

Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range

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Received May 25, 2006. In Final Form: August 8, 2006

In this study, we report on a simple two-step casting process designed to create a stable superhydrophobic surface. This method possesses the advantages of being both simple and inexpensive as well as utilizing non-fluorine-containing compounds. Most interestingly, we found that the as-prepared surface possesses superhydrophobic properties not only for pure water but also for corrosive water under both acidic and basic conditions. Furthermore, the superhydrophobic polybenzoxazine surfaces had excellent environmental stability with regard to both heating and organic solvent treatment in terms of the contact angle to water.

Introduction

A solid surface's water repellency is one of its most important characteristics in both theoretical research and industrial applications. The hydrophobicity of a surface is determined by a combination of its chemical properties and topographical microstructures. The chemical modification of a surface can alone lead to water contact angles of up to 120° by using fluoropolymeric coatings or silane layers.¹ This is insufficient to produce a superhydrophobic surface, which usually requires a water contact angle larger than 150°.² If a surface is microtextured with low surface free energy, the contact angle of water can reach as high as 180°, with the surface remaining dry.^{3,4} Two different hypotheses are generally proposed to explain the cause of this effect. Surface roughness increases the surface area of the solid and thus enhances its hydrophobicity (Wenzel model).⁵ In addition, air becomes trapped within the grooves beneath the liquid, leading to superhydrophobic behavior, because the drop sits partially on air (Cassie model).⁶ Over the past 10 years, there have been numerous reports concerning superhydrophobic surfaces.^{7–17} However, multistep processes, stringent preparation

specifications, and the high cost of forming large-area superhydrophobic surfaces have heretofore limited their practical applications.

In our previous study,¹⁸ we discovered a new class of non-fluorine, non-silicon low surface free energy polymeric material: polybenzoxazine. The polybenzoxazine possesses a surface free energy ($\gamma = 16.4 \text{ mJ/m}^2$) that is even lower than that of pure poly(tetrafluoroethylene) (PTFE) ($\gamma = 21 \text{ mJ/m}^2$). Although polybenzoxazines and fluoropolymers both possess low surface free energies, the former is cheaper to prepare and easier to process. Furthermore, polybenzoxazine also possess unique properties such as a high glass-transition temperatures (T_g),¹⁹ excellent resistance to chemicals²⁰ and UV light,²¹ and a low degree of water absorption.²² Herein, we report on a simple two-step casting process to create a stable superhydrophobic organic–inorganic hybrid coating based on polybenzoxazine. These films possess superhydrophobicity over the whole range of pH values.

Experimental Section

2,2-Bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazine) propane (BA-m benzoxazine) was supplied by the Shikoku Corporation of Japan. Silica nanoparticles, Tokusil 233G, were kindly provided by the Oriental Silicas Corporation. The nanoparticle is a 22 nm precipitated hydrated silica.

Superhydrophobic coating on a glass slide was performed through a two-step process. First, BA-m benzoxazine (0.5 g) was mixed with nanoparticles (0.05–0.5 g) in tetrahydrofuran (THF) (10 mL) (Table 1). After keeping the solutions in an ultrasound bath for 2 h, the mixture was spin-coated onto a glass slide (100 × 100 × 1 mm³) at 1500 rpm for 45 s and then cured in an oven at 210 °C for 1 h. Subsequently, the polybenzoxazine–silica hybrid surface was modified with the pure BA-m polybenzoxazine film. The BA-m benzoxazine solution, in different concentrations (Table 2), was spin coated onto a rough surface for 45 s at 1500 rpm and then cured at 210 °C for 40 min.

Thermal stability was evaluated by treating the film at various temperatures for 8 h. After the thermal treatment, the contact angle was measured at room temperature. The film's durability to organic solvents was evaluated by immersing it in an organic solvent and

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Table 1. Surface Roughness of Polybenzoxazine–Silica Hybrid Films with Various Nanoparticle Contents

sample no.	THF (mL)	benzoxazine (g)	SiO ₂ nanoparticle (g)	rms roughness (nm)
a	10	0.50	0.05	16.9 ± 2.3
b	10	0.50	0.10	38.6 ± 4.8
c	10	0.50	0.15	45.8 ± 5.2
d	10	0.50	0.30	190 ± 12
e	10	0.50	0.50	196 ± 12

Table 2. Surface Roughness and Contact Angles (Water) on the Polybenzoxazine–Silica Hybrid Surface after Modification with the Pure BA-m Polybenzoxazine Film

sample no.	concentration of benzoxazine solution (mg/mL)	rms roughness (nm)	water contact angle (deg)
1	0.5	182 ± 12	168 ± 1
2	1.0	175 ± 9	167 ± 2
3	5.0	150 ± 8	164 ± 1
4	10	129 ± 7	152 ± 3
5	30	117 ± 5	138 ± 2
6	50	103 ± 5	130 ± 2

then drying at 60 °C. After being immersed in diesel oil, the film was then washed with THF and dried as above. The contact angle was measured on the dried film.

The microstructure of the polymer surface was characterized using a Hitachi-S-4700 scanning electron microscope (SEM) with an acceleration voltage of 5 kV. The specimen was coated with a thin layer of Pt/Pd before SEM observations. The contact angle and sliding angle were measured on a Krüss GH-100 contact angle goniometer. The advancing contact angle was read by injecting a 5 μ L liquid drop. The receding contact angle was measured by removing about 3 μ L of liquid from the drop; the static contact angle and the sliding angle were obtained from a ca. 5 μ L drop. Water droplets (about 5 μ L) with different pH values (prepared by HCl and NaOH) were dropped carefully onto the superhydrophobic polybenzoxazine films. Each of the reported contact angles represents the average of six measurements. Atomic force microscopy (AFM) results were acquired using a Digital Instruments multimode scanning probe microscope. Damage to both the tip and the sample surface was minimized by employing AFM in tapping mode. AFM data were acquired by using ultrasharp silicon cantilevers (E-V NanoTech Inc, SEIHR) having a force constant of 15 N/m and a resonance frequency of 138 kHz. The rms roughnesses were calculated over scanned area of 5 μ m \times 5 μ m. Each of the reported rms roughnesses represents the average of five measurements (in air).

Results and Discussion

BA-m benzoxazine was spin coated onto a glass slide and then cured at 200 °C for 1 h; a smooth surface was obtained (Figure 1a). The rms roughness on the surface was about 0.19 nm, and the resulting water contact angle (CA) was about 108° (Figure 2a). A superhydrophobic coating on a glass slide can be achieved by combining BA-m benzoxazines and silica nanoparticles. These silica nanoparticles were mixed with benzoxazine monomers in solution, spin coated onto a glass slide, and then cured. The resulting rough surface of the polybenzoxazine–silica hybrid thin film was further modified with a thin film of the pure BA-m polybenzoxazine.

Table 1 lists the roughness of polybenzoxazine–silica hybrid films with various nanoparticle contents. The benzoxazine monomer concentration was kept constant in solution while increasing the nanoparticle content up to certain extent leading to an increase in the resultant surface roughness of the polybenzoxazine–silica hybrid film. However, in our system, nanoparticle contents that are too high (sample e) tend to reduce the adhesion of the polybenzoxazine–silica hybrid film on the

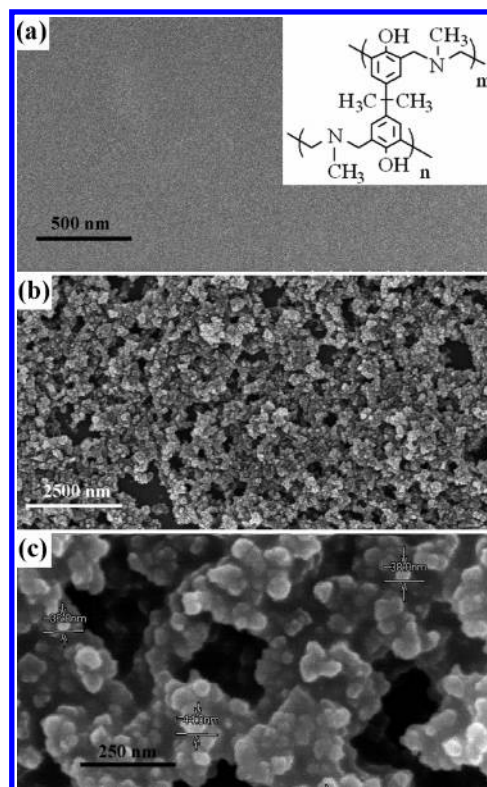


Figure 1. SEM images of different polymer surfaces. (a) Film prepared from pure BA-m polybenzoxazine. The inset is the chemical structure of BA-m polybenzoxazine. (b) Polybenzoxazine–silica hybrid surface modified with BA-m polybenzoxazine. (c) Enlarged view of the image in b.

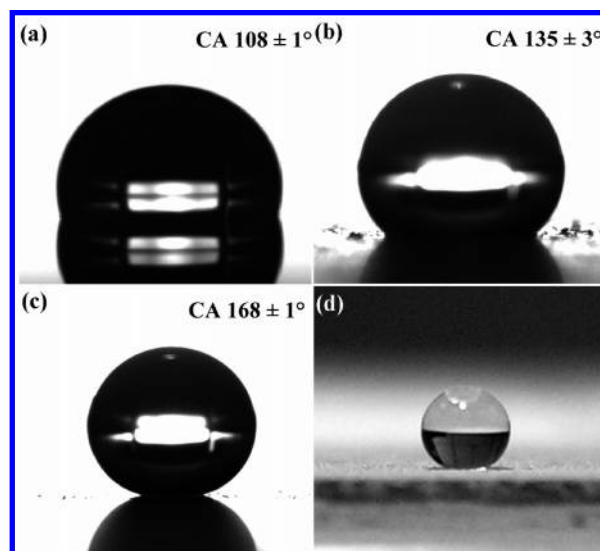


Figure 2. Profiles of water drops on (a) a smooth cross-linked polybenzoxazine surface, (b) a polybenzoxazine–silica hybrid surface, and (c) the as-prepared superhydrophobic surface. (d) Optical image of a water droplet on a polybenzoxazine–silica hybrid surface modified with BA-m polybenzoxazine.

glass substrate. In this letter, we chose the optimum content (sample d) to carry out a detailed investigation. The polybenzoxazine–silica hybrid surface (sample d) had a surface roughness of 190.7 ± 11.9 nm and a CA of $135 \pm 3^\circ$ for water (Figure 2b); although hydrophobic, this value is too low for the material to be classified as superhydrophobic. To increase the CA for water, the polybenzoxazine–silica hybrid surface was modified with a pure BA-m polybenzoxazine film. Table 2 lists the roughness and contact angles for water on the polybenzoxazine–silica hybrid surface modified with BA-m polybenzoxazine.

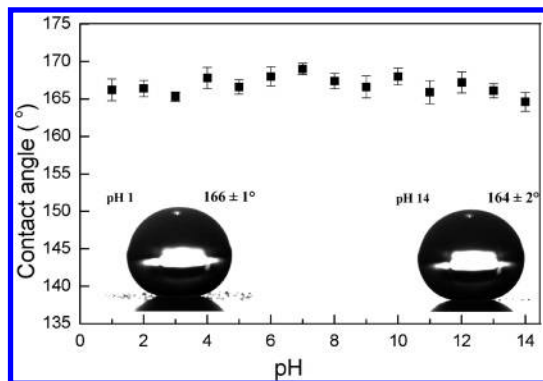


Figure 3. Relationship between pH and water contact angle on the superhydrophobic surfaces of polybenzoxazine.

oxazine–silica hybrid surfaces after they were modified with the pure BA-m polybenzoxazine film. The rms roughness of rough polybenzoxazine surfaces decreased continuously from 182.3 to 103.1 nm upon increasing the concentration of benzoxazine monomer solution from 0.5 to 50 mg/mL. We also discovered that decreasing the surface roughness of rough polybenzoxazine surfaces leads to a decrease in the water CA. This observation can be explained by eq 1 derived by Wenzel¹⁵ to describe the CA for a liquid droplet at a rough solid surface.

$$\cos \theta_r = r \cos \theta \quad (1)$$

Wenzel's equation corresponds to the lowest-energy state on a rough surface. In eq 1, θ is the intrinsic CA on a smooth surface, θ_r is that on a rough surface made of the same material, and r is the roughness factor. The ratio of the true surface area A (taking into account the peaks and valleys on the surface) to the apparent surface area A' is defined as the roughness factor $r = A/A'$. This equation indicates that increasing surface roughness results in an actual CA decrease for hydrophilic materials ($\theta < 90^\circ$) and an increase for hydrophobic materials ($\theta > 90^\circ$). The BA-m polybenzoxazine is a hydrophobic material with a water CA of 108° . It is clear that the CA for water will decrease upon decreasing the roughness of the rough surface created by the coated BA-m polybenzoxazine film, according to eq 1.

Because sample 1 possesses the highest water CA of $168 \pm 1^\circ$ (Figure 2c and d), the minute hysteresis H ($H = \text{advancing angle of } 168^\circ - \text{receding angle of } 167^\circ = 1$) and the smallest sliding angle (lower than 3°), only the superhydrophobic polybenzoxazine surface prepared under sample 1 conditions will be discussed hereafter. Figure 1b and c shows top-view scanning electron microscopy (SEM) images of the as-prepared superhydrophobic surface on a glass slide. This superhydrophobic polybenzoxazine surface gives a rough surface possessing both micro- and nanoscale binary structures. Each microisland (300–700 nm) on the polybenzoxazine surface (Figure 1b) was covered with nanospheres (from 20 to 60 nm; Figure 1c). Such a structure dramatically increases the surface roughnesses and leads to composite interfaces²³ in which air becomes trapped within the grooves beneath the liquid and thus induces superhydrophobicity. It is interesting that the as-prepared surface possesses superhydrophobic properties not only for pure water but also for corrosive water under both acidic and basic conditions.

Figure 3 shows the shapes of aqueous solution droplets on the superhydrophobic polybenzoxazine film with pH values of 0.98 and 13.85, respectively. To our surprise, these two droplets remain spherical with high CA values of $166 \pm 1^\circ$ and $164 \pm 2^\circ$,

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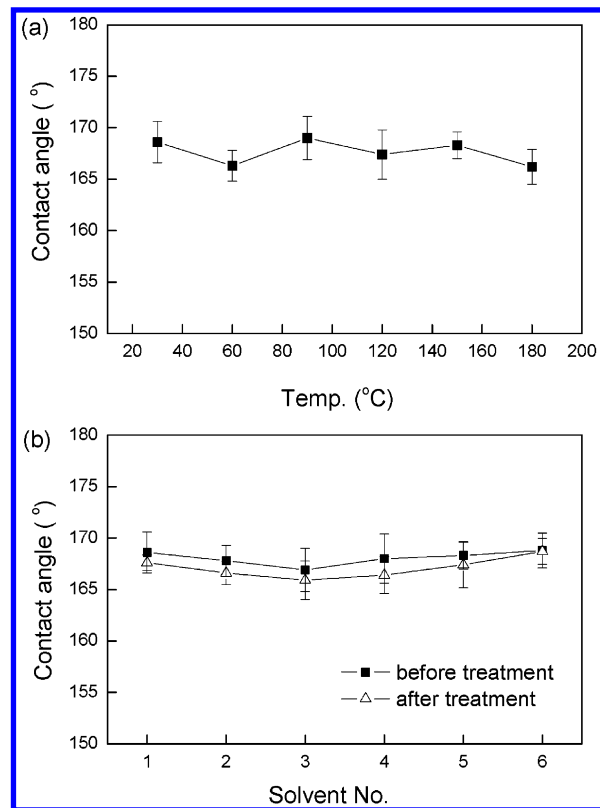


Figure 4. (a) Thermal stability of the superhydrophobic polybenzoxazine film treated at various temperatures for 8 h. (b) Durability of the superhydrophobic polybenzoxazine film on treatment with organic solvent and diesel oil (1, tetrahydrofuran; 2, dichloromethane; 3, acetone; 4, water; 5, ethanol; and 6, diesel oil).

respectively. In fact, such superhydrophobic behavior covers the entire pH range from 1 to 14 as shown in Figure 3. Over the whole pH range, the water droplet can be moved easily when the surface is slightly tilted. These results imply that the superhydrophobic polybenzoxazine surface can be used in a wide pH range of corrosive water. To the best of our knowledge, the superhydrophobic surfaces suitable for both acidic and basic aqueous droplets have been reported only in a few studies. Feng et al. previously reported that nanostructured carbon films prepared from aligned polyacrylonitrile nanofibers show superhydrophobic properties in the pH range from 1.07 to 13.6.²⁴ Recently, Guo et al. reported the formation of superhydrophobic surfaces suitable for all pH environments by treating aluminum and its alloys with sodium hydroxide solution followed by modification with perfluorononane and vinyl-terminated poly(dimethylsiloxane), respectively.²⁵ Zhu et al. found that the polyaniline/polystyrene composite film prepared by an electrospinning method showed stable superhydrophobicity and conductivity, even in acidic or basic solutions over a wide pH range.²⁶ The method we described herein possesses the advantages of being simple and inexpensive while being able to utilize non-fluorine-containing compounds.

The effect of thermal treatment (8 h) on the wettability was also systemically studied to evaluate the thermal stability of the resulting film in terms of water CA. Figure 4a indicates that increasing temperature has little or no effect on the film's CAs. BA-m polybenzoxazine is a cross-linked polymer with a high

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T_g (180 °C). Similarly, the effects of treatment with organic solvents and diesel oil on the wettability were also evaluated in terms of the CA with respect to that of pure water. Figure 4b shows the effect of the superhydrophobic polybenzoxazine film upon treatment with various organic solvents and diesel oil. The CA of the film is nearly unchanged after treatment. Excellent solvent resistance to various organic solvents for polybenzoxazine has been reported.²⁷ In this investigation, the superhydrophobicity was measured over different time intervals. These films are stable after 5 months under ambient conditions, resulting in very little change in their water CAs.

Conclusions

The superhydrophobic polybenzoxazine surface can be prepared through a simple and inexpensive method. The as-prepared

film shows superhydrophobicity covering the entire pH range. The non-fluorine superhydrophobic polybenzoxazine film also possess marvelous environmental stability to both thermal and organic solvent treatments in terms of the water CA. Our results are considered to be significant in terms of their importance to academic research and industrial applications.

Acknowledgment. This work was partially supported by the Ministry of Education “Aim for the Top University” program (MOEATU program).

Supporting Information Available: Video clips showing continuous roll-off of water droplets on the superhydrophobic polybenzoxazine surface tilted by 3°. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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LA061480W