Superhydrophobic/icephobic coatings developed by atmospheric pressure plasma polymerization of HMDSO in nitrogen plasma jets

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Abstract: Icephobic coatings have gained a lot of interest due to their vast range of possible applications, from construction to power engineering to aerospace industry. In this study, a superhydrophobic/icephobic coating is developed using an APPJ operating with nitrogen as the plasma gas and HMDSO as the precursor. The effects of various plasma parameters on surface properties, particularly on ice adhesion strength, is studied and surfaces' stability against multiple cycles of icing/deicing is evaluated.

Keywords: atmospheric plasma polymerization, APPJ, superhydrophobicity, icephobicity

1. Introduction

Atmospheric icing of outdoor structures during icing events can pose serious socioeconomic issues in several industries and countries around the world. If left unaddressed, it can lead to power shortages, driving and aviation accidents and significant life hazards. Icephobic coatings are developed to delay, reduce or prevent ice accumulation in icing conditions, thus protecting the exposed structures against excessive loads related to ice accumulation. Conventionally, there is a close relationship between superhydrophobicity (water-repellency) and icephobicity. The unique characteristics of a superhydrophobic surface can reduce the nucleation rate of ice crystals while hindering the energy transfer between the surface and super-cooled water droplets. Furthermore, the increased mobility of water droplets on a superhydrophobic surface can reduce the extent of ice accumulation.

In this study, a superhydrophobic surface is developed using an atmospheric pressure plasma jet (APPJ) with nitrogen as the working gas and HMDSO as the precursor. The effects of plasma parameters on some of the surface properties is studied and ice adhesion strength is measured on different coatings. The best coating studied here can reduce the ice adhesion strength by a factor of 3, and can retain its icephobic behaviour even after 10 cycles of icing/deicing.

2. Experimental procedure

An OpenAir AS400 APPJ manufactured by PlasmaTreat is used for plasma deposition. At first, Al-6061 samples are exposed to three passes of air plasma treatment with a relatively short jet-to-substrate distance (5 mm). This was found to create a micro-porous alumina-based structure on the surface (Figure 1), which will be used as the substrate for the subsequent coating deposition step. Such micro-roughening of the Al sample can be ascribed to plasma-transferred arcs [1].

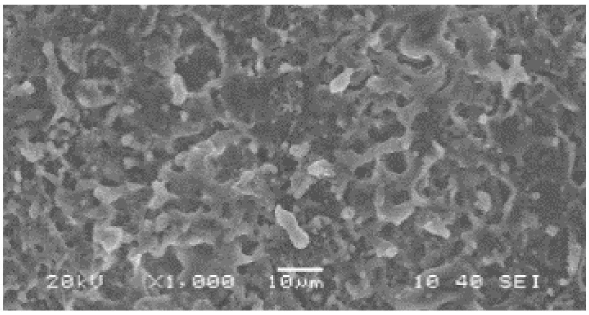

Figure 1. Micro-structure formed on the surface of Al-6061 after three passes of air plasma treatment.

These porous Al-based surfaces are cut into 50 x 30 mm samples and the deposition process in nitrogen plasma is carried out in the same APPJ but at larger jet-to-substrate distances (30 mm). In addition, the jet was confined by a quartz tube to reduce the interaction of plasma-generated species with ambient air (see Figure 2). Plasma conditions used for deposition are presented in Table 1.

To study the effects of precursor flow rate on surface properties, three samples are considered with HMDSO flow rates of 3, 5 and 7 gr/h, referred to as PT3, PT5 and PT7, respectively. Furthermore, to study the effects of multiple deposition passes on surface properties, PT5x3, and PT5x6 are created by exposing the surface to 3 and 6 passes of plasma deposition.

Surface morphology was studied via scanning electron microscopy. The chemical composition of the surface was studied by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Wetting behaviour of the surface was studied through water contact angle goniometry. Ice accumulation was carried out using a wind tunnel equipped with three water sprays operating in -10 °C. This method of ice accumulation is preferred because it closely resembles the natural conditions under which glaze ice is formed. Finally, ice adhesion strength was determined through a centrifugal experiment.

Figure 2. Picture of the APPJ used in this study.

Table 1. Plasma deposition parameters used in this study.

Plasma power	2.7 kW
Precursor flow rate	3, 5 and 7 gr/h
Number of deposition passes	1, 3 and 6 passes
Plasma duty cycle	50%
Jet speed	1 m/min
Jet-substrate distance	30 mm
Ionization gas flow rate (N_2)	500 lit/h
Carrier gas flow rate (N_2)	400 lit/h

3. Results and discussion

Figure 3 shows the effect of precursor flow rate on surface morphology. PT5 is the only case in which the surface features originated from the pre-treatment process are sufficiently pronounced along with the surface features originated from the plasma-deposited structure. In PT3, precursor flow rate is not high enough for complete coverage of the pre-treated surface. In PT7 on the other hand, the pre-treated surface porosity is largely covered by the coating materials, and therefore a significant level of surface roughness is lost.

Figure 4 shows the chemical composition of PT5 by FTIR and XPS. The features common to siloxane-based coatings dominate the FTIR spectrum. The wide band located at around 1100 cm^{-1} is assigned to Si-O-Si stretching and the peaks located at around 1275 cm^{-1} along with the peaks located between 500 cm^{-1} and 800 cm^{-1} are suggestive of Si-$(CH_3)_n$ functions. The intense band between 1000 cm^{-1} and 1200 cm^{-1} is generally assigned to Si-O-Si and Si-O-C asymmetric stretching modes [2]. This band is usually assumed to be the sum of three Gaussian components which correspond to different bond angles in Si-O-Si: TO_2 mode at 1120 cm^{-1} (170°-180° bond angle), TO_1 mode at 1070 cm^{-1} (140° bond angle), and TO_3 mode at 1030 cm^{-1} (120° bond angle). TO_2 mode is often associated to fragments of Si-O-Si chains, but in organic films this wavenumber is also populated by Si-O-C stretching mode. In Figure *4*, TO_2 appears as a shoulder on TO_3 mode, which is related to coesite-like structures, but in $SiO_xC_yH_z$ films, such low Si-O-Si bond angle is often observed because of the methyl environment of the bond [3].

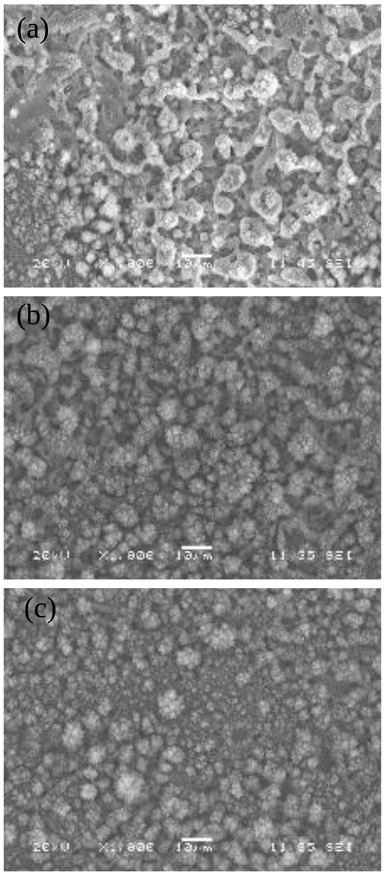

Figure 3. SEM images of (a) PT3, (b) PT5, and (c) PT7

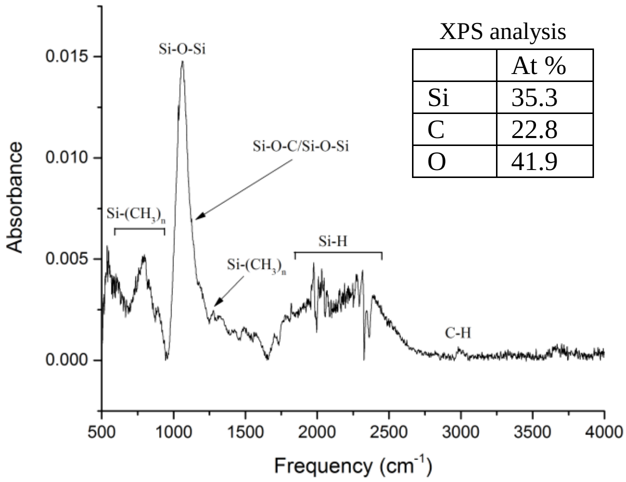

Figure 4. XPS quantification results and FTIR spectrum acquired from PT5.

The chemical state of silicon is also studied by developing a synthetic curve model on Si 2p core peak high-resolution spectrum according to the method introduced by O'Hare et al for curve-fitting of siloxane-based coatings [4]. In this method, various silicon states are distinguished by the number of bonds with oxygen (Q, T, D, and M for 4, 3, 2, and 1 bonds with oxygen, respectively). The results of this process are presented in Figure 5. The absence of Q functions in Figure *5* suggests that the plasma-deposited coating consists of a silica-like structure with organic functions largely replacing oxygen atoms, so that every silicon atom is bonded with at least one methyl group.

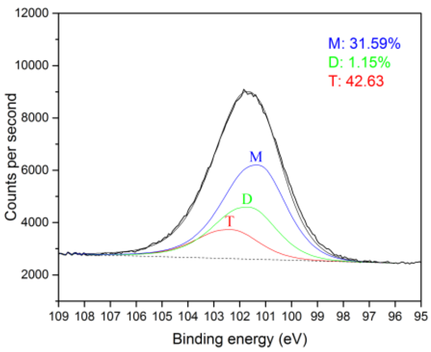

Figure 5. Curve-fitting model used for component quantirication of Si 2p core peak along with the quantification results.

Practical icephobic coatings should be able to withstand aggressive environmental conditions. To increase coating's thickness and improve its stability in natural conditions, particularly against multiple icing/deicing cycles, two different coatings were prepared through multiple deposition passes of PT5. These coatings are expected to be thicker with an identical or similar chemical composition to that of PT5. Static contact angle, contact angle hysteresis and ice adhesion strength are measured on each coating for multiple cycles of icing/deicing and the results are presented in Figure *6*. In all cases, static contact angle decreases with the number of icing/deicing cycles while contact angle hysteresis and ice adhesion strength increase with the number of icing/deicing cycles. This is largely due to coating removal after each deicing. The sample prepared with only one pass of deposition (PT5) is expected to be thinner than the other two, and therefore even a slight loss of coating material during icing or after deicing can have a significant effect on surface properties, resulting in a rapid deterioration of hydrophobic/icephobic properties with the number of icing/deicing cycles.

It is worth highlighting that the sample prepared with three passes of plasma deposition (PT5x3) exhibits the highest stability against icing/deicing cycles. Therefore, to reliably evaluate its mechanical stability, surface properties were studied for up to 10 cycles of icing/deicing. The sample prepared with 6 passes of plasma deposition (PT5x6) is expected to be significantly thicker, therefore the variations in the wetting behavior with the number of icing/deicing cycles is almost negligible. However, we believe that the higher amount of silica powder that forms on the surface due to the higher number of deposition passes, which may be easily removed during icing, is responsible for the higher ice adhesion strength observed in PT5x6.

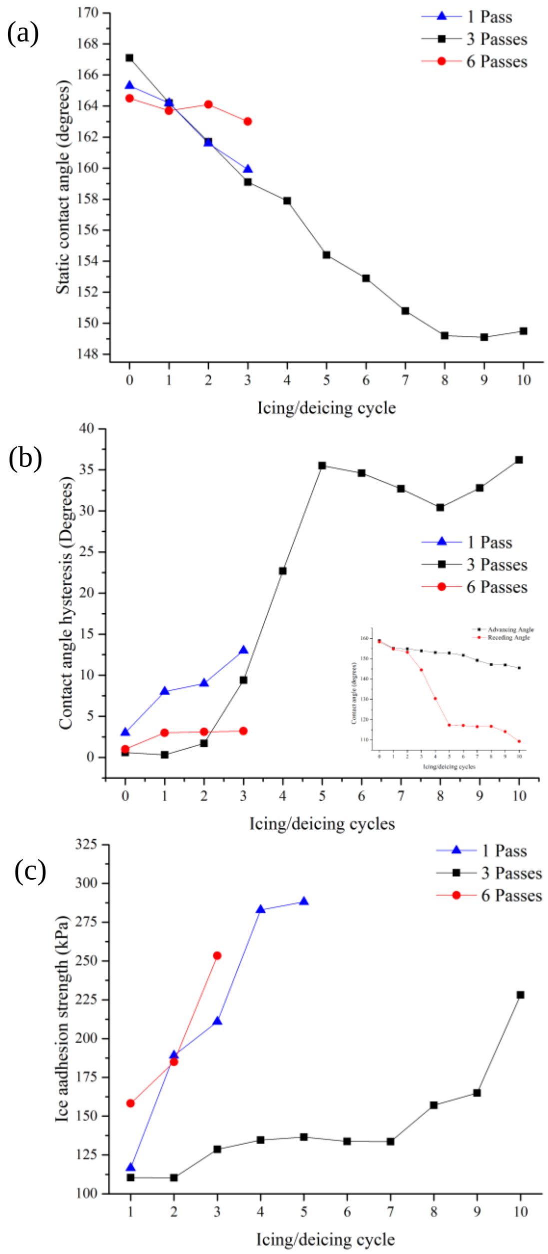

Figure 6. Static contact angle, contact angle hysteresis and ice adhesion strength for samples prepared using 5 g/h of HMDSO after 1, 3 and 6 deposition passes. The inset on (b) shows the advancing and receding angles for the sample with 3 passes of deposition.

4. Conclusions

In this study, superhydrophobic/icephobic coatings are developed using an atmospheric pressure plasma jet operating with nitrogen plasma and HMDSO as the precursor. In all cases, deposition is carried out on a micro-porous surface structure created through multiple passes of intensive air plasma treatment. Three samples were prepared with a precursor flow rate of 3, 5 and 7 g/h. It was shown that the lowest flow rate studied here is not enough for a full coverage of the surface. On the other hand, by increasing the precursor flow rate above a threshold value, surface roughness originated from the pre-treatment step is fully covered by deposition, and a significant level of roughness is lost. The median precursor flow rate (5 g/h) is thus chosen for further study. Two extra samples are prepared through 3 and 6 passes of plasma deposition with the same conditions as PT5. It is shown that PT5x3 shows the best hydrophobic/icephobic properties among the samples studied here. Wetting and icing behaviour of PT5x3 was studied during multiple icing/deicing cycles, and it was shown that PT5x3 can maintain its superhydrophobic and icephobic properties even after 10 cycles of icing/deicing.

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