



## Amphiphilic icephobic coatings

Vinod Upadhyay\*, Teluka Galhenage, Dante Battocchi, Dean Webster\*

Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, United States

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### ABSTRACT

A series of amphiphilic siloxane polyurethane (AmSiPU) coatings were investigated for their icephobic properties. The use of coatings having amphiphilic surfaces for anti-icing applications has not been studied to a large extent although these types of coatings have more recently been studied for anti-fouling (AF)/foul release (FR) applications. Several polyurethane based amphiphilic coatings were prepared having variations in the composition as well as molecular weight of hydrophobic polydimethyl siloxane (PDMS), and hydrophilic polyethylene glycol (PEG). Surface characterizations of the coatings revealed the presence of both PDMS and PEG moieties, implying amphiphilic surface characteristics. The icephobic properties of these coatings were evaluated to investigate if amphiphilic formulations can deter ice adhesion. Water absorption and barrier behaviors of these coatings and their correlation to anti-icing properties were also studied.

### 1. Introduction

The accumulation and adhesion of ice is a serious concern to aircraft flying through adverse weather conditions with temperatures at or below freezing. In cold regions, snow and ice build-ups on infrastructure such as wind turbine blades, power transmission lines, railway lines, communication towers, and electrical power plants can compromise their performance and efficiency. In addition, the socio-economic impact due to ice accretion can be enormous [1,2]. It is therefore no surprise that the quest for a suitable anti-icing coating system has been ongoing for several decades now. Organic coatings designed to this date, are mostly fluorocarbon-based [3–8], silicone-based [9–14], or a mixture of both [14–17]. Designing icephobic coating systems has historically been based on the premise that a hydrophobic or superhydrophobic low energy surface will result in a low work of adhesion, and hence discourage ice accumulation [9,14,18–20]. A similar strategy has been used in the design of silicone elastomer antifouling/fouling-release (AF/FR) coatings.

Amphiphilic polymers are polymers containing both hydrophobic and hydrophilic moieties. The use of amphiphilic polymers for the design of AF/FR surfaces is a more recent approach. Several studies have been performed with encouraging results. Coatings have been designed with a small amount of hydrophilic moieties (such as polyethylene glycol (PEG)) added to an otherwise hydrophobic system, and their AF/FR performance have been studied. The earliest published example of amphiphilic AF/FR coatings were based on crosslinking mixtures of hyperbranched fluoropolymer (HBFP) and diamino-terminated poly

(ethylene glycol) (PEG). Such coatings exhibited promising AF/FR performance compared to a standard poly(dimethylsiloxane) elastomer coating, suggesting their unique applicability in AF/FR applications [21,22]. Subsequently more research followed. Krishnan et al. investigated AF/FR properties of a block copolymers consisting of a polystyrene block and an amphiphilic block with PEG and fluoroalkyl groups in comblike side chains, and observed that such surfaces displayed high removal of both *Ulva* and *Navicula*, marine algae that exhibit differing adhesion preferences. They ascribed possible environment dependent surface reconstruction to the fouling release mechanism [23]. Martinelli et al. [24] prepared FR amphiphilic coatings by blending diblock copolymers of a poly (dimethylsiloxane) block and a PEGylated-fluoroalkyl modified polystyrene block into a PDMS matrix. They studied the fouling release performance based on the ease of removal of the sporelings of *Ulva linza* (a macroalga) attached to the coated surface, and observed that the coatings exhibited 3–14 fold improvement compared to the pure hydrophobic PDMS control. Other lab assays and field trials have also showed promising AF/FR results, but displayed influence of surface composition and structures [25]. In other work by Sundaram et al. [26], amphiphilic polymers consisting of a mixture of PEG and two semifluorinated alcohols were blended into polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene matrix, and effective fouling release performance were observed against both *Ulva* and *Navicula*. Similar studies with amphiphilic surfaces rich in PEG showed excellent FR performance compared to the PDMS standard [27]. Wang et al. [28] prepared amphiphilic coatings by photocuring blends of 10 wt% PEG-monomethacrylates (with varying

\* Corresponding authors.

E-mail addresses: [vinodzz@gmail.com](mailto:vinodzz@gmail.com) (V. Upadhyay), [dean.webster@ndsu.edu](mailto:dean.webster@ndsu.edu) (D. Webster).

molecular weights) into dimethacryloxy functionalized perfluoropolyether matrix and observed notable AF/FR performance against spores of *Ulva* and the cypris larvae of barnacles. In other similar work they also concluded that such amphiphilic formulations could provide an insight into optimum AF/FR formulation strategy by fine tuning PEG flexibility [29]. Bodhke et al. [30] applied a self-stratification approach to the design of polyurethane coatings having amphiphilic fouling-release surfaces whose hydrophilic character was provided by carboxylic acid groups attached to the PDMS component. They demonstrated that such surfaces having both hydrophobic and hydrophilic contents could be used for a fouling-release strategy, but highlighted the importance of fine tuning the surface composition for optimized FR performance against a broad range of marine organisms.

This work is inspired by the hypothesis that if coatings for AF/FR and icephobic applications have similar design strategies, then the design of amphiphilic polymers as AF/FR coatings may also be a suitable approach for icephobic coatings. “Icephobic coatings” as implied in this, and other works, are coatings whose surfaces display low adhesion to ice [31–33], though other definitions based on the time delay of heterogeneous ice nucleation on surfaces, and repulsion of incoming droplets (e.g. fog/rain) below the freezing point, also exists in the literature [5,14,31,34–38]. Recently, research on amphiphilic icephobic coatings has also been reported [39–41]. In this work, a series of amphiphilic coatings designed initially for investigation as AF/FR coatings were evaluated for their icephobicity. In a previous publication, the surface and fouling-release properties have been studied, and very promising results were shown by several amphiphilic coating formulations in laboratory assays against marine bio-foulants such as bacterial biofilms, barnacles and marine mussels [42]. To form the amphiphilic siloxane polyurethane coatings a series of polyisocyanate pre-polymers were initially prepared by reacting a polyisocyanate with monofunctional PDMS and PEG, and then the pre-polymers were mixed with an acrylic polyol and additional polyisocyanate and cured to form coatings. The overall PDMS and PEG contents were maintained at 5 and 10 wt% based on coating solids. Several variations of the pre-polymers and resulting coatings were obtained by varying the molecular weight of PDMS and PEG. In this work, these same amphiphilic siloxane polyurethane (AmSiPU) coatings were evaluated for their anti-icing performance. To verify that the hydrophilic content of the coatings does not absorb significant water and the coatings maintained good barrier behavior, single frequency EIS (SF-EIS), as well as multi frequency EIS (MF-EIS) measurements were done. Moreover, the influence of varying molecular weight and composition of PDMS and PEG on the water absorption and barrier behavior of the coatings, and their correlation to anti-icing behavior was also investigated.

## 2. Experimental

### 2.1. Coating preparation

Details of the coating preparation and characterization are reported in a previous publication [42]. The preparation of the coatings was carried out in three steps. In the first step, twelve different isocyanate-functional pre-polymers were prepared by reacting a commercially available isophorone diisocyanate trimer polyisocyanate (Desmodur Z 4470, Covestro) with monocarbinol terminated PDMS (Gelest) and monofunctional PEG (SigmaAldrich). The molecular weight of monofunctional PEG was varied between 550 (PEG-550) and 750 (PEG-750), whereas the molecular weight of PDMS was varied from 1000, 5000, and 10,000 g mol<sup>-1</sup>. In the second step, the pre-polymers were mixed with an acrylic polyol, additional polyisocyanate, solvents and catalyst to form the coating formulations. The coatings formulations were applied onto primed aluminum panels using a drawdown bar and allowed to cure to form the siloxane-polyurethane coatings. The compositions of the coating systems were designed such that the overall PDMS and PEG contents in the final AmSiPU coatings were maintained at 5 and 10 wt%

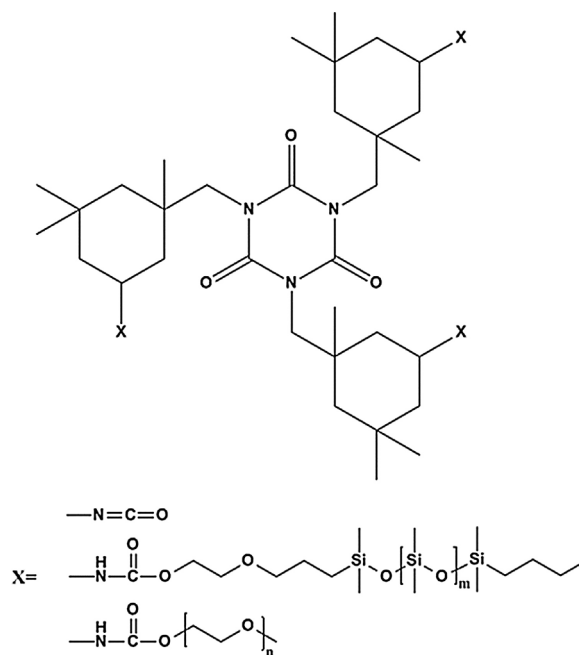


Fig. 1. General structure of the IPDI-PDMS-PEG pre-polymers [42]. [Reprinted with permission from Springer™].

based on coating solids. Fig. 1 illustrates the general structure proposed for the pre-polymers synthesized. In the structure, X can either be an unreacted isocyanate group, PEG chain linked through urethane, or a PDMS chain linked through urethane. Coatings looked smooth visually. Their roughness (measured using OSP370 non-contact laser surface profilometer from Princeton Applied Research) were in the range of  $13.32 \pm 0.84 \mu\text{m}$ .

Table 1 summarizes the details of the coatings prepared for this study. Briefly, Formulation 1 consists of coatings having PDMS and PEG at 5 wt% each, with PDMS and PEG having molecular weight of 1000 and 550 respectively. Formulation 6 consists of coatings having PDMS and PEG at 5 wt% each, with PDMS and PEG having molecular weight of 10,000 and 750, respectively. Similarly, Formulation 12 consists of coatings having PDMS and PEG at 10 wt% each, with PDMS and PEG having molecular weight of 10,000 and 750 respectively. Anti-icing results were compared against an industrial icephobic coating named PhaseBreak Flex MPD Anti-Icing Coating (purchased from Microphase Coatings Inc., Garner, NC), and labeled as PB\_C, and a siloxane-polyurethane system without PEG (labeled SP\_C) [43]. The barrier and water uptake properties were compared against SP\_C.

### 2.2. Ice adhesion test experimental apparatus and procedure

Various ice adhesion test procedures have been reported in the literature [9,44–59], although a universally accepted standard ice adhesion test procedure has not yet been realized. Detail about the experimental set-up and testing procedure is provided as a supplemental information. Briefly, ice was grown in-situ on the surface of the experimental (coated) flat substrates and the peak shear force required by a force gauge to dislodge the ice from the sample surface was measured. An average of six such measurements was considered. The lower is the shear force required higher is the coatings icephobicity.

### 2.3. Water absorption and barrier measurements

An IFC 1000 Potentiostat/Galvanostat/ZRA, purchased from Gamry Inc., was used for the EIS measurements performed to characterize coatings barrier and water absorption characteristics. For water absorption studies, single frequency EIS (SF-EIS) measurements were

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