

# Preparation of Super-Hydrophobic Film with Fluorinated-Copolymer

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**ABSTRACT:** Organic superhydrophobic films were prepared by utilizing TA-N fluoroalkylate (TAN) and methyl methacrylate (MMA) copolymer as water-repellent materials and inorganic silica powder as surface roughness material has been developed. Coating solutions prepared by adding silica powders into copolymer solution directly (one-step method) and by adding silica powders into monomers and allowing them to react (two-step method). The results showed that contact angles of the films prepared by one-step method (37.6 wt % of silica powders in the coating solution) were greater than 150°, but the transmittance of the film at visible light was only 30%. On the other hand, the contact angle of films prepared by two-step

method (20 wt % of silica powders in the coating solution) was greater than 160° and the transmittance of the film was greater than 90%. The contact angle of the film prepared by poly(octyl acrylate), POA, was 32.1°, but while introducing silica powder into the system, the contact angle of the film was reduced to be smaller than 5°. Thus, superhydrophobic and superhydrophilic films can be obtained by introducing a roughening material on the hydrophobic surface and the hydrophilic surface, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1646–1653, 2007

**Key words:** fluorinated-copolymer; superhydrophobic; contact angle; silica powders; lotus effect

## INTRODUCTION

Nature has many magical properties. One of the plants that possess such a property is the lotus. Lotus shows a hydrophobic property as well as a self-cleaning phenomenon. It is found from the natural lotus that superhydrophobic phenomena must constitute two important elements: One is low surface energy substances and the other is roughness. Any materials with these two elements simultaneously are said to be having the "Lotus Effect." Therefore, surface energy and surface roughness are the dominant factors that influence the performance of the surface property. For the formation of superhydrophobic films, modification of surface chemistry is always in conjunction with enhancement of surface roughness.<sup>1–5</sup>

For low surface energy substances, fluorine is the most effective element because of its small atomic radius and its electronegativity, which is the largest among all atoms, so that a covalent bond could be formed with carbon to generate low surface energy of the surface.<sup>5</sup> This chemical modification leads to an increase in the contact angle of water drop, with a maximum value of approximately 120° as reported

for smooth CF<sub>3</sub>-terminated surfaces.<sup>4,6–8</sup> The van der Waals force of the fluorine-based hydrophobic coatings against the substrates is very weak and hence it is necessary to copolymerize with other monomers to offset this drawback.

Wetted surface between solid and liquid is first described by Young's equation. However, it is suitable for flat smooth surface. Two models, the Wenzel model<sup>9</sup> and Cassie model,<sup>10</sup> have been put forward to explain the impact of wettability<sup>11</sup> on surface roughness. The modified equation between contact angle and surface roughness of the Wenzel model is given below

$$\cos \theta_W = \frac{A_r}{A} \times \cos \theta_Y = r \times \cos \theta_Y$$

where  $\theta_W$  is the contact angle of a rough surface,  $\theta_Y$  is the contact angle of a smooth surface, and  $r$  is the roughness factor based on the ratio of actual surface area to the projected surface area. This doctrine stated that while the contact angle on smooth surfaces is less than 90°, the contact angle of the surface decreases with increase in roughness of the surface. On the contrary, when the contact angle on the smooth surface is greater than 90°, the contact angle increases with increase in roughness on the surface.

In general, increasing the roughness of a hydrophobic surface would increase its hydrophobicity markedly.<sup>9–10,12</sup> Over the past few years, most papers

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were devoted to discover approaches on the enhancement of surface roughness. Synthetic superhydrophobic surfaces have been fabricated through various approaches, including sol-gel method,<sup>5,13</sup> organic/inorganic hybrid method,<sup>14,15</sup> CVD method,<sup>16</sup> electrochemical method,<sup>17</sup> embossing method,<sup>18</sup> plasma method,<sup>19</sup> phase separation method,<sup>20–22</sup> and template method.<sup>23–25</sup>

Granville<sup>26</sup> reported that superhydrophobic surface was achieved by synthesis of diblock architecture, poly(methyl acrylate)-*block*-poly(pentafluoropropyl acrylate), using the complicated fabrication of atom transfer radical polymerization (ATRP) method and casting it onto the porous silica substrates to obtain superhydrophobic thin films. In this research, TAN (fluorine-based) and MMA copolymer were prepared as low surface energy substance and silica powders were added into this copolymer solution to improve roughness of the surface. The coating solution prepared by different methods and transmittance of the film were discussed. To point out effect of roughness on the surface, superhydrophilic film prepared by introducing silica powders into POA solution was also discussed.

## METHODS

### Materials

TA-N fluoroalkylate ( $R_f\text{CH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$ ) (TAN) was purchased from DuPont, where  $R_f$  is fluoroalkane chain composed of  $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_8\text{F}_{17}$ ,  $\text{C}_{10}\text{F}_{21}$ ,  $\text{C}_{12}\text{F}_{25}$ ,  $\text{C}_{14}\text{F}_{29}$  and higher is used as a control standard. Silica powders (A200 and H70) were obtained from Degussa. Other reagents were as follows: methyl methacrylate (MMA) (Merck, reagent grade), *t*-butyl methacrylate (*t*-BMA) (Showa, reagent grade), *n*-butyl methacrylate (*n*-BMA) (Wako, reagent grade), octyl acrylate (OA) (Showa, reagent grade), AIBN (Showa, reagent grade), methyl ethyl ketone (MEK) (TEDIA, reagent grade).

### Preparation of copolymer

The fluorinated copolymers **1** (C 1, the as-prepared copolymer with PMMA and PTAN,  $T_g = 50^\circ\text{C}$ ), with various TAN/MMA weight ratios, were synthesized in MEK (monomer : MEK = 20 : 80) at  $70^\circ\text{C}$  for 24 h. Two kinds of silica powders, A200 and H70, were then added into the above copolymer solution followed by ultrasonication for 30 min. This is the so called one-step method. However, the two-step method was different from one-step method in that the silica powders were directly added into TAN and MMA monomer solutions before copolymerization. On the other hand, the copolymerization of TAN and MMA was reacted with silica simultaneously. Acrylic

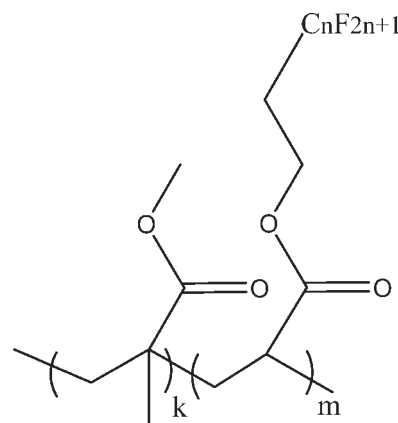


Chart 1 The structure of as-prepared copolymer.

polymer was also prepared by using the same method as above condition.

### Preparation of thin films

In all case, the slide glass substrates were cleaned respectively with HCl (0.1N), NaOH (0.1N), deionized water, and isopropylalcohol for 30 min. Next, the films were coated by using 200  $\mu\text{L}$  coating solution with spin-coating at 4500 rpm onto the slide glass substrates. The as-prepared films were then dried under ambient conditions at  $50^\circ\text{C}$  for 2 h in the oven.

### Instrumentation

Surface morphologies of the films were observed under scanning electron microscopy (SEM, Hitachi S-4200) and the variation of roughness was analyzed by atomic force microscopy (AFM, Seiko SPA400) with tapping mode. Water contact angles of prepared films were measured using manual contact angle goniometer (Kyowa interface sciences CA-D) as follows: water droplet was gently placed onto the films and the average value measured over five different locations for each sample were taken. Applying the  $\theta/2$  method and regulating the droplet size to about 20 scale, the droplets were observed through the eyepiece. The optical transmittance was determined by UV-VIS scanning spectrophotometer (JASCO V-530). The particle distribution was obtained by dynamic light scattering (DLS, Malvern instruments zetasizer 3000).

## RESULTS AND DISCUSSION

### Contact angle of different polymer

The hydrophobic or hydrophilic properties of polymers are directly related to polarity. In general, all acrylic polymers are somewhat polar because of the

**TABLE I**  
The Contact Angle of Water Drop of Films Prepared with Different Polymers

Polymer	Contact angle (°)
PTAN	123.3
P( <i>t</i> -BMA)	93.3
P( <i>n</i> -BMA)	86.8
PMMA	73.6
POA	32.1

ester linkage and the C=C double bond; however, this polarity can largely be offset by the backbone structure of the polymer. To investigate these effects, different acrylic monomers, methyl methacrylate (MMA), *t*-butyl methacrylate (*t*-BMA), *n*-butyl methacrylate (*n*-BMA), TAN fluoroalkylate (TAN), and octyl acrylate (OA), were polymerized, respectively. All polymer films were prepared by spin-coating onto glass substrates under appropriate experimental conditions. Hydrophobic and hydrophilic properties of the polymer films were measured by contact angle goniometer and the results were shown in Table I. It showed that PTAN film (fluorine based) had the biggest contact angle, which was 123.3°. The contact angle of PBMA was larger than that of PMMA because of its ester structure containing more carbon number, which reduced the hydrophilic properties. However, the contact angle of P(*t*-BMA) was greater than that of P(*n*-BMA). This is because there are three methyl group of side chain in the P(*t*-BMA) structure, on the other hand, the P(*n*-BMA) has only a long chain. However, the contact angle of POA was only 32.1°, implying that the larger carbon number of ester (octyl ester) did not promote the hydrophobic property of films. Hare et al. predicted that the closest hexagonal packing of  $-\text{CF}_3$  groups on the surface would give the lowest surface energy of the materials<sup>27</sup> because of the highest electron-fluorine affinity. However, the fluorine-based hydrophobic materials are via van der Waals force and, thus, are very weak so that such materials are copolymerized with other monomers to form copolymers to increase the solubility in solvent and adhesion with substrates. Besides, the other advantage was to reduce the expensive price and damage of environment. In this research, MMA was chosen to copolymerize with TAN and the experimental data of copolymer films produced were summarized in Table II. The result pointed out that with increasing the TAN content in the copolymer, the contact angle of the copolymer film was increased. Especially, the contact angle of the copolymer films was greater than 100° when the content of TAN of the copolymer was exceeded 20%. Even if the content of TAN of the copolymer was exceeded 70% (TM70), the contact angle of the copolymer maintained at about 120°. This was due

**TABLE II**  
The Contact Angle of Water Drop of Films Prepared with Different Composition of TAN/MMA Copolymer

Polymer name	TAN/MMA <sup>a</sup> (wt %)	Contact angle (°)
TM00 <sup>b</sup>	0	73.6
TM09	9	93.8
TM20	20	104.8
TM44	44	117.2
TM70	70	119.4
TM100	100	123.3

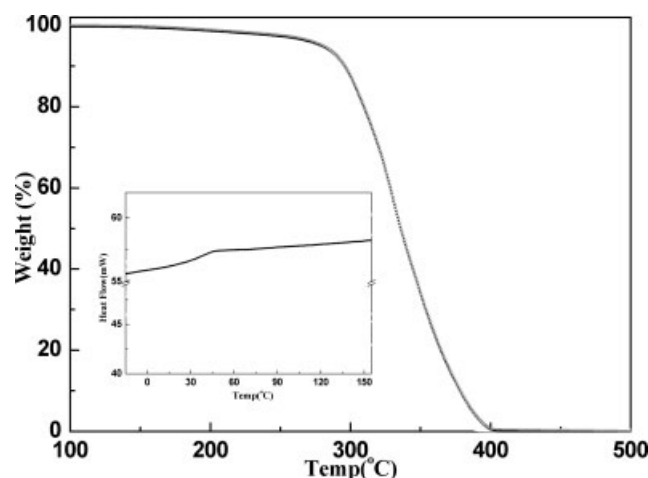
<sup>a</sup> The composition of TAN and MMA.

<sup>b</sup> TM00 means the weight ratio of TAN/MMA = 0/100. The relative condition of TM09 (9/91), TM20 (20/80), TM44 (44/56), TM70 (70/30), TM100 (100/0) were the same as that of TM00.

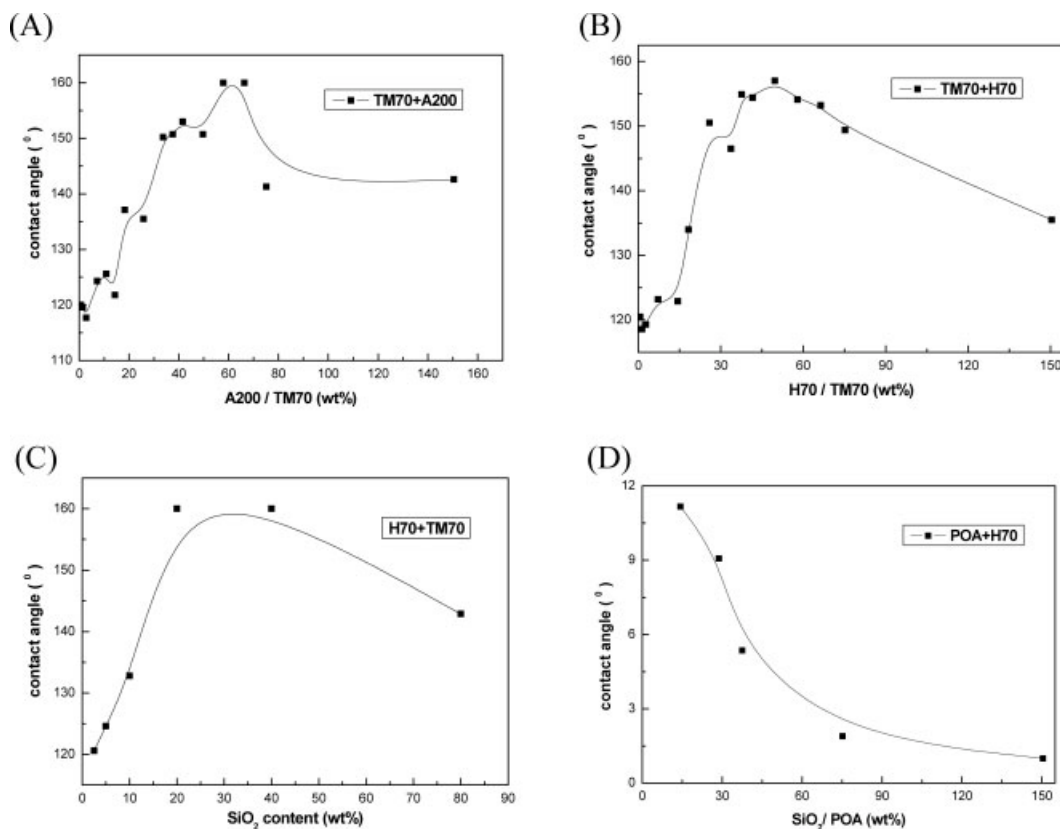
to the addition of the TAN monomer, which resulted in promoting the ratio of fluorine atom on the surface. It thus caused to reduce the surface energy of the copolymer and raise the contact angles of the copolymer. When the content of TAN monomers reached 44%, the contact angle of the copolymer was greater than 115°. Hence, to lower the cost and enhance the application of bare-Fluorine polymer, TM70 was chosen as the sample for follow-up experiment. TGA and DSC analysis of TM70 were showed in Figure 1, which shows that most of the degradation events occurred between 250 and 400°C. On the other hand, the thermal stability of the copolymer was kept before 250°C. The inset diagram of DSC analysis showed that  $T_g$  of TM70 was 50°C.

#### Preparation of superhydrophobic film by one-step method

Roughness and low surface energy are two important factors that influence the property of superhydrophobic film. These two factors should be



**Figure 1** TGA and DSC diagram of TM70 copolymer.



**Figure 2** (A) Contact angles of water droplet on films prepared with various A200 concentration in TM70 solution by one-step method. (B) Various H70 concentration in TM70 solution by one-step method. (C) Various H70 concentration in TM70 solution by two-step method. (D) Various H70 concentration in POA solution by one-step method.

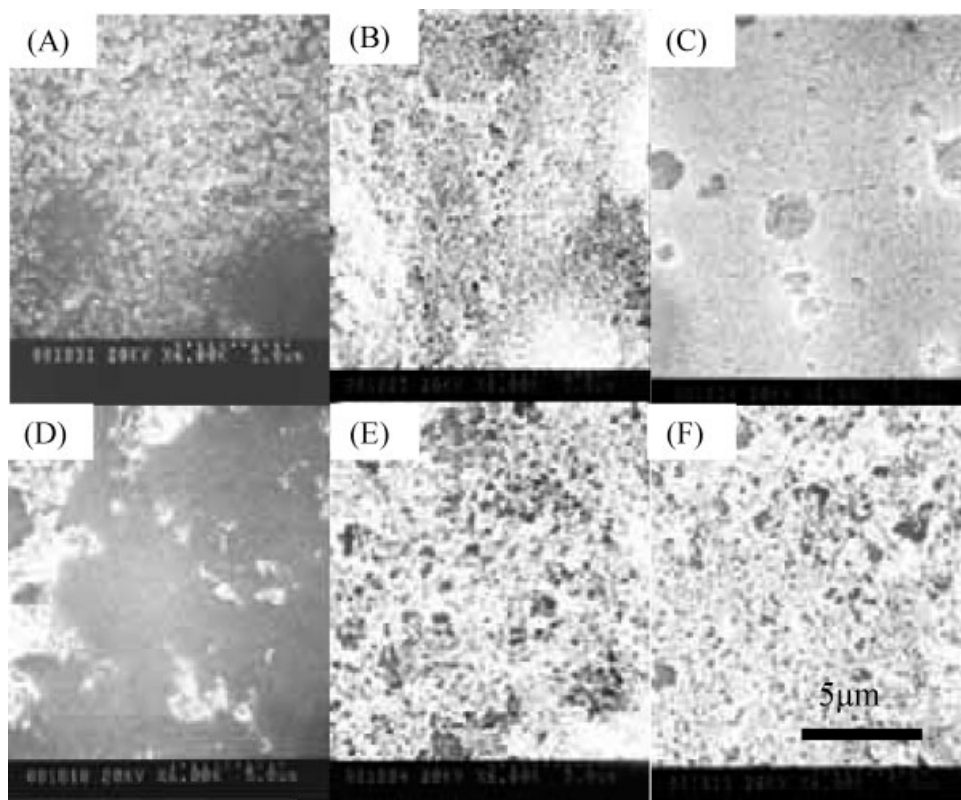
coexisted simultaneously. Based on the fact that films prepared from TM70 on smooth substrate would present hydrophobic property and adding silica powders into TM70 solution would enhance roughness of the surface, there are two methods to prepare coating solution with hydrophobic property. One of which is one-step method, that is to mix silica powders and TM70 solution directly. The other one is the two-step method, that is to firstly mix silica powders with MMA, TAN monomers, then copolymerize to form the coating solution.

First, the preparation of superhydrophobic film by one-step method was discussed. Silica powders (A200 or H70) were introduced into TM70 copolymer solution directly to obtain the surface roughness before coated onto a substrate. The suspension coating solutions were well mixed in the ultrasonic container. In addition, the hydrophobic films were prepared by spin-coating onto glass substrates.

The contact angles of ultra water-repellant rough films prepared by adding various amount of A200 and H70 into coating solution were shown in Figure 2(A) and 2(B), respectively. These diagrams indicate that the contact angle increased with increasing weight ratio of silica powders in TM70 solution from 0% to about 60%, and decreased with increasing that from

60 to 150%. It was obvious that superhydrophobic film with contact angle greater than 150° can be obtained by adding 37.6% weight ratio of silica powders in TM70 copolymer solution. The results showed that by adding silica powders in TM70 copolymer solution, the hydrophobic surface of substrates became superhydrophobic. Figure 3(A) showed the SEM image of the surface prepared by coating TM70 solution containing 14.4% weight ratio of A200 silica powders. It was observed that A200 silica powders did not cover the surface of the substrate continuously. Nevertheless, the surface of the substrates was continuously covered when TM70 solution was added to 37.6% and 75.2% weight ratio of A200 silica powders, respectively, [Fig. 3(B,C)]. The same phenomena were also observed when surface of the film prepared by coating TM70 solution containing H70 silica powders. The average roughness ( $R_a$ ) of the surfaces prepared by coating TM70 solution containing A200 and H70 silica powders were measured by AFM. It showed that the excellent data of roughness ( $R_a$ ) can be obtained when the coating solution containing silica powders of weight ratio was 37.6% for A200 and H70. On the other hand, the maximum  $R_a$  of the surface can be obtained by coating TM70 solution containing appropriate amount of silica powders as





**Figure 3** SEM micrographs of films prepared by one-step method with various weight ratio of A200/TM70 (A) 14.4%, (B) 37.6%, (C) 75.2%; and H70/TM70 (D) 14.4%, (E) 37.6%, (F) 75.2%.

roughness of the surfaces. However, increasing too many silica powders could fill up the roughness on the substrate and become a flat surface so that the contact angle of the film was reduced.

Optical transmittance of the film measured within wavelengths ranging from 400 to 700 nm was shown in Table III. With increasing amount of silica in coating solution, the transparency of the film was decreased. In other words, film coated with TM70 solution containing 37.6% silica powders displayed lower transparency, which was below 30%, but displayed larger contact angle and thus maintaining the superhydrophobic property. There was a marked

decreased in the transmittance for films prepared by both kinds of silica powders. This is because too many powders in the coating solution results in increasing roughness but the solution became opaque.

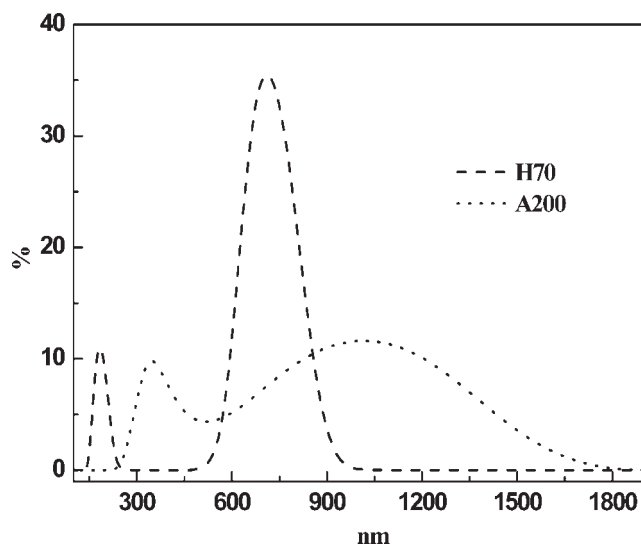
So far, high contact angles of films can be prepared by adding silica powders into TM70 copolymer coating solution. In brief, the contact angles of the superhydrophobic films were dependent on the kinds of silica powders in the coating solution. Comparing with data shown in Figure 2(A,B), superhydrophobic films prepared by adding H70 in coating solution were more stable than A200. Besides,

**TABLE III**  
Contact Angle of Water Drop and Transmittance ( $T\%$ ) of Light of Films Prepared by One-Step Method with Different Silica Powders

SiO <sub>2</sub>	SiO <sub>2</sub> /TM70 <sup>a</sup> (wt %)	Contact angle (°)	$T\%$ 400 nm (%)	$T\%$ 550 nm (%)	$T\%$ 700 nm (%)
A200 <sup>b</sup>	1.4	119.6	85.3	89.8	94.1
	14.4	121.8	57.3	82.2	90.5
	37.6	149.5	21.6	26.9	27.7
H70 <sup>b</sup>	1.4	118.6	78.1	86.3	91.4
	14.4	122.9	40.1	60.9	71.4
	37.6	154.8	18.1	22.9	31.5

<sup>a</sup> TM70 means the weight ratio of TAN/MMA = 70/30.

<sup>b</sup> Two kinds of silica particles.



**Figure 4** Size distribution of A200 and H70 in MEK solution measured by DLS particle size distribution analyzer.

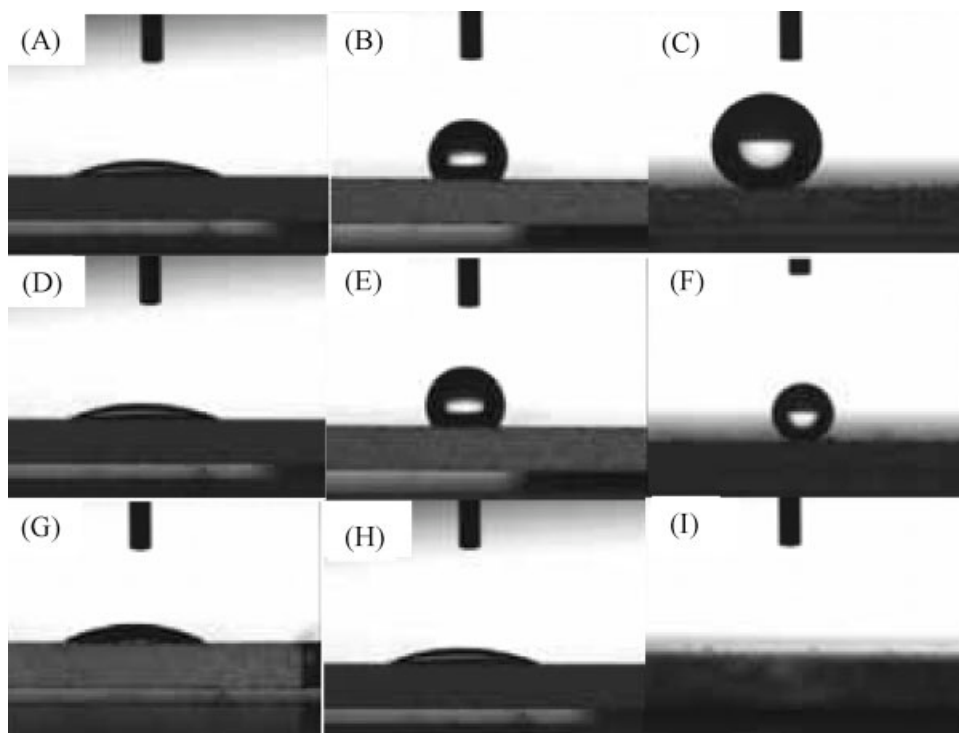
Figure 4 showed the measurement of DLS of these silica powders in MEK solution. The diagram indicates that the size distribution of H70 was narrower than that of A200 and size of H70 was smaller than that of A200 so that the films prepared by H70 were more homogenous and transparent than that by A200.

What the passage made clear at once was that superhydrophobic films can be acquired by adding silica powders, with corresponding contact angles images of films as represented in Figure 5(A–C). The contact angles of films was greater than  $150^\circ$  prepared by adding appropriate amount of silica powders into the copolymer solution, but the transparency of the films was decreased to below 30%. The viscosity of the coating solution was high when more silica powders were added in the copolymer solution. The consideration is because that silica powders were easily aggregated in the polymer solution.

#### Preparation of superhydrophobic film by two-step method

As mentioned already, it was difficult to prepare homogenous coating solution by one-step method. That is, by adding silica powders into copolymer solution directly. However, superhydrophobic films can be obtained by this coating solution. There was another method, the two-step method, to prepare the coating solution by adding silica powders in monomer solution followed by polymerization. It was expected that silica powders was easily and homogeneously dispersed in the final coating solution.

Contact angle of superhydrophobic films prepared by two-step method was shown in Figure 2(C). Silica



**Figure 5** Pictures captured from the goniometer for a water drop on different surfaces by one-step method (A) glass, (B) TM70 film, (C) H70/TM70 film (37.6 wt %). By two-step method (D) glass, (E) TM70 film, (F) H70/TM70 film (20 wt %). By one-step method. (G) Glass, (H) POA film, (I) H70/POA film (75.2 wt %), complete wetting.

**TABLE IV**  
**Contact Angle of Water Drop and Transmittance (*T*%) of Light of Films Prepared by Two-Step Method with H70 Silica Powder**

SiO <sub>2</sub>	SiO <sub>2</sub> /HM70 <sup>a</sup> (wt %)	Contact angle (°)	<i>T</i> % under 400 nm (%)	<i>T</i> % under 550 nm (%)	<i>T</i> % under 700 nm (%)
H70	2.5	120.6	94.9	96.5	98
	20	>160	87.7	92.4	94.9
	40	>160	82.1	87.5	89.9
	80	142.9	70.5	79.7	85.7

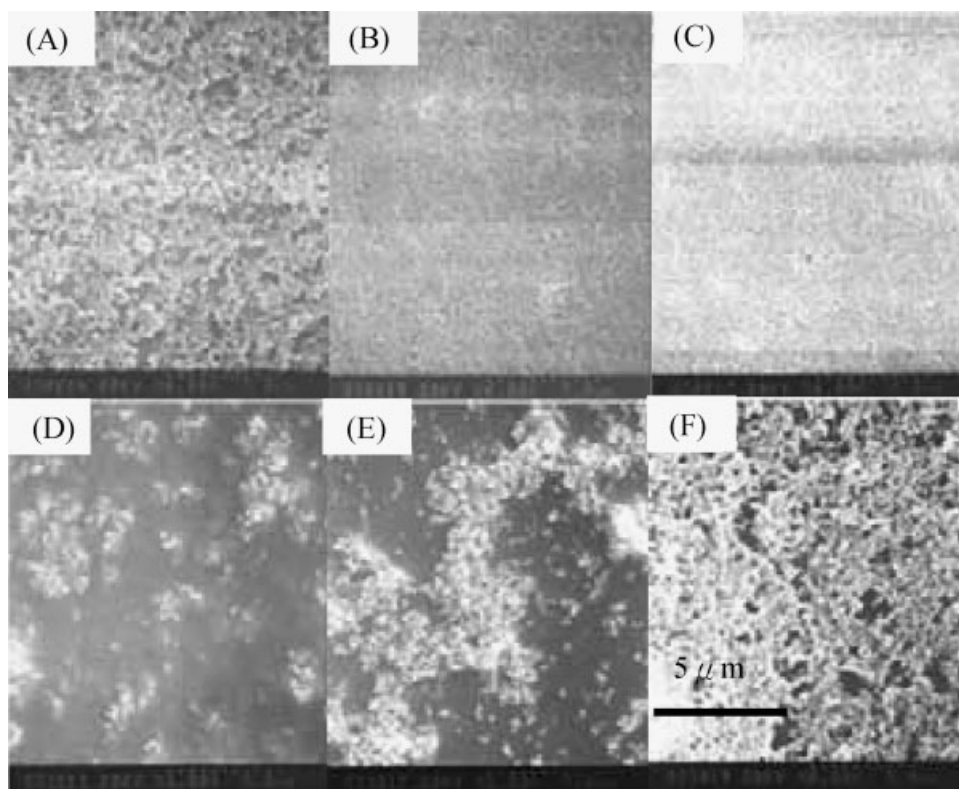
<sup>a</sup> TM70 means the weight ratio of TAN/MMA = 70/30.

powders of H70 were mixed with the monomer and MEK. It was difficult to mix silica powders well in the copolymer solution by one-step method. This diagram indicated that contact angles were increased with increasing weight ratio of silica powders from 0% to about 20% but decreased from 40 to 80%. This phenomenon was the same as the result of one-step method. But when contact angle of the film was greater than 150°, the weight ratio of silica powders prepared by the two-step method was smaller than that prepared by one-step method.

Comparing one step and two step methods, it was obvious that lesser silica powders were needed in the two-step method for preparation of superhydrophobic film. This is because that by adding lesser silica powders into the prepared solution in the two-step method, transmittance of the films could be

enhanced. Table IV shows the data of optical transmittance of the film measured within the wavelengths ranging from 400 to 700 nm. Transmittance of the films was decreased with increasing amount of H70 in the coating solution. However, when the contact angle was greater than 160°, the transmittance was greater than 90%. While comparing Table III and IV, it was obvious that the transmittance of films prepared by two-step method were better than that of the one-step one. In addition, the transmittance of almost all superhydrophobic films prepared by two-step method was greater than 80%.

The microstructure images were measured by SEM and shown in Figure 6(A–C). It was clear that H70 silica powders have not covered the surface of the substrate at 5% weight ratio in the coating solution. Nevertheless, surface of the substrate was



**Figure 6** SEM micrographs of films prepared by two-step method with various weight ratio of H70/TM70: (A) 5%, (B) 20%, (C) 80%. The films prepared by one-step method with various weight ratio of H70/POA (D) 14.4%, (E) 37.6%, (F) 75.2%.

continuously covered by the coating solution with increasing weight ratio of silica powders to 20%. The variance of average roughness (Ra) of films prepared by two-step method was observed by AFM and the data indicated that maximum of Ra can be obtained when weight ratio of H70 in TM70 solution was 20%. Therefore, we can obtain continuous rough surface just at 20% weight ratio of H70 in TM70 solution [from Fig. 6(A–C)]. It was obvious that the surface roughness became continuous as silica powders were increased in the coating solution. But when there are too many silica powders in the coating solution, the roughness and the contact angle of the film would be reduced.

From the data mentioned earlier, lesser silica powder in the coating solution is enough to obtain continuous and rough surfaces by two-step method. Contact angle images of water drop on the films were represented in Figure 5(D–F). It has been proven that the problem of particles' dispersion can be improved by applying the modified procedure of the two-step method.

#### Preparation of superhydrophilic film by using POA polymer

The equation of relationship between surface roughness and contact angle was developed by Wenzel in 1936 based on Young equation, which was known that the contact angle of flat surface was greater than 90°, and that was increased with roughness. In other words, the characteristic of superhydrophobic films prepared as mentioned earlier could be proven by the earlier-mentioned experimental data for increased roughness on hydrophobic flat surface (greater than 90°). On the contrary, superhydrophilic films can be obtained by increasing the roughness of hydrophilic flat surface.

In this section, POA polymer solution (with contact angle = 32°) was chosen to prepare superhydrophilic film by adding H70 silica powders. The experimental data were graphically represented in Figure 2(D). It was quite obvious to find that contact angle was decreased with increasing H70. However, the minimum contact angle (smaller than 2°) of the film was appeared when the weight ratio of silica powder of H70 was 75.2%. This phenomenon was also observed by SEM as shown in Figure 6(D–F). The images of water drop on the films were shown in Figure 5(G–I), which indicates superhydrophilic film is obtainable by introducing silica powders into POA solution.

### CONCLUSIONS

Superhydrophobic films have been prepared by using coating solutions prepared by adding silica powders in TAN and MMA copolymer solution. The TAN and MMA copolymer was used as the

hydrophobic materials and silica powders were used to improve surface roughness. Ultra-water repellent films can be obtained by both one-step and two-step method, but the films prepared by two-step method produced better transmittance, which was greater than 90%. Wenzel's equation was verified by using PTAN copolymer as hydrophobic material and POA polymer as hydrophilic material, respectively. In other words, superhydrophobic and superhydrophilic films were obtainable by introducing roughness into the hydrophobic surface and hydrophilic surface, respectively.

### References

1. Woodward, I.; Schofield, W. C. E.; Roucoules, V.; Badyal, J. P. S. *Langmuir* 2003, 19, 3432.
2. Feng, X.; Feng, L.; Jin, M.; Zhai, J.; Jiang, L.; Zhu, D. *J Am Chem Soc* 2004, 126, 62.
3. Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2004, 43, 357.
4. Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* 2003, 299, 1377.
5. Shang, H. M.; Wang, Y.; Limmer, S. J.; Chou, T. P.; Takahashi, K.; Cao, G. Z. *Thin Solid Films* 2005, 472, 37.
6. Coulson, S. R.; Woodward, I.; Badyal, J. P. S.; Brewer, S. A.; Willis, C. J. *Phys Chem B* 2000, 104, 8836.
7. Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Oner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* 1999, 15, 3395.
8. Nishino, T.; Meguro, M.; Nakamae, K.; Matsushita, M.; Ueda, Y. *Langmuir* 1999, 15, 4321.
9. Wenzel, R. N. *Ind Eng Chem* 1936, 28, 988.
10. Cassie, A.; Baxter, S. *Trans Faraday Soc* 1944, 40, 546.
11. Xuedong, W.; Lijun, Z.; Dan, W. *Langmuir* 2005, 21, 2665.
12. Lei, Z.; Fevzi, C. C.; Robert, E. C.; Michael, F. R. *Nano Lett* 2004, 4, 1349.
13. Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C. *Langmuir* 2003, 19, 5626.
14. Satoh, K.; Nakazumi, H. *J Sol-Gel Sci Technol* 2003, 27, 327.
15. Gu, Z. Z.; Uetsuka, H.; Takahashi, K.; Nakajima, R.; Onishi, H.; Fujishima, A.; Sato, O. *Angew Chem Int Ed* 2003, 42, 894.
16. Lau, K. K. S.; Bico, J.; Teo, K. B. K.; Chhowalla, M.; Amaratunga, G. A. J.; Milne, W. I.; McKinley, G. H.; Gleason, K. K. *Nano Lett* 2003, 3, 1701.
17. Li, M.; Zhai, J.; Liu, H.; Song, Y.; Jiang, L.; Zhu, D. *J Phys Chem B* 2003, 107, 9954.
18. Lee, W.; Jin, M. K.; Yoo, W. C.; Lee, J. K. *Langmuir* 2004, 20, 7665.
19. Teshima, K.; Sugimura, H.; Inoue, Y.; Takai, O.; Takano, A. *Langmuir* 2003, 19, 10624.
20. Fu, Q.; Rao, V. R.; Basame, S. B.; Keller, D. J.; Artyushkova, K.; Fulghum, J. E.; López, G. P. *J Am Chem Soc* 2004, 126, 8904.
21. Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2004, 43, 357.
22. Zhai, L.; Cebeci, F. C.; Cohen, R. E.; Rubuner, M. F. *Nano Lett* 2004, 4, 1349.
23. Feng, L.; Li, S.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2002, 41, 1221.
24. Feng, L.; Song, Y.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, D. *Angew Chem Int Ed* 2003, 42, 800.
25. Jin, M.; Feng, X.; Feng, L.; Sun, T.; Zhai, J.; Li, T.; Jiang, L. *Adv Mater* 1977, 2005, 17.
26. Anthony, M. G.; William, J. B. *Macromol Rapid Commun* 2004, 25, 1298.
27. Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J Phys Chem* 1954, 58, 236.