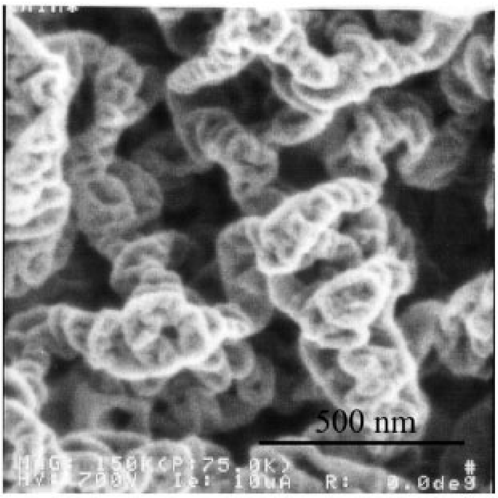
Summary: In this study, a method for producing super-amphiphobic surfaces through plasma modification of benzoxazine films is presented. Microroughening and fluorination of the benzoxazine films occurs during the plasma treatment process and a rugged surface with a micro/nano binary structure is formed. The combined effect of low surface energy and substrate roughness results in high advancing contact angles (157° for water, 152° for diiodomethane) and low contact angle hysteresis.



SEM image of a cross-linked polybenzoxazine film treated with Ar plasma (7 min) heated to 200 °C (1 h) and treated with CF_4 plasma for 30 s.

Fabrication of Biomimetic Super-Amphiphobic Surfaces Through Plasma Modification of Benzoxazine Films

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Introduction

Liquid repellency is an important property for a material if it is to be useful in many industrial and biological applications.[1] Although poly(tetrafluoroethylene), i.e., Teflon, is regarded as a benchmark low-surface-free-energy material that displays water repellency[2] in combination with other desirable properties,[3] its low oil repellency and microcrystalline surface structure limit its application. One method to improve the liquid repellency of a surface is to combine a suitable chemical structure (surface energy) with a topographical microstructure (roughness). Previous attempts have included preparing a fractal surface,[4] plasma treating polymer surfaces,[5,6] functionalizing roughened substrates with perfluoroalkyl groups,[7] preparing gel-like roughened polymers through solvent processing,[8] phase separating polymer blends,[9] densely packing aligned carbon nanotubes,[10–12] self-assembling monolayers of *n*-alkanoic acids on electrochemical deposition copper films,[13] and other approaches.[14] Both super-hydrophobic and super-amphiphobic surfaces can result from increased surface roughness, for example, this effect occurs naturally on the lotus leaf.[15,16] The surfaces of these leaves possess a micrometer-level roughness and they are covered with nanosized crystals of wax.[11] The water contact angles of these leaves can be as high as 160° because air is trapped between the water droplets and the wax crystals at the plant surface to minimize the contact area.[17]

Polybenzoxazines have been developed recently as a new type of phenolic resin. This class of polymer has many advantageous features, such as superior mechanical properties,[18] low cost, excellent resistance to both chemicals[19] and UV light,[20] and high glass transition temperatures.[21] In this paper, a novel method for producing super-amphiphobic surfaces through plasma modification of benzoxazine monomer thin films is presented.

Experimental Part

2,2-Bis(3,4-dihydro-3-methyl-2*H*-1,3-benzoxazine)propane (BA-m benzoxazine) was supplied by Shikoku Corp. Diiodomethane (99%) was obtained from Aldrich.

Super-amphiphobic coatings on silicon wafers were formed by a four-step process. All plasma treatment processes were performed using a reactive ion etching (RIE) system (TEL, model TE5000) operated at a frequency of 13.56 MHz. Firstly, BA-m benzoxazine dissolved in tetrahydrofuran (50 $mg \cdot mL^{-1}$) was spin-coated for 45 s onto a 6 inch silicon wafer using a photoresist spinner (CONVAC 801/ST) operated at 1 500 rpm. The solvent was then allowed to evaporate for 1 h at 60 °C. Secondly, argon plasma roughening of the benzoxazine monomer thin film was performed in the RIE system for a desired period of time. The flow rate of argon was 1 000 sccm, the pressure was 800 mTorr, and the power was 500 W. Thirdly, cross-linking of these plasma-roughened benzoxazine films was performed by placing them onto a digital hot plate for 1 h at 200 °C. Fourthly, rugged polybenzoxazine surfaces were fluorinated for 30 s with CF_4 plasma at a pressure of 800 mTorr, a flow rate of 30 sccm, and a power of 25 W.

The microstructure of the polymer surface obtained after plasma treatment was characterized using an HITACHI-S-6280H scanning electron microscopy (SEM) instrument. Contact angles were measured on a Krüss GH-100 contact angle goniometer. Each reported contact angle is the average of six measurements. The advancing contact angle was read by injecting a 5 μL liquid droplet. The receding contact angle was measured by removing about 3 μL of liquid from the drop. The static contact angle was obtained from a drop of ca.5 μL. Atomic force microscopy (AFM) images were acquired using a Digital Instruments DI5000 scanning probe microscope. Damage to both the tip and to the sample surface was minimized by employing AFM in the tapping mode. The values of root-mean-square (rms) roughness were calculated over scan areas of 5 μm × 5 μm. X-Ray photoelectron spectroscopy (XPS) analysis of the sample was performed on a VG Microlab 310F spectrometer with an Al Kα X-ray source (1 486.6 eV).

Results and Discussion

Smooth thin films of polybenzoxazine are obtained after spin-coating 2,2-bis(3,4-dihydro-3-methyl-2*H*-1,3-benzoxazine)propane (BA-m benzoxazine) onto silicon wafers and then curing them at 200 °C for 1 h. AFM results suggest an rms thin-film roughness of 0.19 nm. A water droplet placed on such a surface has a contact angle of $108 \pm 1°$ (Figure 1a). To increase the contact angle, an RIE system is used for CF_4 plasma treatments on the BA-m polybenzoxazine film. The plasma-treated film has a surface roughness of 0.31 nm and a water contact angle of $111 \pm 1°$. Although hydrophobic, this value remains too low for the material to be classified as super-hydrophobic. Herein, a novel method for producing super-amphiphobic surfaces is described. This method, which can improve the water contact angle from 108° to 155° (Figure 1b), is cheap, rapid, durable, and can be applied readily to a variety of substrates.

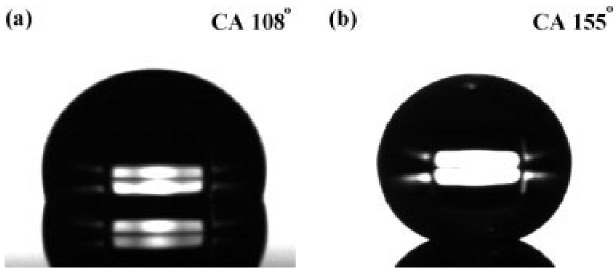
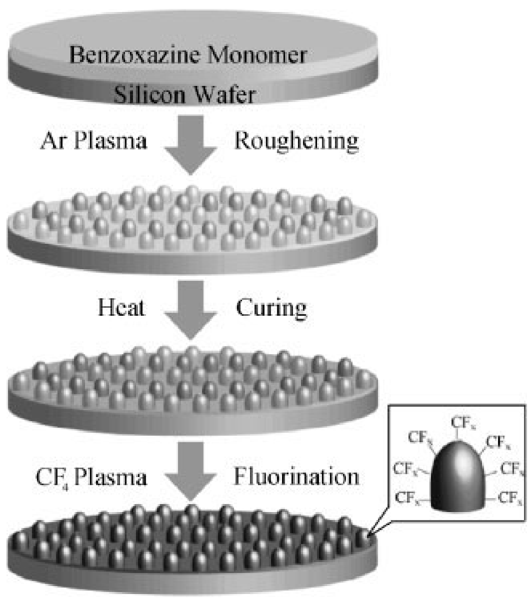


Figure 1. Profiles of water drops on a) a smooth cross-linked polybenzoxazine surface, and b) a super-amphiphobic polybenzoxazine film coated on a silicon wafer and treated by the following process: Ar plasma, 1 min; 200 °C, 1 h; CF_4 plasma, 30 s. CA: Contact angle.

The formation of super-amphiphobic coatings on silicon wafers is achieved by applying the four-step process displayed in Scheme 1. Table 1 lists the exact conditions of the plasma treatment processes. SEM is used to observe



Scheme 1. Procedure for forming super- hydrophobic films from benzoxazine monomers.

Table 1. Parameters of the plasma treatment processes.

Sample No.	Ar plasma treatment time	Curing time at 200 °C	CF_4 plasma treatment time
	min	h	s
1	0.5	1	30
2	1	1	30
3	3	1	30
4	5	1	30
5	7	1	30

the morphologies of the polybenzoxazine surfaces. After argon plasma treatment, the benzoxazine film exhibits a rugged surface that possesses papillae-like structures (Figure 2a–c). The dimensions of the papillae and the rms roughness of the benzoxazine surfaces increases upon increasing the plasma exposure time, e.g., the samples in Figure 2a (30 s exposure) and 2c (7 min) have an rms roughness of 27 and 62 nm, respectively. The water contact angle of the benzoxazine monomer thin film decreases abruptly (from 75 to 38°) after exposure to the argon plasma for 30 s. Increasing the exposure time to 7 min has little

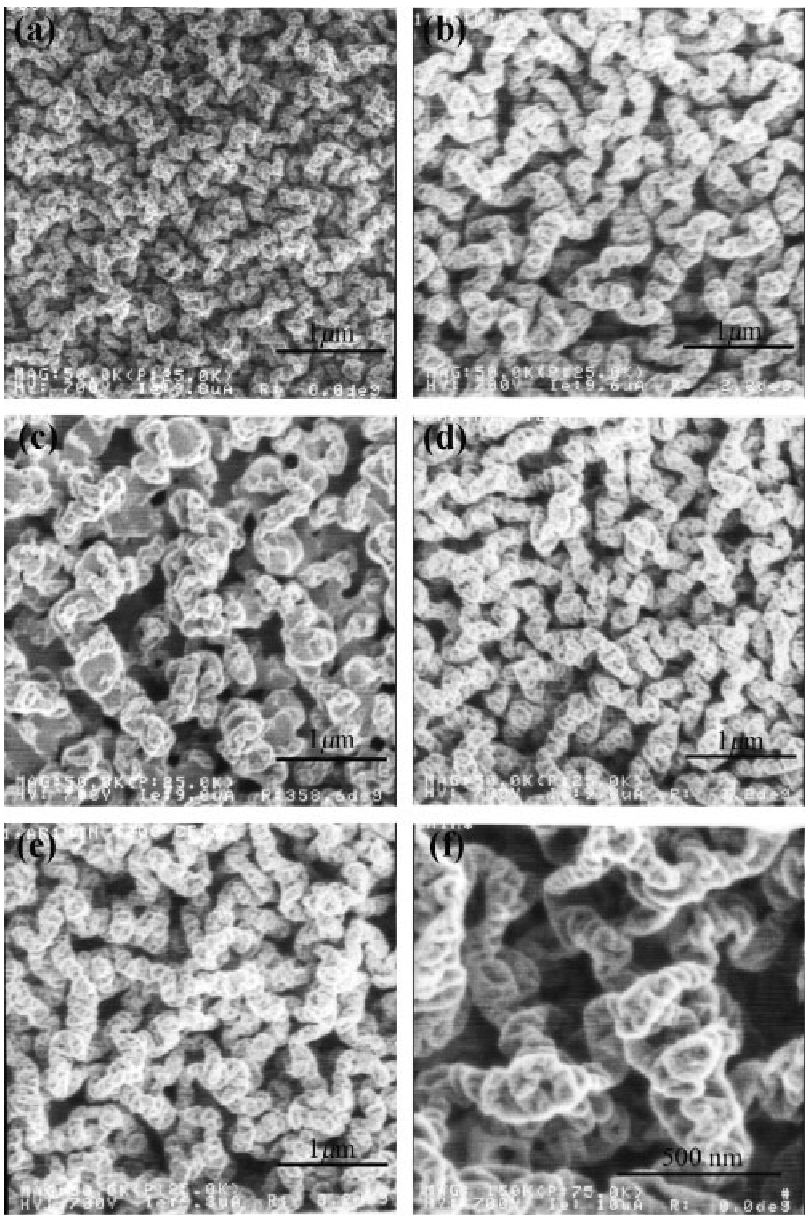


Figure 2. SEM images of different polybenzoxazine surfaces. Benzoxazine films treated with Ar plasma for a) 30 s, b) 1 min, and c) 7 min. d) The rough polybenzoxazine film from (b) after its curing for 1 h at 200 °C. e) The cross-linked polybenzoxazine film from (d) after its treatment with CF_4 plasma for 30 s. f) Enlarged view of the image in (e).

effect on the water contact angle, which remains at ca. 35°. The SEM images of the thermally cured (Figure 2d) and uncured (Figure 2b) films reveal that no significant morphological change occurs at the surface. The water contact angle of each of the rough benzoxazine surfaces increases after curing, and increases with respect to the degree of roughness (Figure 3a), but the water drops remain pinned to these surfaces. The rugged polybenzoxazine (Figure 2d) exposed to CF_4 plasma for 30 s does not undergo any significant change to its surface morphology (Figure 2e).

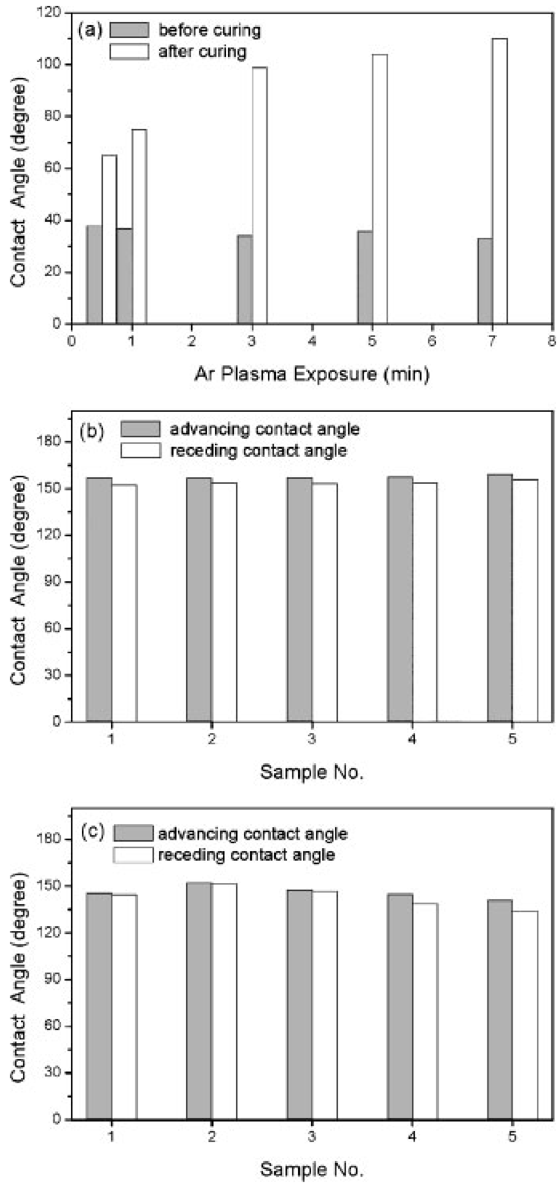


Figure 3. a) Static water contact angles of Ar plasma-treated benzoxazine films before and after curing for 1 h at 200 °C. b) The advancing and receding water contact angles of each of the fully treated polybenzoxazine films. c) The advancing and receding diiodomethane contact angles of each of the fully treated polybenzoxazine films.

After fluorination with the CF_4 plasma, super-hydrophobic surfaces (water contact angles >150°) are obtained for all of the polybenzoxazine films (Figure 1b).

Contact angle hysteresis is another criterion for characterizing the hydrophobicity and lyophobicity of solid surfaces. For an ideal surface, there exists only one contact angle, i.e., a true equilibrium contact angle. For a real surface, however, several contact angles may be observed, which results in contact angle hysteresis. The difference between the advancing (θ_A) and receding (θ_R) angles provides the extent of hysteresis (H). A single static or advancing contact angle does not adequately describe the hydrophobicity of a surface. The hysteresis is more important for determining the true hydrophobicity (and lyophobicity) than achieving a maximum contact angle. The contact angle hysteresis can be regarded as the force required to move a liquid droplet across a surface.[22] When the contact angle hysteresis is small or negligible, only a very small force is required to move the droplet and, thus, it can roll off easily. Figure 3c indicates that a super-hydrophobic character (advancing contact angle >150°, and the difference between the advancing angle and receding angle is small) is observed for all of the fully treated polybenzoxazine films. The water contact angle hysteresis of all surfaces is below 5°. The water drops roll easily on the horizontal surfaces. Not only do these polymer surfaces exhibit improved hydrophobicity but they also display lyophobic properties. Figure 3c presents the advancing and receding contact angles of diiodomethane on all of the fully treated polybenzoxazine surfaces. One of the benzoxazine films (specific treatment process: argon plasma, 1 min; 200 °C, 1 h; CF_4 plasma, 30 s) exhibits diiodomethane contact angles, θ_A and θ_R, of 152° and 151°, respectively, such that diiodomethane droplets move easily when the surface is slightly tilted. Most interestingly, it is found that the polybenzoxazine film treated in this way has a rough surface possessing both micrometer- and nanometer-scale binary structures: each micro-papilla (200–600 nm) on the polybenzoxazine surface (Figure 2e) is covered with nanopapillae (from 30 to 60 nm, Figure 2f). This binary structure is similar to that of the self-cleaning lotus leaf.[11] Such structures possess a dramatically increased surface roughness that leads to the formation of composite interfaces[17] in which air becomes trapped within the grooves beneath the liquid. This phenomenon significantly minimizes the contact area between the polybenzoxazine surface and the liquid. On this polybenzoxazine surface, water and diiodomethane droplets both possess near spherical shapes and roll off with ease.

The chemical resistance, thermal stability, and mechanical durability of these argon-plasma-roughened polybenzoxazines are found to improve after cross-linking. In contrast, bulk cross-linking causes negligible changes to the surface morphology, which suggests that the surface regions have already undergone extended structural rearrangement (cross-linking) during the prior argon plasma treatment process.[6,23] A substantially lower water contact angle (112°) is obtained after cross-linking (but prior to argon plasma roughening and CF_4 plasma fluorination), which indicates that a sufficient degree of monomer mobility occurs during the argon plasma treatment process to induce surface roughness. The surface elemental compositions of the CF_4-plasma-treated (argon plasma treatment, 5 min; curing, 1 h at 200 °C) and untreated rough polybenzoxazine film are obtained from XPS analysis. After treatment with the CF_4 plasma, a significant increase in the fluorine content (from 0 to 33%), is observed in conjugation with depletion of the other elements. Combining the results of the XPS and SEM images (Figure 2d and 2e), it is clear that after a short treatment time (30 s), the CF_4 plasma induces a drastic modification of the surface chemistry, but it does not cause any significant change to the surface morphology. The results indicate that these super-amphiphobic polybenzoxazine films are stable for 6 months under ambient atmospheric conditions. No change is observed in their physicochemical characteristics.

Conclusion

The plasma treatment of BA-m benzoxazine films is used to mimic the well-known two-level surface texture of the lotus leaf. Argon plasma microroughening of the benzoxazine thin films creates their rugged surfaces. Subsequent bulk cross-linking leads to a significant enhancement in the chemical resistance, thermal stability, and mechanical durability of these films. Fluorination of rough polybenzoxazine thin films using CF_4 plasma improves the liquid repellency and yields super-amphiphobicity. The net result is a stable super-amphiphobic surface that exhibits high contact angles and low contact angle hysteresis.

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