Icephobicity of polydimethylsiloxane-*b*-poly(fluorinated acrylate)

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ABSTRACT

A facile process to fabricate icephobic surfaces was developed by spin-coating the polydimethylsiloxane-*b*-poly(fluorinated acrylate) (PDMS-*b*-PFA) block copolymers on the substrate. The surface microstructure and chemical composition of the block copolymer films can be adjusted by changing the PDMS content. Icephobic properties of the copolymer surface were mainly ascribed to "flexible-hard" microphase separation and the ratio of fluorine to silicon. The appropriate microphase domain size and the fluorine/silicon ratio could weaken the interaction of ice and copolymer surface and delay icing of water droplets on the copolymer surface. The co-polymers containing 15 wt.% PDMS showed the most outstanding icephobicity by depressing the interaction between ice and the copolymer surface.

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1. Introduction

Excessive ice accretion on the surfaces of power and communication networks, aircraft and ships might lead to undesired service outages or costly safety issues [1]. An ideal solution would be preventing ice accumulation rather than de-icing which is time-consuming and expensive. This could be accomplished by depositing icephobic coatings [2,3].

Low surface energy coatings including fluorinated and organic silicone materials have been studied for decades to prepare anti-icing coatings [4–7]. Generally, the interactions between the substance and ice include electrostatic force, hydrogen bonding and mechanical adhesion. Due to the flexible mobility of polydimethylsiloxane (PDMS) chains at lower temperatures, the PDMS-based polymer can prevent mechanical adhesion and reduce ice adhesion strength, which makes it a good candidate for icephobic coatings. Because of the low dielectric constant ($\varepsilon \approx 2.1$), fluoropolymer can also reduce the electrostatic force between the substrate and ice, resulting in low ice adhesion strength [3]. However, the interaction energy between the fluorocarbon group and water is three times larger than that between the siloxane group and water [8]. The water droplet could hardly slide on the surface of the fluoropolymer because of the strong interaction between fluorocarbon groups and water. 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 effect of silicon and fluorine would contribute to the reduction of contact angle hysteresis and lead to low ice adhesion strength [8].

At the present, relative reports have shown that certain microstructures of the coating surface could contribute to improving anti-icing performances [9,10]. The surface morphology can have a spectacular influence on hydrophobicity and icephobic behaviors. For example, in Cassie–Baxter state, a water drop can be supported by air which is jammed between the water drop and the rough surface of the substrate [11]. In such aspect, water drops tend to behave like pearls and can roll down from the surface. It was well known that the incompatibility of block compositions could result in microphase separation both in bulk and on surface of the block copolymers. Usually, the domain size of microphase on the block copolymer surface generated by self-assembly could be controlled from 5 nm to 100 nm, but it also could be as large as several microns by selecting proper materials and methods [12].

In this paper, the polydimethylsiloxane-*b*-poly(fluorinated acrylate) block copolymers (PDMS-*b*-PFA) with various PDMS contents were synthesized by radical solution polymerization using PDMS macroazoinitiator (PDMS-MAI), and microphase separation, surface elements composition and roughness, wettabilities and icephobic properties of PDMS-*b*-PFA were systematically studied. It was assumed that the anti-icing properties of the block copolymer strongly relied on both the domain size of microphase and the ratio of fluorine to silicon on the surface. The appropriate microphase domain size and fluorine/

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silicon ratio could weaken the interaction of ice and copolymer surface and delay icing of a water droplet on the copolymer surface.

2. Experimental methods

2.1. Materials

α,ω-Dihydrogen-terminated polydimethylsiloxane (H-PDMS-H) with molecular weight of about 12,500 was supplied by Hangzhou Silong Material Technology Co., Ltd., China. 4,4′-Azobis(4-cyanovaleric acid) was purchased from Aldrich. 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl methacrylate (DFHMA) was supplied by Xeogia Fluorin-Silicon Chemical Co., Ltd., China. Methy1methacrylate (MMA), n-butyl acrylate (nBA), hydroxyethyl methacrylate (HEMA) and solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. All the monomers were treated with 5 wt.% aqueous NaOH to remove inhibitor, dried overnight with anhydrous sodium sulfate and stored at low temperature prior to use.

2.2. Synthesis

PDMS macroazoinitiator (PDMS-MAI) was synthesized as shown in our previous report [13]. Briefly, PDMS-MAI was prepared by esterification with hydroxyl terminated PDMS (HO-PDMS-OH) with 4,4′-azobis(4-cyanovaleric acid), whereas HO-PDMS-OH was synthesized by hydrosilylation of allyl alcohol and H-PDMS-H by using a platinum catalyst. The PDMS-b-PFA block copolymers with various PDMS contents were prepared by radical solution polymerization using PDMS-MAI. The polymerization was carried out under nitrogen atmosphere in a 250-mL four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel and a nitrogen inlet. The monomer compositions were listed in Table 1. After MMA, nBA and HEMA were polymerized using PDMS-MAI as the initiator in MIBK at 60 °C for 4 h, DFHMA was added drop-by-drop within 1 h. Afterward, the reaction mixture was stirred for another 5 h at 65 °C. The reaction was stopped by cooling to room temperature. The prepared copolymers were purified by dissolution and reprecipitation with tetrahydrofuran (THF) and hexane, respectively. The PDMS-b-PFA copolymer was soluble in THF but insoluble in hexane, whereas the poly(fluorinated acrylate) (PFA) homopolymer was insoluble in THF. After several cycles of the dissolution and reprecipitation process, the PDMS-b-PFA copolymer was purified, and then dried under vacuum at 40 °C for 24 h.

2.3. Preparation of the PDMS-b-PFA film

The PDMS-b-PFA films were prepared by spin-coating of the copolymer solution in ethyl acetate on the substrate at room temperature. The spinning speed was set at 300 rpm (6 s) and 2000 rpm (10 s) for the first and second steps, respectively. The thickness of the copolymer films was around 210 ± 15 nm.

2.4. Characterizations

Fourier transform infrared (FT-IR) spectra of samples were recorded between 4000 cm^{-1} and 400 cm^{-1} in an AVATER-360B spectrophotometer using KBr pellet technique.

^{1}H nuclear magnetic resonance (^{1}H NMR) measurements were carried out in Varian machines (INOVA 500 MHz and Infinity plus 300WB, USA) by dissolving the samples in deuteriochloroform or deuterated dimethyl sulfoxide.

The molecular weight and polydispersity of the prepared PDMS-b-PFA copolymers were determined in a Waters 1515–2414 gel permeation chromatography (GPC) with THF as the eluent flowing at 1 mL/min. Polystyrene standards were used to generate a calibration curve.

Differential scanning calorimetry (DSC) measurements were carried out with a DSC200F3 differential scanning calorimeter (NETZSCH, Germany) under N$_2$ atmosphere at a heating rate of 10 °C min^{-1} from −150 °C to 150 °C.

Atomic force microscope (AFM) experiments were performed using an AFM machine (CSPM5500A of Ben Yuan Ltd., China) equipped with E-type vertical engage piezoelectric scanner and operated in a tapping-mode at room temperature.

Copolymer morphologies were also observed under a transmission electron microscope (TEM) (JEOL JEM100CXII 100 kV, Japan). The diluted copolymer solution was deposited onto a copper net and stained with ruthenium tetroxide (RuO$_4$) vapor for 2 h.

The surface chemical composition of the PDMS-b-PFA copolymer film was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using at a 90° take-off angle under an ultrahigh vacuum less than 6.7×10^{-6} Pa at 45° with Al K radiation (1486.6 eV) operating at 24.2 W. The tested area was a circle of 100 μm diameter.

Water contact angles and contact angle hysteresis on the surfaces were measured in a modified optical contact angle meter system with a cold plate (JC2000D, Shanghai Zhongchen Equipment Ltd., China). A droplet of distilled water (5 μL) was placed on the sample surface and then expanded or shrunk at a flow rate in the range of 0.1–1.0 μL/s via a syringe needle. Images of the droplets were captured by a CCD camera and analyzed to obtain the advancing and receding contact angles, and values of the water contact angle hysteresis were calculated [13]. The surface energies of the polymers were evaluated by measuring the static water and hexadecane contact angles on the surface [13]. All the presented values are averages of at least five or six measurements each. The modified optical contact angle meter system with a high speed CCD camera was also utilized to observe the freezing profiles of individual water droplets on sample substrates at −20 °C. The freezing process of water droplets in 4 μL was recorded by the high speed CCD camera at a speed of 25 fps. The sample substrates were mounted on a cold plate controlled at −20 °C under nitrogen (relative humidity <10%). The icing delay time of the water droplet on the copolymer surfaces was recorded as the start time of freezing.

Ice adhesion strength was measured using a universal testing machine (QJ211, Shanghai Qingji Instrumentation Science and Technology Co., Ltd., China) equipped with a 100 N load cell (Transcell Technology,

Table 1
Compositions, molecular weight and polydispersity index, and yields of the prepared PDMS-b-PFA copolymers.

Sample	PDMS-MAI (wt.%)	Monomer (g)				$\overline{M}_n$ ($\times 10^4$)	$\overline{M}_w$ ($\times 10^4$)	$\overline{M}_w / \overline{M}_n$	Yield (%)
		MMA	nBA	HEMA	DFHMA				
HO-PDMS-OH	–	–	–	–	–	1.25	2.14	1.71	–
PDMS-MAI	–	–	–	–	–	2.17	3.31	1.53	–
PF1	50	6	4.5	1.5	3	2.73	4.12	1.51	78.3
PF2	40	6	4.5	1.5	3	2.85	7.04	2.47	68.6
PF3	30	6	4.5	1.5	3	4.11	6.83	1.66	54.2
PF4	15	6	4.5	1.5	3	6.42	11.29	1.75	43.9