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Preparation and evaluation of hydrophobic surfaces of polyacrylate-polydimethylsiloxane copolymers for anti-icing

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ABSTRACT

Two series of polyacrylate-polydimethylsiloxane (PDMS) copolymers, namely, polyacrylate-*b*-PDMS and polyacrylate-*g*-PDMS with three different molecular weights of PDMS blocks or side chains, were synthesized for formation of hydrophobic surfaces for anti-icing. The main purpose of this paper was to investigate the relationship between ice adhesion strength and the surface structure of the copolymers, and to find out how the prepared PDMS-containing polyacrylate copolymers are potentially used for anti-icing. The microphase-separated structure and the surface chemical composition were analyzed by transmission electron microscopy, atomic force microscopy and X-ray photoelectron spectroscopy, and ice adhesion strength was measured using a universal testing machine in a pull off mode. Results suggested that microphase separation appeared clearly in all the copolymers, especially for the block ones. The PDMS chains aggregated on the top of the polymer surfaces caused by microphase separation could weaken the interaction between the polymer surface and water, mainly hydrogen bond, which was demonstrated because of decrease of water contact angle hysteresis. Then, ice adhesion strength was decreased by the contribution of PDMS in the block copolymers or the graft copolymer with longer PDMS side chains. It is suggested that the polyacrylate-*b*-PDMS or polyacrylate-*g*-PDMS copolymers would have practical applications in preparation of anti-icing coatings.

1. Introduction

Anti-icing coatings with icephobic characteristics to reduce ice adhesion strength or eliminate ice attachment have been widely investigated in recent years [1–5]. Low surface energy and superhydrophobicity are the two main strategies for anti-icing. Superhydrophobic coatings, which were generally prepared from fluorine- or silicon-containing polymers and organic or inorganic nanoparticles, presented good anti-icing performances in inhibiting ice formation based on micro- and nano-scaled roughness [6–12]. Patterned surfaces with fluorinated treatment could also generate superhydrophobic surfaces [13]. From the practical point of view, most of the methods to obtain the superhydrophobic surfaces or coatings cannot be easily industrialized because of their low stability or the complex processes with higher resolutions [13,14]. The recent report on sandblasted aluminium alloys plus boehmite nanostructure formation could be a feasible way to prepare superhydrophobic coatings, and the lubricant-infused textured surface combined of a superhydrophobic surface and an infused low surface energy liquid exhibited excellent icephobic properties [15].

It is well known that the interaction between the substance and ice is a combination of chemical interactions (mainly hydrogen bond), electrostatic force and mechanical bonding [3]. According to these principles, when water condenses on a surface with rough structure in a humid atmosphere, the mechanical interaction between ice and the porous superhydrophobic surface could lead to very large values of ice adhesion strength [16,17]. There was pro and con discussion on ice-releasing properties of the rough superhydrophobic surfaces [14,16–19]. The size of the microcracks at the solid-ice interface can be considered as a critical parameter that governs ice adhesion strength, and some superhydrophobic surfaces can have strong ice adhesion if they do not provide sufficiently large voids at the interface [18]. Therefore, uniform nanoscaled surfaces would possibly demonstrate the most significant ice-repellent behaviours [15,19]. These phenomena encourage us to investigate the coating itself in detailed polymer structures for anti-icing.

Polydimethylsiloxane (PDMS) with lower glass transition temperatures (T_g), was considered as one of the best candidates to

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prepare anti-icing coatings. One of its advantages, low dielectric constant ($\varepsilon = 2.3–2.8$), guarantees its lower electrostatic adhesion for applications in protection of electronic transportation equipments [9,20,21]. The repulsion between water molecules and siloxane groups also endows PDMS with hydrophobicity [3,21]. In comparison with fluoropolymers, more flexible mobility of PDMS chains at lower temperatures is another advantage of silicone-based polymers to inhibit ice adhesion. In fact, silicone has been used to generate anti-icing surfaces. For example, room-temperature-vulcanizated silicone coating on the nanostructured surface could possibly be used as icephobic surfaces [21]. Silicone-based polymers could also be compounded with nano-particles to obtain hybrid superhydrophobic coatings for anti-icing [9,12,22].

From the above statement, it is possible for silicone-based polymers to hinder ice attachment. Additionally, chemical-modified silicone copolymers are more attractive with integrated advantages of both silicones and the modified components. PDMS-polyurea segmented copolymers exhibited high level of mechanical strength coupled with enhanced fouling release characteristics for anti-fouling coatings [23]. Ice releasing coatings prepared from poly(dimethyl-siloxane)-*b*-polycarbonate copolymers were ever tested in the earlier indication [24]. A heterogeneous polymer coating of polysiloxane grafted with fluoropolymer has been attempted to decrease ice adhesion strength, and the heterogeneity of this polymer brings about a synergistic effect of polysiloxane and fluoropolymer, leading to low ice adhesion strength [25].

Acrylate-modified PDMS, such as a heterophase material of poly(methyl methacrylate)-*g*-poly(dimethylsiloxane) (PMMA-*g*-PDMS), can be synthesized via copolymerization of PDMS macromonomer with methyl methacrylate (MMA), and the surface stability of the hydrophobic soft phase of the graft polymer architecture was ever evaluated for anti-fouling [26,27]. PMMA-*b*-PDMS block copolymer could also be synthesized via the macro-azo-initiator [28].

Though the preparing methods and the anti-icing performances of silicone-containing coatings have been widely studied, there were a few reports on anti-icing performances of the modified silicone-polyacrylate polymers. In this study, two series of polyacrylate-PDMS block and graft copolymers were synthesized and evaluated. The polymer surface characterizations including microphase morphology, surface chemical composition, contact angles and ice adhesion strength were investigated, and effects of the PDMS chain length and the copolymer types on anti-icing performance were emphasized.

2. Experimental methods

2.1. Materials

Three of methacryloxypropyl terminated poly(dimethylsiloxane) (PDMS-MA) macromonomers with molecular weight of about 1000, 5000 and 13,000 were supplied by Gelest Inc., USA. Three Si–H capped PDMS in about 2000, 10,000 and 13,000 of molecular weight were supplied by Hangzhou Silong Material Technology Co., Ltd., China. Methacryloisobutyl POSS (POSS-MA) was purchased from Hybrid Plastics, Inc., USA. 4,4′-Azobis(4-cyanovaleric acid) (ACVA) was purchased from Aldrich, and freeze-dried under vacuum for 24 h before use. 4-(Dimethylamino) pyridine (DMAP) and dicyclohexyl carbodiimide (DCC) were supplied by GL Biochem Ltd., Shanghai, China. *p*-Toluenesulfonic acid (PTSA), azobisisobutyronitrile (AIBN), methylmethacrylate (MMA), *n*-butyl acrylate (*n*BA), hydroxyethyl methacrylate (HEMA), and solvents including dichloromethane, *N,N*-dimethyl formamide (DMF), toluene and benzene were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd., China. The liquid monomers (MMA, *n*BA, HEMA) were purified and solvents were dried before use. 4-(Dimethylamino) pyridinium-*p*-toluenesulfonate (DPTS) was synthesized from DMAP and PTSA for the further use. Others were used as received.

2.2. Synthesis

The block copolymers polyacrylate-*b*-PDMS (I in Fig. 1) were synthesized by initiation of PDMS macro-azo-initiators (PDMS-MAI) and polymerization of monomers including MMA, *n*BA, HEMA and POSS-MA. PDMS-MAI were synthesized from hydroxypropyl functioned PDMS (PDMS-ROH) which were prepared by hydrosilylation of allyl alcohol and Si–H functional PDMS according to the references [28–30]. Briefly described, PDMS-ROH was reacted with ACVA under DPTS and DCC (PDMS-ROH/ACVA/DPTS/DCC = 1:1:0.4:3, molar ratio) in a mixture of dichloromethane and DMF (6/1, w/w) at room temperature for 24 h to obtain PDMS-MAI. The copolymerization of PDMS-MAI with MMA, *n*BA, HEMA and POSS-MA in 10/6/2/1/1 mass ratio (Table 1) was carried out under nitrogen at 65 °C for 12 h. The resulting polyacrylate-*b*-PDMS copolymers were purified by slow precipitation in methanol and re-precipitation in benzene from the solution in a mixture of *n*-hexane and ethanol (1/2, *v*/*v*), and vacuum-dried at 40 °C. POSS-MA was introduced as a monomer for reinforcement.

As shown in Fig. 1, the graft copolymers polyacrylate-*g*-PDMS (II) were obtained by copolymerization of PDMS-MA with MMA, *n*BA, HEMA and POSS-MA in given compositions (Table 1) by using AIBN as the initiator.

The copolymer films of PDMS-*b*-polyacrylate or polyacrylate-*g*-PDMS were prepared by spraying the copolymer solutions in *n*-butyl acetate with a concentration of 20 wt% on polished aluminium plates (30 mm × 30 mm), and allowing the solvent to evaporate completely at room temperature in air. A given amount of the curing agent was supplied. The prepared films were used for the surface characterizations.

2.3. Characterizations of the polyacrylate-PDMS copolymers

Average molecular weights of PDMS-*b*-polyacrylate and polyacrylate-*g*-PDMS copolymers were determined in gel permeation chromatography (GPC, TDA305, Malvern Instruments Ltd., UK) by using THF as the eluent. Values of yield, $\bar{M}_n$, $\bar{M}_w$ and polydispersity index (PDI) of the synthesized copolymers are shown in Table 1.

Fourier transformed infrared spectroscopy (FTIR) spectra of samples were recorded in a Spectrum 100 FT-IR spectrometer (Perkin-Elmer, USA) in the range from 4000 cm^{-1} to 400 cm^{-1} using KBr pellet technique. ^1H Nuclear magnetic resonance (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. Differential scanning calorimetry (DSC) were measured with a Diamond differential scanning calorimeter (Perkin-Elmer, USA) under nitrogen atmosphere at a heating rate of 10 °C min^{-1} from −150 °C to 150 °C.

Transmission electron microscope (TEM) samples were prepared by dropping a droplet of the copolymer solutions (1 wt% in butyl acetate) on a carbon-coated copper grid. After a few seconds, excess solution was removed by blotting with filter paper. Staining was performed with ruthenium tetroxide (RuO_4) vapour for 3 h to increase the contrast of PDMS and polyacrylate domains [26,27]. Those samples were observed under a field emission TEM machine (Tecnai G2 F20 200 kV, the Netherlands).

Atomic force microscope (AFM) observation was operated in tapping-mode at a scan rate of 1.0 Hz at room temperature in an AFM machine (NanoscopeIIIa multimode, Veeco Instruments Inc.,