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Mechanical properties of polyelectrolyte multilayer self-assembled films

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Abstract

The mechanical properties of electrostatic self-assembled multilayer films from polyacrylic acid (PAA) and C_{60}-ethylenediamine adduct (C_{60}-EDA) or poly(allylamine hydrochloride) (PAH) were evaluated by atomic force microscopy (AFM) wear experiments. Because of the higher molecular weight of PAH, the wear resistance of the $(PAH/PAA)_{10}$ film is higher than that of the $(PAH/PAA)_2(C_{60}\text{-EDA/PAA})_8$ film; that is, the former is mechanically more stable than the latter. The mechanical stability of both films can be improved significantly by heat treatment, which changes the nature of the linkage from ionic to covalent. The AFM measurement also reveals that the $(PAH/PAA)_2(C_{60}\text{-EDA/PAA})_8$ film is softer than the $(PAH/PAA)_{10}$ film. The friction properties of the heated films were measured. These films can be developed as potential lubrication coatings for microelectromechanical systems.

Keywords: Polymers; Multilayers; Tribology; Atomic force microscopy

1. Introduction

The so-called "layer-by-layer" (LBL) self-assembly or electrostatic self-assembly (ESA) is a relatively new method to fabricate organic ultrathin films [1,2]. By alternately dipping an initially charged surface in a polycation and a polyanion solution, a coating is easily fabricated with finely controlled thickness and composition [3]. This method has received a growing amount of attention since it was first introduced in 1991 [1]. A large number of bio-, electro- or photoactive thin films have been prepared by incorporating biopolymers, electroactive polymers or photoactive polymers into the films [4–6].

For their application, some fundamental characteristics, such as optic and electrical properties, are also important issues. Recently, the electrical (dielectric and impedance) characteristics of certain ESA films have been examined carefully by Durstock and Rubner [7] in terms of temperature, moisture content and deposition conditions. Mechanical properties are another important issue for the application; however, little is known about these properties up to now [3].

Investigations of the mechanical properties of ESA films have been limited mostly to tape peel tests so far [3]. The introduction of the scanning force microscopy (SFM) technique opened the possibility to study the surface mechanical properties with a submicron resolution. In a SFM experiment the tip acts as a model single-asperity contact, combining careful control of the applied force with in situ microscopic analysis of the modified region. So it is easy to examine the effect of tip scanning on the surface and evaluate the mechanical wear stability. In this paper, mechanical properties of several ESA films were evaluated using this method. Their microtribological properties were also reported.

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2. Experimental details

2.1. Materials and instruments

C_{60}-ethylenediamine adduct (C_{60}-EDA) was synthesized according to Ref. [8]. Element analysis results correspond to $C_{60}(NH_2CH_2CH_2NH_2)_4$ (C: 57.93, N: 8.38 and H: 3.44). Its hydrochloric salt was obtained by reacting with hydrochloric acid [9]. Polyacrylic acid (PAA) was prepared at 70 °C by free radical polymerization of acrylic acid in water using isopropyl alcohol as a chain transfer agent and potassium persulfate as an initiator. Poly(allylamine hydrochloride) (PAH) (average molecular weight ca. 70,000) was obtained from Aldrich.

Ultraviolet–visible (UV–vis) spectra were measured on a Shimadzu UV 1601 PC spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on a Bruke Equinox 55 FT-IR/FAR 106 spectrophotometer.

2.2. Self-assembled film fabrication

For the substrate, quartz and silicon slides were treated before use in boiling H_2O_2–H_2SO_4 mixture (3:7 v/v) for 30 min. They were washed with water thoroughly and then air-dried. The slides were first immersed in a cationic solution (C_{60}-EDA or PAH) for 4 min and then washed with water thoroughly. They were then immersed in a PAA solution (pH 7) for another 4 min, followed by washing with water thoroughly. Films were fabricated by repeating this deposition cycle. Before the deposition of C_{60}-EDA/PAA bilayers, two bilayers of PAH/PAA were first synthesized.

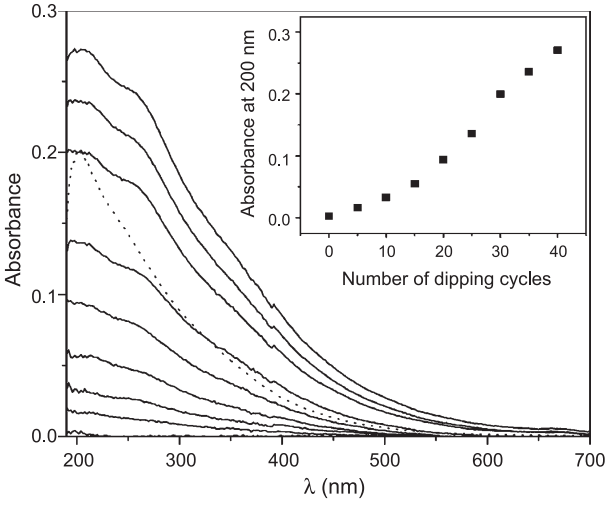

Fig. 1. The absorption spectra of the self-assembled film from C_{60}-EDA and PAA with various dipping cycles. Number of dipping cycles (from bottom to top): 1, 5, 10, 15, 20, 25, 30, 35 and 40. The dashed line is the spectrum of C_{60}-EDA.

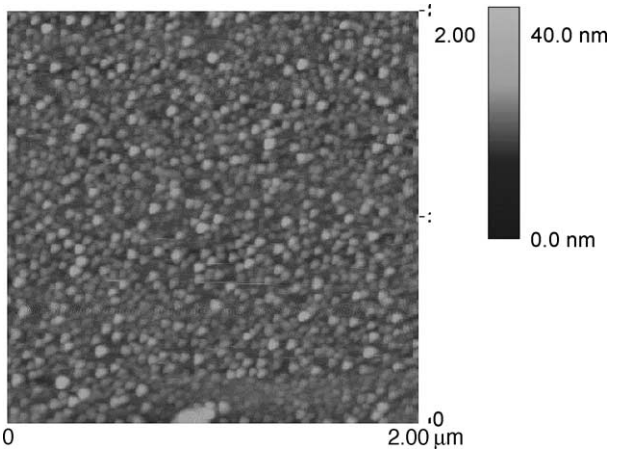

Fig. 2. Tapping mode AFM image of a $(PAH/PAA)_2(C_{60}$-EDA$/PAA)_4$ film on silicon slide.

2.3. Micromechanical property measurement

The morphology and microtribology measurements were performed by atomic force microscopy (AFM)/friction force microscopy on a Nanoscopy IIIA (Digital Instruments) equipped with a bioscope J scanner in contact mode. A commercial Si_3N_4 cantilever with a spring constant of K=0.06 N m^{-1} was employed. Tapping mode images were obtained using commercial silicon probes (model TESP-100) with a typical resonant frequency around 300 KHz. For wear resistance testing, contact mode scanning was done within a selected 1×1 μm area at different normal loads. The extent of the surface modification was then determined by re-imagining at lower load and magnification. Friction forces were obtained from scanning probe microscopy friction loops under different normal loads. All measurements were carried out in air at room temperature and a relative humidity of about 30%.

3. Results and discussion

3.1. Film fabrication

In this study we chose PAA as polyanion and C_{60}-EDA and PAH as low- and high-molecular-weight polycations, respectively, to fabricate self-assembled films. UV–vis absorption spectra were used to trace the fabrication process of the C_{60}-EDA/PAA film. As shown in Fig. 1, the absorption spectra of the film are almost identical to that of C_{60}-EDA since PAA is almost transparent in this range. The absorption intensity of the film increases with increasing dipping cycle number, indicating the fabrication is successful, but poor linearity between the absorbance at 200 nm and the dipping cycle number was found (see inset). Films from PAA and PAH and ternary films containing PAA, PAH and C_{60}-EDA were fabricated in the same way.

The morphology of resulting films was studied by AFM in tapping mode. A typical image was shown in Fig. 2. The