Precursor fragmentation dynamics in atmospheric pressure plasma polymerization of HMDSO in nitrogen plasma

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Abstract: The fragmentation dynamics of HMDSO molecules in a high-density arc-based atmospheric pressure plasma jet of nitrogen is studied through characterization of plasma and the deposited coating. Available energy per precursor molecule is introduced as a qualitative parameter that can determine the coating chemical composition and morphological features. It is shown that in the case of organosilicon-based coatings, higher energy per precursor molecule leads to higher precursor fragmentation and subsequently higher oxide content and lower organic content in the coating.

Keywords: APPJ, HMDSO, Wetting, Superhydrophobicity, FTIR

1.Introduction

Plasma-based surface treatment methods have gained a significant amount of interest for coating deposition and surface modification applications. In particular, processes carried out in atmospheric gas pressures are of great interest due to their lower cost and faster growth rates. Generally, in plasma-based deposition methods, highenergy plasma-generated-species are used to induce molecular fragmentation in a precursor compound, generating free radicals that may be deposited onto the substrate under the right conditions. In this context, the fragmentation dynamics is of great importance since it dictates the gas phase composition from which the coating grows. This in turn depends on several plasma parameters, including the presence of precursor molecules in different regions of the discharge, the energy density of the plasma, the plasma gas being used, and electron and neutral species temperatures.

One of the most common precursors used in atmospheric pressure plasma polymerization is hexamethyldisiloxane (HMDSO). This organosilicon molecule is consisted of a siloxane (Si-O-Si) group along with 6 methyl (-CH₃) groups, which allows for deposition of coatings with a wide range of properties based on how the molecule is fragmented. In this study, the fragmentation dynamics of HMDSO in a high-density arc-based atmospheric pressure plasma jet operating with nitrogen gas is studied. The amount of available plasma energy per precursor molecule is introduced as a significant factor in precursor fragmentation, and its effects on gas phase species and coating properties is studied through optical emission spectroscopy, Fourier transform infrared spectroscopy, scanning and electron microscopy and water contact angle goniometry.

2. Experimental Procedure

Al6061 sheets with 1.4 mm thickness are acquired from ALCAN Canada and are cut into 30 mm x 50 mm pieces. All plasma treatment procedures reported here are done using an OpenAir AS400 APPJ reactor manufactured by PlasmaTreat GmbH. Prior to coating deposition, the samples are exposed to multiple passes of air plasma

treatment with a short jet-substrate distance and high plasma power to form an alumina based micro-roughened structure is formed on the surface. The details of this process have were published elsewhere [1]. An SEM image of this porous microstructure may be seen in **Figure 1**.



Figure 1. Alumina-based micro-porous structure formed after pre-treatment with multiple passes of air plasma.

This structure is then used as the substrate for coating deposition in nitrogen plasma. To limit the interaction between the discharge species and ambient air, a 30 mm quartz tube is mounted on the jet-head (see **Figure 2**). 3 samples are prepared with different precursor flow rates and plasma powers, referred to as PT3, PT5, and PT5P75 Plasma parameters used in coating deposition for these samples are summarized in Table 1.



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

Table 1. Plasma parameters used in coating deposition

Plasma gas	Nominally pure nitrogen
Plasma gas flow rate	500 L/h
Precursor flow rate	<i>PT3:</i> 3 g/h <i>PT5 and PT5P75:</i> 5 g/h
Carrier gas flow rate	400 L/h
Plasma power	<i>PT3 and PT5:</i> 500 W <i>PT5P75:</i> 750 W
Jet-substrate distance	30 mm
Jet speed	1 m/min

These parameters are chosen in a way to highlight the effect of available energy per precursor molecule on coating characteristics. Plasma characterization is carried out through optical emission spectroscopy, while surface characterization is carried out through scanning electron microscopy, Fourier transform infrared spectroscopy and contact angle goniometry.

3. Results

Figure 3 shows the optical emission spectra acquired from the nitrogen discharge during coating deposition.



Figure 3. Optical emission spectra acquired from the nitrogen afterglow during the coating deposition for PT3, PT5, and PT5P75.

Naturally, the optical emission intensity in the higher power discharge (PT5P75) is significantly stronger than other cases. In lower power cases (PT3 and PT5), the near UV region of the spectra is dominated by the NO γ system. However, at higher plasma powers, this system is much weaker while atomic oxygen lines may be observed between 700 nm and 850 nm, which is consistent with higher precursor fragmentation in higher plasma powers.

Figure 4 shows the surface morphology for all coatings investigated here. In PT3, precursor concentration is not enough for a complete coverage of the pre-treated aluminium surface. In PT5 on the other hand, the substrate is fully covered by the deposited material, while the roughness features originated from the pre-treatment procedure are maintained. In PT5P75, due to a higher presence of oxygen in the discharge (see **Figure 3c**), which subsequently leads to a higher growth rate of silica-like structures, large deposited features are observed on the surface which can eliminate an important level of roughness, created during pre-treatment procedure.



Figure 4. SEM images of (a) PT3, (b) PT5, and (c) PT5P75.

Chemical composition of the coatings was studied through FTIR spectroscopy and the results are presented in **Figure 5**.



Figure 5. FTIR spectra for the pre-treated surface before coating deposition, PT3, PT5, and PT5P75.

The most notable feature in the FTIR spectra of the coatings being investigated here is the wide band observed between 1000 and 1200 cm⁻¹, which is assigned to Si-O-Si groups which form the backbone of all siloxane-based structures. The intensity of this band is significantly stronger for PT5P75, which suggests a thicker coating in the case of PT5P75. This is in agreement with the larger deposited features observed in **Figure 4**.

In the IR spectra of most siloxane coatings, the 500-1700 cm⁻¹ range can provide valuable information regarding the order and chemical composition of the siloxane network. For instance, the wide band at around 1100 cm⁻¹ is usually assumed to be the sum of three Gaussian spectral

components which correspond to the Si-O-Si bond angle: TO1 mode at 1070 cm⁻¹ (bond angle of 140°, assigned Si-O-Si asymmetric stretching vibrational mode in quartz-like structures), TO2 mode at 1120 cm⁻¹ (bond angle of 170-180°, assigned to fragments of Si-O-Si chains), and TO3 mode at 1030 cm⁻¹ (bond angle of 120°, assigned to Si-O-Si groups in the presence of methyl groups) [2]. To better identify such subtleties in the IR spectra, the 500-1700 cm⁻¹ range is deconvoluted into its spectral components in **Figure 6**.



Figure 6. Synthetic curve models developed on the IR spectra of (a) PT3, (b) PT5, and (c) PT5P75.

In Figure 6, peak index 1 is assigned to Si-C rocking vibration in Si-(CH₃)_n [3], peak index 3 is assigned to TO2 component (Si-O-Si in quartz-like structures), and peak index 4 is assigned to TO2 (fragments of siloxane chains) [2,4]. Therefore, the ratio between the surface area of peak index 1 to that of peak index 3 can be regarded as the ratio between organic and oxide content in the coating. Similarly, the ratio between the surface area of the peak index 4 to that of peak index 3 can be regarded as an indicator for disorder in the siloxane network. These ratios are calculated for all three coatings and are presented in **Table 2**.

Table 2. Ratios between surface areas under some of the IR spectral components for PT3, PT5, and PT5P75.

•	A_1/A_2	A_4/A_2
	(Si-(CH ₃) _n /Si-O-Si)	(TO_2/TO_1)
PT3	0.35	0.67
PT5	0.52	0.64
PT5P75	0.22	0.81

Since the plasma power is identical for PT3 and PT5, the amount of available energy per HMDSO molecule is higher in the case of PT3. Therefore, higher monomer fragmentation is expected in lower precursor flow rates, which leads to lower Si-(CH3)n/Si-O-Si ratio. This is manifested as a lower A1/A3 ratio for PT3 than PT5. Similarly, since precursor flow rate is identical for PT5 and PT5P75, higher power leads to higher energy per precursor molecule, which in turn increases the fragmentation and leads to lower Si-(CH3)n/Si-O-Si ratio in the case of PT5P75. Furthermore, to study the structural integrity of the siloxane network, A4/A3 ratio is investigated. For PT3 and PT5, this ratio is almost identical, which is suggestive of similar siloxane structure integrity in both cases. In the case of PT5P75, it is shown that increasing the generation power has a significant effect on the Si-O-Si network, leading to shorter siloxane chains (higher TO2 intensity). This is consistent with higher precursor fragmentation with higher plasma energies.

To demonstrate how the precursor fragmentation can be correlated to real characteristics of the deposited coating, the wetting behaviour of PT3, PT5, and PT5P75 was studied through static and dynamic contact angle measurements. Static contact angle was measured on a resting 4 μ L droplet while dynamic contact angle was measured by slowly increasing and decreasing the droplet volume while monitoring the contact angle at both three phase interfacial points. The details of dynamic contact angle measurement is already published elsewhere [5]. The results from wetting studies are presented in **Figure 7**.

All coatings are shown to be superhydrophobic (water contact angle > 150°). However, a significant difference is observed in contact angle hysteresis, which is heavily affected by surface roughness and the wetting regime. In this context, PT5P75 exhibits the lowest CAH here due to its high roughness and larger deposited features. However, larger silica-like features observed in the case of PT5P75 have an adverse effect on the mechanical stability of the coating. On the other hand, PT3 shows the highest CAH due to the lower amount of deposition and large micrometric porosity of the substrate. PT5 seems to be a suitable compromise between the two cases, where the complete coverage of the substrate occurs while the deposited features are not large enough to become unstable.



Figure 7. Static and dynamic contact angle for PT3, PT5, and PT5P75.

4. Conclusions

Fragmentation dynamics of HMDSO molecules in a high-density arc-based atmospheric pressure plasma jet operating in nitrogen plasma is studied. Available energy per precursor molecule is introduced as a qualitative parameter that determines the extent of precursor fragmentation in the discharge and the chemical composition of the resulting coating. It is suggested that understanding the fragmentation dynamics of the precursor molecules may reveal efficient paths to design and optimization of functional coatings. For hydrophobic applications for instance, it was shown that lower fragmentation leads to higher organic content and more suitable surface structure.

5. References

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