Superhydrophobic Surfaces on Phase-separated Nanostructures of Polystyrene/Polymethyl Methacrylate Films Fabricated by the Double-spray Technique

Satoshi Watanabe¹*, Motoharu Fujisaki², Kazuki Murai³, and Mutsuyoshi Matsumoto²

¹ Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Chuou-ku, Kumamoto 860-8555, JAPAN
² Department of Materials Science and Technology, Tokyo University of Science, 6-3-1 Nijuku, Katsushika-ku, Tokyo 125-8585, JAPAN
³ Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, JAPAN

Abstract: Rapid large-area printing techniques are required to fabricate superhydrophobic surfaces of polymer films on solid substrates. Here, we report a double-spray technique for fabrication of mixed phase-separated films of polystyrene (PS), poly(methyl methacrylate) (PMMA), and PS-b-PMMA. The surface wettability of the films changes to superhydrophobic by immersing the samples in cyclohexane, which is a good solvent for only PS. The rinsing process forms nanostructures in the remaining PMMA films that have flat surfaces before the rinsing treatment. The highest contact angle is about 150° on the film with a PMMA ratio of 0.2. X-ray photoelectron spectroscopy shows that a small amount of PS remains on the surface of the PMMA films, making the films superhydrophobic. Addition of PS-b-PMMA to the PS/PMMA films forms smaller phase-separated structures than those in the original PS/PMMA films because of an increase in the compatibility between PS and PMMA. The contact angle hysteresis in the films decreases with increasing PS-b-PMMA ratio, indicating an increase in the homogeneity of the phase-separated structures.

Key words: superhydrophobicity, spray coating, phase separation, polystyrene, poly(methyl methacrylate)

1 INTRODUCTION

The surface roughness and heterogeneity of the wettability and water contact angle have been studied since Wenzel’s and Cassie’s initial publications¹⁻³. Superhydrophobic surfaces that have water contact angles greater than 150° have been obtained by controlling the surface topography of hydrophobic materials using various processing methods, such as machining and etching⁴⁻⁶. Superhydrophobic surfaces that exhibit water contact angles as high as 174° have been prepared from an n-alkyl ketene dimer. The unusually high contact angles are ascribed to the fractal nature of the surfaces⁷. Super-water-repellent alumina coatings have been prepared by hydrophobizing porous alumina gel films with fluoroalkyl-trimethoxysilane, and a water contact angle of 165° has been reported⁸. Polymer coating techniques have attracted much attention because they can be used to simply and inexpensively fabricate superhydrophobic surfaces based on phase separation. Erbil et al.⁹ formed a superhydrophobic polypropylene surface by adjusting the temperature to induce phase separation of the solvent mixture. Cao et al.¹⁰ reported phase separation and a selective solvent treatment technique to enhance the hydrophobicity of the surface of poly (methyl methacrylate) (PMMA, a hydrophilic polymer) and polystyrene (PS, a hydrophobic polymer).

In this study, we used double-spray nozzles to prepare mixed PS/PMMA films and fabricate nanoscale phase-separated structures and then selectively removed PS, leading to formation of superhydrophobic surfaces. The first and second spray nozzles were used for ejection of the polymer solution and nitrogen gas to rapidly dry the polymer solution, hindering phase separation of PS and PMMA. The samples were analyzed by contact angle measurements, optical microscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

2 EXPERIMENTAL PROCEDURES

2.1 Materials

PS (Mₐ = 208,000, Wako), PMMA (Mₐ = 120,000, Sigma-Aldrich), PS-b-PMMA (Mₐ = 70,000, PDI = 1.5, Sigma-Al-

---

*Correspondence to: Satoshi Watanabe, Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Chuou-ku, Kumamoto 860-8555, JAPAN
E-mail: watasato@kumamoto-u.ac.jp
Accepted April 21, 2018 (received for review April 5, 2018)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/ http://mc.manuscriptcentral.com/jocs
drich), tetrahydrofuran (THF, Wako), and cyclohexane (Wako) were used for fabrication of the mixed polymer films and removal of PS from the mixed polymer films. Suction-type spray nozzles with a nozzle diameter of 20 μm were obtained from Kirino Ikeuchi, Co., Ltd. (spray code BIMV 8002 SS303 ND S303). The ammonia and hydrogen peroxide solutions used for cleaning the silicon wafers were purchased from Wako. The (001)-surface silicon wafers with native SiO₂ (n-type, 1–10 Ω, mirror polished) purchased from Furuuchi Chemical Corp. were cut into 1.0 cm × 2.5 cm pieces.

2.2 Preparation

PS and PMMA were dissolved in THF at a total concentration of 5 wt%. The mixed solution (30 mL) in a beaker was connected to suction-type spray nozzles (Fig. 1a). The distance between the spray nozzles and the substrate was 15 cm and the distance between the spray nozzles and the surface of the solution in the beaker was 0 cm. The second spray nozzle at an angle of 0° was used to eject N₂ gas for immediate evaporation of the sample. The N₂ gas pressures of the first and second spray nozzles were the same. The solution from the first spray nozzle was sprayed on Si wafers under blowing N₂ gas from the second spray nozzle (Fig. 1b). The prepared polymer films were dried in a vacuum desiccator for more than 1 h. After measurement of the contact angles, the polymer films were immersed in cyclohexane at 70°C for 20 min for selective removal of PS (Fig. 1c and 1d). After drying in a vacuum desiccator, the films were characterized.

2.3 Measurements

The optical microscopy observations were performed with a BX-60 optical microscope (Olympus, Japan). The SEM observations were performed with an S-4200 microscope (Hitachi, Japan). XPS was performed with a Kratos analytical spectrometer (Kratos Nova, Shimadzu, Japan) using a monochromated AlKα X-ray source (45°, 1486.6 eV) operating at a power of 150 W (voltage 15 kV, current 10 mA). The contact angles of water droplets (4 μL) at eight points were measured with a CA-DT contact angle meter (Kyowa Interfacial Science, Japan). The angle at which a water droplet rolled off when the sample was tilted (sliding angle) was measured at six points by a DM-501 sliding angle meter (Kyowa Interfacial Science).

3 RESULTS

3.1 Mixed PS/PMMA films

First, we fabricated spin-coated PS/PMMA films with different fabrication conditions and cyclohexane treatment. Cyclohexane treatment leads to an increase in the water contact angle from 100° to 135°. This is because of formation of nano- and microporous structures in the films. Superhydrophobic films were not obtained even by varying the fabrication conditions. Solvent evaporation causes excess phase separation, resulting in difficulty in formation of nanosize structures in the films.

We fabricated 80/20 (wt%) PS/PMMA films with single and double sprays to increase the evaporation speed, and then treated the films in cyclohexane to remove PS. The angles of the spray nozzles, distance between the spray nozzles and the sample, and substrate temperature were optimized to maximize the contact angle of water on the sample. Figure 2a shows the contact angle of water on the films plotted against the nitrogen pressure of the single spray nozzle. Before cyclohexane treatment, the contact angle of the film fabricated at a nitrogen pressure of 0.15 MPa is about 95°. Films did not form at nitrogen pressure below 0.15 MPa. Increasing the nitrogen pressure to 0.3 MPa leads to an increase in the contact angles to 125°. After cyclohexane treatment, the contact angle increases by 5–10° for all of the samples. Figures 2b and 2c show SEM images of the films fabricated at a nitrogen pressure of 0.3 MPa before and after cyclohexane treatment. Some aggregates with sizes of several tens of micrometers are

Fig. 1 Scheme of fabrication of superhydrophobic surfaces of structured PMMA films. (a) Single- and double-spray coating of PS/PMMA solutions on substrates, (b) formation of phase-separated PS/PMMA films, (c) selective removal of PS by immersion in cyclohexane, and (e) formation of structured PMMA films.
present on the smooth surface of the film before cyclohexane treatment. Some tens of micrometer aggregates and random mesh structures are present on the film after cyclohexane treatment. This increase in the surface roughness results in an increase in the water contact angle. The reason the contact angle does not increase to $150^\circ$ might be that nanostructures do not form on the surface of the film. This indicates that PS and PMMA phase separation occurs during solvent evaporation, leading to nanostructures not forming on the surface of the film.

To prevent excess phase separation, the evaporation rate was increased by preparing the film under nitrogen blown from the second spray nozzle. The pressures of the two spray nozzles were the same. Figure 2d shows the water contact angles on the films before and after the cyclohexane treatment plotted against the nitrogen pressure. Before cyclohexane treatment, the contact angles are about $90^\circ$ for all of the nitrogen pressures. After cyclohexane treatment, the contact angles of all of the films increase to $150^\circ$. Figures 2e and 2f show SEM images of the films before and after cyclohexane treatment. Compared with the single-sprayed films, there are less microsized aggregates. Cyclohexane treatment results in a drastic change of the films. The amount of film substance greatly decreases and nanometer to micrometer sized pores and particles form on the films. Formation of a superhydrophobic surface can be explained by considering that an increase in the surface area of the hydrophobic surface and formation of air holes in the nanostructure increase the hydrophobicity of the surface according to Wenzel and Cassie–Baxter.

Next, we varied the mixing ratio of PS and PMMA in the films fabricated with double-spray nozzles. Figure 3 shows the relationships between the contact angle of water on the PS/PMMA film and the PMMA ratio for the as-prepared films and the films after cyclohexane treatment. For the as-prepared films, the contact angles are about $100^\circ$ and $85^\circ$ for the pure PS and PMMA films, respectively. The contact angles of the PS/PMMA films at PMMA ratios from 0.2 to 0.8 are between those of the pure PS and PMMA films. After cyclohexane treatment, the pure PS film completely dissolves, and the contact angle on the pure PMMA film does not change. The highest contact angle is about $150^\circ$ on the film with a PMMA ratio of 0.2. Increasing the PMMA ratio decreases the water contact angle on the film. The insert SEM images in Figure 3 show the morphologies of the films fabricated at PMMA ratios of 0.5 and 0.8 before and after cyclohexane treatment. Before cyclohexane treatment, there are some microscale aggregates on the films, as with a PMMA ratio of 0.2. After cyclohexane treatment, microscale network structures are present on the films. Decreasing the PMMA ratio increases the micropore fraction in the film.

According to Cao et al., the methyl groups of PMMA
are selectively oriented on the surface of porous PMMA films after cyclohexane treatment. We performed XPS of the PS/PMMA films fabricated with double-spray nozzles. Before cyclohexane treatment (Fig. 4a), the five peaks at 284.7, 285.6, 286.7, 288.7, and 291.2 eV are attributed to the C–C bonds, C–H bonds, β-shifted C–C bonds, C–O bonds of PMMA, and π–π* bonds of PS, respectively. Cyclohexane treatment greatly decreases the peaks of the C–C (284.7 eV) and π–π* bonds (291.2 eV) with respect to the intensity of the O–C bond (288.7 eV), indicating selective removal of PS. As shown in the insert of Fig. 4b, a small PS peak at 291.2 eV is still present, suggesting that a small amount of PS remains on the film. The hydrophobicity of this residual PS and the nanostructures in the films increase the contact angle of water on the films.

3.2 Addition of PS-b-PMMA dopant to the mixed films

Next, we added a small amount of PS-b-PMMA to decrease the size of the phase-separated structures of PS and PMMA in the films fabricated by double-spray and spin-coating techniques. Figures 5a and 5b show the contact angles of water on the PS/PMMA films (80/20 wt%) doped with PS-b-PMMA before and after cyclohexane treatment plotted against the PS-b-PMMA ratio. The contact angles of both the spin-coated and double-spray-coated films are about 90° before cyclohexane treatment. The contact angles of water on the spin-coated films at PS-b-PMMA ratios of 1 and 3 wt% are about 120° and 90° after cyclohexane treatment, respectively. After cyclohexane treatment, the double-sprayed films have water contact angles of about 150° for all of the dopant ratios. Figure 5c shows the contact angle hysteresis and sliding angle of water on the double-sprayed films. Increasing the PS-b-PMMA ratio from 0 to 3 wt% decreases the contact angle hysteresis from 24° to 5° and the sliding angle from 10° to 2°. Figure 5d shows the PS ratios of the surfaces of the PS/PMMA films calculated from the XPS results. After cyclohexane treatment, the PS ratio increases with increasing PS-b-PMMA ratio.

Figure 6 shows SEM images of the double-sprayed PS/PMMA films and PS/PMMA films with PS-b-PMMA after cyclohexane treatment. A nanoscale network and particle structures are present in the films doped with PS-b-PMMA, and the sizes of the nanostructures are smaller than those in the undoped films. Therefore, the PS-b-PMMA dopant increases the PS ratio on the surface and decreases the size of the nanostructures, resulting in a decrease in the contact angle hysteresis and sliding angle.
4 CONCLUSION

We have reported a double-spray technique for fabrication of superhydrophobic phase-separated PS/PMMA films. The films show superhydrophobicity and small sliding angles after cyclohexane treatment. This approach can be used for other polymers if good solvents are selected for both polymers. Spray techniques are useful for fabrication of films with large-scale continuous short-time processes, and they can easily be scaled up for industrial applications. In addition, film coating can be performed on three-dimensional materials as well as flat substrates, indicating that this technique can be used to modify the hydrophobicity of three-dimensional materials.

ACKNOWLEDGMENT

We gratefully thank Prof. Taniguchi, Prof. Yuasa, and Kondo in Tokyo University of Science for the sliding angle measurements, and XPS. We thank Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

References

1) Wenzel, R.N. Surface roughness and contact angle. J. Phys. Colloid Chem. 53, 1466-1467 (1946).
2) Wenzel, R.N. Resistance of solid surfaces to wetting by water. Ind. Eng. Chem. 28, 988-994 (1936).
3) Cassie, A.B.D. Contact angles. Discuss. Faraday Soc. 3, 11-16 (1948).
4) Chen, W.; Fadeev, A.Y.; Hsieh, M.C.; Jeffrey, D.O. Ultra-hydrophobic and ultralyophobic surfaces: some comments and examples. Langmuir 15, 3395-3399 (1999).
5) Öner, D.; McCarthy, T.J. Ultrahydrophobic surfaces. Effects of topography length scales on wettability. Langmuir 16, 7777-7782 (2000).
6) Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. Super-water-repellent fractal surfaces. Langmuir 12, 2125-2127 (1996).
7) Tadanaga, K.; Katata, N.; Minami, T. Formation process of super-water-repellent Al₂O₃ coating films with high transparency by the sol-gel method. J. Am. Ceram. Soc. 80, 3213-3216 (2005).
8) Erbil, H.Y.; Demirel, A.L.; Avciı, Y.; Mert, O. Transformation of a simple plastic into a superhydrophobic surface. Science 299, 1377-1380 (2003).
9) Ma, Y.; Cao, X.; Feng, X.; Ma, Y.; Zou, H. Fabrication of super-hydrophobic film from PMMA with intrinsic water contact angle below 90 degree. Polymer 48, 7455-7460 (2007).