Effect of alkyl chain length on the hydro/ice-phobic properties of self-assembled monolayers (*SAMs*) coatings on aluminum alloy 6061 surfaces

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Abstract- The effects of alkyl chain length on hydro/ice-phobic properties were studied through self-assembled monolayers (SAMs) thin films of an alkylsilane compound, OT (trichloro(octyl)silane, 8C) and OD (trichloro(octadecyl)silane, 18C), on a flat aluminum alloy (AA6061) substrate. The contact angle (CA) values for OD and OT coatings after a 12-hours immersion time (IT) were ~140^o and ~120^o, respectively. The contact angle hysteresis (CAH) for the OD sample was ~38^o and ~55^o for the OT sample after the 12-hour immersion. The ice adhesion reduction factor (ARF) of the OD and OT samples showed that the ice adhesion strength values are ~1.24 and ~1.05 times smaller than those obtained on a polished Al sample, respectively. It was shown that the hydro/ice-phobic properties of the OD sample was more improved compared to the OT sample. This behavior could be explained by the reduction of the molecular reactivity caused by the *steric effect* in case of the OT sample on a polished Al surface. The surface morphology of the surfaces was analyzed by scanning electron microscopy (SEM). The SEM micrographs of the coated surfaces demonstrated the presence of a rough structure at micro/nanoscale levels on the mirror-polished Al substrate.

Keywords: self-assembled monolayers (*SAM*s); hydro/ice-phobic properties; scanning electron microscopy (SEM); ice adhesion reduction factor (*ARF*); steric effect.

INTRODUCTION

Atmospheric icing occurs when surfaces of exposed structures are hit with supercooled water droplets or snow particles. For instance, overhead transmission lines and their substations can be subjected to ice accumulations for an extended period of time each year [1,2]. These may cause damage to power network equipment [3-5]. Reducing or preventing ice accumulation on exposed surfaces can be accomplished by developing ice-phobic coatings [6-10]. The wetting behavior of a surface can be determined by the contact angle (CA) which is the angle between the surface and a water liquid drop [11]. Development of self-assembled monolayer (*SAM*) coatings with -CH_3 or -CF_3 groups oriented outward from the ice surface is one of the most successful approaches to chemically modified hydrophilic surfaces [12]. The *SAMs* through processes involving adsorption, hydrolysis, and polymerization can lead to spontaneously assembled low energy surfaces on many solids and oxides (Al_2O_3, SiO_2, etc.) [13-16]. In the present study, the effects of alkyl chain length on the hydrophobic and ice-phobic properties of *SAM*s coatings of OT (trichloro(octyl)silane, 8C) and OD (trichloro(octadecyl)silane, 18C) on polished aluminum alloy 6061 (AA6061) will be investigated.

I. EXPERIMENTAL PROCEDURE

Aluminum alloy 6061 composed of Al 97.9 wt.%, Mg 1.0 wt.%, Si 0.60 wt.%, Cu 0.28 wt.%, Cr 0.20 wt.% from industrial rolled sheets was cut into 5.1 × 3.2 cm samples, that were used as substrates. This alloy is widely used for power transmission and distribution line conductors. Organic molecules providing low surface energy, Trichloro(octadecyl)silane ($C_{18}H_{37}Cl_3Si$) and Trichloro(octyl)silane ($C_8H_{17}C_{l3}Si$), were purchased from Sigma-Aldrich®. The as-received AA6061 samples were ultrasonically cleaned in acetone and distilled water each for 5 minutes. Subsequently, the cleaned samples were first mechanically polished using 320-800-1200 and 4000-grit sand paper, then with successively finer SiC abrasive. Finally, they were mirror-polished with aqueous 1.0 µm alumina slurry. The polished substrate were then cleaned and degreased ultrasonically in organic solvents of methanol (99.8%), acetone (99.5%) and finally de-ionized water. The cleaned and polished Al plates were then blow-dried in a N_2 gas flow followed by a 1-hour post-treatment in oven at 70 ^{o}C. Later, they were placed in *SAM*s baths of octadecyltrichlorosilane (OD) in toluene (1 mM) and octyltrichlorosilane (OT) in toluene (1 mM) by the dip coating method. The substrates were then removed from their respective solutions after 15 minutes, 2, 6, and 12 hours. They were then rinsed with toluene and blow dried under nitrogen gas. Finally, they were post-treated in an oven for 2 hours, drying at 70 ^{o}C.

The dried samples were characterized by measuring their hydrophobic and ice-phobic properties. The wetting characteristics reported in this study were obtained following the standard sessile drop method on a fully automated contact angle goniometer (DSA100 from Krüss) with controllable volume (4 µl) of water droplets. Surface topographies were studied via scanning electron microscopy (SEM, Hitachi S-4700 Field-Emission SEM with accelerating voltages from 500 V to 25 kV) to take surface images of the coated samples and therefore reveal their surface characteristics. The ice-repellent performance of bare as well as prepared coatings was evaluated using a home-made centrifugal apparatus which was placed in a climate room at subzero temperature (-10^{o}C). The detail of the ice preparation procedure has been described previously [7].

II. RESULTS AND DISCUSSION

Figure 1 shows the IT effect of alkylsilane with short chains (OT) on the hydrophobic properties. The concentration of OT in this series of experiments was 1 mM OT diluted in toluene. By increasing IT from 2 h to 12 h, the CA value of aluminum coated with OT increased from ~ 90° to ~ 121° while the CAH values decreased from ~ 77° to ~50°.

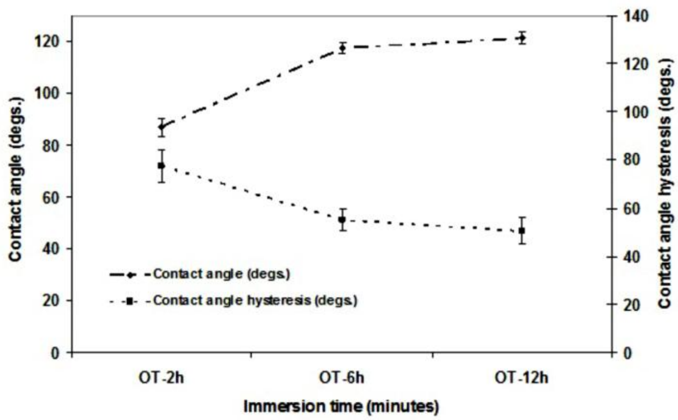


Figure 1: Contact angle and contact angle hysteresis values of coated samples with OT (1mM) for different ITs.

In order to study the effect of chain length on wetting characteristics and ice-phobic properties, dissimilar alkylsilanes in term of chain length were chosen, i.e. 18 carbon (trichloro(octadecyl)silane, OD) with similar chemical component to 8 carbons (trichloro(octyl)silane, OT). Figure 2 shows the CA and CAH values of sample surfaces coated with OD (1 mM). By increasing the IT from 15 min to 12 hours, the CA values of the coated samples increased, in such a way that, a remarkable enhancement of CA to ~152° was observed after 12-h IT, with regards to superhydrophobic characteristics. As seen from Figure 2, CAH decreased over time, as IT increased from 15 minutes to 12 hours. A CAH decrease of ~ 32° was also obtained in the case of coatings with 12-h IT, whereas the CAH of other coatings was ~40-70° (for samples with15 min, 2 and 6 h IT).

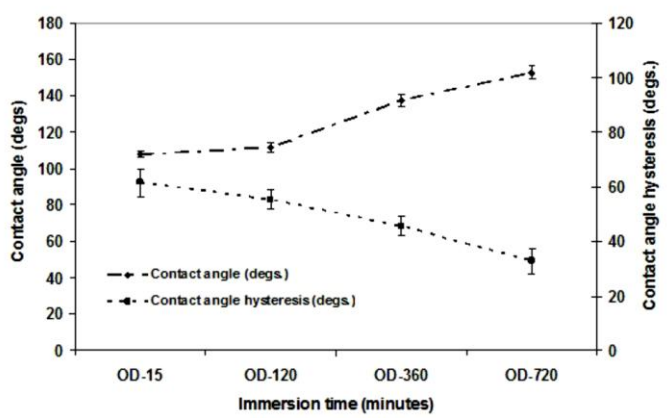


Figure 2: CA and CAH values of coated samples with OD (1mM) for different ITs.

As observed earlier, increasing IT from 15 min to 12h resulted in a significant enhancement of the hydrophobic properties of the samples coated with OD (1 mM) as compared to the short chain alkylsilane (OT). Thus, the IT parameter plays a very important role on the self-assembly process [17]. The reason of the observed results concerning the wetting properties of OD coatings as well as the remarkable increase in CA by increasing the IT is probably due to well-ordered *SAM* structure on the aluminum oxide layer compared to that of the shorter IT [18, 19]. However, in case of short chain alkylsilane, this is probably due to the rise of the *steric effect* that prevents *SAM*s molecule structures on the aluminum oxide layer from ordering well [20].

Figure 3 shows scanning electron microscopy (SEM) analysis for the OT coated Al surface (1 mM). The SEM images of the surface coated with OT shows a distribution of white points and trenches at the micrometer scale, as seen in Figure 3 (a and b).

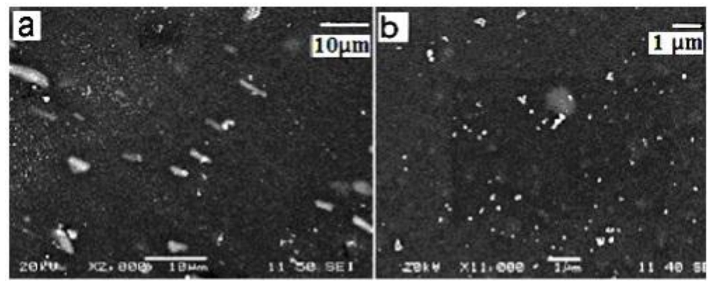
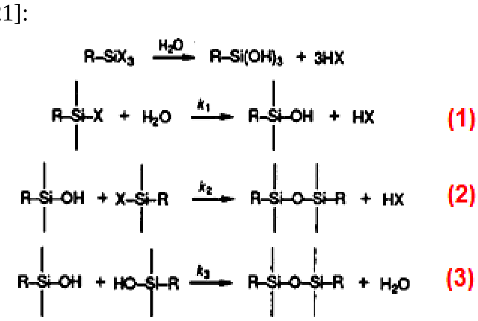


Figure 3: Scanning electron microscopy (SEM) images of sample coated with OT (12 hours). Magnification is (a) 2000X, (b) 11000X.

Figure 4 shows SEM images of the Al sample coated with OD (1 mM) for a 12-hour IT with 2000X and 11000X magnifications. Rough structure at micro-/nano-metre scale as well as the distribution of some branches in several parts on the polished aluminium surface were observed in the case of coated samples with OD (1 mM) (Fig.4 a and b). This micro/nanoscale roughness was obtained following the immersion of aluminium samples in a chemical solution bath, which corresponds to the hydrolysis step of the *SAM*s process, where chloride ions are released to form hydrochloric acid (HCl). More precisely, as HCl contains aggressive ions of Cl^-, the aluminium surface sample are subjected to erosion as IT Is increased. This reaction is expressed by the following equation [21]:



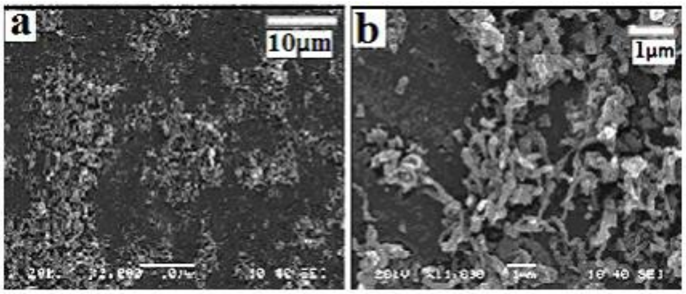


Figure 4: Scanning electron microscopy (SEM) images of sample coated with OD (12 h). Magnification is (a) 2000X and (b) 11000X.

In order to study the effect of IT on the ice-repellent properties of the coatings, the ice adhesion tests were carried out on samples coated with OD. These samples were selected with regards to enhanced hydrophobic properties of long alkyl chain coatings (OD) compared to short alkyl chain OT coated samples. In other words, the first value of shear stress of ice detachment, for sample coated with OT-12h was 220.5 ± 12 compared to 242.5 ± 25 which was obtained on the polished bare Al sample. These two sets of values are very close to each other.

Table 1 presents the first values of shear stress of ice detachment and ice adhesion reduction factor (*ARF*) of coated samples of OD (1 mM) for different IT.

Table 1: Ice adhesion strength and ARF values of OD samples for different IT.

Sample-IT	Ice adhesion strength (kPa)	*ARF*
Polished Al	242.5 ± 26.1	1
OD-15	241.3 ± 25.2	1.005
OD-120	237.3 ± 15.9	1.02
OD-360	202.0 ± 10.1	1.2
OD-720	181.7 ± 8.0	1.33

The difference of ice adhesion strength between the 12-h OD sample and other ones is due to the superhydrophobic characteristics and lower wetting hysteresis (CAH) of this sample. As well, the *ARF* of the prepared sample for 12-h IT showed ice adhesion strength of at least ~ 1.33 times lower than that obtained on the polished bare Al sample.

III. Conclusions

In this study, the effect of alkylsilane chain length on the formation, wetting behavior and anti-ice performance of prepared *SAM*s coatings on flat aluminum alloy (AA6061) surfaces were investigated. For this purpose, self-assembled monolayers of alkylsilane compounds with ITs of 15 min, 2, 6 and 12 hours were elaborated on polished aluminum substrates. It was observed that, by increasing the IT from 15 min to 12h, the hydrophobic properties of the samples coated with OD (1 mM) were significantly enhanced compared to those of the short chain alkylsilane. The *ARF* of the OD sample with 12-h IT demonstrated values of ice adhesion strength ~1.33 times lower than those obtained on a polished bare Al sample. The SEM images of the samples coated with OD and OT (12-hour IT) showed the presence of micro/nano scale roughness which was obtained following aluminum sample immersion in their corresponding chemical baths resulting in the erosion of the aluminum substrate during the *SAM*s process.

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V. References

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