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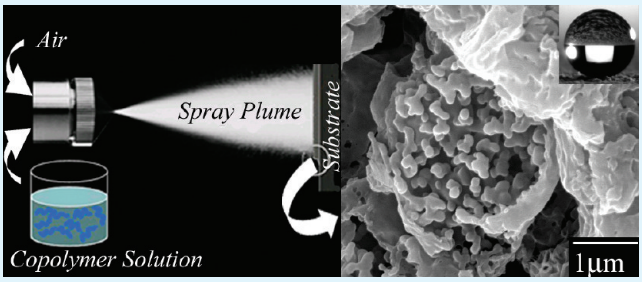
Facile Fabrication of Transparent Superhydrophobic Surfaces by Spray Deposition

Ha Soo Hwang,[†] Nam Hyun Kim,[†] Seung Goo Lee,[‡] Dong Yun Lee,[‡] Kilwon Cho,*[,‡] and In Park*[,†]

[†]Korea Packaging Center, Korea Institute of Industrial Technology, Bucheonsi, Gyeonggido 421-742, Republic of Korea
[‡]Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

S Supporting Information

ABSTRACT: Herein, we present a one-step facile spray-deposition process for fabricating a new superhydrophobic surface with a novel statistical copolymer. The polymeric material is relatively inexpensive, easily prepared, transparent, solvent-processable, very simple, and applicable to rugged substrates. The materials presented herein also feature a near-perfect superhydrophobic surface with a static water contact angle of 178° and a transmittance of higher than 75% at 550 nm wavelength.



KEYWORDS: superhydrophobic, water repellent, polymer particle, spray deposition, lotus effect

INTRODUCTION

In the past decade, water-repellent solid surfaces have become an attractive topic in material sciences because of their scientific significance and variety of applications including self-cleaning, metal refining, adhesion prevention, and drag reduction in fluid flow.[1−4] The superhydrophobic properties of the surface allow water droplets to easily roll across the surface rather than pinning; such surfaces exhibit water contact angles higher than 150° and low-contact-angle hysteresis. It is well-known that the superhydrophobicity of a surface is attributed to low surface energy and a micro/nano binary rough surface.[5−7] In nature, a typical example is the self-cleaning surface of a lotus leaf.[8,9] Because lotus leaves have hydrophobic wax nanostructures covering microstructured papillae, contaminants are easily removed as water droplets roll along the leaf surfaces. Inspired by their unusual characteristics, many methods for the artificial synthesis of superhydrophobic surfaces have been developed, including lithography, electrochemical deposition, self-assembly, and sol−gel processes.[10−13] However, most of the methods disclosed to date require multistep procedures, have limited substrate materials, and feature small flat surfaces, which limit their practical applications.

On the other hand, the spray-deposition process is a well-established technique for painting, graphic arts, and industrial coating. This simple process, with high throughput, is applicable for a variety of substrates and is not limited to small areas. Among the various surface deposition techniques, spray deposition is the most mature technology and is the current choice in the modern surface-coating industry.

In this communication, we present a one-step facile spray-deposition process for the fabrication of a new superhydrophobic surface with a novel statistical copolymer. Compared with the above-mentioned approaches, the raw material used herein is relatively inexpensive, easily prepared, translucent, solvent-processable, very simple, and applicable to rugged substrates. Additionally, the procedure is convenient. The materials presented in this article feature a near-perfect superhydrophobic surface that exhibits static water contact angles of 178° and a negligible sliding angle (i.e., contact angle hysteresis).

EXPERIMENTAL SECTION

For the experiments, we synthesized a low-surface-energy statistical copolymer composed of 3-[tris[(trimethylsilyl)oxy]-silyl]propyl methacrylate (SiMA) and methyl methacrylate (MMA). The SiMA component of the copolymer is responsible for its hydrophobicity, whereas the MMA groups impart rigidity. Details of the synthesis and characterization of the copolymers are given below. A statistical copolymer of SiMA and MMA was prepared by free-radical polymerization under a nitrogen atmosphere. MMA (2 g), SiMA (2 g), toluene (4 mL), and 2,2′-azobis(isobutyronitrile) (AIBN; 0.04 g) were placed in a 25 mL round-bottomed flask under a nitrogen atmosphere. The flask was sealed, and the polymerization was performed for 6 h at 70 °C. After polymerization, the reactor was cooled in ice water, and any unreacted monomer and initiator were removed by precipitation in methanol. The precipitated product was dried in vacuo and then collected and weighed. Other homopolymers and copolymers were also prepared in the same manner for the purpose of control experiments. A glass slide and a silicon wafer are cleaned with acetone, methanol, and isopropyl alcohol before deposition of the copolymer. Other substrates were used as received. For contact- and sliding-angle measurements, 10 μL water droplets were used.

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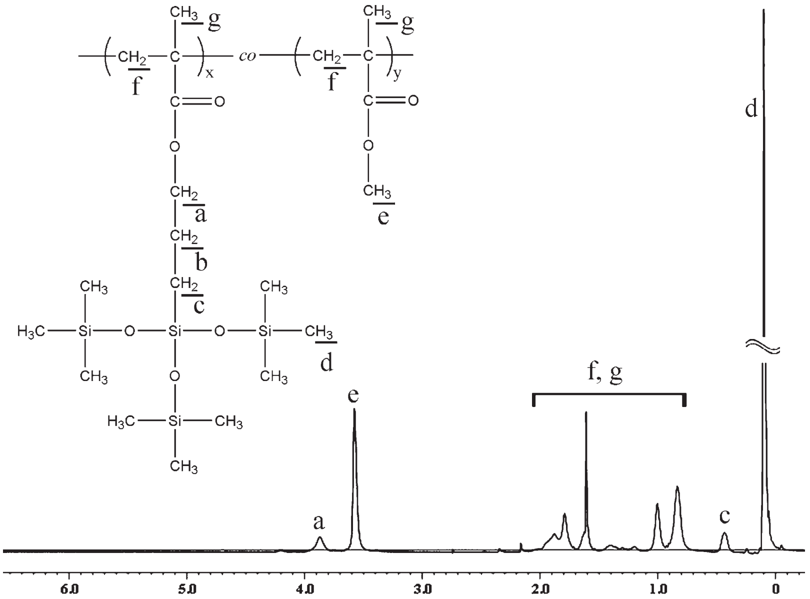

Figure 1. Structure and ^{1}H NMR spectrum of random copolymer poly(SiMA-*co*-MMA).

Table 1. Polymerization Results and Properties of Polymers

polymer	SiMA feed ratio (mol/mol %)	SiMA incorporated ratio (mol/mol %)^a	M_n (g/mol)^b	PDI $^b\overline{M_w}/\overline{M_n}$	yield (%)^c	T_g (°C),^{d} CA (deg)^e
poly(MMA)	0	0	41 000	1.78	78.2	125.9, 63 ± 1
poly(SiMA)	100	100	31 000	1.66	76.1	−32.8, 118 ± 2
poly(SiMA-*co*-MMA) (25:75)	19.1	25.4	44 000	1.82	79.5	62.6, 97 ± 3
poly(SiMA-*co*-MMA) (39:61)	35.8	38.9	57 000	1.87	81	34.5, 97 ± 2
poly(SiMA-*co*-MMA) (50:50)	48.6	50.2	48 000	1.78	78.2	1.2, 99 ± 2

[a] Determined by ^{1}H NMR with $CDCl_3$ as the solvent. [b] Determined by GPC with a poly(MMA) standard. [c] Yields were determined gravimetrically. [d] Differential scanning calorimetry (DSC) data were obtained using a DSC-60 thermal analysis system (Shimadzu Co., Tokyo, Japan). [e] Contact angles of spin-coated films.

RESULTS AND DISCUSSION

The structure and ^{1}H NMR spectrum of the copolymer are shown in Figure 1. The SiMA component of the copolymer is responsible for the low surface energy of the copolymer, whereas the MMA groups make the copolymer less viscous by increasing the glass transition temperature (T_g). The mole content of SiMA with respect to MMA was calculated by comparing the peak integrals between the methylene protons (at 3.87 ppm; a) next to the ester moieties in the SiMA groups and the methyl protons (at 3.56 ppm; e) in the MMA in the ^{1}H NMR spectra of the copolymers.[14] The results of polymerizations are summarized in Table 1. As expected, the proportion of SiMA and MMA incorporated into the copolymer is in well accordance with the feed ratio of the monomers. Gel permeation chromatography (GPC; HP1110 apparatuses) data showed that the molecular weights ($\overline{M_n}$) of the copolymers were in the range of 44 000−57 000 g/mol. Before the copolymer was employed in the deposition process, the T_g of the copolymer was examined. T_g values well above room temperature indicate utilization as rigid structural materials. As shown in Table 1, the T_g values of the copolymers increase with an increase in the mole percentage of MMA and the copolymers containing less than 61.1 mol/mol % of MMA structural units were found to be fluidic at room temperature. Hence, it is clear that the maximum MMA ratio in the copolymer must be higher than 38.9 mol/mol % to generate a rigid surface on the substrate by the deposition process in this work.

Spin- and spray-deposition processes were carried out using acetone as the solvent because all of the polymers used were completely soluble in acetone. First, the inherent water contact angles of poly(MMA), poly(SiMA), and poly(SiMA-*co*-MMA) (25:75) were measured on flat films prepared via the spin-coating process. The shape of the water drop on the poly(MMA) flat surface had a contact angle of 63° (see Figure 1a). Higher contact angles were observed for poly(SiMA) (118 ± 2°) and poly(SiMA-*co*-MMA) (25:75) (ca. 97 ± 3°), which is attributed to the low surface energy of the silicone functional groups in SiMA.

To compare the water contact angles of these samples with those of rough polymer layers prepared by spray deposition, we prepared three polymer coatings on glass slides by spraying from acetone at room temperature. The typical spray-deposition process for a rough polymer surface is as follows: 1 g of poly(SiMA-*co*-MMA) is dissolved in 25 mL of acetone in an ultrasonic bath operating at 40 kHz to form a transparent solution. The airbrush (Badger model 250) was powered by air at 20 psi pressure. The distance of the airbrush nozzle to the substrate and the flow rate were kept constant at 3 cm and approximately 20 μL/min, respectively. During this spray-deposition process, the polymer solution is atomized by pressure at the nozzle and then directed

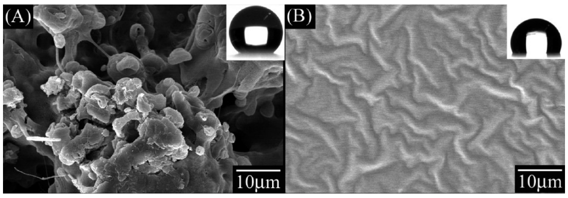

Figure 2. SEM images of the spray-coated surfaces of (A) poly(MMA) and (B) poly(SiMA). Optical images of the water contact angles are inserted in the top-right corner of the SEM images.

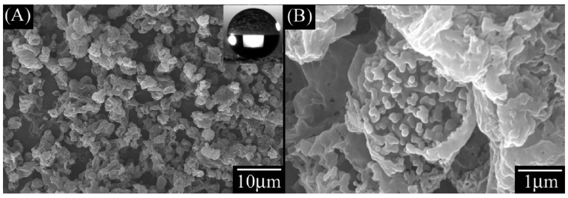

Figure 3. SEM images of the spray-coated poly(SiMA-*co*-MMA) surfaces at (A) low and (B) high magnification. An optical image of the water contact angle is inserted into the top-right corner of the SEM image.

toward the glass slide by an air flow. A random distribution of tiny droplets then lands on the surface, producing a fully wet layer using large air-flow rates. It can also be assumed that there is rapid evaporation of the solvent during spraying, so the droplets of the polymer solution hit the substrate. This leads to the generation of submicrometer-sized polymeric particles and renders a microporous structure.

Figure 2 shows the top-view scanning electron microscopy (SEM; Hitachi S-4300) image of the spray-deposition surfaces and the static water-contact-angle results. From the results of the poly(MMA) spray deposition (Figure 2A), clumpy particles were formed on the surface, which has micrometer-sized roughness. The maximum static water contact angle of the sprayed poly(MMA) was 145°. The reason for the higher water contact angle than that of the spin-coated poly(MMA) surface (Figure 1a) is the presence of micromorphology with a high density of $\sim$5−10 μm poly(MMA) lumps. However, the water droplet on the spray-coated poly(MMA) surface was firmly pinned to the surface even when the sample was turned upside down because of insufficient hydrophobicity. In the case of the poly(SiMA) homopolymer, the filmlike flat surface morphology resulted from the spray deposition of poly(SiMA) due to the low glass transition temperature (T_g) and the good solvent wettability of the homopolymer. A maximum static water contact angle of 119 ± 2° was observed (inset of Figure 2B). Therefore, the spray-coated layer of poly(SiMA) with a low T_g (−32.8 °C) exhibits too high of a fluidity to generate surface roughness.

Interestingly, in contrast with the poly(SiMA) surface, spray-coated poly(SiMA-*co*-MMA) has a microporous structure consisting of an approximately 2-μm-sized polymer particle domain (Figure 3A). Moreover, submicrometer-sized (approximately 0.2 μm) agglomerates were also observed inside the micrometer-sized domain (Figure 3B). It is assumed that the protrusion of the particle domain is similar to that of a lotus leaf, which is important for generating superhydrophobicity. The measured water contact angle is 97° for the spin-coated poly(SiMA-*co*-MMA) flat surface (see Figure 1c), whereas the contact angle for the spray-coated surface increased to 178 ± 1° because of the increase in the surface roughness (see the inset of Figure 3A). The irregular surface morphology of the spray-coated poly(SiMA-*co*-MMA) surface increases the proportion of water/air interfaces, which can greatly intensify the surface hydrophobicity.[15] The sliding angle of spray-coated poly(SiMA-*co*-MMA) is also lower than 1°, allowing water droplets to roll off easily from the surface. We also succeeded in spray depositions of the poly(SiMA-*co*-MMA) (25:75) copolymer on a wide range of substrates including, but not limited to, aluminum, silicon wafer, concrete block, and poly(ethylene terephthalate) film (see Figure S1 in the Supporting Information).

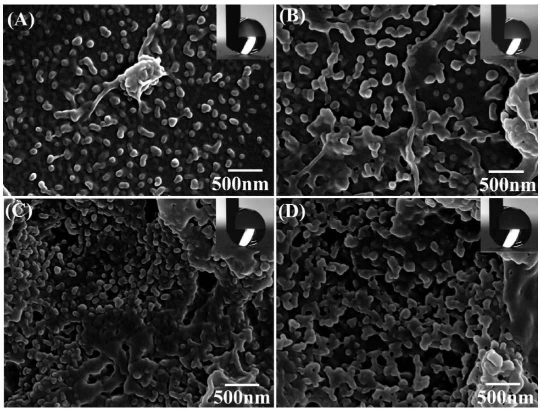

Figure 4. SEM images of the spray-deposited poly(SiMA-*co*-MMA) copolymer layer prepared using the following concentrations of copolymer: (A) 0.2 wt %, (B) 0.5 wt %, (C) 1 wt %, and (D) 2 wt % copolymer in acetone.

It is difficult to prepare a surface with transparency because of the unique rough structure of a superhydrophobic surface in previous investigations. Recently, transparent superhydrophobic surfaces consisting of porous polymeric materials were prepared via surface polymerization using an inert solvent such as a porogen. Levikin et al. found that it is possible to improve the transparency of the superhydrophobic surface which is controlled by the porosity and thickness of the polymeric materials.[16] However, the most practically important point of the spray-deposition process is that the transparent layer can easily be prepared by controlling the copolymer concentration.

In order to improve the transparency with the spray-deposition process, we have to significantly reduce the particle aggregation and the thickness of the sprayed polymer layer. For fabrication of the transparent layers, we have to significantly reduce the particle aggregation and the thickness of the sprayed polymer layer to prevent the scattering of visible light. The particle morphology and thickness of the copolymer layer obtained from spray deposition depend on the concentration of the copolymer in the solvent. Figure 4 shows the representative SEM images of spray-deposited poly(SiMA-*co*-MMA) (25:75) copolymers with various concentrations. The spray deposition carried out with a 0.2 wt % concentration of copolymer resulted in approximately 180-nm-sized particles with 120 nm thickness, and the resultant static water contact angle was found to be 172 ± 2° (Figure 5A). When the concentration was increased to 0.5−2 wt %, an appreciable aggregation of the particles was observed and the transmittance values decreased (see Table S1 in the Supporting Information). The average surface roughness (R_a) for each copolymer layer obtained using 0.2, 0.5, 1, and 2 wt % concentrations are 0.12 ± 0.09, 0.38 ± 0.13, 0.45 ± 0.25, and 1.9 ± 1.5 μm, respectively, as

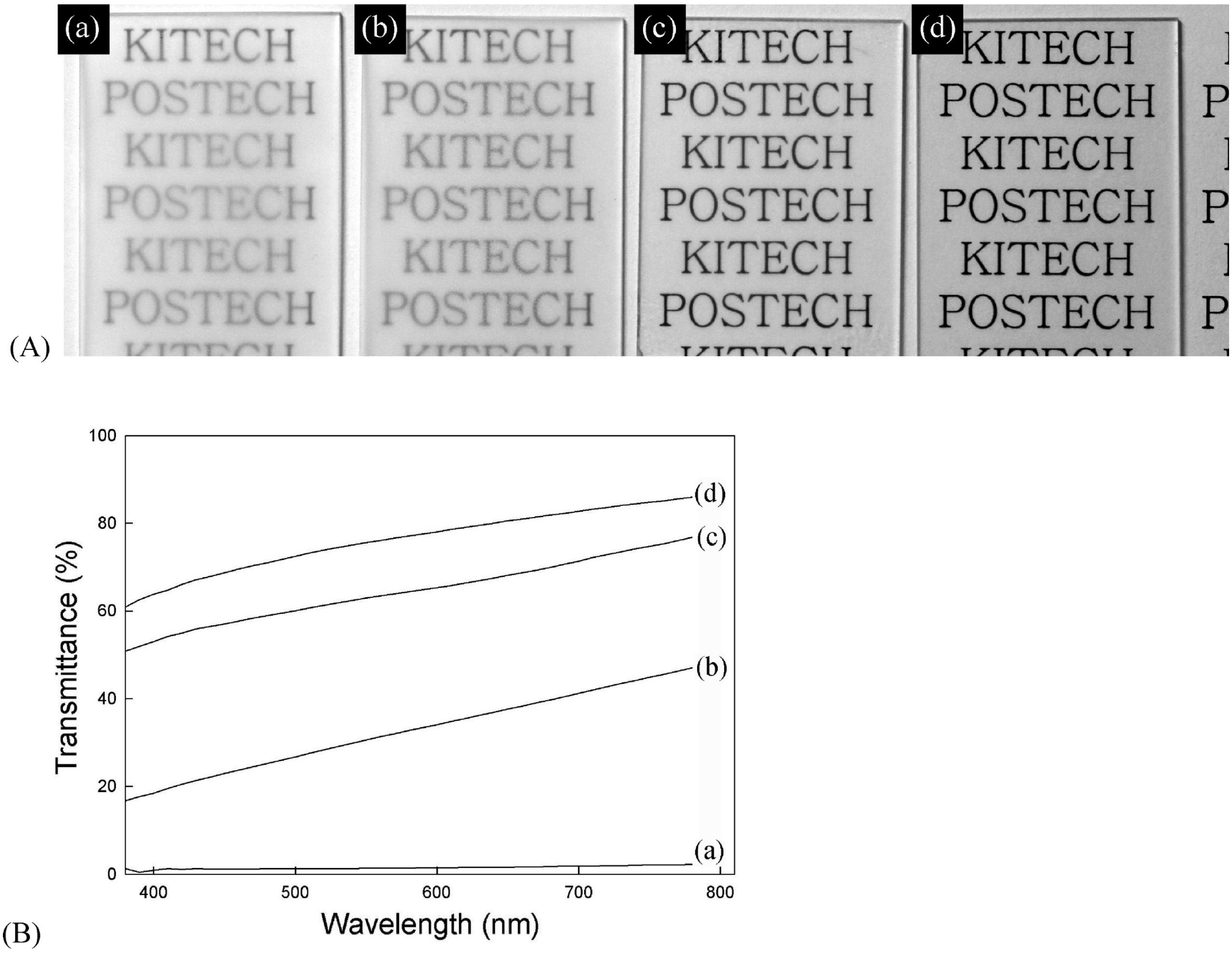

Figure 5. (A) Digital photographs and (B) UV—vis transmittance spectra of the spray-deposited poly(SiMA-*co*-MMA) copolymer layer prepared using the following different concentrations of copolymer: (a) 2 wt %, (b) 1 wt %, (c) 0.5 wt %, and (d) 0.2 wt % copolymer in acetone.

determined by profilometry (Tencor Alpha Step). Thus, the surface prepared using a 0.2 wt % concentration has a relatively low aggregation, a thin layer, and decreased roughness. This morphology change resulted in a significant improvement in the transparency, as shown in Figure 5A. The transmittance measurement data also indicated an increase in the transparency of the layer with decreasing concentration (Figure 5B). The transmittance of the 0.2 wt % layer for the visible-wavelength range, as shown in Figure 5B, was higher than 75% at 550 nm wavelength.

CONCLUSIONS

We have demonstrated a simple and conventional spray-deposition process to create a transparent and near-perfect superhydrophobic surface with a random copolymer composed of SiMA and MMA. The resulting surface has a rough structure similar to that of a lotus leaf, which features a high water contact angle and low contact-angle hysteresis. Moreover, the obtained surfaces are transparent in the visible-wavelength range. The present spray-deposition process is one of the simplest methods to produce superhydrophobic surfaces. This method may even be applicable to a large-scale process and has the potential to be an economical route for industrial applications.

ASSOCIATED CONTENT

Supporting Information. Details of poly(SiMA-*co*-MMA) (25:75, 4 wt % in acetone) deposited on various substrates by spray deposition. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kwcho@postech.ac.kr (K.C.), inpark@kitech.re.kr (I.P.). Tel: +82-54-279-2270 (K.C.), +82-32-624-4776 (I.P.). Fax: +82-54-279-8269 (K.C.), +82-32-624-4770 (I.P.).

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