

Formation of Nanoporous Polycarbonate Surfaces and Their Chemical Modification for Superhydrophobicity

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Polycarbonates (PCs) are a particular group of thermoplastic polymers that contain carbonate groups (-O-CO-O-). PCs are nontoxic and temperature resistant with high mechanical strength, low water absorption, and good optical properties, including transparency. However, they easily dissolve in organic solvents (*i.e.*, dichloromethane or toluene). Nevertheless, PC is a very attractive material for a wide range of applications in housewares, CDs and DVDs, electronic equipments, and machine parts.¹⁻⁵ In the near future, after the further improvement of a few of its physical properties, PC will replace automobile glass. Transparent polymers have already been used as precision optical parts such as optical lenses.⁶ The surface energy and surface structure of PC are controlled by the polymer's surface properties. For instance, the wetting behavior of a PC surface depends on its nanoscale and microscale roughness as well as on the existence of a hierarchical surface structure. A hierarchical surface structure increases the surface roughness which minimizes the contact area between the surface and a water drop. For example, lotus leaves, which are known to be superhydrophobic with a high water contact angle ($< \sim 150^\circ$) and low sliding angle ($> 10^\circ$), are covered by a nanoscale/microscale binary structure that is coated with wax.

Artificial superhydrophobic surfaces can be fabricated by mimicking the properties of lotus leaves. While there have been numerous approaches along these lines, they can be roughly divided into two groups; the creation of nanoscale/microscale roughness on a hydrophobic surface and modification of hierarchical structures with low surface energies.⁷⁻⁹ Fluorinated compounds and long-chain fatty acids, which have low surface energies, have been generally used to modify rough surfaces.¹⁰⁻¹²

Various approaches to fabricate surfaces with roughness on the nanoscale/microscale have been reported and evaluated.¹³⁻¹⁷ However, most of these fabrication methods have significant limitations, in that they are time consuming, or require harsh reaction conditions and expensive chemicals. Recently, simpler phase-separation methods have been applied to polymer materials in order to fabricate superhydrophobic coatings. These phase-separation methods are known to be rapid, simple, and cost effective processes for creating rough superhydrophobic surfaces.¹⁸⁻²⁴ For example, polypropylene can be dissolved in an organic solvent and spread onto a solid surface, which creates a hierarchical super-

hydrophobic surface after the solvent is evaporated.²⁵ In these processes, the solvents and temperature are important factors for controlling the surface roughness and achieving superhydrophobicity. Wang's group and Varanasi's group have reported the preparation of superhydrophobic PC surfaces using phase-separation methods. Wang's group used a process involving dipping the plate sample into the PC solution.²⁶ Varanasi's group created the superhydrophobic surface by dipping a PC plate into acetone for different amounts of time.²⁷ However, a long immersion period (*i.e.*, 30 min) was required to create a superhydrophobic surface, which introduces the possibility of deformation of the PC plate or the formation powder on the surface by the recrystallization of PC after solvent evaporation.

In the present study, we report an inexpensive and facile method for fabricating nanoporous superhydrophobic PC plates by dipping them into organic solvents for a very short period and then modifying them with fluorinated chemicals. The effect of different dipping times, pH values, and organic solvents on the surface morphology and wettability of the PC is also studied. Commercially available PC plate was chosen to prepare the superhydrophobic surfaces at room temperature using the simple dipping and drying process. The nanoporous PC surfaces were studied using scanning electron microscopy (SEM). The chemical composition of surface was studied by X-ray photoelectron spectroscopy (XPS), and the nature of the hydrophobic surface was studied by measuring the contact angle between the surface and water.

Experimental Section

Instrumentation. The water contact angles on the PC plates were measured using a contact angle analyzer (Phoenix 300, Surface Electro Optics) at room temperature. The surface morphologies of the modified PC plates were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S4300, Hitachi Inc.). XPS was performed using an XPS spectrometer (MultiLab 2000, Thermo VG Scientific). Trichloromethyl silane (TCMS) was purchased from Sigma-Aldrich (U.S.A.). The PC substrates were cut into $3 \times 1 \times 0.1$ cm slices and cleaned by sonication in distilled water.

Procedure. The PC plates were immersed in CH_2Cl_2 for 5

s at room temperature and then removed. An air gun was then used to blow the PC plate dry. The treated PC plates were hung inside a 300 mL round-bottom flask, and 1.57 mL of TCMS was added. The flask was connected to a balloon and heated at 80 °C for 10 min.

Results and Discussion

We fabricated superhydrophobic surfaces on PC pieces using the dipping and drying method described above at room temperature with different organic solvents. One of the key factors that need to be controlled in order to obtain a superhydrophobic surface is the surface structure, which should have roughness on the nano-scale/micro-scale and should be hierarchical. Superhydrophobic surfaces often have extrusions on the surface, along with irregular spaces, as can be observed in the SEM images of lotus leaves.

In this study, we tried to investigate the role of organic solvent in the formation of a nanoporous structure on the surface of a PC plate. Different organic solvents were selected to treat the PC plates: CH_2Cl_2 , methyl ethyl ketone, ethyl acetate, toluene, and isopropyl alcohol. Only CH_2Cl_2 created a nanoporous structure in a short period (5 s), as can be seen in Figure 1. The other organic solvents produced a sticky or swollen surface on the PC plate. The rough surface of the PC plate treated with CH_2Cl_2 has a nanoporous surface morphology with nonuniform pore sizes typically ranging from 700 nm to 950 μm . As soon as the PC plate was withdrawn from the organic solvent, it became opaque because a crystallized polymer layer was formed on the surface of the PC plate.

The rough nanoporous structure of the PC surface is very labile in organic solvents, which limits the coating methods

available for depositing a low-surface-energy material. After it was treated with CH_2Cl_2 , the nanoporous PC plate was successfully coated with TCMS vapor with no deformation of its nanoporous surface structure. After modification with TCMS, the surface of the coated nanoporous PC plate had a water contact angle as high as 161° (Fig. 2).

The Cassie-Baxter equation is used to determine the volume of open space in the hierarchical structure of the surface. Because air is trapped in the space, water cannot penetrate into the hierarchical structure. The Cassie-Baxter equation defines the wettability of a porous surface.²⁸

$$\cos\theta^* = \Phi_s(1 + \cos\theta) - 1$$

where θ^* is the water contact angle on a nanoporous surface modified with a low-surface-energy material, Φ_s is the area fraction of the solid surface and θ , is the contact angle on a flat surface. The water contact angle of the fabricated surfaces was $\theta^* = 161^\circ$, and the water contact angle of a flat PC plate treated with TMCS was $\theta = 79^\circ$, as shown in Figure 2. From these data, the Φ_s value of the modified nanoporous surface of the PC was calculated as 0.045. This indicates that 95.5% of the contact area between the nanoporous superhydrophobic surface of the PC plate and the water droplet is made up of air. The nanorough surface contains air that prevents the penetration of water into the open space in the surface. This causes the contact area between the surface and water to decrease, resulting in the lower value of Φ_s . In summary, the nanoporous surface contains a large amount of air, which increases the water contact angle dramatically.

The stability of the superhydrophobic surfaces was studied under different pH conditions. Figure 3 shows the relationship between the pH and water contact angle on the nano-

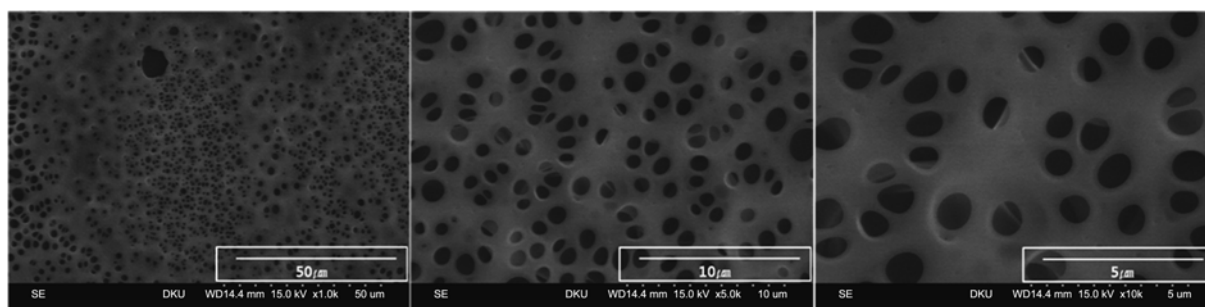


Figure 1. SEM images of PC treated with CH_2Cl_2 for 5 s.

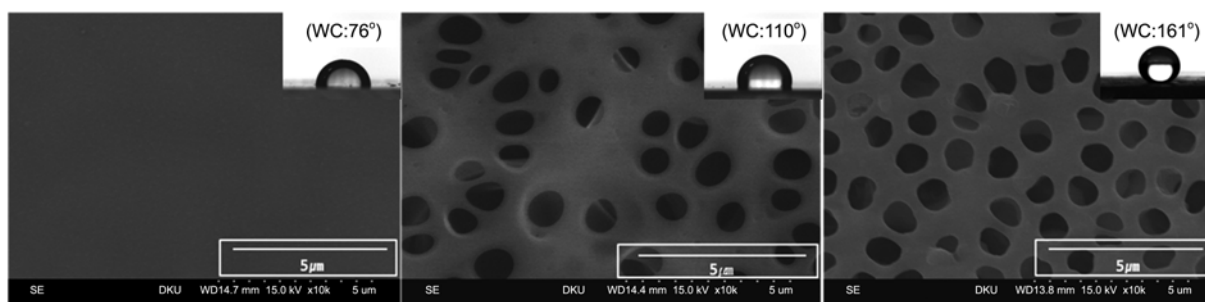


Figure 2. SEM images and water contact angles of (a) untreated PC plate, (b) PC plate treated with CH_2Cl_2 for 5 s, and (c) PC plate coated with TCMS after it was dipped in CH_2Cl_2 .

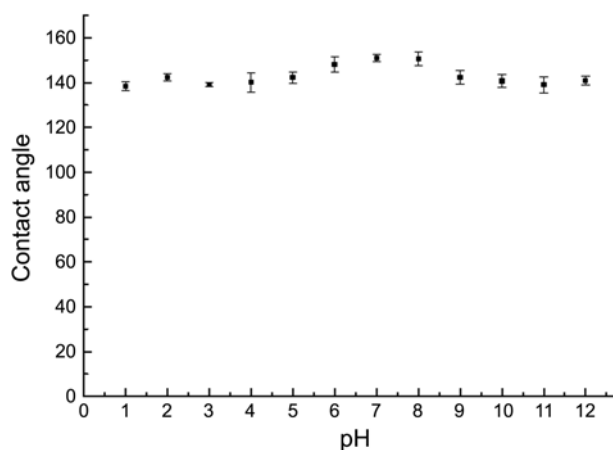


Figure 3. Relationship between pH and water contact angle on superhydrophobic surfaces.

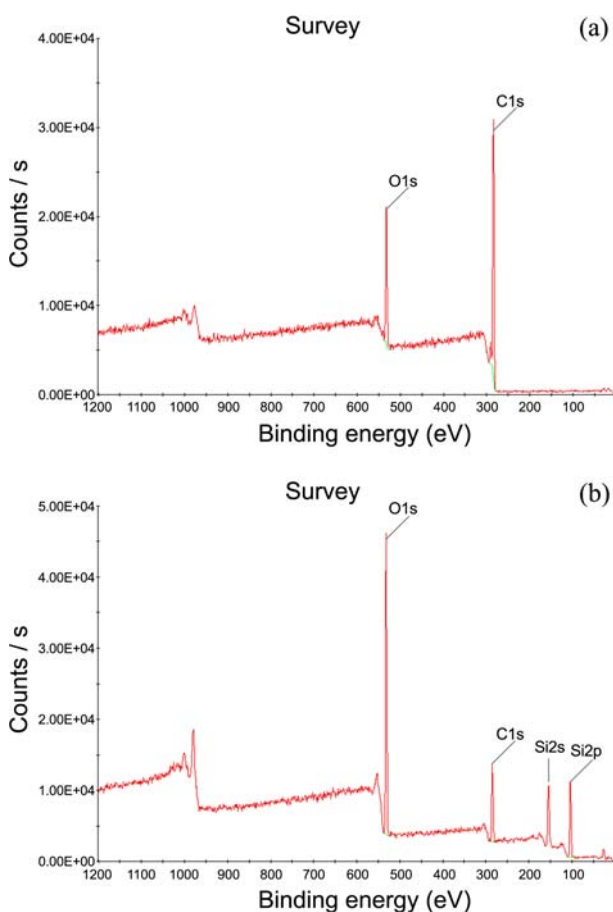


Figure 4. XPS spectrum of porous PC plate (a) before and (b) after modification with TCMS.

porous PC surface modified with TCMS. The contact angle did not change for different pH values. This demonstrates that the modified PC surfaces are stable in acidic and basic solutions at normal temperatures. The superhydrophobicity of the nanoporous PC plate can be maintained over a broad pH range.

XPS was carried out to obtain the elemental composition of the coated surface of the PC plate in terms of the C, O,

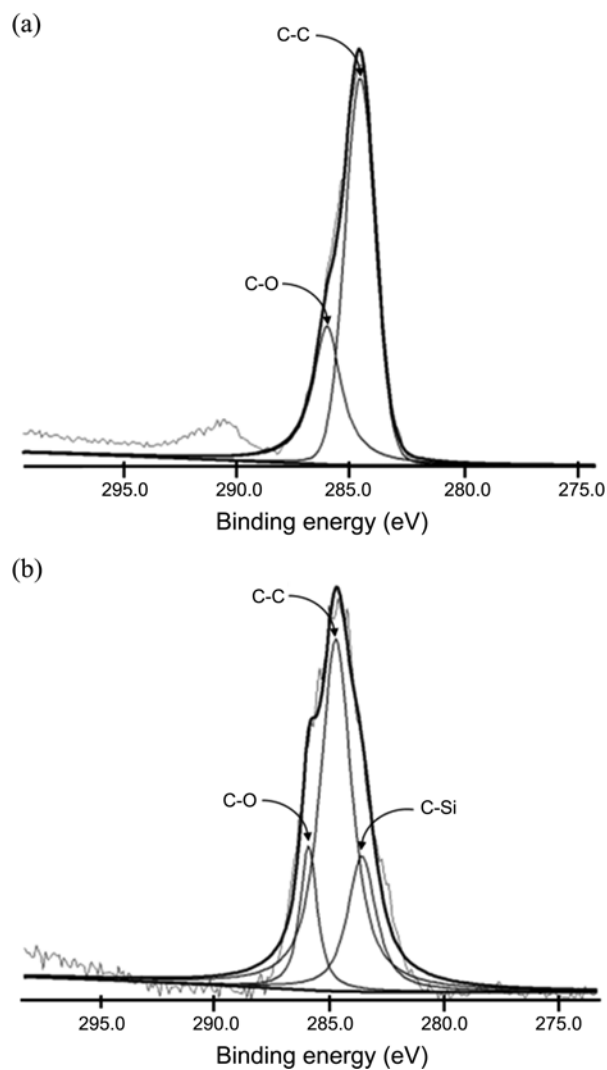


Figure 5. High resolution of C1s XPS pattern of (a) unmodified PC plate and (b) PC plate coated with TCMS.

and Si contents. The XPS analysis revealed the differences in the elemental composition of the surface before and after modification with TCMS. Figure 4 shows the XPS spectra of (a) the unmodified PC plate and (b) the PC plate modified with TCMS. Both Si(2*p*) and Si(2*s*) XPS signals were observed on the PC plate modified with TCMS. Figure 5 shows the high-resolution C1s spectrum. The C1s signal of the unmodified PC plate includes peaks at 284.8 eV and at 286.3 eV. The peak at 284.8 eV was assigned to C participating in C-C bonds, and that at 286.3 eV was assigned to C participating in C-O bonds. However, C participating in C-Si bonds was also identified on the surface of the nanoporous PC plate modified with TCMS as a peak at 283.8 eV. This clearly indicates that the surface of the PC plate was coated with TCMS, and the surface coated with low-surface-energy material became superhydrophobic after the reduction of the surface energy.

In conclusion, superhydrophobic surfaces were fabricated by dipping PC plates into CH₂Cl₂ and then coating them through sublimation of TCMS. Because CH₂Cl₂ is a good

solvent for dissolving PC plates, the dipping time was very short. Because the nanoporous structure of the PC surface is very labile in organic solvents, we used sublimation of TCMS to coat the surface with low-surface-energy material. After the CH₂Cl₂ treatment, the nanoporous PC plate was successfully coated with TCMS vapor with no deformation of its nanoporous surface structure. The PC plate modified with TCMS had a water contact angle as high as 161°, demonstrating its excellent superhydrophobicity. The technique described here can be applied to the creation of superhydrophobic nanoporous surfaces on substrates that are labile in organic solvents.

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