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SHORT COMMUNICATION

Superhydrophobic surfaces of microspheres obtained by self-assembly of poly[2-(perfluorooctyl)ethyl acrylate-*ran*-2-(dimethylamino)ethyl acrylate] in supercritical carbon dioxide

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Abstract Superhydrophobic surfaces were obtained by coating with microspheres formed by the self-assembly of poly[2-(perfluorooctyl)ethyl acrylate-*ran*-2-(dimethylamino)ethyl acrylate] (P[POA-*r*-DAA]) in the presence of dicarboxylic acids in supercritical carbon dioxide. The P[POA-*r*-DAA] random copolymer aggregated into micellar microspheres through the hydrogen bond cross-linking of the amino groups via the carboxylic acids. The size of the microspheres and the amount of the acids needed to produce them were dependent on the kinds of acids. Glutaric acid (Glu) and perfluorosuccinic acid (Psuc) provided microspheres at a 0.5 molar ratio of the acid/DAA. Psuc produced smaller microspheres than Glu. Maleic acid (Ma), succinic acid (Suc), and azelaic acid (Az) required a higher molar ratio to produce the microspheres. These acids provided spherical particles at the ratio of 1.0. The microspheres produced by Suc and Az contained particles with a several hundred nanometer size. The surface coated with the microspheres showed high water contact angles of 164°–172°.

Keywords Poly[2-(perfluorooctyl)ethyl acrylate-*ran*-2-(dimethylamino)ethyl acrylate] · Dicarboxylic acids · Cloud point · Microspheres · Superhydrophobic surface · Contact angles · Supercritical carbon dioxide

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Introduction

A superhydrophobic surface with water contact angles greater than 150° has attracted considerable attention in recent years, because the hydrophobicity of the surface is important in developing new materials and products for the next generation. Expected products, for instance, include fibers and films with a self-cleaning ability, vessels and wet suits with a high floating power, and wiperless vehicles. The hydrophobicity of a surface is dependent both on its chemical properties and physical properties. For improvement of the chemical properties on the surface, modification of the surface is performed using compounds with a low surface free energy such as fluoropolymers. The creation of a rough surface also has the effect of enhancing the hydrophobicity and is often carried out to improve the physical properties of the surface [1]. Recently, a variety of processing methods has been discovered to fabricate superhydrophobic surface. Examples include the deposition of gold clusters [2], plasma fluorination of polymer films [3–7], phase separation of polymer blends [8], fractal structures [9, 10], honeycomb and pincushion structures [11], gel-like porous polypropylene [12], low-density polyethylene controlled by crystallization [13], packed aligned carbon nanotubes [14–16], aligned nanofibers [17] and nanorod films [18], porous microsphere/nanofiber composites [19], nanosphere lithography [20], and nanoparticles of block copolymer micelles [21].

We have released a publication on the synthesis of microspheres by the self-assembly of random copolymers of 2-(perfluorooctyl)ethyl acrylate (POA) and 2-(dimethylamino) ethyl acrylate (DAA) in the presence of perfluoroazelaic acid (Paz) in supercritical carbon dioxide [22]. The microspheres obtained from the poly[2-(perfluorooctyl)ethyl acrylate-*ran*-

2-(dimethylamino)ethyl acrylate] (P[POA-*r*-DAA]) random copolymers were considered as micellar particles having their shells covered with perfluoroalkyl chains and the cores with amino groups cross-linked by the acid. We found that a surface coated with the microspheres showed a superhydrophobicity. The coating processes using supercritical CO_2 have industrial advantages in simplifying the drying process and manufacturing products without organic solvents. This paper describes the preparation of microspheres through the self-assembly of the copolymer using different dicarboxylic acids in supercritical CO_2 and the water contact angles on the microsphere-coated surfaces.

Experimental

Instrumentation

The scanning electron microscopy (SEM) measurements were made using a JEOL JSM-6300 electron microscope. The cloud point measurement was performed with a Nekken variable volume view cell (with a window made of tempered glass) equipped with an Eyela CCA-1110 cooler and a Nihon Seimitsu Kagaku NP-D-321 personal pump.

Materials and methods

A P[POA-*r*-DAA] random copolymer was prepared as reported previously [22]. The molar ratio of POA/DAA was 7/3. The molecular weight (Mn) and molecular weight distribution (Mw/Mn) of the copolymer were Mn=50,400 and Mw/Mn=7.35[1], respectively, based on the size exclusion chromatography with poly(methyl methacrylate) standards. The melting temperature of the copolymer was T_m=47.9 °C[2]. Extrapure dicarboxylic acids of perfluorosuccinic acid (Psuc), maleic acid (Ma), succinic acid (Suc), glutaric acid (Glu), and azelaic acid (Az) were used without further purification.

Cloud point measurement: general procedure

P[POA-*r*-DAA] (30 mg) and Glu (1.7 mg, a molar ratio of Glu/DAA unit=0.5) were placed in a variable volume view cell [22], then CO_2 liquefied with a cooler was added to it. The cloud point was defined as the point at which the contents of the cell turned slightly opaque, indicating precipitation of the polymer from solution.

Preparation of microspheres of P[POA-*r*-DAA] with the dicarboxylic acids: general procedure

Microspheres were prepared as reported previously [22]. P[POA-*r*-DAA] (30 mg) and Glu (1.7 mg) were placed in the variable volume view cell, then liquid CO_2 was added to it. The solution was kept at 209 bar at 35.1 °C for 10 min. The homogeneous solution was brought to the cloud point by the volume expanded. The cloud point pressure was 170.7 bar at 35.2 °C. The pressure of the heterogeneous solution was further reduced 20.7 bar lower, then the heterogeneous state was kept for a few minutes. The solution at 150 bar was sprayed into a plastic bag made of polyethylene to collect the polymer particles. The white polymer powder was quantitatively collected.

SEM measurement of microspheres

The microspheres were put on a carbon adhesive tape and was subjected to SEM measurement after coated with Pt.

Contact angle measurement

The surfaces completely covered with the microspheres were prepared on a carbon adhesive tape attached to a slide glass. The contact angles were measured by dropping water (10 μl) on the microsphere-coated surface at ambient temperature. The surface on the cast film of the copolymer was prepared directly on a slide glass from a copolymer solution in hexafluorobenzene.

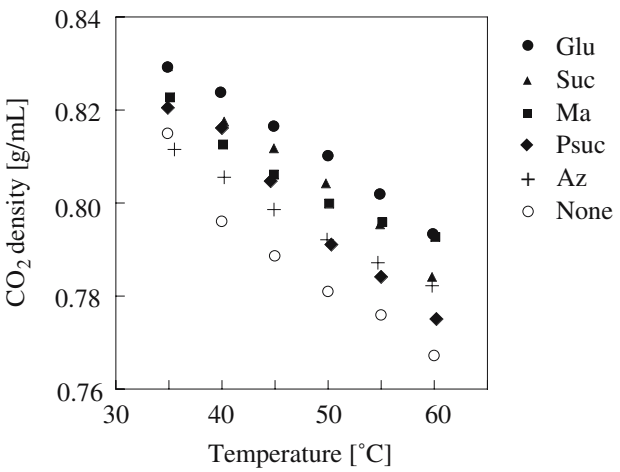

Fig. 1 Plots of the experimental cloud points of the P[POA-*r*-DAA] copolymer in the presence of the dicarboxylic acids at each temperature. The acid/DAA=0.5

[1] The broad molecular weight distribution of the copolymer should be based on the poor solubility of the POA units. In fact, as the molar ratio of the POA to DAA units in the copolymer increased, the molecular weight distribution increased [22]. However, the differential scanning calorimeter analysis confirmed that no POA homopolymer was included in the copolymer.

[2] Poly(POA) showed the melting temperature at 72.2 °C, whereas poly(DAA) had the melting temperature below −50 °C.

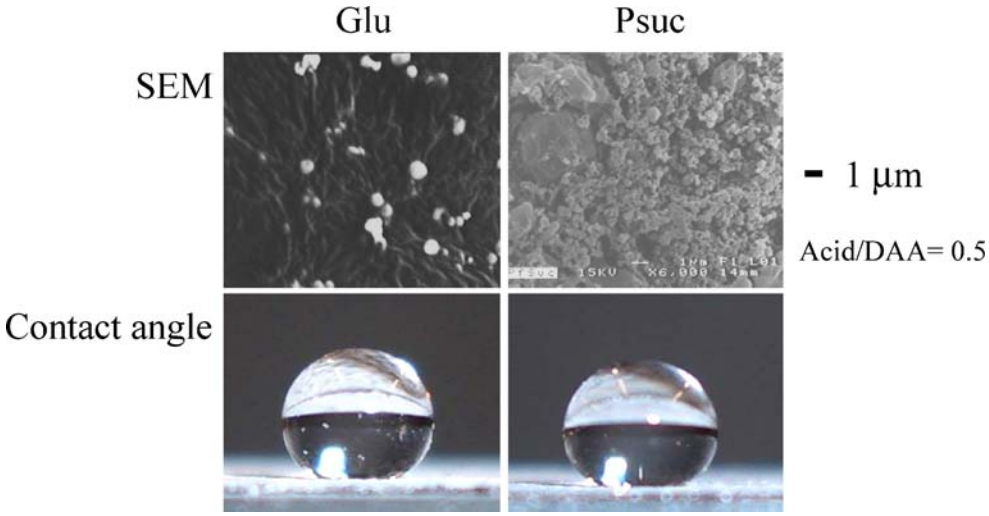

Fig. 2 SEM images of the particles produced by the copolymer in the presence of Glu and Psuc, and photographs of water droplets placed on the surface coated with the particles

Results and discussion

We reported that P[POA-*r*-DAA] formed microspheres in the presence of Paz at a Paz/DAA molar ratio of 0.5 [22]. The microspheres were produced in the heterogeneous state at a pressure lower than the cloud point pressure. Accordingly, the cloud points of the copolymer were determined in the presence of different dicarboxylic acids at the 0.5 ratio of the acid/DAA. Figure 1 shows the plots of the experimental cloud points of the copolymer at each temperature for Psuc, Suc, Glu, Az, and Ma. The CO_2 density at the cloud point decreased as the temperature increased, indicating that the solubility of the copolymer to supercritical CO_2 increased with the increase in the temperature. Similarly, the CO_2 density at the cloud points were shifted to a lower density in the order of Glu > Suc >

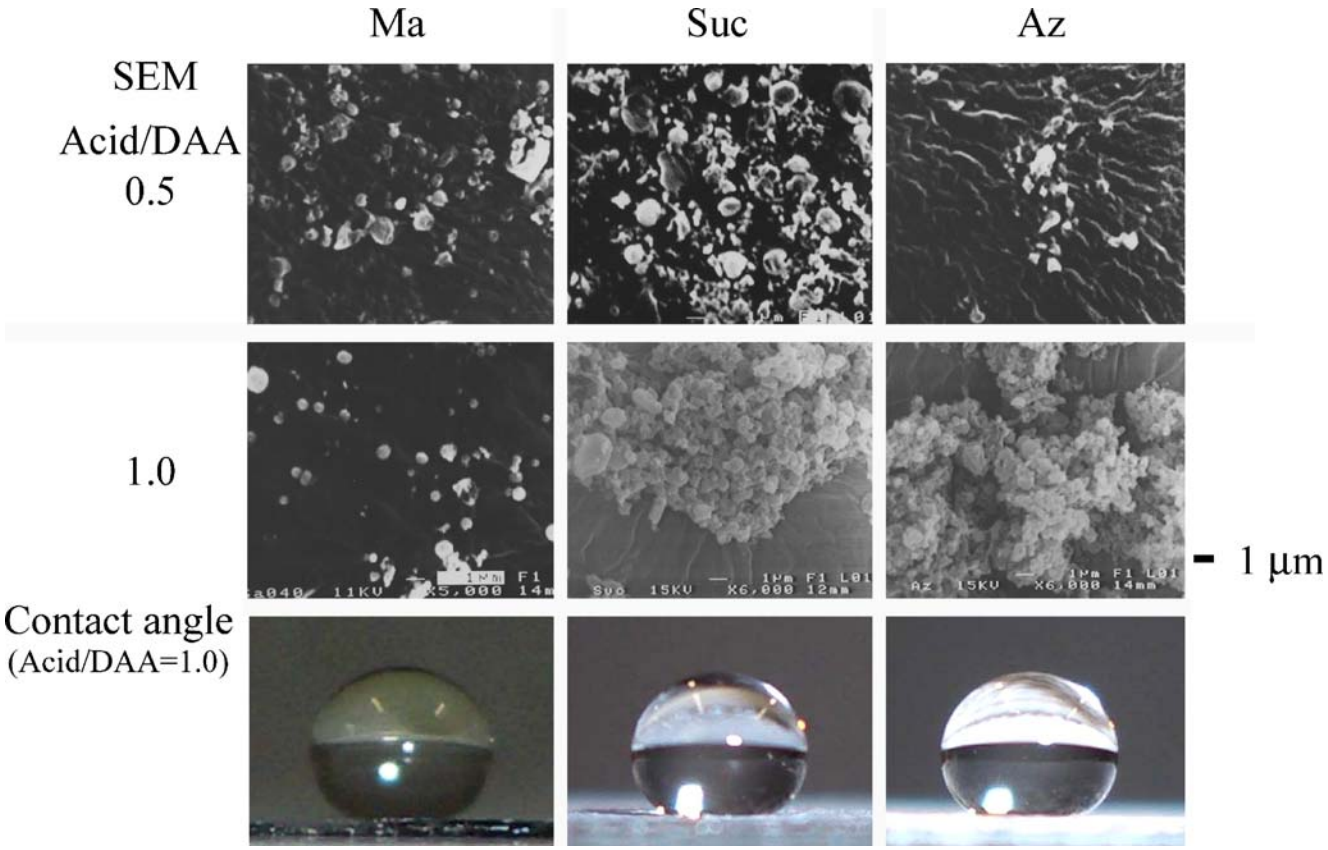

Fig. 3 SEM images of the particles produced by the copolymer in the presence of Ma, Suc, and Az, and photographs of water droplets placed on the surface coated with the particles

Table 1 Water contact angles (CA) on the surface coated with microspheres of P[POA-*r*-DAA] and carboxylic acids

Acid	Glu[a]	Psuc[a]	Ma[b]	Suc[b]	Az[b]	None[c]	None[d]
CA (°)	171.5	170.0	165.5	164.7	171.0	161.5	96.5

[a] Acid/DAA=0.5
[b] Acid/DAA=1.0
[c] The copolymer placed in supercritical CO_2
[d] Casted from a hexafluorobenzene solution of the copolymer under atmosphere

Ma > Psuc, Az. This indicated that the solubility of the particles formed by the copolymer and the acids increased in this order.

SEM observations revealed that the solubility of the particles to supercritical CO_2 was dependent on the size and forms of the particles. Figures 2 and 3 show the SEM images of the particles produced by the copolymer in the presence of the respective acids. Glu and Psuc provided spherical particles at 0.5 of the acid/DAA (Fig. 2). Psuc produced smaller microspheres than Glu. On the other hand, Ma, Suc, and Az provided random forms of the copolymer rather than spherical particles at this ratio (Fig. 3). Ma produced microspheres at 1.0. Suc and Az also produced spherical particles at 1.0; however, there were very smaller particles with a several hundred nanometer size along with the microspheres. These three acids had a lower ability to make the copolymer aggregate into microspheres because of the weak acidity and too short or too long chain length. Consequently, there was a tendency that the solubility of the particles decreased as the form of the copolymer became spherical from the random forms. The formation of the smaller particles seems to increase the solubility of the copolymer.

The microspheres have shells composed of the perfluoroalkyl chains from the POA units and cores of the DAA units cross-linked through the hydrogen bonding via the acids. Therefore, the surface on the microspheres is expected to have a high water repellence based on the perfluorinated shell. It was found that the surface coated with the microspheres had water contact angles greater than 164° (Table 1). The largest contact angle was obtained for Glu at 171.5°. It has been reported that the copolymer produced random forms in the absence of the acid in supercritical CO_2 [22]. The random forms had a contact angle at 161.5° (Fig. 4). The roughness of the surface due to the random forms should contribute to enhancing the hydrophobicity of the surface. On the other hand, the small contact angle of the surface on the cast films should be based on its smoothness.

Conclusion

Superhydrophobic surfaces with water contact angles of 164°–172° were obtained by forming microspheres covered with shells composed of the perfluoroalkyl chains. The microspheres were prepared through the self-assembly of the copolymer with the amino groups by the dicarboxylic acids. The easy formation of the microspheres was dependent on the kinds of acids. The acids with a weak acidity and short chain length had a lower effect on the formation of the microspheres. The microspheres were produced in the heterogeneous state at a pressure lower than the cloud point pressure. The solubility of the particles decreased as the copolymer became spherical from the random forms and as the size of the particles was smaller. Using supercritical CO_2, this should be a convenient method to easily obtain superhydrophobic surfaces.

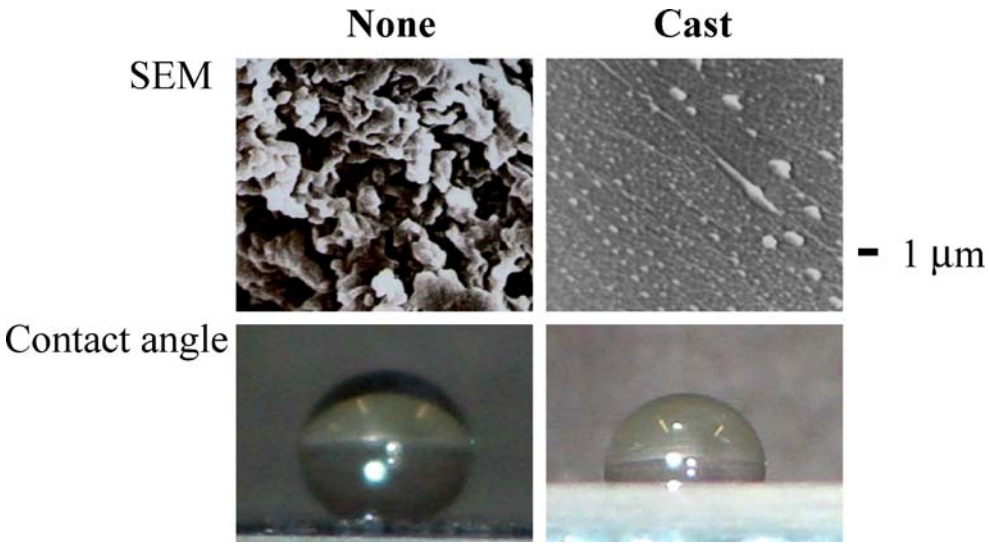

Fig. 4 SEM images of the random forms produced by the copolymer and of the surface on the cast films. Also shown are photographs of water droplets placed on the surface of the random forms produced by the copolymer and of the surface on the cast films

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