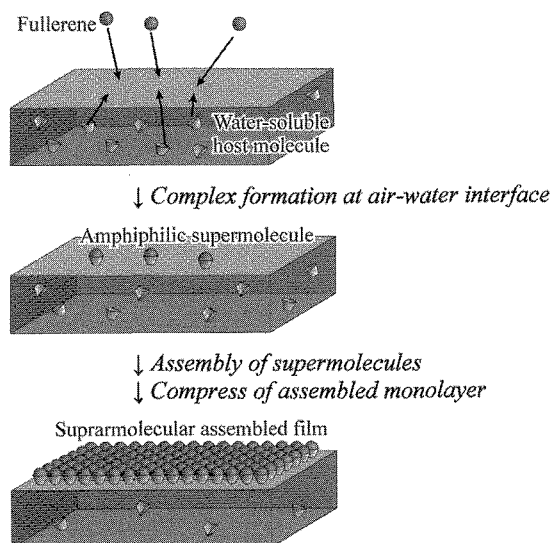
Key words: fullerene / supramolecular assembly / molecular bearing / lateral force microscopy / solid lubricant

1. INTRODUCTION

Nano- and micro-machines have been expected to trigger the creation of a future prominent industry. However, previous works on micromachine bearings have produced poor results. Thus far, micromachines have been considered 'machines incapable of movement'. At this time, a C₆₀ thin film has been expected to be a suitable lubricant because of the nearly spherical shape of C₆₀ molecules, low surface strength and high robustness [1, 2]. However, a pin-on-disk experiment for the C₆₀ thin film has a large frictional coefficient of 0.8, which suggests that the C₆₀ thin film is not a good lubricator [3]. Furthermore, a few studies in air and in ultrahigh vacuum (UHV) have cast doubt on the possibility of low friction. In UHV experiments [4, 5], molecular-resolution images have been presented using both an atomic force microscope (AFM) and a lateral force microscope (LFM), but it has, unfortunately, been concluded that the frictional forces of C₆₀ films up to 18 nN load are larger than that at a NaCl (001) surface. In an experiment conducted in air [6], the behavior of frictional force up to a load of 20 nN has been investigated using the LFM, but it was concluded that the frictional force acting between the probe tip and the first C₆₀ layer is larger than that acting between C₆₀ layers. In a recent study by Miura et al. [7], it was found that a graphite flake placed on a C₆₀ monolayer on graphite stacks in the same way as the C₆₀ molecules on graphite. The C₆₀ molecules act as molecular bearings, assisted by the nanogears of the six-membered carbon ring between C₆₀ molecules and graphite, in which the mean dynamical frictional forces are 0 up to a load of 100 nN. However, it is not always evident that the superlubricity of the C₆₀ monolayer film proposed by Miura et al. [8] arises over a larger area because the

contact between the C₆₀ monolayer and the graphite flake is on the order of nanometers. For the application of the C₆₀ monolayer film in a microsystem, the occurrence of superlubricity over a larger area is crucial.

We have investigated the preparation technique of the supramolecular assembled film of C₆₀ [9]. Scheme 1 illustrate the preparation scheme of C₆₀ assembled film. In the Brewster angle microscope (BAM) image, the monolayer-like C₆₀ film spread beyond 1-cm long. And it was reported that the fullerene C₆₀ rotates in the cavity of calixarene from the ¹³C-NMR spectra [10]. In this study, the frictional behavior was investigated for the supramolecular assembled film of C₆₀ using LFM.



Scheme 1. Schematic illustration for the preparation of supramolecular assembled films at the air-water interface.

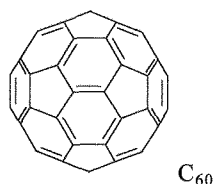
Furthermore, the usefulness of the C_{60} monolayer as a molecular bearing film was discussed through the wear resistance.

2. EXPERIMENTAL

2.1 Materials

Fullerene C_{60} was purchased from SES Research Co. and it was used without further purification. Water-soluble azocalix[6]arenes, CA6, were synthesized as described elsewhere [11]. Cyclodextrins were purchased from Wako Pure Chemical Industries, Ltd. and used as received. The structure and abbreviation for each compound is shown in Figure 1.

Spherical guest



Water-soluble hosts

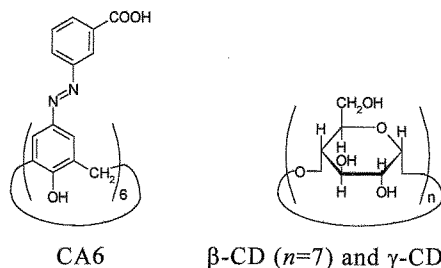


Figure 1. Chemical structures and their abbreviations of host and guest molecules.

2.2 Measurements

Surface pressure–area isotherm: The surface pressure – area (π – A) isotherms were measured with a Langmuir trough (HBM AP3, Kyowa Kaimenkagaku Co. Ltd.). Distilled water purified by EasyPure RF (Barnstead) with a resistivity of higher than 18.0 $M\Omega$ ·cm. Fullerene C_{60} was dissolved into toluene, ca. 0.069 mmol/L, in order to spread on the water surface. Appropriate amounts of the solution were spread on a water surface at 10°C. The planar density of C_{60} in a water surface was initially kept lower than 0.166 molecule/ nm^2 , which inhibited self-aggregation of C_{60} and promoted the host–guest interaction at the air–water interface [9]. The C_{60} films were compressed at a speed of 10 cm^2/min . Homemade BAM was employed for the *in situ* observation of the film morphology at the air–water interface.

Transfer of the assembled films onto the solid substrate: The films were transferred from water surface onto the substrates for the observation by atomic force microscope. The transfers were carried out by the Langmuir–Blodgett method, the Langmuir–Scheafer method [12], and the inverse Langmuir–Scheafer method [13, 14]. Polished silicon wafers (Shin-Etsu Chemical Co., Ltd., DP050000) were used as substrates. The glass slides were cleaned in an oxidative sulfuric acid.

The wafers were sonicated in toluene, acetone, ethanol, and distilled water. After then the substrate was cleaned by irradiating O_2 plasma (Yamato Science Co. Ltd., PR300) to remove a trace of organic contaminants. The cleaning procedure made the silicon surface hydrophilic.

Sample Characterization: UV-VIS absorption spectra of C_{60} were obtained with a Shimadzu UV-Visible spectrophotometer, PharmaSpec UV-1700. The spectra for the supramolecular assembled films were compared with that for the hexane solution of C_{60} to discuss the aggregation of fullerenes. Contact-mode measurements were performed with a scanning force microscope (Seiko Instruments Inc., SPI3700) on the transferred films. Triangular cantilevers with a normal spring constant of 0.08 N/m and a pyramidal Si_3N_4 tip (Olympus Optical Co., Ltd., Micro Cantilever) were used in this study. All measurements were performed with a 150- μm scanner at loading forces of 0.087 nN. The scanning area and the scanning frequency were fixed at $40 \times 40 \mu m$ and 1 Hz, respectively. Frictional coefficients of the deposited films were also recorded on Tribostation Type 14FW (Shinto Scientific Co. Ltd.) by sliding a Si_3N_4 ball (5 mm) on the substrates in width of 20 mm at the rate of the 200 mm/min under the loading of 0.20 N.

3. RESULTS AND DISCUSSIONS

3.1 Preparation of supramolecular assembled film

Figure 2 shows the typical π – A isotherms of fullerene C_{60} on the aqueous solution of CA6 at 10 °C. On the ultrapure water, the surface pressure began to rise at the smaller area than the intrinsic molecular area of C_{60} , 0.98 $nm^2/molecule$. BAM observation of this film revealed that the fullerene C_{60} forms three-dimensional aggregates immediately after spread on the water surface because of their high cohesive energies, 31 kcal/mol [15]. However, when the fullerene C_{60} was spread onto the aqueous solution of CA6 or cyclodextrins, the surface pressure rose sharply and the limiting molecular areas were 1.17 $nm^2/molecules$ on the CA6 aq. and 1.02 $nm^2/molecule$ on β -CD aq. On aqueous solutions of both hosts, the limiting molecular areas were slightly larger than the intrinsic molecular area of C_{60} , and the subphases contained large excess of host; the molar

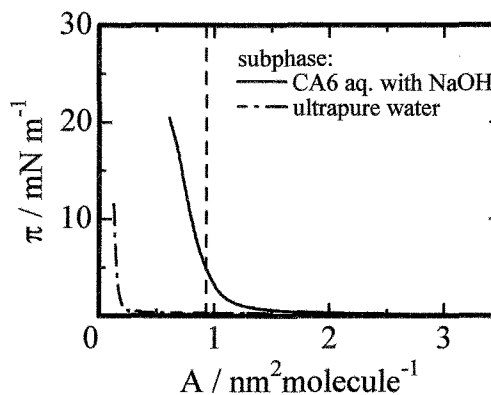


Figure 2. π – A isotherms for the films of fullerene C_{60} on aqueous solution of CA6. The vertical dashed line represents the intrinsic molecular area of C_{60} .

ratios of host and C_{60} were $C_{60}/CA6 = 240$ and $C_{60}/\beta\text{-CD} = 470$. The results are consistent with our estimation that C_{60} make an amphiphilic supermolecule by captured in the cavity of the host molecules.

3.2 Transfer of assembled film onto the solid support

A layer of supramolecular assembled films could be transferred onto the hydrophilic solid support, such as a silicon wafer and a glass slide, by the Langmuir-Blodgett method and the inverse Langmuir-Scheafer method. When the films were deposited at a surface pressure of 10 mN/m, only smooth surface was observed in AFM.

3.3 UV-VIS absorption spectroscopy

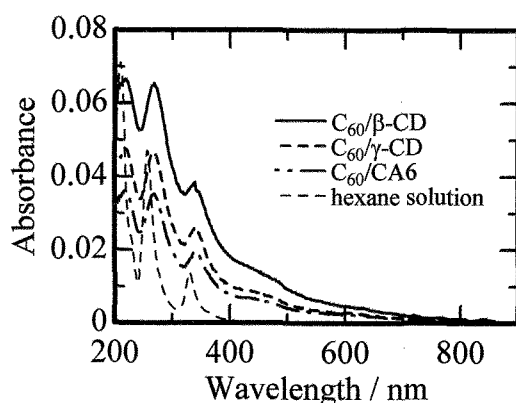


Figure 3. UV-VIS absorption spectra for the supramolecular assembled films of C_{60} on glass slide and a hexane solution of C_{60} . —: $C_{60}/\beta\text{-CD}$, ---: $C_{60}/\gamma\text{-CD}$, — · —: $C_{60}/CA6$ and · · · ·: hexane solution of C_{60} .

Figure 3 shows the UV-VIS absorption spectra for the supramolecular assembled films of C_{60} and a dilute hexane solution of C_{60} . When fullerene C_{60} makes a aggregate, the absorption bands are red-shifted and are broadened [16, 17]. Cast film of C_{60} rarely shows absorption peaks in a UV-VIS region. The absorption peaks for all supramolecular assembled films were slightly red-shifted, but the peaks certainly recognized in UV region, which means C_{60} molecules are almost separated each other. These C_{60} films were transferred onto glass slide when the molecular area is around $1 \text{ nm}^2/\text{molecule}$, so C_{60} should be encapsulated with the host cavity to isolate them.

3.4 Lateral force microscopy and friction measurement

Figure 4 shows typical height profile and friction loop for the $C_{60}/CA6$ assembled film. The films were deposited on the silicon wafer by the inverse Langmuir-Scheafer method when the average occupied areas were 2.0 nm^2 per one C_{60} . Height profile shows that two isolated islands of the supermolecules exist in this molecular occupied area region. The difference in the outputs between two scans is proportional to the actual lateral force of the monolayers. The assembled film exhibited a lower lateral force than bare silicon surface. The frictional coefficients obtained by

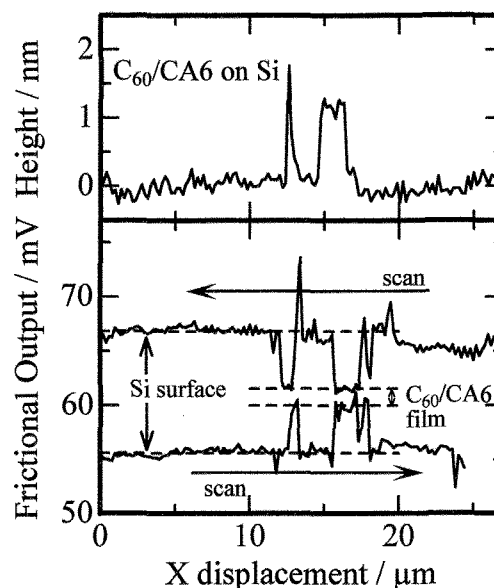


Figure 4. Height profile (top) and friction loop (bottom) for the $C_{60}/CA6$ assembled film on Si wafer.

the surface tester were 0.023 for $C_{60}/CA6$ monolayer and 0.67 for Si wafer. These results showed that the deposited film acts as a lubricant. However, the $C_{60}/CA6$ assembled film had higher friction coefficient, 0.45, when the film was deposited at well-compressed state, $1.0 \text{ nm}^2/\text{molecule}$. The phenomena shows that the low frictional force could be attributed to the rotation of fullerene C_{60} in the host cavity. The lubrication efficiency is dependent on the loading force as shown in Figure 5. At lower loading force, the film was sufficient lubricant, e.g. when the loading force was 0.60 nN, the friction forces were 0.43 nN and 1.89 nN for the supramolecular assembled film and Si wafer, respectively. Figure 6 shows lateral forces for $C_{60}/CA6$ monolayer and C_{60} aggregated film. Friction coefficients are 0.25 and 0.55 for $C_{60}/CA6$ monolayer and C_{60} aggregated film, respectively. The $C_{60}/CA6$ monolayer had smaller friction

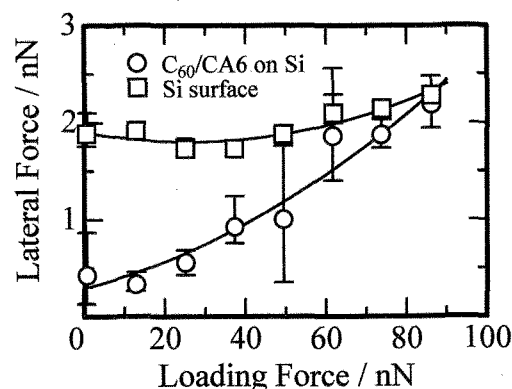


Figure 5. Loading-force dependence of friction force of the C_{60}/CA assembled film. The film was deposited on the silicon wafer at 0 mN/m and $2.0 \text{ nm}^2/\text{molecule}$.

coefficients than that reported previously for the C_{60} thin films [3]. The C_{60} /CA6 monolayer is atomically flat [9] and that seems to make the friction lowered.

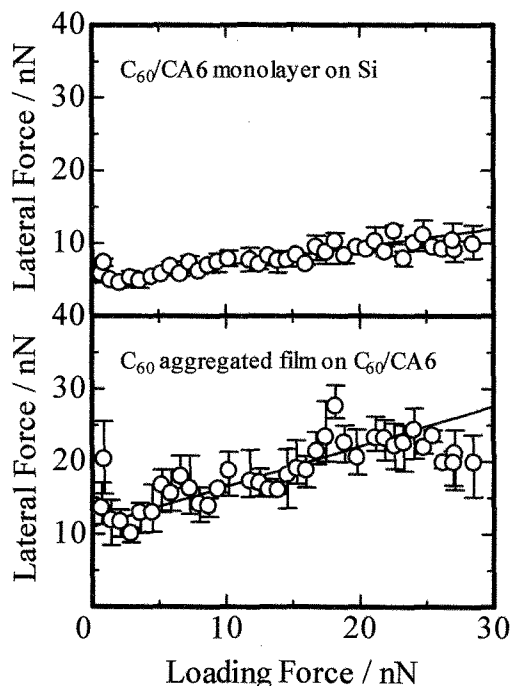


Figure 6. Lateral force for the C_{60} films as a function of loading force. C_{60} /CA6 monolayer (top) and C_{60} aggregated film (bottom) were transferred on the silicon wafer at 2 mN/m.

3.5 Wear resistance

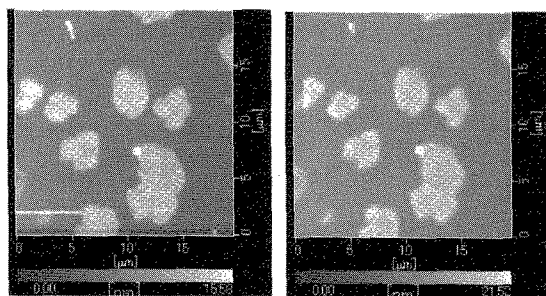


Figure 7. AFM images of C_{60} /β-CD assembled films before (right) and after (left) scratching with an AFM tip. The film was deposited on Si wafer at 0 mN/m and 2.0 nm²/molecule.

Figure 7 provides the representative height images for the C_{60} /β-CD assembled films before and after scratching with an AFM tip at the top limit of loading force, 99.5 nN. Two images had almost the same feature, which shows that the C_{60} films do not wear at this loading force. The C_{60} film had a high wear resistance comparing with same monolayers of poly(alkyl acrylate) which wear easily at 0.1 nN [18]. The supramolecule is consisted with a hydrophobic C_{60} and a hydrophilic host molecule. The polar OH groups in the host molecules would increase the affinity between the supramolecular film and native oxide on silicon surface to show this high resistance against wearing.

4. CONCLUSIONS

Supramolecular assembled films of fullerene C_{60} were prepared and their nanotribological behavior has been investigated with lateral force microscope and surface property tester. The supramolecular assembled film showed lower lateral force and friction coefficients than silicon wafer, which showed that the films acted as solid lubricant. The scratching test with AFM revealed that the supramolecular films had high wear resistance comparing with other solid lubricants made from polymer monolayers.

5. ACKNOWLEDGEMENT

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