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Coating of silica particles by fluorinated diblock copolymers and use of the resultant silica for superamphiphobic surfaces

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ABSTRACT

Factors affecting the grafting of fluorinated diblock copolymers onto silica particles and the repellency of films prepared from the coated silica particles were investigated. The three copolymers used for silica coating were of the poly[3-(triisopropyloxysilyl)propyl methacrylate]-*block*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA) family possessing different relative block lengths. They were grafted onto silica under acidic conditions *via* the sol–gel chemistry of the PIPSMA block in binary solvent mixtures that solubilized the PFOEMA block but not necessarily the PIPSMA block. Depending on the solvent property, the silica type, the polymer composition, and the acid catalyst used, the coated silica could be non-dispersible or dispersible. The morphology of the coating on silica could be lumpy, smooth, or bumpy. Further, the amount of polymer grafted was also affected by these parameters. The various experimental results and observations were rationalized. In addition, the coated silica was cast to yield either smooth or rugged particulate films. The water and oil repellency or amphiphobicity of the films improved as the particle coating was changed from being smooth to bumpy, as the relative PFOEMA-to-PIPSMA block length of the coating polymer was increased, or as the roughness of the particulate film increased.

1. Introduction

Fluorinated silica particles or other particles can be cast alone or together with a polymeric binder to yield particulate films that repel water- and oil-borne contaminants alike [1–8]. The repellency arises due to three reasons [9–14]. Firstly, the surface tension of the particles is reduced by fluorination. Secondly, the particles do not pack densely, giving rise to a large particle/air interfacial area and surface roughness. Thirdly, the particles possess re-entrant sites on the surfaces of their bottom halves.

Traditionally, silica and other particles have been fluorinated using fluorinated silane coupling agents such as perfluorooctylethyl triethoxysilane [3,7,8,15–17], where the triethoxysilane groups graft onto silica *via* sol–gel chemistry and the perfluorooctyl groups protrude outwardly to provide the desired low surface tension. We recently demonstrated that diblock copolymers consisting of a fluorinated block and a grafting/crosslinking block can replace fluorinated silane coupling agents for the surface modification of silica [1,2,18] or other substrates [19–21]. For example, a poly[3-(triisopropyloxysilyl)propyl methacrylate]-*block*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA, Scheme 1) sample consisting of 10 units of IPSMA and FOEMA, respectively, was prepared by anionic polymerization and used to coat silica particles [1]. In that case, the PIPSMA and PFOEMA blocks served the functions of the triethoxysilane groups and the perfluorooctyl group, respectively. Compared with the traditional coupling agents, diblock copolymer coupling agents have the following perceived advantages. First, the grafting reaction may be facilitated by the greater abundance of trialkoxysilane groups found in the grafting block than the three found in a traditional coupling agent. Second, a thick grafted and crosslinked layer formed from a sol-gelling block would be more stable than the thin layer formed by the triethoxysilane groups. Third, the thickness of the fluorinated layer can be adjusted by changing the molecular weight of the fluorinated block. A thick PFOEMA layer would better shield the grafting layer and silica and thus enhance the anti-smudge properties of fluorinated silica. Additionally, it impedes surface reconstruction and coating permeation by reagents and etchants. While some of these advantages such as the improved etching resistance have been demonstrated [1], the advantages

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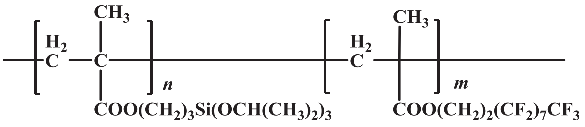

$$-\left[H_2C-\overset{CH_3}{\underset{COO(CH_2)_3Si(OCH(CH_3)_2)_3}{C}}\right]_n-\left[H_2C-\overset{CH_3}{\underset{COO(CH_2)_2(CF_2)_7CF_3}{C}}\right]_m-$$

Scheme 1. Chemical structure of PIPSMA-*b*-PFOEMA.

offered by an increased PFOEMA block length had not been verified because only one PIPSMA-*b*-PFOEMA sample has been used to coat silica.

We report in this paper the coating of silica by three PIPSMA-*b*-PFOEMA samples with different PIPSMA and PFOEMA block lengths. These samples are $PIPSMA_{15}$-*b*-$PFOEMA_{31}$ (P1), $PIPSMA_{19}$-*b*-$PFOEMA_{23}$ (P2), and $PIPSMA_{12}$-*b*-$PFOEMA_{30}$ (P3), respectively, with the subscripts denoting the repeat unit numbers for the different blocks. Since the repeat unit numbers of the PFOEMA blocks here are substantially longer than 10, these PFOEMA chains became insoluble in normal organic solvents such as tetrahydrofuran (THF) or had reduced solubility even in α,α,α-trifluorotoluene (TFT). Thus, our formally established coating conditions for $PIPSMA_{10}$-*b*-$PFOEMA_{10}$ using a TFT/THF mixture as the solvent became irrelevant and a new systematic study was initiated to establish solvent choices for coating silica using the new polymers. In the current study, we used, as solvents, mixtures of TFT and methyl perfluorobutyl ether (MFB), which is a good solvent for PFOEMA and a precipitant for PIPSMA. This systematic study revealed that the coating solvent composition critically affected the dispersibility of the coated silica as well as the morphology and amount of polymer grafted on silica. Even the choice of the catalyst, HCl versus trifluoroacetic acid, or the type of silica particles affected the morphology and amount of the grafted polymer. Only under optimized conditions, PIPSMA-*b*-PFOEMA could be grafted on silica as a smooth layer. Alternatively, a precipitate could be formed. More interestingly, we were even able to produce a novel bumpy coating on silica under certain conditions. Therefore, we report new insights gained from this systematic study. In addition, the silica particles bearing smooth or bumpy coatings were cast onto glass plates to yield uniform or rough amphiphobic particulate films. Further reported are the effects of changing the roughness of the particulate film, the block copolymer composition, and the roughness of the silica film on water and oil repellency.

2. Experimental section

2.1. Materials

Tetraethoxysilane (Aldrich, ≥99%), ammonia solution (2.0 M in isopropanol, Aldrich), isopropanol (Fisher, 99.5%), TFT (Acros, 99+%), methoxyperfluorobutane (MFB, Aldrich, 99%), trifluoroacetic acid (TFA, Fisher, ≥97%), and hydrogen chloride solution (HCl, Aldrich, 4.0 M in dioxane) were used as received. P1, P2, and P3 were synthesized *via* sequential atom transfer radical polymerization (ATRP) and were characterized as described in the Supporting Information (SI).

Silica particles were synthesized *via* a modified Stöber procedure [22]. First, 48 mL of isopropanol, 40 mL of deionized water, and 20 mL of an ammonia solution (2.0 M in isopropanol) were added into a 250 mL round-bottom flask and stirred vigorously at 60 °C for 30 min. Tetraethoxysilane (16.70 g) was added to this flask and the reaction was allowed to proceed for 20 h at 60 °C. The resultant silica particles were settled *via* centrifugation at 3050 *g* for 10 min. The supernatant was discarded and the particles were re-dispersed into 20 mL of isopropanol. The particles were settled again by centrifugation and the supernatant was discarded. This rinsing process was repeated thrice. The final particles were dried overnight at room temperature under vacuum to yield 5.33 g of silica particles (denoted as S1-1). Some of the particles were further vacuum-dried at 120 °C for 3 h to yield S1-2 particles or dried in a furnace at 550 °C for 10 h to produce S1-3 particles.

Smaller silica particles denoted as S2 were prepared in an analogous manner. In this case, 12.0 mL of isopropanol, 10.0 mL of deionized water, 5.0 mL of an ammonia solution (2.0 M in isopropanol) and 4.29 g of tetraethoxysilane were used. After the particles had been vacuum dried at room temperature overnight, 1.33 g of silica was obtained. The particles were subsequently vacuum-dried at 120 °C for 3 h before use.

2.2. Silica coating

In a typical silica coating procedure, 10.0 mg of S1-2 was ultrasonicated for 4 min in 1.40 mL of TFT to disperse the particles. Subsequently, 0.26 mL MFB and 1.20 mg of P1 dissolved in 1.60 mL of TFT were added under stirring. This mixture was stirred for 1 h at room temperature prior to the addition of 9.0 μL of a 0.10-M TFA solution. After an additional 3 h of stirring, 20 μL of a 13.0 M TFA solution was added. The mixture was further stirred for 16 h before it was centrifuged at 3000 *g* for 5 min to settle the particles. After the supernatant was removed, the particles were re-dispersed into a 1.50 mL TFT/MFB mixture (8.0 vol% MFB). The particles were settled again by centrifugation and the supernatant was discarded. The final particles were dried under vacuum at 120 °C for 2 h to yield 9.0 mg of coated silica.

A similar protocol was used to coat other silica particles with other polymers in different MFB/TFT mixtures. When a 4.0-M HCl solution in dioxane was utilized as the catalyst, 30 μL of this solution was used.

2.3. Sol-gelled PIPSMA-b-PFOEMA

Sol-gelled PIPSMA-*b*-PFOEMA samples were prepared by performing sol–gel reactions of the polymers using the silica coating protocol described above but without actually using silica particles. After the reaction, the solution was centrifuged at 17,000 *g* for 10 min to settle the product. The supernatant was removed, and the product was re-dispersed into a 1.50 mL TFT/MFB mixture (8.0 vol% MFB). The polymer was then settled again by centrifugation and the supernatant was discarded. The final product was dried under vacuum at 120 °C for 2 h.

2.4. Particulate films

To prepare films from coated silica, 2.0 mg of coated silica was dispersed into 40 μL TFT. To prepare a smooth film, 10 μL of MFB was then added to the solution before the dispersion was cast onto a glass plate with an area of ~1.3 cm^2. To prepare a rough film, 10 μL of decane was added to the TFT/MFB solution before it was cast onto a glass plate of ~1.3 cm^2 area. The films were left to dry at room temperature before they were further dried at 120 °C for 15 min.

2.5. Characterization

For atomic force microscopy (AFM) analysis, coated silica particles were dispersed into TFT and subsequently aero-sprayed [23] onto mica substrates. AFM height and phase images were obtained using a Veeco Multimode instrument equipped with a Nanoscope IIIa controller that was operated in the Tapping Mode. Rectangular-shaped silicon probes (AppNano, ACT) with a 300 kHz resonance frequency and a spring constant of 40 N/m were used.