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NANO-TRIBOLOGICAL STUDY ON A SUPER-HYDROPHOBIC FILM FORMED ON ROUGH ALUMINUM SUBSTRATES*

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ABSTRACT: A novel super-hydrophobic stearic acid (STA) film with a water contact angle of 166° was prepared by chemical adsorption on aluminum wafer coated with polyethyleneimine (PEI) film. The micro-tribological behavior of the super-hydrophobic STA monolayer was compared with that of the polished and PEI-coated Al surfaces. The effect of relative humidity on the adhesion and friction was investigated as well. It was found that the STA monolayer showed decreased friction, while the adhesive force was greatly decreased by increasing the surface roughness of the Al wafer to reduce the contact area between the atomic force microscope (AFM) tip and the sample surface to be tested. Thus the friction and adhesion of the Al wafer was effectively decreased by generating the STA monolayer, which indicated that it could be feasible and rational to prepare a surface with good adhesion resistance and lubricity by properly controlling the surface morphology and the chemical composition. Both the adhesion and friction decreased as the relative humidity was lowered from 65% to 10%, though the decrease extent became insignificant for the STA monolayer.

KEY WORDS: nano-tribology, adhesion, friction, super-hydrophobic, AFM/FFM

1 INTRODUCTION

The fast developing micro-electro-mechanical systems (MEMS) are known for their superior performance and low unit cost[1]. The large surface-area-to-volume ratios, however, raise serious adhesive and frictional problems for their operations.With typical surface separations in the range of 500~2000 nm, water droplets can be easily entrapped in the micromachined structures of high surface tension and produce strong capillary forces[2]. In order to alleviate these adhesive related problems, both the topography and the chemical composition of the contacting surfaces must be controlled in order to reduce the surface hydrophilicity and hence decrease the adhesion. As apart of the efforts in this respect, the surfaces with super-hydrophobic (with water contact angles above 150°) properties have been largely focused on and several typical super-hydrophobic surfaces been successfully prepared[3~11]. Nevertheless, the report on the tribological studies of super-hydrophobic surfaces has been so far unavailable, though which is imperative to the tribology research and engineering application of the surfaces.

In a previous study, we reported a novel ultrathin film with super-hydrophobic properties, prepared by chemically adsorption of stearic acid onto the polyethyleneimine coated rough Al surface[12]. The present article deals with the adhesive and frictional behaviors of the super-hydrophobic film.

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2 EXPERIMENT SECTION

2.1 Materials

The polyethyleneimine solution (-[$C_2H_5NHC_2H_5$-$N(C_2H_5NH_2)C_2H_5NH]_n$-, MW is 50 000 ~ 60 000, coded as PEI) with a concentration of 50 wt.% in water was obtained from ACROS (New Jersey, USA). Analytically pure stearic aicd (abridged as STA) and N,N'-dicyclohexylcarbodiimide (DCCD) were commercially obtained from Shanghai Sheshan Chemical Plant of China and used after purification. The solvent n-hexane (purity > 98%) was used as received.

2.2 Preparation of the Super-hydrophobic Film

Polished aluminum wafer substrate was boiled in water for 5 minutes to allow the surface roughening and hydroxylating. Since the branched PEI with primary and secondary amino groups can be easily adsorbed onto any hydroxylated solid surfaces through hydrogen bonds and van der Waals forces[13~16], while the primary and secondary amine groups in PEI can be readily modified by phosgene, thiophosgene, cyanuric chloride and glutaraldehyde[13], thus a layer of PEI was first prepared on the rough Al surface by immersing it into a dilute aqueous solution of PEI of 0.2 wt.% for 15 min. After rinsing with ultra-pure water, the PEI-coated Al substrates were then put into a dilute solution of STA and DCCD mixture in n-hexane. At the completion of a reaction duration of 24 h, a monolayer of STA was presumably produced on the top of the PEI film since the amine groups of the PEI could react with the STA molecules to form chemical bonds. At the end of the reaction, the samples were sequentially washed with n-hexane, acetone, and ultra-pure water in order to get rid of the physically adsorbed impurities. As determined by ellipsometric measurment, the overall thickness of the PEI coating and the STA monolayer was about 3.4 nm.

2.3 Characterization of the Super-hydrophobic Film

The contact angles of water on various surfaces were measured with a contact-angle goniometer (Model 100-00; Ramé-hart Inc, USA). The topographies and nano-tribological properties of the films were evaluated on an atomic force microscope (AFM) controlled by RHK electronics (RHK Technology, Rochester Hills, MI, USA), using commercially available Si_3N_4 cantilevers/tips with a nominal force constant of 0.5 N/m and tip radius of less than 50 nm (Park Instruments, Sunnyvale, CA, USA). To obtain the adhesive force between the AFM tip and the sample surface, the force-distance curve was recorded and the pull off force reckoned as the adhesive force, which was calculated according to the method reported[17]. All the friction and adhesion tests were conducted at room temperature and relative humidity of 10% or 65%.

3 RESULTS AND DISCUSSION

3.1 Wettability

It is well known that the water contact angles on smooth hydrophobic surfaces are generally not exceeding 115° ~ 120°. For example, the contact angles of water on self-assembled monolayers of long chain hydrocarbon and fluorocarbon are about 112° and 115°, respectively[18]. However, the situation will be quite different when the surface is roughened[19]. Such a kind of roughening can be well illustrated as in Fig.1, where the AFM images of the original aluminum wafer and that boiled in water for 5 min indicate that a rougher aluminum surface is prepared after boiling, with the surface roughness rms increasing from 1.2 nm to 18.5 nm.

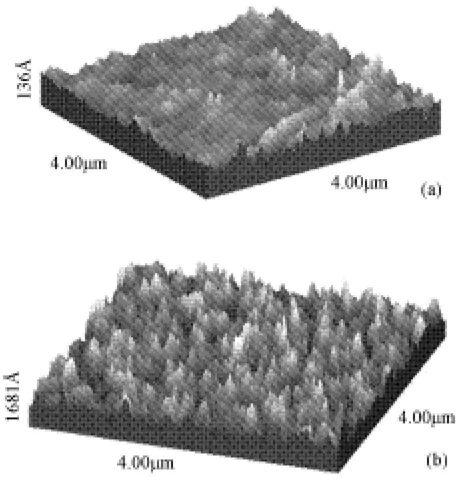


Fig.1 AFM images of polished aluminum wafer (a) and that boiled in water for 5 min (b)

Table 1 shows the surface roughness and contact angles for water on various surfaces. The contact angle of water on the polished Al surface is about 62°, it decreases to be less than 5° after the Al was boiled in water or coated with PEI, indicating that both the rough and PEI-coated Al surfaces are strongly hydrophilic. Once the STA monolayer is generated on the PEI coating, the water droplet thereon is spherically-shaped (as shown in Fig.2) and has a

Table 1 Surface roughness and water contact angles for various surfaces studied

Surface	Polished Al	Rough Al	PEI	STA
surface roughness/nm	1.2	18.5	22.0	21.3
contact angle/(°)	62	< 5	< 5	166

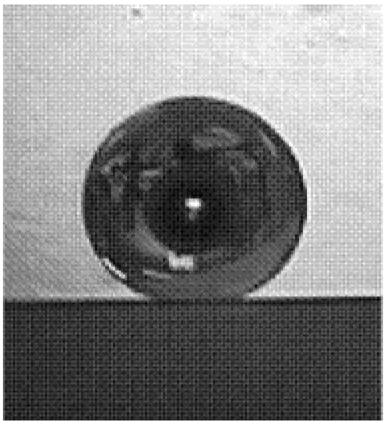


Fig.2 Photo of a water droplet ($\sim 3\,\mu$L) on a rough STA monolayer surface with super-hydrophobicity

contact angle as high as 166°, indicating that the STA monolayer on the PEI-coated Al surface is super-hydrophobic. As discussed elsewhere[12], the composite interface is supposed to be responsible for the super-hydrophobic behavior of the STA monolayer. In other words, due to the larger roughness and the STA of hydrophobicity, air was entrapped in the crevices to form a composite interface when water droplets were placed on the rough STA monolayer surface. According to Cassie's equation[20], the fraction of air in the composite interface is calculated to be 96%. This means that the composite interface is almost totally possessed by air, which makes the film surface extremely water-repellent.

3.2 Nano-tribological Behavior

The adhesive forces between the AFM tip and the sample surfaces at different relative humidity are shown in Fig.3. Relative strong adhesion is observed on the polished Al surface. Once the Al substrate is boiled in water, or coated with PEI or STA monolayer, the adhesive forces are greatly decreased. The smallest adhesive force is recorded on the STA super-hydrophobic surface. It is also seen that relative humidity has an important influence on adhesion. Namely, the adhesive forces increase with increasing relative humidity from 10% to 65%, However, the sensitivity of the adhesion to the humidity is different for various surfaces. For example, the polished Al surface registers an adhesion force increase of 6.3 nN at relative humidity 65% than 10%, while the other three surfaces record an adhesion force increase of only about 1 nN under the same conditions. Tsukruk et al. studied the wettability and the adhesive forces of several kinds of self-assembled monolayers and they reported that the stronger of the surface hydrophilicity, the higher of the adhesive forces[21], which may seemingly contradict to ours. In our experiments, at a relative humidity of 10% and 65%, the adhesive forces are determined to be about 14.4 nN and 20.7 nN for the polished Al surface with a contact angle of 62°, however, they are only about 3.8 nN and 4.9 nN for the rough Al surface, and 3.6 nN and 5.0 nN for PEI surface which have the contact angles less than 5°. Such inconsistency can be well understood by taking into account the great changes in the topography of the polished Al surface after boiling in water (see Fig.1; similar morphologies of the rough Al coated with PEI and STA films are obtained, which are not shown in this paper). On the rough and needle-like Al surface (Fig.1(b)), the contact area between the AFM tip and the film surface will be significantly decreased as compared to that between the relatively smooth polished Al surface and the AFM tip (Fig.1(a)). Thus, the adhesive force is greatly decreased although both the rough Al and PEI surfaces possess strong hydrophilicity. Besides, the hydrophobicity of the film itself may also play an important role in decreasing the adhesion. For example, the lowest adhesive forces are obtained on the super-hydrophobic STA monolayer surface (Fig.3) and which only increases by 0.6 nN (from 2.8 nN to 3.4 nN) when the relative humidity increases from 10% to 65%.

For a further understanding of the effect of rough

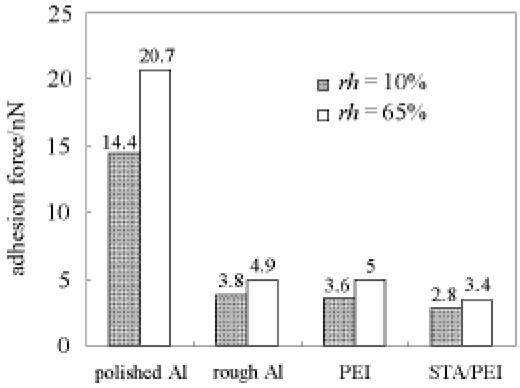


Fig.3 Adhesive forces between an AFM tip and various surfaces at relative humidity of 10% and 65%

surface on adhesion, the adhesive forces at 20 different points on the rough Al surface (Fig.2(b)) are measured at relative humidity of 65% and the results are listed in Table 2. It is seen that the measured adhesion forces show relatively larger scattering, with the smallest value to be only 1.1 nN while the largest one to be as high as 13.6 nN. This is also largely attributed to the contact area between the AFM tip and the rough surface. Such a contact between an AFM tip and the rough surface is schematically illustrated in Fig.4. It is obvious that the contact area at point A is smaller while that at point B larger. Therefore quite different adhesions were measured at points A and B, owing to the different contact area corresponding to points A (weaker adhesion) and B (stronger adhesion).

Table 2 Adhesive forces (nN) at 20 different points on the rough Al surface (relative humidity 65%)

1.1	2.6	4.1	2.8	7.0
4.2	5.2	3.6	1.4	2.6
11.0	3.6	6.6	5.8	3.2
7.0	4.3	13.6	4.8	2.8

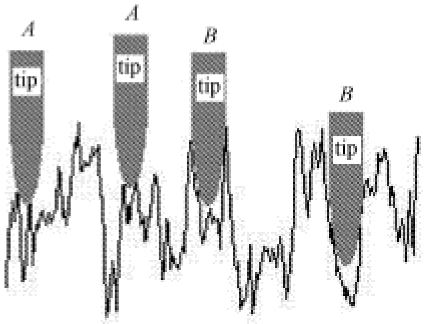


Fig.4 A schematic view of the contact between an AFM tip and a rough surface

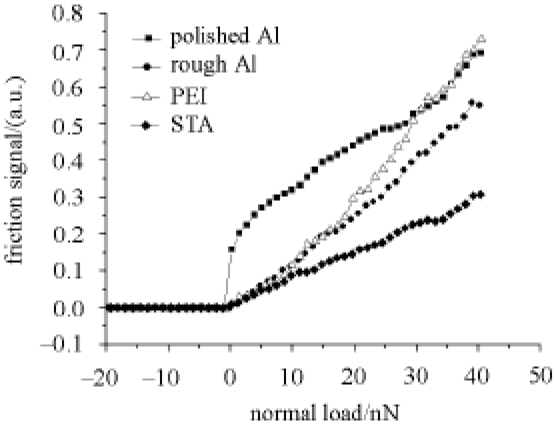
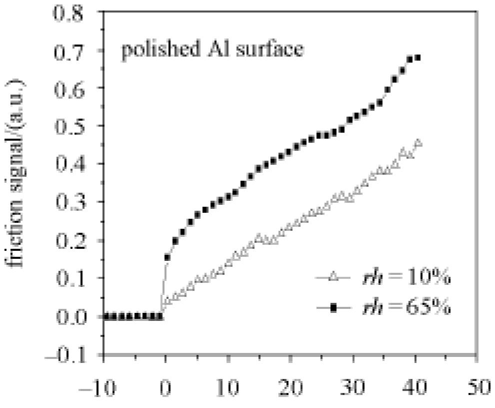


Fig.5 Friction-versus-load curves for various surfaces at a scanning velocity of 0.5 μm/s ($rh = 65\%$)

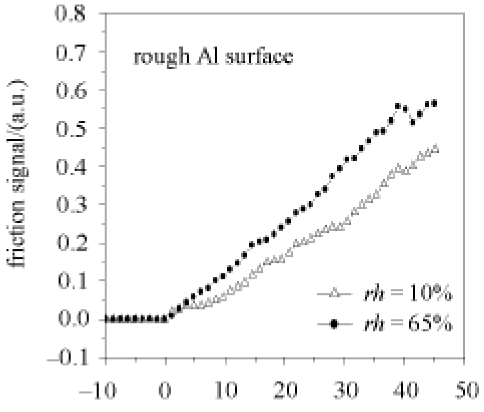
The friction-versus-load curves for various surfaces at a humidity of 65% are shown in Fig.5. Although these curves show somewhat irregularity in shape, they have some common features. First, the STA super-hydrophobic film possesses good lubricity as compared with the other surfaces, because the long-chains of STA molecules with one end attached to the substrate surface have a significant freedom to swing and rearrange along the sliding direction under shear stress and hence yield a smaller resistance. Secondly, large non-zero friction signal on the polished Al surface is observed at zero external load, which is attributed to the jump-to-contact instability caused by the attractive forces during the approach of the AFM tip to the sample surface and reflects that the polished Al surface has large adhesion. Such a phenomenon is not observed on the other surfaces, which is well consistent with the results shown in Fig.3. Thirdly, although the friction force of the polished Al surface is larger than that of the rough and the PEI-coated Al surfaces, the slopes of the friction-versus-load curves for the latter two surfaces are much bigger than that for the former. Since the curve slope is supposed to be proportional to the friction coefficient of the surface, it is therefore deduced that the friction coefficients of the rough and PEI-coated Al surfaces are larger than that of the polished Al surface, which might be attributed to the larger surface roughness of the rough and PEI-coated Al surfaces. In this respect, the Al surface coated with the STA monolayer will have the smallest friction coefficient, due to the good lubricity of the STA monolayer.

The effect of humidity on friction is also studied, and the results are shown in Fig.6. On the polished Al surface, the decrease of the relative humidity from 65% to 10% results in a friction reduction, while the jump of the tip onto the surface at a zero external load becomes extremely slight. The friction reduction with decreasing relative humidity on both the rougher and PEI-coated Al surfaces becomes insignificant, while the STA super-hydrophobic surface records almost the same friction at relative humidity of 65% and 10%, Since the large variation in the friction corresponds to a large variation in the adhesive force (Fig.3) with the decreasing of the relative humidity from 65% to 10%, the reduction of the friction might be attributed to the decreased adhesion, which is closely related to the surface hydrophobicity and the contact area between the AFM tip and the sample surface, as discussed above.

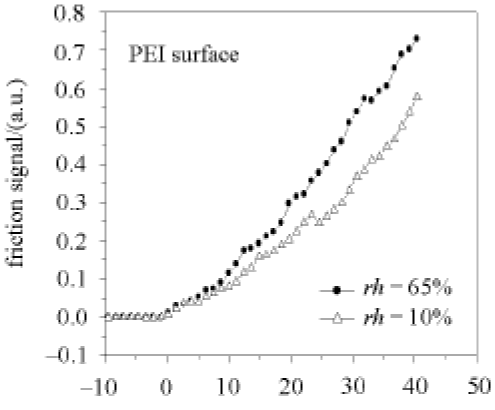
It is worth pointing out that, although the STA superhydrophobic surface possesses good lubricity and adhesion resistance, the super-hydrophobicity does not necessarily lead to super-lubricity. In other words, although the contact angle for water shows an abrupt increase with respect to the PEI-coated Al surface and the STA/PEI-coated Al surface (Table 1), such an abruptness is not reflected in the micro-tribological test results (Fig.3 and Fig.5). This might be because the super-hydrophobicity of the STA surface was originated from the composite interface mechanism but not from a surface with actually super-low surface energy. Thus in terms of the tribological behavior, the STA superhydrophic surface behaves similar as conventional self-assembled monolayers.



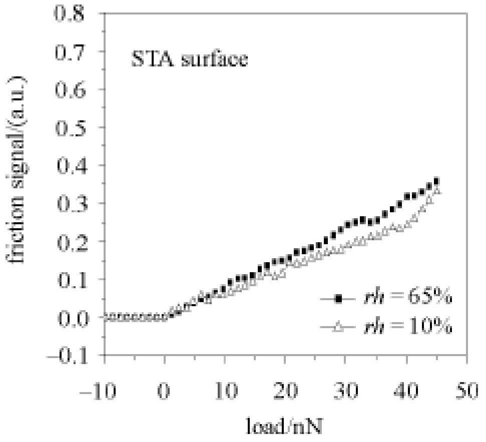
(a)



(b)



(c)



(d)

Fig.6 Friction-versus-load curves for various surfaces at the relative humidity of 10% and 65% and a scanning velocity of 0.5 μm/s

4 CONCLUSIONS

The rough aluminum wafer coated with PEI was made to show super-hydrophobicity with a water contact angle about 166°, by chemically adsorption of an STA monolayer thereon. The composite interface between the water droplet and the STA monolayer surface was supposed to be responsible for the super-hydrophobicity of the composite film. The micro-tribological behavior of the super-hydrophobic STA monolayer was compared with that of the polished and PEI-coated Al surfaces. The effect of relative humidity on the adhesion and friction was investigated as well. It was found that the STA monolayer showed decreased friction, while the adhesive force was greatly decreased by increasing the surface roughness of the Al wafer to reduce the contact area between the AFM tip and the sample surface. Thus it might be feasible and rational to prepare a surface with good adhesion resistance and lubricity by properly controlling the surface morphology and the chemical composition. Both the adhesion and friction decreased as the relative humidity was lowered from 65% to 10%, though the decrease extent became insignificant for the STA monolayer. The findings that the surface nanostructures (including chemical composition) were close related to the tribological properties might be instructive and referenced to seek for resolving of the tribological problems in MEMS.

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