Microtribological properties of a novel C_{60}-containing self-assembled film

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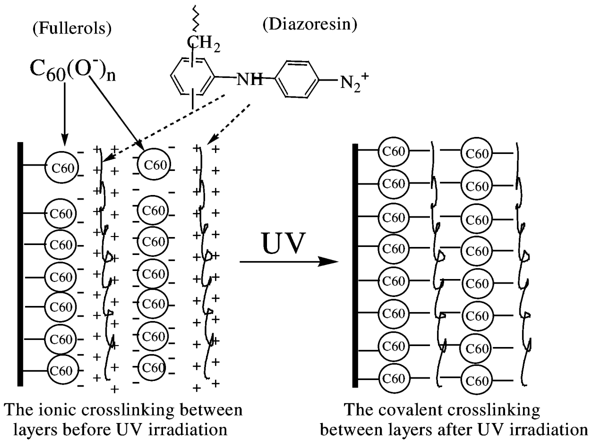
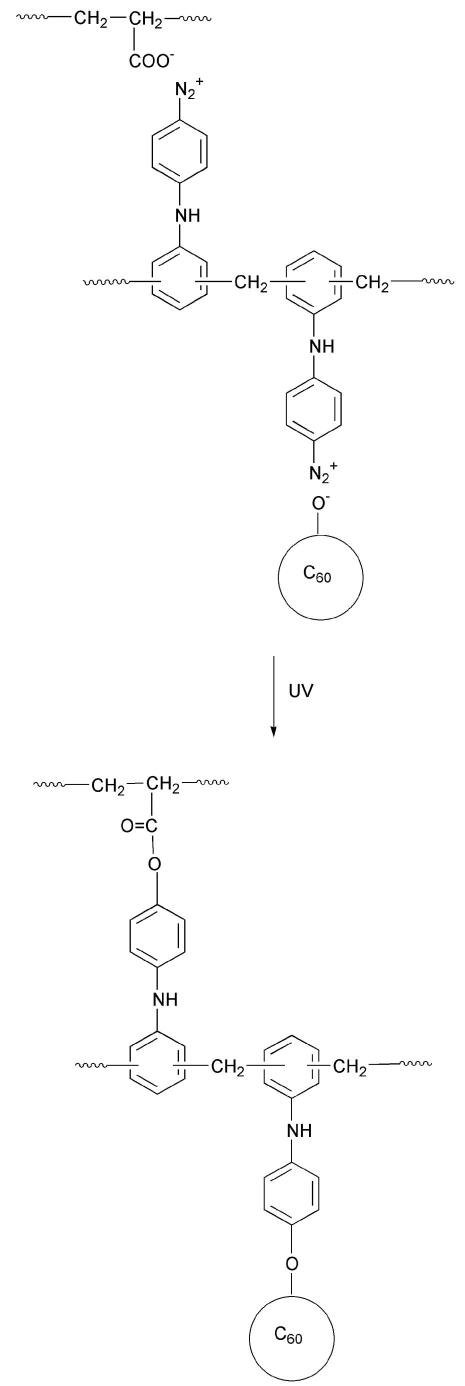
Using the self-assembly technique, we have fabricated a novel, ternary-component ultra-thin film based on rigid C_{60} molecules and soft poly(acrylic acid) chains through electrostatic attractions with diazoresin. Under UV irradiation, the film is linked by covalent bonds, following the decomposition of diazonium, and shows good stability, contrasting with ionic bond linkages. Using AFM/FFM, the microtribological properties of the ternary film were investigated. Because of the inclusion of rigid molecules and soft polymer chains having a covalent linkage, the film shows not only good load-bearing, but also low friction, properties.

In recent years, there has been increasing interest in the use of ultra-thin organic films as boundary lubricants in several technological applications, such as information storage devices and micromechanical systems.[1] In addition, the tribological properties of C_{60} films have been widely studied because of their structural uniqueness and chemical identity.[2–4] Despite the theoretical prediction of exceptional rigidity and load-bearing capacity,[3] experimental observations of the lubricating properties of C_{60} films have been inconsistent.[4] Although low frictional properties of the films have been reported, the accompanying wear and the mobility of wear debris complicate the characterization of C_{60} films. Moreover, many of the C_{60} films reported thus far exhibit "island" formation due to insufficient coverage or aggregation by sublimation of C_{60} onto the substrates.[5] To overcome these difficulties, researchers have explored the attachment of C_{60} moieties to the tail groups of self-assembled monolayers.[3,6] Common methods to produce mono- or multi-layer thin films are Langmuir–Blodgett (L-B)



Scheme 1 Schematic illustration of the structural changes in the $C_{60}(OH)_n$-DR-PAA multi-layer film under UV irradiation.



Scheme 2 The photoreaction occurring in the multi-layer film fabricated from $C_{60}(OH)_n$, DR and PAA.

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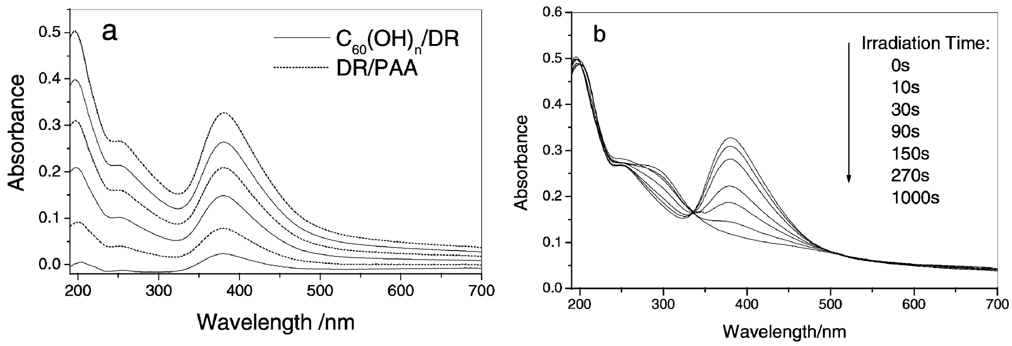

Fig. 1 (a) UV-vis spectra of the multi-layer film fabricated from $C_{60}(OH)_n$, DR and PAA with three cycles: (——) absorbance determined after fabrication of a DR-$C_{60}(OH)_n$ layer, (······) absorbance determined after fabrication of a DR-PAA layer. (b) UV-vis spectra of the three-cycle film irradiated under UV light (230 μW, 360 nm) for different times.

deposition[7] and self-assembly techniques.[8] But most L-B films are bonded to the substrate by weak Van der Waals forces, and common self-assembled films are linked by electrostatic attractions, hydrogen bonds or charge transfer, thus the interaction between layers is too weak for films to bear load and wear. In this short communication, we report the fabrication of a novel ternary film from fullerol [$C_{60}(OH)_n$], diazoresin (DR), and poly(acrylic acid) (PAA), which covalently attach between layers after UV irradiation (as shown in Scheme 1). The microtribological properties of the C_{60}-containing multi-layer film were initially investigated by atomic force microscope/friction force microscope (AFM/FFM). In our novel ternary film, the soft polymer chains are reasonably expected to reduce friction efficiency, while the C_{60} cores are expected to be beneficial for the load-bearing capacity.

In our previous works, some multi-layer thin films from diazoresin were prepared *via* H-bonding or electrostatic self-assembly techniques. Following the decomposition of the diazonium group under UV irradiation, all of the films are attached by covalent bonds and become stable towards polar solvents.[9] Using this distinctive property of diazoresin, we have fabricated a C_{60}-containing film through the self-assembly technique; the linkage between the film layers is ionic, which can easily be converted into covalent bonds under UV irradiation.[10]

Diazoresin is a photosensitive polymer, which has an abundance of diazonium group on its chain. While some of the diazonium groups (cationic) can link with the hydroxyl groups of $C_{60}(OH)_n$, the remainder can link with the carboxyl groups of PAA through electrostatic attractions; thus we can get a –BABCBABC– type ternary composite film layer-by-layer, where A, B, C represent $C_{60}(OH)_n$, diazoresin and poly(acrylic acid), respectively. When the ternary composite film is submitted to UV light irradiation, the ionic bonds in both the DR-$C_{60}(OH)_n$ and DR-PAA layers will be converted into covalent bonds, as shown in Scheme 2.

The self-assembly procedure can be simply described as follows. A quartz slide or freshly cleaved mica was used as the substrate. Firstly, the wafer was immersed in aqueous DR solution (0.5 mg ml^{-1}) for 5 min, rinsed with deionized wafer for 3 min and dried. It was then immersed in an aqueous solution of $C_{60}(OH)_n$ (0.5 mg ml^{-1}) for 5 min, rinsed with deionized water for 3 min and dried. Subsequently the wafer was again immersed in the DR solution, and after rinsing and drying it was immersed in an aqueous PAA solution (0.5 mg ml^{-1}) for 5 min, rinsed with deionized water for 3 min and dried to complete a full fabrication cycle. In each cycle of immersion into DR plus $C_{60}(OH)_n$ or DR plus PAA solutions, a bilayer of DR-$C_{60}(OH)_n$ or DR-PAA is formed on the substrate. Fig. 1(a) shows the UV-vis spectra of $C_{60}(OH)_n$-DR-PAA films recorded on a Shimadzu 2100 spectrophotometer on a quartz wafer to trace the self-assembly process.

The mica or quartz substrates present a negatively charged surface. Diazoresin, which is cationic, is easily absorbed onto these substrates through electrostatic interactions. Subsequently, the fullerol or poly(acrylic acid) can be easily attracted to the DR molecules. This process was investigated in detail by Caruso *et al.*[11] The absorbance at 380 nm is assigned to the absorption of the diazonium group of DR. From Fig. 1(a), we can see that the stepwise fabrication is regular, which indicates that both $C_{60}(OH)_n$ and PAA are incorporated into the films by linking with diazonium groups. Since the diazonium group is photosensitive, it decomposes very easily under UV irradiation, as shown through disappearance of the 380 nm band [Fig. 1(b)].

The morphology and microtribology measurements of the ultra-thin films were performed by AFM/FFM with a Nanoscopy IIIa (Digital Instruments, Inc.) equipped with a bioscope G scanner in contact mode. A commercial Si_3N_4 cantilever with spring constants of $K = 0.06$ N m^{-1} was used to obtain the roughness and friction images in air at 25 °C and 50% relative humidity. The typical scan rates were 2 Hz. Roughness images and the RMS (roughness mean square) were obtained simultaneously when the scan angle was 0°. Friction images in trace and retrace scan directions were recorded when the scan angle was 90°, the friction forces (V) were then plotted as a function of load to yield a friction–load map.[12]

We have studied the surface morphology of the DR-$C_{60}(OH)_n$ film (1 bilayer on mica substrate) before UV irradiation in contact mode of AFM. Because of the relatively weak interaction of the ionic bond between the layers, the film is easily scratched by the tip in contact mode at a low load of

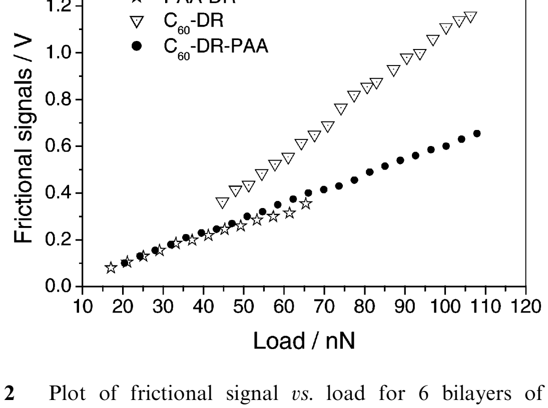

Fig. 2 Plot of frictional signal *vs.* load for 6 bilayers of DR-$C_{60}(OH)_n$, DR-PAA and $C_{60}(OH)_n$-DR-PAA films.

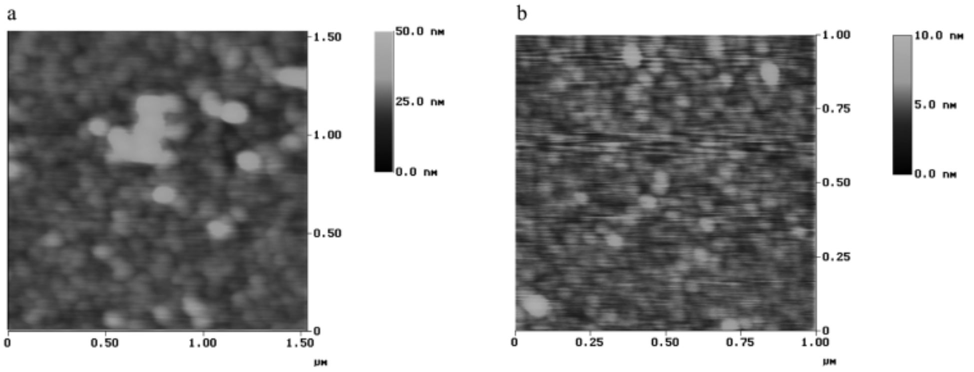

Fig. 3 Morphology of the (a) DR-$C_{60}(OH)_n$ and (b) $C_{60}(OH)_n$-DR-PAA films.

about 10 nN, and thus the microtribological study of the film could not proceed further.

Fig. 2 shows the friction force signal *versus* applied load for three kinds of UV-irradiated films. In contrast with the un-irradiated films, the irradiated films show significantly increased load-bearing properties in contact mode of AFM/FFM. All the tribologic measurements of the three films were carried out in succession with the same V-shaped cantilever tip under the same conditions. The force curves of each film were found to be uniform before and after the measurement, which confirms that the tip is not contaminated with molecules from the films.

From the data shown in Fig. 2, for the DR-PAA self-assembled film, a low friction force and low load-bearing ability are clearly observed; this film can be considered to have good lubrication properties but insufficient load-bearing capacity. Comparably, the load-bearing properties of the DR-$C_{60}(OH)_n$ film are obviously very good. Because of the limitations of the AFM/FFM device, the applied load cannot be further increased; the C_{60}-containing film shows no damage under the highest applied load. The subsiding disadvantage of the DR-$C_{60}(OH)_n$ self-assembled film is the low lubrication function corresponding to the applied load. The ternary $C_{60}(OH)_n$-DR-PAA composite film combines the merits of the DR-PAA and DR-$C_{60}(OH)_n$ films as it exhibits both good load-bearing (or anti-wear) properties and a better lubrication capacity, compared to the DR-PAA and DR-$C_{60}(OH)_n$ films.

To understand the characteristic microtribological properties of the three films, the roughness of UV-irradiated DR-$C_{60}(OH)_n$ (6 bilayers) and ternary $C_{60}(OH)_n$-DR-PAA (6 bilayers) composite films were obtained in contact mode of the AFM and are shown in Fig. 3. The surface roughness (RMS) of the DR-$C_{60}(OH)_n$ self-assembled film is 1.618 nm. The film readily forms an "island" structure, because the diazoresin has a hydrophobic chain containing many phenyl groups and thus has a tendency to aggregate under UV irradiation. The surface roughness (RMS) of the ternary $C_{60}(OH)_n$-DR-PAA composite film is 0.567 nm and the film is very flat, as shown in Fig. 3(b), which can be attributed to the fact that the soft PAA chain lying on the film surface can gloss over the "island" structure formed by the DR-$C_{60}(OH)_n$ layers through segment movement. The soft PAA layer on the outside of the film can also reduce friction force, while the rigid C_{60} molecules embedded in the film can endure a higher load. Thus, this novel ternary film supports the prediction that it would have better anti-wear and lubrication properties and may have potential use as a good solid lubricant in microelectromechanical systems.

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