Macromol. Symp. 2008, 264, 73–79 DOI: 10.1002/masy.200850412

Polymer-Based Superhydrophobic Coating Fabricated from Polyelectrolyte Multilayers of Poly(allylamine hydrochloride) and Poly(acrylic acid)

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Summary: Superhydrophobic films mainly based on poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) polyelectrolyte multilayer have been deposited onto cleaned glass substrate by a layer-by-layer dip coating method. 3 bilayers of the PAH and PAA was directly coated onto the substrate as an underlying layer for subsequent coating. Desired surface roughness on the polyelectrolyte bilayers was created by etching the bilayers in hydrochloric acid solution so as to create the open pore having suitable size at the surface. Then, nanoparticles such as SiO_2 and TiO_2 of various sizes were deposited onto the etched polyelectrolyte bilayers. Finally, the surfaces were further modified with semifluorinated silane followed by cross-linking at 180 °C for 2 h to obtain desirable surface morphological features. The effect of etching time and addition of nanoparticles on surface morphology was investigated using an atomic force microscope (AFM). Wetting ability of the prepared film was determined by measuring water droplet contact angle using a goniometer. Adhesion between the superhydrophobic films and the substrate was evaluated by using a standard tape test method (D3359). The adhesion was improved by reducing the organic content in the films.

Keywords: poly(acrylic acid); poly(allylamine hydrochloride); polyelectrolyte; superhydrophobic

Introduction

The surface having high hydrophobic and self-cleaning property is generally found in nature such as butterfly's wing and lotus leaf. The best known example of a superhydrophobic self-cleaning surface is the lotus leaf. It consists of protruding nubs, which are about 20–40 micrometer apart and the whole surface is covered with tiny waxy crystal of about 0.2–2 microns.[1] Such feature makes the surface superhydrophobic. When water droplets roll off the leaf surface, they carry off dirt, leaving the surface perfectly clean. Scientists have tried to fabricate the substrate's surface similar to natural surface to make it superhydrophobic because of its promising practical applications including water-repellence, self-cleaning and anti-fouling. Techniques used for preparation of the superhydrophobic surface can be simply classified into two categories. One is making a rough surface from a low surface energy material.[2–5] The materials having low surface energy used to make the superhydrophobic surface are fluorocarbon, silicones and organic materials (polyethylene, polystyrene, etc.), and inorganic materials (ZnO and TiO_2). The other is modifying a rough surface with a material having low surface energy. There are many approaches to create rough surfaces such as mechanical

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stretching, laser/plasma/chemical etching,[6–8] lithography,[9] sol-gel processing,[10] layer-by-layer and colloidal assembly.[7]

This present work attempts to mimic such natural surface feature by controlling surface roughness of the underlying polyelectrolyte layer simply by chemical etching, followed by deposition of oxide nanoparticles such as Degussa P25 TiO_2, Colloidal SiO_2 and fumed SiO_2, and finally thin layer of organic molecules to further lower the surface energy. This method is inexpensive and can be coated on various substrates such as plastics, metals and ceramics with no limitation on shape complexity.

Experimental Part

The glass substrate was ultrasonically washed with cleaning agents (ethanol, acetone and de-ionized water, respectively) and then dried at 60 °C. The cleaned substrate was coated with 3 PAH/PAA bilayers by dipping it in the PAH followed by in the PAA solutions. Desired surface roughness on the bilayers was obtained by etching with hydrochloric acid so as to create the open pore with diameters at micrometer scale in the polyelectrolyte multilayer film. Then, oxide nanoparticle was deposited onto the etched multilayer film, giving the surface roughness at very fine scale. Finally, the surface was modified with low surface energy substance by coating of semifluorinated silane followed by cross-linking at 180 °C for 2 h to preserve desirable surface morphological features.

The effect of etching time (5, 15, 30 and 60 min) and addition of nanoparticles having various types and sizes (shown in Table 1) on the surface morphology and hydrophobicity was also explored. In some experiment, the polyelectrolyte bilayers coated with nanoparticles were heated at a temperature range of 300–500 °C to reduce the organic content before deposition the silane layers. It was expected that such treatment would improve the film's adhesion.

Table 1.
Details of oxide nanoparticles deposited onto the etched polyelectrolyte bilayers.

Name	Types of nanoparticle	Particle size (nm)
P 25 TiO_2	TiO_2	30–60
Colloidal SiO_2	SiO_2	20–25
Fumed SiO_2	SiO_2	40–45

Surface's wetting ability of the prepared films was investigated by contact angle measurement (ram'e-hart instrument co.). Several droplets of de-ionized water were mounted on ten different areas of the film's surface using a microsyring. Photos of water droplets on the film's surface were recorded using a CCD camera, and then a curvature profile was created using the software provided by the manufacturer and finally the contact angle measured. Surface topography was studied by using an atomic force microscopy (AFM, Seiko instrument SPA 400) performed in a non-contact mode. Film's adhesion was evaluated by using a standard tape test method (D3359). An adhesive tape was pressed onto the film's surface and then peeled off. Images of these films before and after tape testing were taken by using an optical microscope to evaluate the films' adhesion.

Results and Discussion

Figure 1 shows AFM images of the surface prepared by modifying the polyelectrolyte bilayers with the P25 TiO_2 and then coated with silane. Photos of water droplet on the film's surface recorded by using a CCD camera are also provided to reflect the films' wetting ability. Contact angle values and surface roughness of these films are summarized in Table 2. As shown in Figure 1, the film surface was quite flat consisting of particles of around 50–100 nm in size. These particles were P25 TiO_2. Note that the particles seen on the film's surface were about double the average size of the P25 TiO_2, indicating that the TiO_2 deposited onto the film were agglomeration of few TiO_2 particles. The average peak-to-valley value was 2.7 nm, providing contact

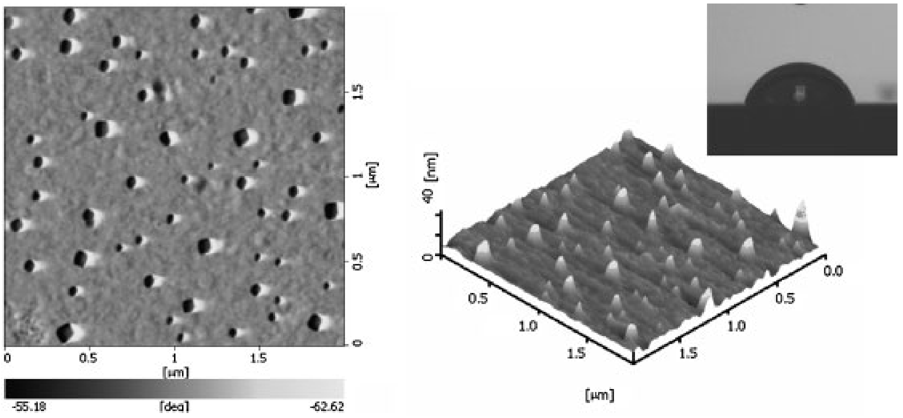

Figure 1.
2-dimensional (left) and 3-dimensional (right) AFM images of the P25 TiO_2-modifiled polyelectrolyte film.

angle of 69 degree. AFM topographical images of the surface prepared by similar manner but the polyelectrolyte film was modified with colloidal SiO_2 are shown in Figure 2. The surface had similar feature to that of the film modified with the P25 TiO_2. However, this film consisted of more and finer SiO_2 particles. Such surface provide the surface roughness of 4.4 nm and give the contact angle of 111 degree.

Surface topography significantly changed when the films were prepared by modifying the bilayers with fumed SiO_2 as shown in Figure 3. It shows hill-like feature rather than protrusion. The surface had much higher surface roughness of about 39 nm and did not consist of particles on its surface as in the case of P25 TiO_2- and colloidal SiO_2-midified samples. This surface had high contact angle of 152 degree, which was superhydrophobic and exhibited self-cleaning characteristics (contact angle $\geq$150 degree). These results gave positive indicator that the approach of using acid etching of the polyelectrolyte film followed by deposition of fumed SiO_2 nanoparticle and low surface energy organic substance is feasible to achieve true self-cleaning property. According to the superhydrophobic theory, the substrate surface requires both appropriate surface roughness and low surface energy. Therefore, it can be explained that the superhydrophobic characteristics of this film resulted from the appropriate particle size of fumed SiO_2 particles (40–45 nm) which are deposited in the suitable pore size of the etched film. Chemical bonding between the silanol group (–Si–OH) of the fumed SiO_2 and the silane may also play an important role. This bonding was not expected in the case of colloidal SiO_2 as it was stabilized by a surfactant.

Table 2.
Summary of the water contact angle and surface roughness of the polyelectrolyte film modified with different nanoparticles.

Sample	Contact angle	Surface Roughness
	(degree)	(nm)
PAH_PAA_ P 25 TiO_2	68.8 ± 2	2.7
PAH_PAA_ Colloidal SiO_2	110.9 ± 4	4.4
PAH_PAA_ Fumed SiO_2		
Etched 5 min	136.4 ± 4	32.1
Etched 15 min	137.7 ± 1	30.4
Etched 30 min	140.3 ± 2	31.9
Etched 60 min	152.4 ± 5	38.9

It is well known that increasing the roughness of a hydrophobic surface can increase its hydrophobicity dramatically. In this research, the diverse porous multilayer films were prepared by etching them in acid solution for different time. The contact angle measurements were carried out on these different films after they were coated with the silane to investigate the relationship between contact angle and etching time (and therefore roughness). The result

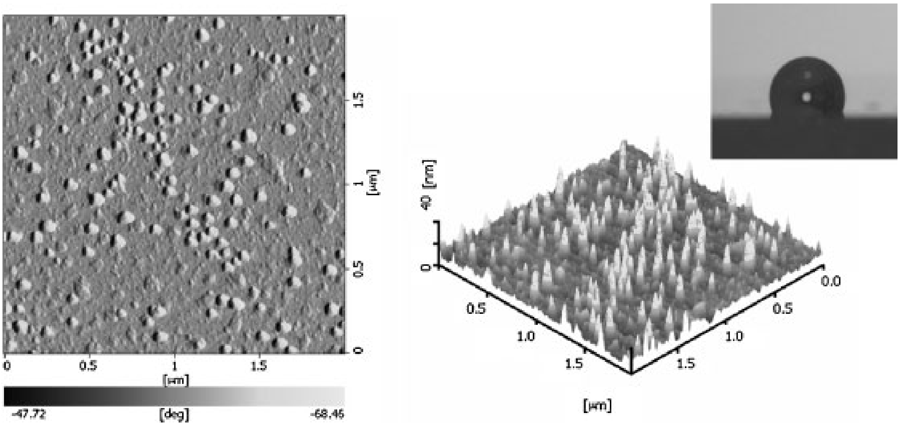

Figure 2.
2-dimensional (left) and 3-dimensional (right) AFM images of the colloidal SiO_2-modified polyelectrolyte film.

is summarized in Table 2. It was found that the water contact angle and surface roughness increased with increasing the etching time. It is believed that the acid treatment at longer time resulted to more porous surface having more suitable pore size for nanoparticle deposition.

Figure 4 shows optical images of the films before and after adhesion test. All the films before adhesion test had uniform and smooth surface. After testing, part of the film detached from the substrate as observed by white regions in the OM images - the larger the white region, the lower the film adhesion. The film adhesion was quantitatively illustrated in Figure 5. It is clearly seen that the as-prepared film had poor adhesion. The adhesion was improved after the polyelectrolyte had been burnt off. The adhesion increased when the polyelectrolyte bilayers was burnt off at higher temperature. The film prepared by heating the polyelectrolyte at 500 °C (referred to as "PAH_PAA_SiO_2_500_FSF") had the best adhesion.

The poor adhesion can be explained based on the content of the polyelectrolyte bilayers which bonded to the substrate. According to thermal analysis result (Figure 6), the PAA had 3 major weight

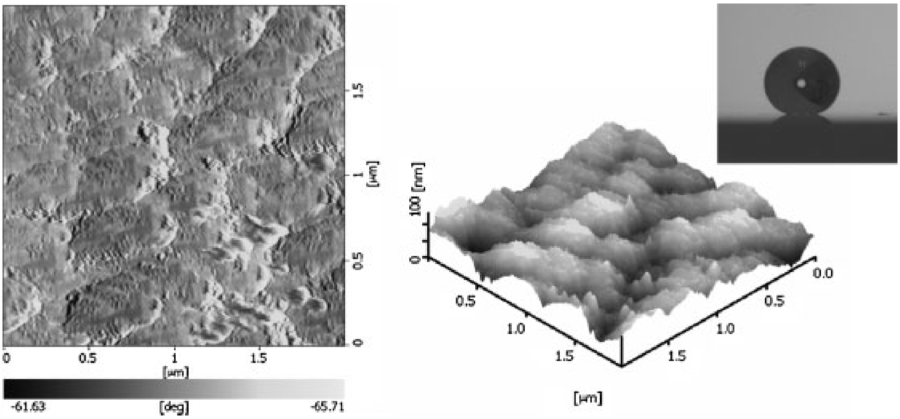

Figure 3.
2-dimensional (left) and 3-dimensional (right) AFM images of fumed SiO_2-modified polyelectrolyte film.

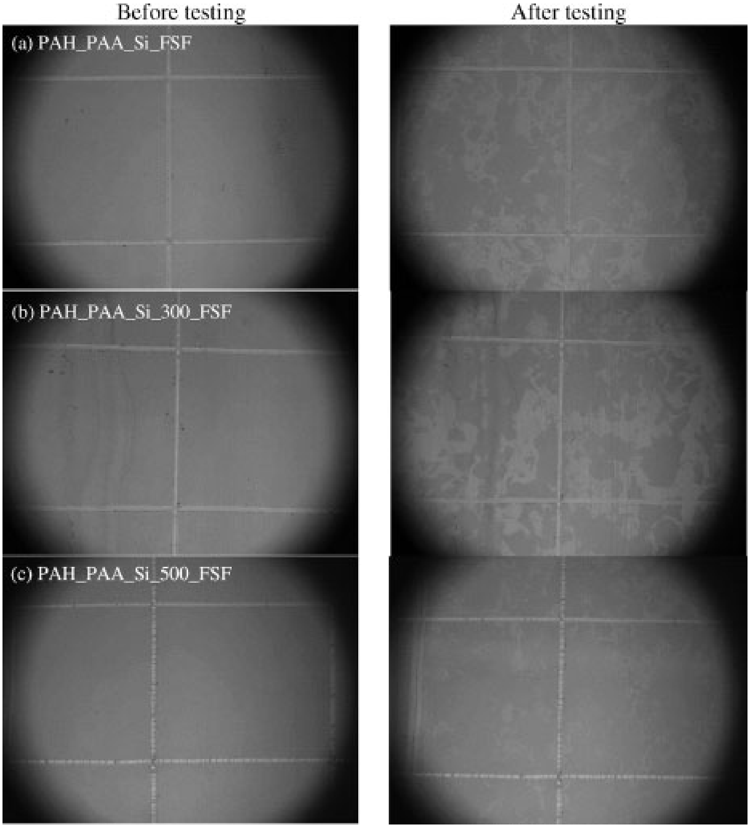

Figure 4.
Optical microscope images of the superhydrophobic films before and after adhesion test.

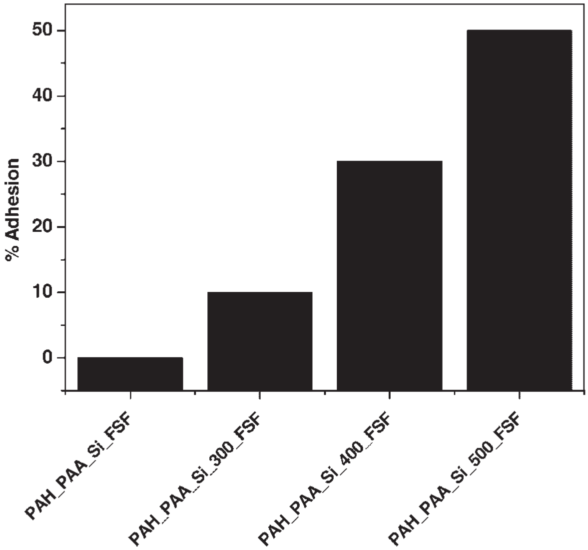

Figure 5.
Percentage of adhesion of modified polyelectrolyte multilayer films.

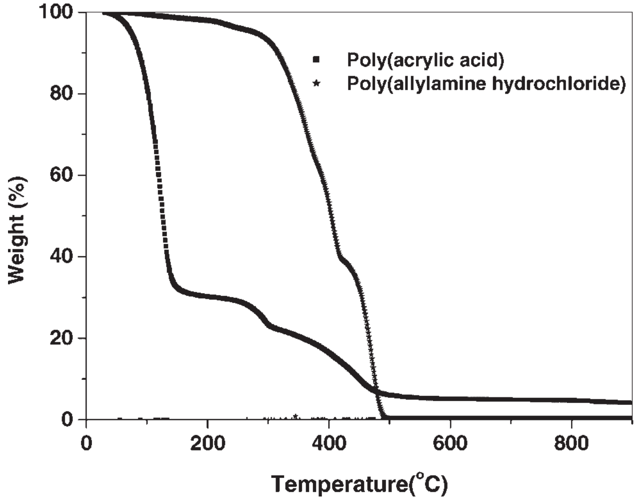

Figure 6.
A thermogram of the poly(acrylic acid) and poly(allylamine hydrochloride).

losses. The weight rapidly decreased at the temperature of about 100–150 °C, and then gradually decreased at 150–300 °C and finally at 300–500 °C. The weight loss at 100 °C resulted from water evaporation from the PAA solution while the weight loss at higher temperatures was attributed to decomposition of the PAA molecules. However, the PAA had residue of around 10 wt% which could not be decomposed even at 900 °C. In the case of PAH, the weight loss began at temperature of about 200 °C and became significant at 300 °C as a result of PAH decomposition. Complete decomposition was observed at 500 °C. Based on the TGA result, weak binding between the remaining PAH/PAA polyelectrolyte and the silicate structure of the substrate would be expected, particularly on the as-prepared film. The TGA result support the result of adhesion test that the as-prepared film had the poorest adhesion, and the film prepared by heating the polyelectrolyte bilayers at 500 °C (the maximum temperature employed) had the highest adhesion. The adhesion increased with the increase of heating temperature. The improved adhesion was attributed to strong chemical binding between the SiO_2 particles and the silicate glass substrate.

Conclusions

Super-hydrophobic self-cleaning surface on glass substrate have been fabricated by deposition of fume SiO_2 nanoparticles on the etched polymer polyelectrolyte film having suitable pore size and finally modifying the rough surface with thin layer of silane molecules to further lower surface energy. By chemical etching at longer time, the films were more porous which were suitable for deposition of the SiO_2 nanoparticle, providing high surface roughness and resulting to higher contact angle. The durability of these films in terms of adhesion was improved by removing the polyelectrolyte underlying layer by heat treatment before further deposition of the silane. Adhesion was improved as a result of good chemical binding between the SiO_2 particles and the silicate glass.

Acknowledgements: This research was supported by the National Metal and Materials Technology Center, the National Science and Technology Development Agency, Thailand (Grant MT-B-49-ATO-07-020-I).

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