

SUPERHYDROPHOBIC SURFACES FROM A SPRAY COATING PROCESS

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Keywords: *superhydrophobic, spray coating, composite, water contact angle*

1 Introduction

In recent years, the strategy to prepare superhydrophobic surfaces with water contact angles higher than 150° is of intense interest because of their potential applications in self-cleaning, metal refining, adhesion preventing and drag reduction in fluid flow [1-3]. Remarkable achievements have been recently made in superhydrophobic surfaces with tailoring the surface topography and using techniques such as anodic oxidation, template extrusion, the electrodeposition and/or chemical etching, plasma etching, laser treatment, electrospinning and chemical vapor deposition [4-8]. Despite improvements in these techniques, most of the methods are expensive and require multistep procedures, limited substrate materials, and small flat surfaces, which limit practical applications. Thus many of these methods are not readily suitable for the coating of the surfaces of complex substrates with large area.

In this study, silica/polymer composites were synthesized and utilized as superhydrophobic surfaces. The surfaces were prepared by spray deposition of silica/polymer composites in organic solvent. The spray-deposition process is a well-established process for industrial coatings such as photoresist coating, printing and painting. This simple process, with a high throughput, is applicable for a variety of substrates and is not limited to small areas. Among the various surface deposition processes, spray-coating is one of the most mature techniques.

2 Experimental

2.1 Materials

Methylmethacrylate (MMA) and Zonyl[®] TM (Zonyl) were purchased from Aldrich and purified

by passing the liquids through a neutral alumina column to remove inhibitors. 2,2'-azobisisobutyronitrile (AIBN, Aldrich) was purified by recrystallization in methanol. 3-(trimethoxysilyl)propyl methacrylate (γ -MPS), NH₄OH (25 wt% aqueous solution), ethanol, methanol, tetrahydrofuran (THF), tetra-ethylorthosilicate (TEOS, 95%), and toluene were purchased from Aldrich and used as received.

2.2 Synthesis of SiO₂ particle and surface modification

SiO₂ particles were synthesized using the Stöber procedure [9]. Absolute ethanol (200 mL) and 15 mL of 28 wt% ammonia solution were placed into a round flask. The mixture was stirred at 300 rpm to homogenize the mixture, which was then heated to 60 °C. Subsequently, 12 mL of TEOS was added to the solution and the reaction was carried out for 24 h. The product was isolated by an ultracentrifuge operated at 10000 rpm for 30 min and dried in vacuum at 40 °C. For SiO₂ surface functionalization, an excess of γ -MPS was added to 10 g of the SiO₂ particles dispersed in 100 mL of toluene, and the mixture was stirred at 100 °C for 24 h, in an argon atmosphere. Modified γ -MPS-SiO₂ was isolated by an ultracentrifuge and washed several times with toluene to remove the unreacted γ -MPS. The calculated amount of grafted MTS was approximately 15.7% from the result of thermogravimetric analysis (TGA, see Fig.3(a)).

2.3 Synthesis of silica/polymer composite by free radical polymerization

A typical procedure for synthesizing the silica/poly(Zonyl-co-MMA) composite is as follows: 0.8 g of MMA, 0.2 g of Zonyl, 0.1 g of γ -MPS-SiO₂, 0.1 g of AIBN, 4mL of toluene and a Teflon-coated stir bar were placed in a 10 mL round flask equipped

with a reflux condenser. The flask was purged with nitrogen and heated to 70 °C. Polymerization was continued for 10 h. After polymerization, the flask was cooled to room temperature and the reaction mixture was precipitated in methanol. The product was filtered and dried in a vacuum oven.

2.4 Coating procedure

A typical spray coating process for rough polymer surface is as follows: 1 g of silica/poly(Zonyl-*co*-MMA) composite dissolved in 25 mL of THF under ultrasonic bath operating at 40 kHz to form a transparent solution. An airbrush, a commercially available Badger Model 250, was powered by air at 20 psi. The distance of the airbrush from the nozzle to the substrate and the flow rate were kept 3 cm and 20 mL/min, respectively.

2.5 Adhesion test

The adhesion between the silica/poly(Zonyl-*co*-MMA) composite layer and the slide-glass was studied by the standard ASTM D3359 Scotch tape test (cross-cut tape test) which consists in applying and removing pressure-sensitive adhesive tape over 16 cross-hatched squares of 1 mm × 1 mm made in the film by an Elcometer Cross Hatch cutter (Elcometer 107 X-Hatch ASTM Kit). The scotch tape was applied to the cut surface and rubbed with eraser and then removed after 90 s [10].

2.6 Characterization

Fourier transform infrared (FT-IR) characterizations of pristine and functionalized SiO₂ were performed using a Varian 660-IR spectrometer. Scanning electro microscopy (SEM) observation was performed with a HITACHI S2700. TGA curves were recorded on Perkin-Elmer TGA-7.

3 Results and Discussion

Spherical silica nanoparticles with mean diameter of 210 nm determined by SEM images were first reacted with γ -MPS. Fig.1(A) shows a SEM image of the γ -MPS-SiO₂ particles. After treatment with γ -MPS, the surface functionalized SiO₂ was characterized by FT-IR measurement. The FT-IR spectra of γ -MPS-SiO₂ showed the absorption bands at 2943, 1723, and 1635 cm⁻¹ resulting from the

stretching vibration of CH₃, C=O, and C=C groups of γ -MPS, respectively (see Fig.1(B)). These peaks were not observed in the FT-IR spectrum of the pristine SiO₂ particles. The reaction scheme and the structure for silica/poly(Zonyl-*co*-MMA) are illustrated in Fig.2. The radical copolymerization of Zonyl and MMA with γ -MPS-SiO₂ nanoparticles dispersed in THF was attempted in the presence of AIBN as an initiator. Due to the low dispersibility of γ -MPS-SiO₂ in the reaction medium, the particle was precipitated at the initial stage of polymerization. The solution became cloudy during the polymerization because of poly(Zonyl-*co*-MMA) chains formed on the silica surface.

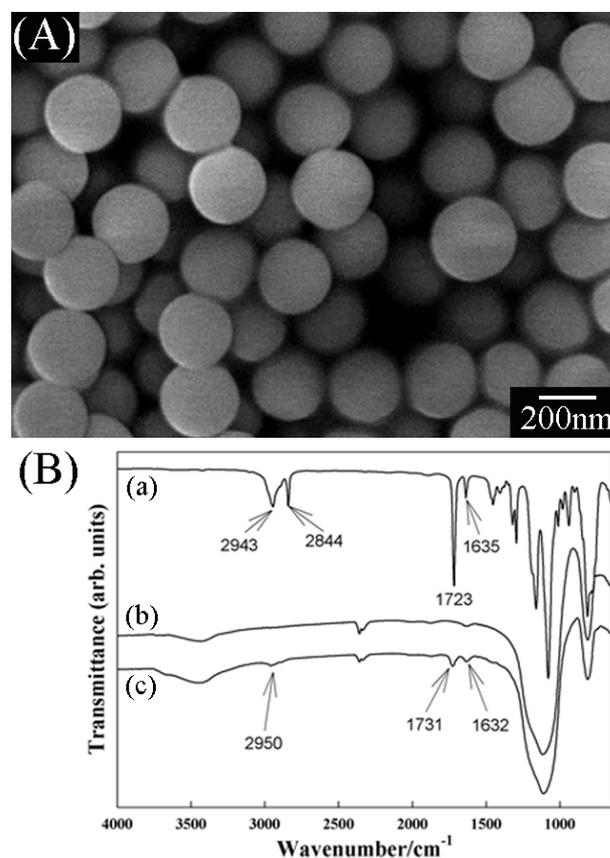


Fig.1. (A) a SEM image of silica particles, (B) FT-IR spectra of (a) γ -MPS, (b) SiO₂, (c) γ -MPS-SiO₂.

The resulting silica/poly(Zonyl-*co*-MMA) composite could be well dispersed in THF that is a good solvent for poly(Zonyl-*co*-MMA). The Zonyl component of the composite is responsible for low surface energy of the copolymer whereas MMA

groups make the copolymer more soluble than Zonyl homopolymer in an organic solvent.

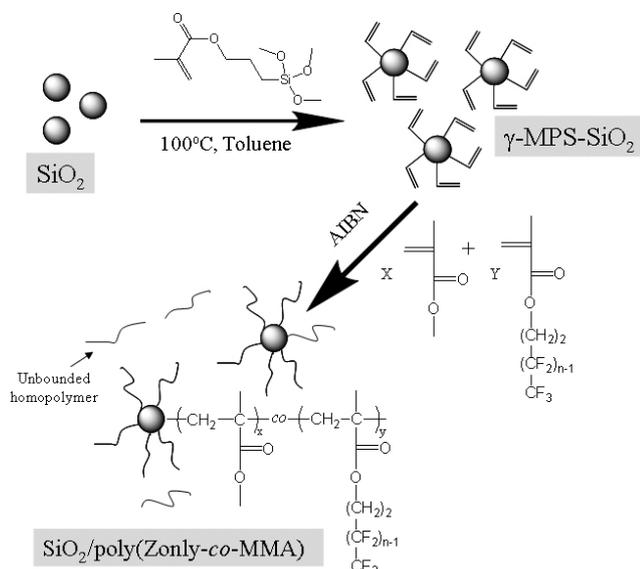


Fig.2. Schematic representation of the process for the synthesis of silica/poly(Zonyl-co-MMA) composite.

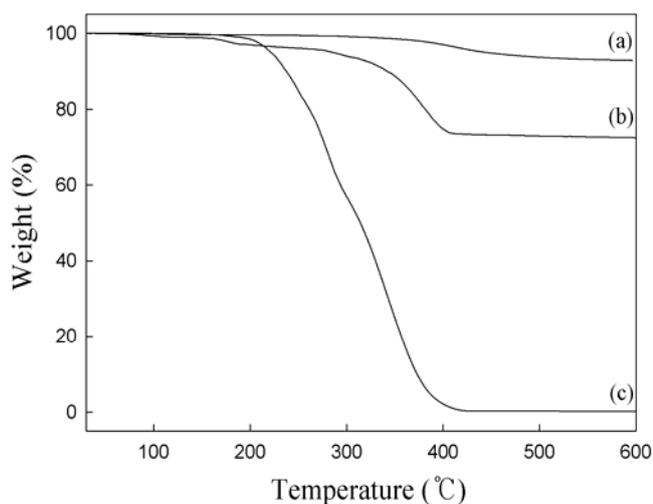


Fig.3. TGA plots of (a) $\gamma\text{-MPS-SiO}_2$, (b) silica/poly(Zonyl-co-MMA) and (c) poly(Zonyl-co-MMA) copolymer.

Fig.3 (b) and (c) show the TGA plots of silica/poly(Zonyl-co-MMA) composite and poly(Zonyl-co-MMA) copolymer, respectively. Consistent with the degradation of pure poly(Zonyl-co-MMA) copolymer, the weight loss between 350 and 450 °C is attributed to the existence of poly(Zonyl-co-MMA).

The residual amount of silica/poly(Zonyl-co-MMA) composite was determined to be 73%.

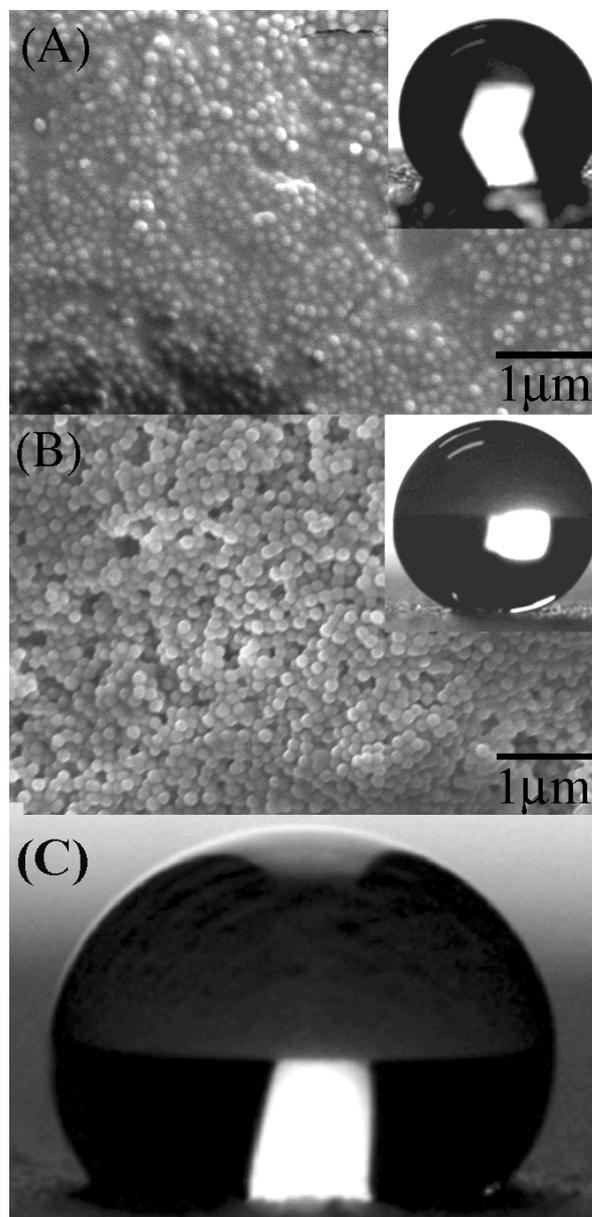


Fig.4. SEM images of silica-Zonyl composite layers by (A) spin coating and (B) spray coating. The inset photographs are shapes of a water droplet on each surface. (C) The shape of CH_2I_2 droplet on the (B).

To determine the water contact angle, we prepared silica/poly(Zonyl-co-MMA) composite coated on glass-slides by spraying the composite in THF at room temperature. For comparison, the spin coating was also performed under the same condition. Fig.4 (A) and (B) are the top views of SEM images of the

spin coating and spray-deposition surface, respectively.

As shown in Fig.4(B), with a spray coating process, the surface structure transits from non-grooved flat surface (Fig.4(A)) to microporous morphology. The spray coated silica/poly(Zonyl-co-MMA) composite has a rough structure consisting of silica particles assembled by poly(Zonyl-co-MMA) copolymer.

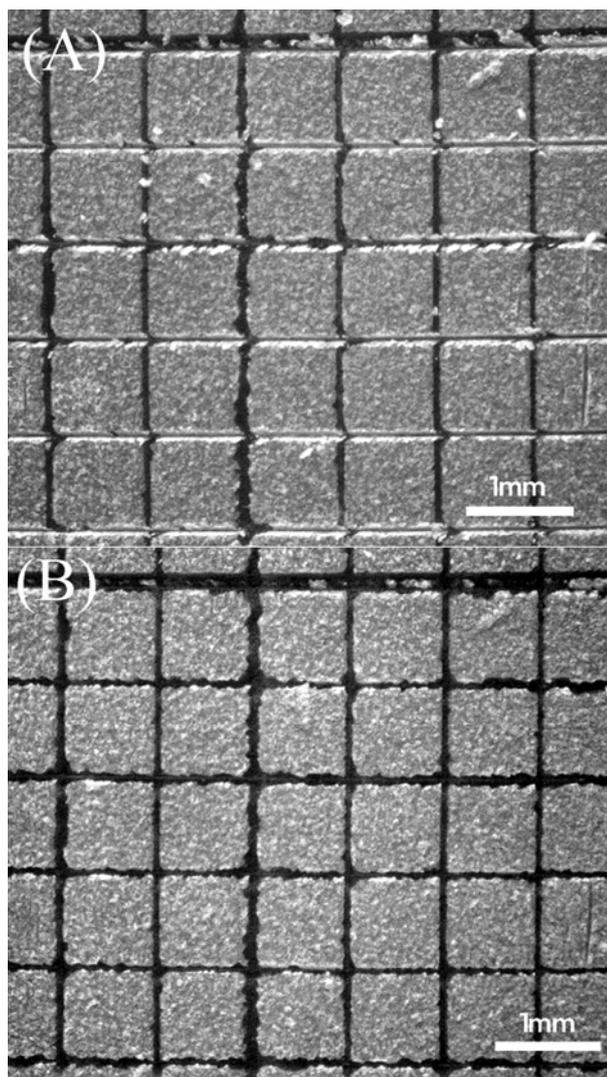


Fig.5. Optical camera images of silica-Zonyl composite layers (A) before and (B) after a cross cut adhesion test by the ASTM standard D 3359-02, Method B.

Moreover, sub-micron sized pores also observed inside of the composite layer. This can be assumed that the micro/nano binary structure similar to a lotus leaf, which is important for generating super-

hydrophobicity [11,12]. This transition can be explained by considering the solvent evaporation rate. The composite solution is atomized at the nozzle by pressure and then directed toward the substrate by an air flow.

If one considers an individual composite droplet, the grafted copolymer chain collapses onto silica surface because of the rapid evaporation during spraying. Therefore, this effect leads to make the submicron-sized composite particles and the microporous structure. The measured water contact angle was 130° for the spin-coated silica/poly(Zonyl-co-MMA) surface (see the inset of Fig.3(A)), whereas the contact angle for the spray-coated surface increased to 176° due to the increase in surface roughness (see the inset of Fig.3(B)). The irregular surface morphology of the spray-coated silica/poly(Zonyl-co-MMA) surface increases the proportion of water/air interfaces, which can greatly intensify the surface hydrophobicity. The sliding angle of spray coated silica/ poly(Zonyl-co-MMA) was also lower than 1° , allowing water droplets to roll off easily from the surface. Moreover, the silica/poly(Zonyl-co-MMA) coated surface exhibits oleophobicity due to the low solubility of semifluorinated material in organic solvent. In Fig. 4(C), the measured CH_2I_2 (oil) contact angle values for this silica/ poly(Zonyl-co-MMA) surface was as high as 137° . This results indicated that the spray-coated silica/poly(Zonyl-co-MMA) surface has omniphobic property [13].

The ASTM cross-cut tape test for adhesion demonstrates the strong adhesion of silica/poly (Zonyl-co-MMA) to the slide glass. The test layer exhibited the highest adhesion rating of 5B according to the ASTM. Fig. 5 reveals little removal of silica/poly(Zonyl-co-MMA) from the slide glass substrate along sides of the cross-cuts.

4 Conclusions

We have demonstrated a simple and conventional spray deposition process to create a superhydrophobic surface with silica/poly(Zonyl-co-MMA) copolymer composite. The resulting surface has a micro/nano binary structure similar to a lotus leaf, which exhibits a high water contact angle. The coating created has excellent adhesion to the slide glass substrate. The present spray deposition process is one of the simplest methods to produce superhydrophobic surfaces. This method may even

be applicable to large-scale coatings and has the potential as an economic route for industrial applications.

Acknowledgement

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (Ministry of Education, Science and Technology). [NRF-2010-355-D00028]

References

- [1] R. Blossey “Self-cleaning surfaces—virtual realities”. *Nature Materials*, Vol. 2, pp 301-306, 2003.
- [2] A. Nakajima, K. Hashimoto, T. Watanabe, K. Takai, G. Yamauchi, A. Fujishima “Transparent superhydrophobic thin films with self-cleaning properties”. *Langmuir*, Vol. 16, pp 7044-7047, 2000.
- [3] H. Y. Erbil, A. L. Demirel, Y. Avci, O. Mert “Transformation of a simple plastic into a superhydrophobic surface”. *Science*, Vol. 299, pp 1377-1380, 2003.
- [4] L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu “Super-Hydrophobic surface of aligned polyacrylonitrile nanofibers” *Angewandte Chemie International Edition*, Vol. 41, No. 7, pp 1221-1223, 2002.
- [5] D. Öner, T. J. McCarthy “Ultrahydrophobic surfaces. effects of topography length scales on wettability”. *Langmuir*, Vol. 16, No.20, pp 7777-7782, 2000.
- [6] F. Shi, Z. Wang, X. Zhang “Combining a layer-by-layer assembling technique with electrochemical deposition of gold aggregates to mimic the legs of water striders”. *Advanced Materials*, Vol. 17, No. 8, pp 1005-1009, 2005.
- [7] J. T. Han, X. Xu, K. Cho “Diverse access to artificial superhydrophobic surfaces using block copolymers”. *Langmuir*, Vol. 21, No. 15 pp 6662-6665, 2005
- [8] J. T. Han, D. H. Lee, C. Y. Ryu, K. Cho “Fabrication of superhydrophobic surface from a supramolecular organosilane with quadruple hydrogen bonding”. *Journal of the American Chemical Society*, Vol.126, No. 15, pp 4796-4797, 2004.
- [9] W. Stöber, A. Fink, E. Bohn “Controlled growth of monodisperse silica spheres in the micron size range” *Journal of Colloid and Interface Science*, Vol. 26, No. 1, pp 62-69, 1968.
- [10] G. J. E. Davidson, L. A. Lane, P. R. Raithby, J. E. Warren, C. V. Robinson, J. K. M. Sanders “Coordination polymers based on aluminum(III) porphyrins”. *Inorganic Chemistry*, Vol.47, No. 19, pp 8721– 8726, 2008.
- [11] W. Barthlott, C. Neinhuis “Purity of the sacred lotus, or escape from contamination in biological surfaces” *Planta*, Vol. 202, pp 1-8. 1997.
- [12] L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang, D. B. Zhu “Super-hydrophobic surfaces: From natural to artificial” *Advanced Matererials*, Vol 14, pp. 1857-1860, 2002.
- [13] A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen “Robust omniphobic surfaces” *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 105, No. 47, pp 18200-18205, 2008.