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Formation of zwitterionic coatings with an aqueous lubricating layer for antifogging/anti-icing applications

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ABSTRACT

Zwitterionic coatings with high transparency were developed by combining poly(methacryloxyethylsulfobetaine-*co*-hexafluorobutyl methacrylate-*co*-allyl methacrylate) (P(SBMA-*co*-FMA-*co*-AMA)) with different contents of oligoethylene glycol dimethacrylate (OEGDMA) via UV curing for antifogging and anti-icing applications. The prepared coatings exhibited excellent antifogging behavior under moist conditions owing to the hydrophilic and hygroscopic capacities of the coating. Water droplets on the zwitterionic coatings with 2% OEGDMA demonstrated maximal freezing delay time (126.3 ± 4.0 s) at −18 °C in comparison with bare aluminum (about 3 s). Results of differential scanning calorimetry analysis further confirmed that the bond water and non-freezable bond water in the zwitterionic coatings could be the main factors contributing to the antifogging/anti-icing performances. It was assumed that the zwitterionic SBMA component in the coating could bond with water to generate an aqueous lubricating layer for the excellent antifogging/anti-icing performances, while hydrophobic FMA was introduced for modulation of the surface wettability of the coatings. The zwitterionic coating could be a potential candidate for antifogging and anti-icing applications.

1. Introduction

Fogging on eyeglasses, lenses, optical instruments, windshields and so forth would cause light scattering and reduce light transmittance [1–3]. During fogging, small water beads are formed due to the condensation of vapor in the air on the substrate [4]. For versatile applications, antifogging coatings could be combined with multifunctional properties such as frost-resisting [4–7], antimicrobial [8] or self-healing [9–11].

Anti-icing coatings, including low surface energy coatings [12,13], superhydrophobic coatings [14] and lubricated coatings [15–20], have drawn the attention of researchers to solve icing and frosting problems. In addition to oil-lubricated coatings, water-lubricated coatings were also developed for antifogging or anti-icing coatings with aqueous lubricating layer [21–25].

Polyelectrolytes are water-soluble due to electrostatically enhanced hydrogen bonds [26]. Sun et al. fabricated self-healable, antifogging/frost-resisting coatings with poly(ethylenimine) (PEI) and a blend of hyaluronic acid (HA) and poly(acrylic acid) (PAA) polyelectrolytes via layer-by-layer (LbL) assembly [5]. Hydrogen bonds formed between water and PEI or HA and PAA endowed the coating remarkably water-absorbing capability, and antifogging and frost-resisting properties. Several robust and durable water-lubricated anti-icing coatings have also been prepared from polyelectrolytes such as crosslinked HA [24], dimethylolpropionic acid [23] and PAA [27], respectively. The aqueous lubricating layer of coatings made from polyurethane and DMPA could remain stable at as low as −53 °C [23]. When the hydrophilic component is introduced, bond water could appear and form a very thin lubricating layer in a few molecules thickness in favor of boundary lubrication. The favorable anti-icing property resulted from hydrophilic pendant groups contributing to melting of ice after ionizing in water. In addition, the freezing point of bond water inside the aqueous lubricating layer was much lower than that of bulk water [28]. Chen et al. provided solid evidence to prove the existence of nonfrozen lubricating layer by using solid-state NMR [29]. Bond water results from interactions of water and hydrophilic groups, which is necessary for antifogging and anti-icing behaviors. As a result, antifogging coatings with adequate hydrophilic materials could be also anti-icing under low temperatures.

Zwitterionic coatings, which were widely used for the anti-fouling purpose [30,31], recently show potential in antifogging and anti-frost applications. Ezzat et al. implemented antifogging/anti-frost modification with superhydrophilic poly(methacryloxyethyl sulfobetaine) brushes prepared by surface-initiated atom transfer radical polymerization [32]. However, the rapid absorption of water by zwitterionic polymers could make the coatings unstable in the practice. Combination of

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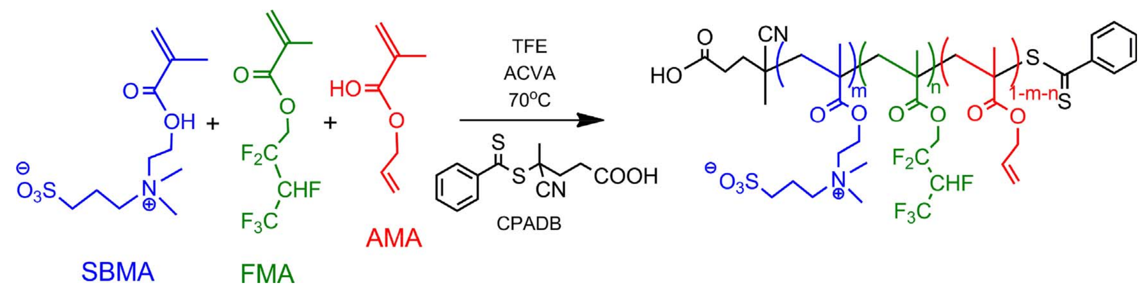

Scheme 1. Synthesis of the random copolymer P(SBMA-*co*-FMA-*co*-AMA) via RAFT copolymerization (m = 0.90, n = 0.07).

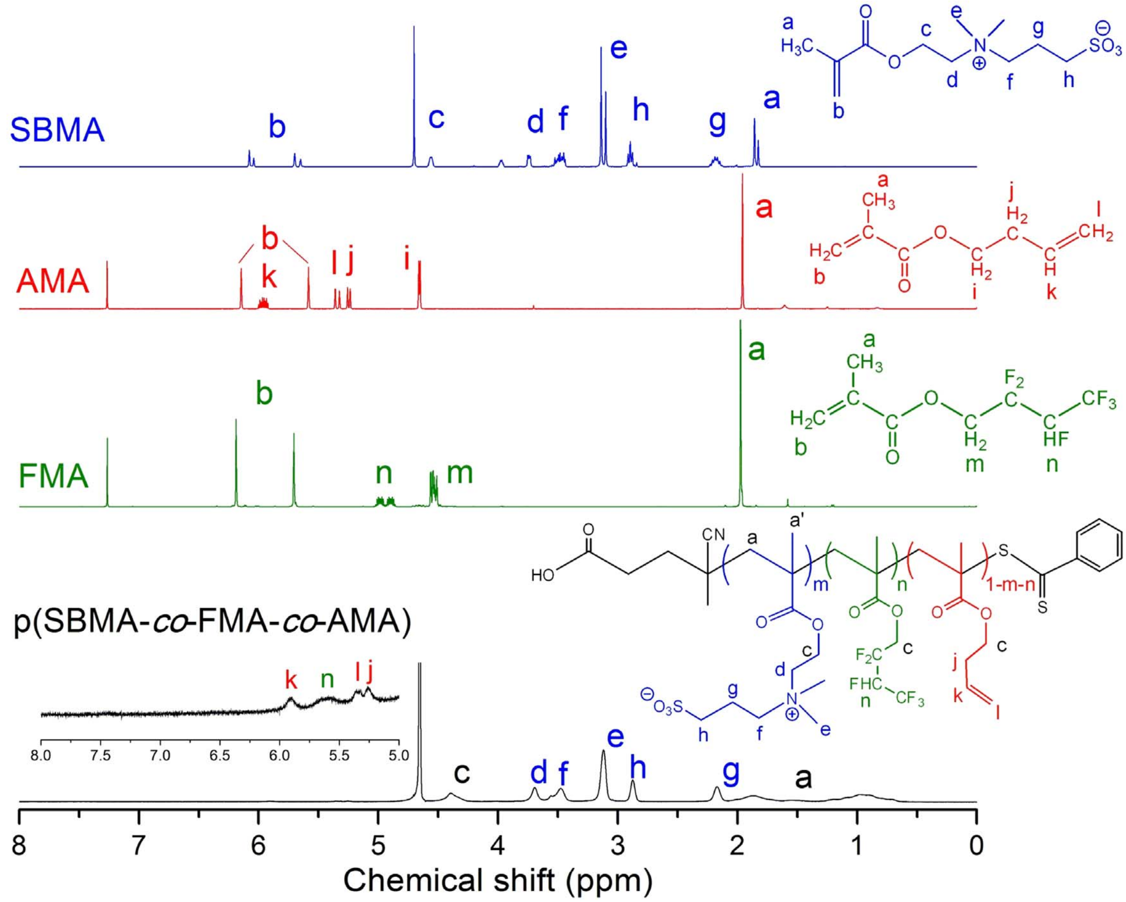

Fig. 1. ^{1}H NMR spectra of SBMA, FMA, AMA and P(SBMA-*co*-FMA-*co*-AMA).

hydrophobicity with hydrophilicity could achieve effective water absorption and meanwhile resistance of water penetration [33]. Cohen et al. designed and fabricated several zwitter-wettable polyelectrolytes coatings with excellent antifogging property. They prepared zwitter-wettable antifogging films with a nanoscale hydrophobic capping layer (chitosan/Nafion) which enabled rapid diffusion of vapor [34]. Acrylic polymers are known as conventional materials for fabrication of anti-fogging and anti-icing coatings [7,35–39]. Ming et al. successfully synthesized random copolymer poly(2-dimethylamino-ethylmethacrylate-*co*-methyl methacrylate) via free radical polymerization. The copolymer, together with crosslinked oligoethylene glycol dimethacrylate (OEGDMA), formed a semi-interpenetrated polymer network (SIPN). The delicate balance of hydrophilicity and hydrophobicity was proved to be effective for the antifogging and frost-resisting properties of the SIPN [7].

Hydrophilic groups could bond with water via hydrogen bonds, inducing the formation of different states of water including free water, freezable bond water and non-freezable bond water, which can affect the formation of lubricating layer [29]. Free water shares the same phase transition temperature of bulk water, while that of freezable bond water is below 273 K [40]. Due to their different thermal properties, diverse states of water could be investigated by studying their phase transition via differential scanning calorimetry (DSC) [41–43].

In this work, dual-functional antifogging/anti-icing coatings were prepared based on a random copolymer synthesized from methacryloxyethyl sulfobetaine (SBMA) as the main component, which is expected to decrease the water freezing-point by forming an aqueous lubricating layer due to the electrostatically enhanced hydrogen bonds with water so as to keep high transmittance under foggy conditions and display the anti-icing properties. The zwitterionic coatings were cured under UV irradiation by using OEGDMA. The effect of different amount of OEGDMA in the prepared coatings on the wettability and antifogging properties were investigated. Hexafluorobutyl methacrylate (FMA) and allyl methacrylate (AMA) were introduced to balance hydrophobicity and hydrophilicity as well as to improve stability of the coatings, respectively. Particularly, we combined hydrophilic SBMA with