Higher Water Repellency Caused by a Reduced Employment of Low Surface Energy Structures

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Fluorine-containing random copolymers based on methyl methacrylate (MMA) and 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl acrylate (FAEA) have been prepared by solution polymerization. Superhydrophobic surface was attained by casting the polymer solution from a fluorine-containing solvent at a constant temperature. The contact angles of water drops on the prepared surface were measured. SEM was adopted to detect the fine structures of the prepared polymeric surface. The mechanism of forming these films was studied.

Great attention has been attracted on superhydrophobic surfaces since late 1990s according to the progress of the preparing technique, the characterizing methods, and especially the potential application in industry and our daily life.[1] Since the super-hydrophobic surfaces have such special characteristics as self-cleaning, anticontamination, in certain cases also oleophobic, etc., the coatings can be adopted widely.[2] A combination of enhanced roughness and low surface energy is often used for attaining the superhydrophobic surfaces.[3] However, the limitation of the wide application of such superhydrophobic surfaces is mainly due to the high cost or the strict and complicated processes of the preparation.

In our research, fluorine-containing random copolymers based on methyl methacrylate and 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl acrylate have been exploited for superhydrophobic surfaces. Certain factors affecting the water repellency of the final polymer surface have been discussed here.

Monomer MMA was washed with 5% NaOH and deionized water, dried through CaH_2, and then vacuum-distilled. FAEA was kindly supplied from Clariant Company. FAEA was stirred over CaH_2 overnight at 40 °C and then distilled under reduced pressure. The FAEA used in current study is a mixture of $CH_2{=}CHCO_2CH_2CH_2(CF_2)_nCF_3$ with different n ($n = 5$, 7, 9, 11, and 13; average $n \approx 8.6$). 1,1,2-Trifluoro-1,2,2-trichloroethane (FREON 113) was distilled and the distillate of 47–48 °C was collected for use. Other chemicals are commercially purchased analytical reagents and were used as received.

A general procedure for the polymerization is as follows: Designate amounts of MMA, FAEA, and azobisisobutyronitrile (AIBN) were dissolved in cyclohexanone and followed by a 15-min N_2 bubbling. Then, the polymerization was performed at 70 °C for 24 h with mechanical stirring. The product mixture was dissolved into acetone and then precipitated into methanol for three times in order to remove all the residue monomers. Later the prepared PMMA-co-PFAEA was dried in high vacuum at 50 °C till constant weight.

Table 1 shows the structures of the prepared PMMA-co-PFAEA random copolymers. No. 2 with higher fluorine content was prepared with the same initiator/monomer molar ratio for a comparison of No. 1. However, since the high fluorine content results in poor solubility in the GPC eluent phase THF, the GPC measurements were failed to be performed. The fluorine content was obtained through fluorine elemental analysis by ignition method.

Table 1. Molecular structure of the prepared PMMA-co-PFAEA

Samples	$M_n \times 10^{-4}$	PDI	FEA[a]/%
No. 1	3.99	1.47	12
No. 2	—	—	33

[a]Results of the fluorine element analysis.

The dried sample was dissolved in FREON 113 (the concentration is 100 mg/mL) and coated on a 1-cm^2 clean glass wafer. The surface was prepared directly by the solvent evaporation at a constant temperature. Contact angle measurements were performed at 20 °C with a JC-2000A surface tension instrument (Shanghai Zhongchen digital equipment Ltd. Co.). The volume of the water drop was 5 µL. SEM measurements were taken on a JEOL JSM-6360LV instrument with 20 kV acceleration voltage.

$$\cos\theta_r = f_1 \cos\theta - f_2 \qquad (1)$$

The contact angle (θ_r) on a rough surface composed of a given (co)polymer structure, can be expressed by eq 1.[4] Here, θ_r and θ are the contact angles on the hierarchically rough surface and the smooth surface composed of the same structures, respectively. f_1 and f_2 are the fractional interfacial areas of the solid structures and of the air in the troughs, respectively (i.e., $f_1 + f_2 = 1$). Since θ should be a constant value for the smooth surface of a given structure, it is obvious that θ_r can be increased by increasing the value f_2, the fraction of air in the surface. f_2 is fully corresponding to the roughness of the prepared surface, which can be generally understood as a rougher surface affords higher f_2 value. The discussion of different effects on the hydrophobicity of the coating surfaces in this paper is based on the above-mentioned mechanism.

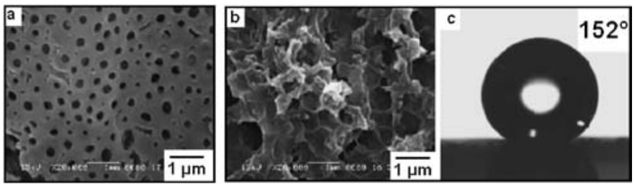

Figure 1. SEM images of polymer surfaces prepared at 27 °C. (a) the surface morphology prepared with sample No. 2; (b) the surface morphology prepared with sample No. 1, (c) the image of the water drop on surface (b).

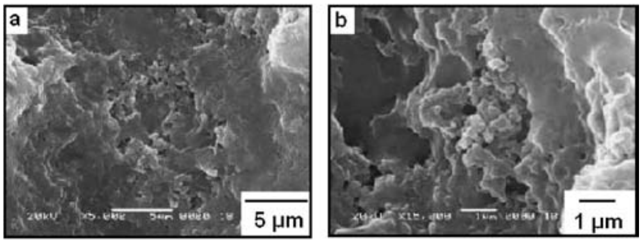

Figure 2. SEM images of polymer surfaces prepared at 20 °C with sample No. 1. (a) and (b) images with different scale bars.

Since the surface morphology as well as the water repellency of the copolymer films is greatly affected by the polymer structures, the effect of fluorine content of the PMMA-co-PFAEA is investigated by a comparison of samples 1 and 2 as shown in Figure 1.

The polymer surface composed of sample No. 1 (Figure 1b) is rougher than that of No. 2 (Figure 1a). The greater roughness makes the "f_2" value (eq 1) and the corresponding hydrophobicity higher. The water contact angle on surface "a" is 141° while on surface "b" is 152°, which is already in the range of superhydrophobic surface. In FREON 113, the PFAEA structures can be well highly dissolved; however, the PMMA part is insoluble. Therefore, aggregates formed with a PMMA core and a PFAEA shell. The smoother surface morphology obtained on the surface "a" is partially caused by the high degree of interdigitation between the relatively thick corona shells of these fluorine-containing structures. In other words, higher water repellency was attained by a reduced employment of low surface energy structures (here fluorine-containing structures) in this special case.

Figure 2 shows the surface image of the sample No. 1 prepared at lower temperature. Since the boiling point of the solvent FREON 113 is 48 °C, the evaporating speed is much high at room temperature. At lower cast temperature 20 °C, the evaporation of FREON 113 can be slower than that of 27 °C, so the corona shells of these fluorine-containing structures have more time for interdigitation, which results in a smoother surface morphology, a lower "f_2" value as well as a lower water contact angle of 145°.

The fluorinated units' movement to the air–polymer surface is affected by the heat treatment. For the surfaces prepared by typical fluorine-containing block copolymers from nonfluorinated solvent, the heat treatment promotes the microphase segregation and leads to a decrease of the surface energy of the surfaces and an elevation of the water repellency, which has been demonstrated by our previous work.[5] However, the heat treatment for the surface prepared by fluorine-containing random copolymers from FROEN 113 shows effects different from our expectation, which is shown in Figure 3. The heat treatment was performed at 120 °C, which is higher than the glass-transition temperatures of both PMMA (104 °C) and PFAEA (58 °C), so the full microphase segregation of PMMA and PFAEA should be achieved through the heat treatment of suitable long time.

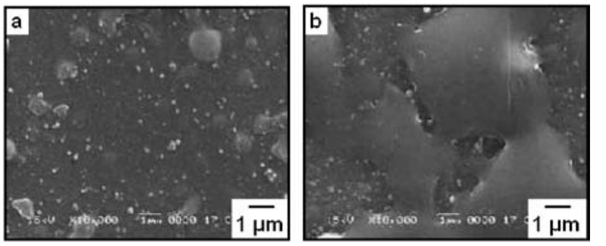

Figure 3. SEM images of polymer surfaces prepared at 20 °C with sample No. 1. (a) after 3 h of heat treatment and (b) after 6 h of heat treatment at 120 °C.

Figure 3 shows the morphology of the surface during the heat treatment at 120 °C. In Figure 1b it is obvious that the film surface without any heat treatment contains large quantities of convexities and grooves, which were left on the film surface during the cast process and provided the enhanced roughness for the superhydrophobic property. After 3 h and 6 h heat treatment (Figures 3a and 3b) almost all the grooves and convexities disappeared, since the further microphase segregation of the fluorinated structures and the nonfluorinated structures at high temperature eliminated the remained core–shell structures formed in the cast process. This leads to a great decline of the surface roughness, and the contact angle goes down to less than 115°, much lower than the superhydrophobic range.

In conclusion, PMMA-co-PFAEA random copolymers have been used for the preparation of superhydrophobic surfaces by the solvent-evaporation method. The mechanism of the formation of the surface morphology was discussed. The higher fluorine content of the copolymer turns to be an unfavorable factor for the water repellency since a decline of the surface roughness. Furthermore, the cast temperature and heat treatment also show certain effects on the water repellency of the final surface, which leave an interesting space for further investigation of tuning the surface water repellency.

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