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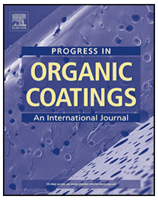

Formation of icephobic film from POSS-containing fluorosilicone multi-block methacrylate copolymers

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ABSTRACT

Polyhedral oligomeric silsesquioxane (POSS)-containing fluorosilicone multi-block methacrylate copolymers (PDMS-*b*-(PMAPOSS-*b*-PFMA)$_2$) were synthesized *via* RAFT polymerization of methacryloisobutyl POSS (MAPOSS) with hexafluorobutyl methacrylate (HFBMA) or dodecafluoroheptyl methacrylate (DFHMA) as different fluorinated side groups. A macro-RAFT chain transfer agent of polydimethylsiloxane with dithiobenzoate groups at both ends was initially used. Characterizations of surface chemical composition and morphology of the copolymer films suggested that the PDFHMA chains with longer fluorinated side groups, as compared with PHFBMA chains, were easy to migrate onto the surface and the surface roughness was enhanced by introducing PMAPOSS segments. The film of multi-block copolymer PDMS-*b*-(PMAPOSS-*b*-PDFHMA)$_2$ produced a fluorine-rich surface due to the enrichment of fluorinated blocks and exhibited the highest receding contact angle (103.8 ± 0.5°) and lowest water contact angle hysteresis (8.7 ± 1.4°) among all the samples, attributed to the introduction of PMAPOSS segments and the synergistic effect of silicon and fluorine. Measurements of icephobic properties demonstrated that the supercooled water droplet could easily slip away from the tilted PDMS-*b*-(PMAPOSS-*b*-PDFHMA)$_2$ surface (45°) at −20 °C and the ice shear strength tended to decrease from 361 kPa to 264 kPa with incorporation of PMAPOSS blocks in comparison with PDMS-*b*-(PFMA)$_2$. However, it was found that decreasing wettability of the block copolymer film did not have significant effect on reducing the ice shear strength. The prepared POSS-containing fluorosilicone multi-block methacrylate copolymers with good icephobicity can be used as icephobic coating materials potentially.

1. Introduction

Ice accumulation on exposed surfaces such as aircrafts, wind turbines, and power lines may result in severe accidents and large economic losses [1,2]. In the past few years, a considerable amount of researches have been conducted on the development of icephobic materials [3–6]. Low surface energy materials, including silicone-based polymers and fluoropolymers, are often applied to prepare hydrophobic surfaces, which can be used as icephobic materials. It is well known that the interaction between the substance and ice includes electrostatic forces, hydrogen bonding, van der Waals forces and mechanical interlocking. Because of flexibility of polydimethylsiloxane (PDMS) chains at low temperature, the PDMS-based polymer can prevent mechanical interaction and reduce ice adhesion strength, which makes it a good candidate for icephobic coatings [7,8]. Fluoropolymers may also be used as icephobic materials due to their low dielectric constant, which can reduce the electrostatic force between the substrate and ice, and result in low ice adhesion strength [9]. However, both PDMS-based polymers and fluoropolymers have drawbacks in actual icephobic coating applications. The former shows poor mechanical properties and low oil repellency, while the latter usually has a higher T_g value.

Recently, increasing attention has been attracted to incorporation of fluorinated polymeric components into PDMS-based polymers to obtain fluorosilicone copolymers. Fluorosilicone copolymers combining the advantages of fluoropolymer and silicone, can possibly surmount their individual weakness and thus may be used as ice or snow repellent coatings [10–13]. Meanwhile, for a heterogeneous polymer surface containing both fluorocarbon and siloxane, the interaction energies between the polymer surface and water would be decreased when both fluorocarbon group and siloxane group close into a water molecule. Thus, the synergistic

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effect of silicon and fluorine would contribute to the reduction of contact angle hysteresis [14,15].

The surface morphology would have great influence on the icephobicity of the materials. Compared with micron scale roughness surfaces, the nanoscaled surfaces would possible possess better icephobic behaviors [7,16–18]. Polyhedral oligomeric silsesquioxane (POSS) has a cage-like inorganic core in the range of 1–3 nm, covalently surrounded by organic corner groups, which endow the POSS molecule with a higher solubility in organic solvents and can be used to modify the properties of polymers at the molecular level [19,20]. The incorporation of POSS units into polymer may improve the properties such as mechanical strength, hydrophobicity and thermostability, and can also increase the surface roughness of polymers [21–23].

Because of compatibility with a wide range of functional monomers and ability to control polymer architecture and molecular weight [24], reversible addition–fragmentation chain transfer (RAFT) polymerization is adopted in the study to synthesize POSS-containing fluorosilicone copolymer with well-defined structure, which allows greater insight into the structure–icephobicity relationship.

In the previous reports, we attempted to synthesize fluorosilicone block copolymers *via* free radical polymerization and RAFT polymerization [25,26]. The icephobicity results showed that the fluorosilicone block copolymer surfaces could decrease ice adhesion strength indeed, but the water droplet could hardly slide off the copolymer surfaces. It was reported that rapid de-wetting surface can be achieved by increasing receding contact angle or by removing water droplets through minimization of contact angle hysteresis [27,28]. In order to improve the icephobicity of the fluorosilicone block copolymer, in this study, a macro-RAFT chain transfer agent of polydimethylsiloxane with dithiobenzoate groups at both ends (CTA-PDMS-CTA) was initially used for RAFT polymerization of methacryloisobutyl POSS (MAPOSS) with hexafluorobutyl methacrylate (HFBMA) or dodecafluoroheptyl methacrylate (DFHMA) as the fluorinated methacrylate (FMA) monomers. The effect of different fluorinated side groups and PMAPOSS segments in the prepared POSS-containing fluorosilicone multi-block methacrylate copolymers (PDMS-*b*-(PMAPOSS-*b*-PFMA)$_2$) on the wettability and icephobic properties of copolymer films were investigated. PFMA with low surface energy was architected as the end block for facilitating fluorinated groups to migrate onto the surface. PMAPOSS was introduced for improving hydrophobicity and modifying the surface morphology of the copolymer film. The relationship between the wettability and the icephobic properties was also investigated. It was hypothesized that this specific integration of PMAPOSS block and enrichment of fluorinated groups on the copolymer surface could enhance the hydrophobic and icephobic properties.

2. Experimental methods

2.1. Materials

α,ω-Dihydrogen-terminated poly(dimethylsiloxane) (H-PDMS-H, 10,000 g/mol) was supplied by Hangzhou Silong Chem-Tech, Hangzhou, China. MAPOSS was purchased from Hybrid Plastics, USA, and used as received. HFBMA and DFHMA were supplied by Xeogia Fluorin-Silicon Chemical Co. Ltd., China, and purified by passing over a column of alumina to remove inhibitor. *N*,*N*′-Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Sigma–Aldrich. 2,2′-Azobisisobutyrobutyl acrylate (AIBN) was obtained from Tianjin Kemiou Chemical Reagent Co. Ltd., China, and used after recrystallization by ethanol. α,α,α-Trifluorotoluene (TFT) was purchased from Tianjin Heowns Biochem Technologies LLC, Tianjin, China. All other reagents were supplied by Tianjin Kermel Reagent Co. Ltd, China, and used without further purification.

2.2. Synthesis

The POSS-containing fluorosilicone multi-block methacrylate copolymers were synthesized by RAFT polymerization (Scheme 1). The detailed compositions of the prepared copolymers are shown in Table 1.

CTA-PDMS-CTA was prepared by the DCC/DMAP catalyzed esterification of 4-cyanopentanoic acid dithiobenzoate (CPADB) with hydroxyl-terminated PDMS (HO-PDMS-OH), whereas CPADB and HO-PDMS-OH were synthesized according to the references [29,30]. Typically, HO-PDMS-OH (10 g, 1 mmol), CPADB (0.837 g, 3 mmol), DCC (0.931 g, 4 mmol) and DMAP (0.116 g, 0.9 mmol) were charged into a 150 mL flask with 50 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred under N_2 protection for 12 h at 0 °C, and then for 20 h at room temperature. The precipitated dicyclohexylurea was filtered off. The crude product was precipitated in methanol for three times and dried under vacuum for 24 h. CTA-PDMS-CTA was obtained as red oil-like liquid.

The synthesized CTA-PDMS-CTA was used as macro-RAFT chain transfer agent to synthesize a PDMS-*b*-(PMAPOSS)$_2$ triblock copolymer *via* RAFT polymerization. In a typical experiment, CTA-PDMS-CTA (0.6 g, 0.05 mmol), MAPOSS (1.028 g, 1.09 mmol) and AIBN (3.6 mg, 0.022 mmol) were dissolved in 1.8 mL of toluene and placed in a 50 mL round-bottom. Then, argon gas was passed through the solution for 30 min to eliminate oxygen. The bottle was immersed in a water bath at 70 °C and the polymerization was carried out for 10 h under argon atmosphere. Pure PDMS-*b*-(PMAPOSS)$_2$ was obtained from precipitation in methanol. The product designated as **S-POSS** was then dried in a vacuum oven overnight for further uses.

Table 1
Composition and molecular weight of the prepared fluorosilicone multi-block copolymers.

Sample	Structure	[M]:[Macro-CTA]:[I]	$\bar{M}_{n,\mathrm{NMR}}$ ($\times 10^4$)	$\bar{M}_{n,\mathrm{GPC}}$ ($\times 10^4$)	DP_n [a] (MAPOSS)	DP_n [a] (FMA)	W_F [b] (wt%)	PDI[c]
–	CTA-PDMS-CTA	–	–	1.06	–	–	–	1.28
S-POSS	PDMS-*b*-(PMAPOSS)$_2$	20:1:0.4	2.10	2.03	11	–	–	1.15
S-6F	PDMS-*b*-(PHFBMA)$_2$	50:1:0.4	1.93	1.51	–	35	0.20	1.18
S-POSS-6F	PDMS-*b*-(PMAPOSS-*b*-PHFBMA)$_2$	100:1:0.4	3.45	2.51	11	54	0.17	1.24
S-12F	PDMS-*b*-(PDFHMA)$_2$	50:1:0.4	2.26	1.81	–	30	0.29	1.09
S-POSS-12F	PDMS-*b*-(PMAPOSS-*b*-PDFHMA)$_2$	50:1:0.4	3.46	2.37	11	34	0.21	1.18

[a] Measured by ^{1}H NMR.

[b] W_F = FMA conversion × F%, F% represents F element content in FMA.

[c] Obtained from GPC.