

Investigation of the Performance of Barrel Atmospheric Plasma Source for the Deposition of Fluorocarbon Coating onto Silicone Polymer Particles

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Abstract

This study reports on the use of a barrel atmospheric plasma source for the deposition of a fluorocarbon coating onto the silicone polymer particles. The (Perfluoro-1-Decene) precursor was introduced into helium plasma and coatings deposited at flow rates in the range 5 to 9 $\mu\text{l}/\text{min}$. The retention of the chemical functionality of the precursor in the plasma polymerized coating was demonstrated using both XPS and FTIR analysis. This study thus demonstrates the success of the barrel reactor for the coating of polymer particles.

Keywords: Atmospheric pressure plasma, Barrel reactor, Polymer particles, Silicone, Fluorocarbon coating, Water contact angle, XPS

Introduction

Plasma treatments have been widely used to tailoring the surface properties of polymers [1]. These treatments can be used for example, to change the chemical composition, increase the surface energy, modify the crystallinity, morphology, and surface topography, or remove contaminants and weak boundary layers [2,3]. One area of interest is in decreasing the surface energy of polymers by creating Teflon-like surfaces which exhibit non-wetting behavior, low permeability and good thermal stability [4]. Polymers are however often processed as granules, for examples with applications in the additive manufacturing and biotechnology (Cell support) [5,6]. The industrial applications of plasma processing have to date largely focused on flat polymer substrates [7]. Amongst the plasma reactor designs, plasma-fluidized bed reactors, plasma downer reactors and plasma batch reactors are reported [8-10].

However, most of the experiments need a long treating time, of up to several hours, and a relatively high gas flow, and in some reactors multiple passes of the powders through the plasma zone are required [11].

This study investigates the performance of the plasma barrel reactor for the deposition of fluorocarbon film on the silicone polymer particles. There have been very few reports on the performance of this reactor type for the treatment of polymer particles and these have all involved low pressure plasma treatments [12-14].

Experimental

The barrel reactor was designed and constructed as shown in Figure 1, it consists of a quartz chamber with dimension of 7 cm length and 4 cm inner diameter. The plasma operating at a frequency 20 kHz was generated between two parallel electrodes using a maximum of 100-watt output from the power supply (Plasma Techniques Inc.). The powder charge of 0.5 g can be agitated by rotating of the glass chamber with speed of approx. 40 revolutions per minute.

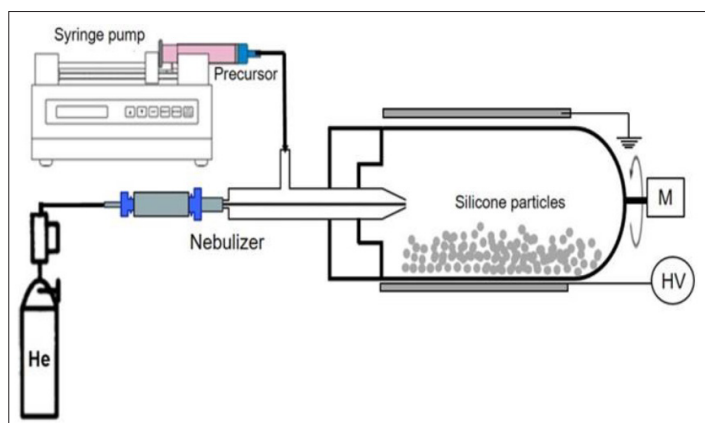


Figure 1: Schematic diagram of the barrel plasma reactor used for fluorocarbon coating of silicone particles

The fluorocarbon 1H, 1H, 2H-Perfluoro-1-Decene ($\text{C}_{10}\text{H}_3\text{F}_{17}$) obtained from Fluorochem was used as the liquid precursor for the coating deposition experiments. The equipment set-up is shown in figure 1. Helium was used as a carrier gas (10 slm). A programmable syringe pump is used to deliver the precursor liquid into the helium plasma. Precursor flow rates of 3, 5, 7, 9 and 10 $\mu\text{l}/\text{min}$ were then

investigated at deposition time of two minutes. For some of the characterization studies silicon wafer substrates were used as the test material to facilitate an evaluation of the deposited coating. The experiment was carried out by mounting the wafer segment using double sided tape, against the chamber wall.

Surface morphology and roughness was measured using a Wyko NT1100 optical profilometer in vertical scanning interferometry (VSI) mode. Scanning electron microscopy (SEM) analysis were obtained using the FEI Quanta 3D FEG DualBeam (FEI Ltd, Hillsboro, USA) and the energy dispersive x-ray spectroscopy (EDX) was carried out with EDAX EDX APOLLO XV Silicon Drift Detector. Variable angle spectroscopic ellipsometry (JA Woollam M-2000) was used to measure the coating thickness. Water contact angle of deposited coating was measured using Dataphysics Instruments OCA 20 Video Based Contact Angle Device using sessile drop technique with a drop volume of 0.5 μl at room temperature. Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Bruker Vertex-70 system. Both the film deposited on the silicone peace and precursor liquid are analyzed. The FTIR sample chamber was purged by N₂ gas before the scans were obtained. Spectra were collected in the range of 400-4000 cm^{-1} using a spectral resolution of 4 cm^{-1} . X-ray photoelectron microscopy (XPS) (Kratos ULTRA DLD spectrometer with a monochromatised Al K α source) was used to study the chemical composition of the deposited coating.

Results and Discussion

Coating Thickness

The thickness of the deposited fluorocarbon coatings was assessed using a silicon wafer substrate (4 x 0.5 cm), mounted on the chamber wall. The deposited layer thickness was measured using spectroscopic ellipsometry. As shown in Figure 2, comparing rotated and non-rotated barrel tests the coating thickness was found to be more homogeneous on the silicon wafer substrate, when deposited using the rotated barrel. The thickness of deposited coating found to increase near the edges of the wafer, probably due to a more intense discharge spark formation during plasma deposition process.

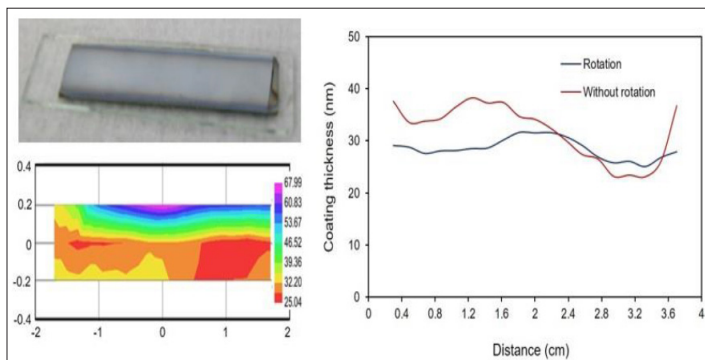


Figure 2: Photograph and spectroscopy ellipsometry scan of coating thickness measurement along the 4 x 0.5 cm silicon wafer substrate. The figure on the right demonstrates the enhanced deposited coating homogeneity when deposited using barrel rotation (Precursor flow rate 5 $\mu\text{l}/\text{min}$ and deposition time 2 min)

The effect of precursor flow rate on the resulting coating thickness was investigated on the silicon wafer substrates. Average thickness values were therefore obtained using measurements along the centre of the wafer (experiments carried out in triplicate). It was found that, coating thickness increase with increasing flow rate

as shown in Figure 3. Comparing the coatings deposited those obtained at a flow rate of 5 $\mu\text{l}/\text{min}$ exhibited the least variation in coating thickness along the length of the wafer surface.

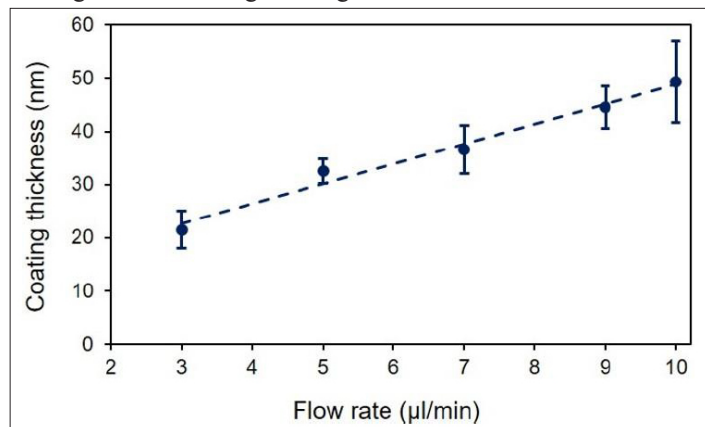


Figure 3: Effect of precursor flow rate on coating thickness after 2 minutes deposition

Water Contact Angle Measurements

Water contact angle measurements were obtained for coatings deposited on silicon wafer and silicone particles at the precursor flow rate setting of 3, 5, 7, 9 and 10 $\mu\text{l}/\text{min}$. Again, the coating obtained at the 5 $\mu\text{l}/\text{min}$ flow rate exhibited the most homogeneous water contact angle. In general, however, there is no significant difference of water contact angle for the varying range of flow rates investigated. The approx. 107° mean value obtained was just above that of the 101° value obtained for the coated silicone particles (precursor flow rate 5 $\mu\text{l}/\text{min}$). Note that the contact angle for the uncoated particle is 145°. The lower value for the contact angle on the polymer may reflect lower fluoropolymer coverage on the comparably rough particle surface. The effect of precursor flow rate on the WCA of coating deposited on the both silicon wafer and silicone particles is shown in Figure 4.

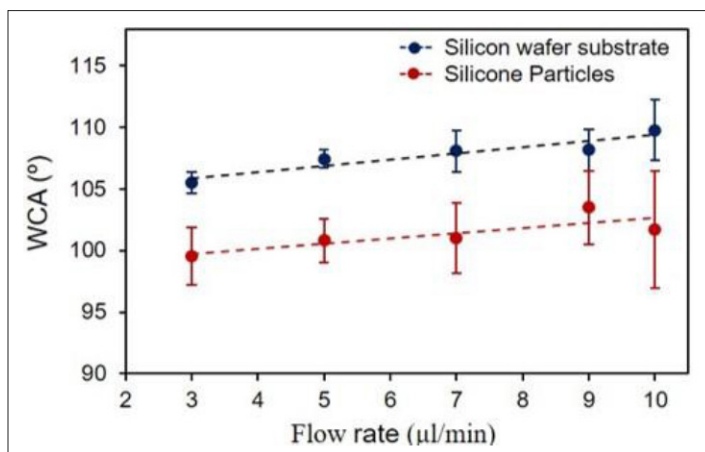


Figure 4: Effect of precursor flow rate on WCA of coating deposited on the silicon wafer and silicone particles substrates (Deposition time 2 minutes)

Surface Chemistry

Energy Dispersive X-Ray Spectroscopy (Edx) Analysis

EDX analysis of the coated particles demonstrated the presence of fluorine as shown in Figure 5.

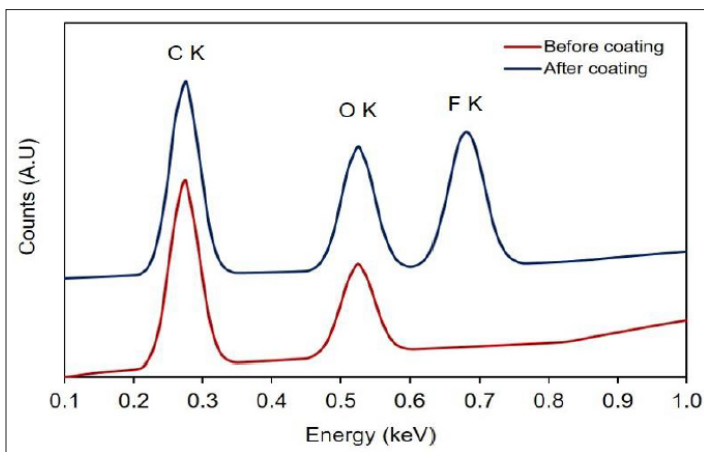


Figure 5: EDS analysis of silicone powder before and after coating demonstrating the presence of fluorine (K alpha peak) in the deposited layer

Fourier Transform Infrared (Ftir) Analysis

FTIR spectroscopy was used to examine the chemistry of the deposited coatings. Spectra from a typical coated sample, and from the monomer liquid, are shown in Figure 6. The fluorocarbon (CF₃ and CF₂) peaks were observed in the range 1100- 1250 cm⁻¹ [15]. The strong peaks at 1246 and 1207 cm⁻¹ corresponding to asymmetric and symmetric stretching of the - CF₂ - moiety, respectively [16]. The peak at 1153 cm⁻¹ is corresponding to -CF₂-CF₃ end group [17]. The spectra for the monomer liquid and polymeric coatings are largely similar, indicating that the deposited film retains the CF₂ and CF₃ moieties originating from the pendant functional group of the monomer [18].

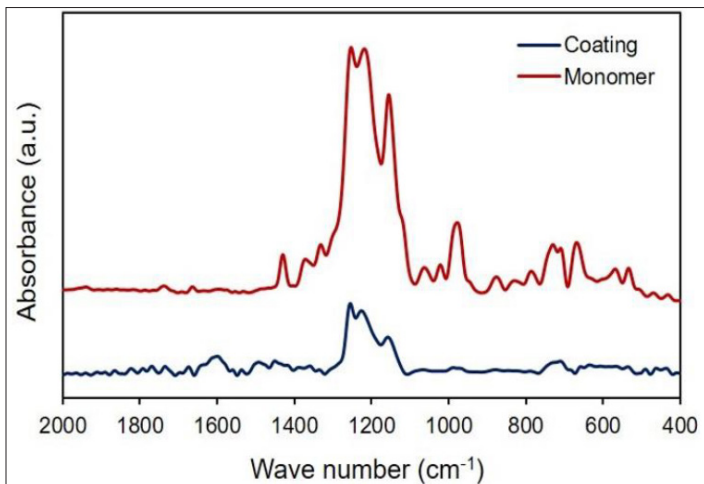


Figure 6: FTIR spectra of liquid monomer and deposited coating

X-Ray Photoelectron Spectroscopy (Xps) Analysis

XPS was used to examine the surface chemistry of coatings deposited at precursor flow rates of 5 to 9 μl/m onto silicon wafer substrates. A typical survey spectrum is shown in Figure 7. As expected the elements F and C were detected along with O probably due to oxidation of the fluorocarbon coating due to reactions with atmospheric oxygen [19].

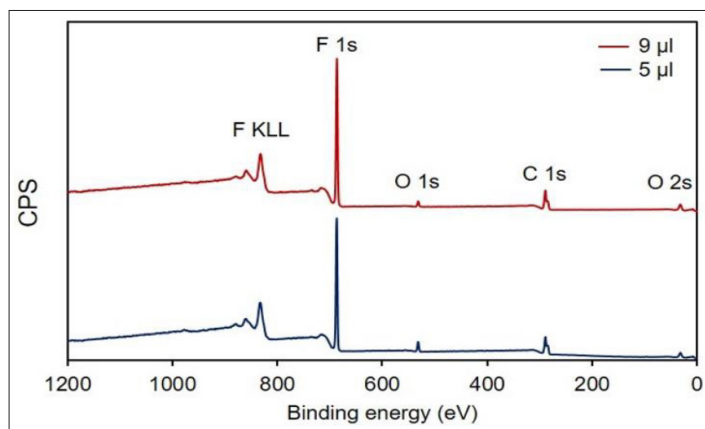


Figure 7: XPS survey spectrum indicating which elements are present

The theoretical elemental composition calculated from the chemical formula of the monomer based on the relative concentration of the elements in the 1H, 1H, 2H - Perfluoro - 1 - Decene molecule is 37% carbon, 63% fluorine giving an F:C ratio of 1.7:1. Table 1 shows the experimental values for the elemental composition of the analysed samples. The F:C ratio was less than that expected from an ideal polymerisation reaction, suggesting that any fragmentation of the molecule is minimal and that a controlled polymerisation reaction has taken place through the acrylate group [20, 21].

Table 1: XPS data for coatings deposited with 5 and 9 μl/min precursor flow rate

	%C	%F	%O	F:C
Theoretical	37	63	-	1.7:1
5 μl/min	42.7	51.5	5.8	1.2:1
9 μl/min	43.1	53.8	3.1	1.2:1

To further investigate the chemistry of the coatings, curve-fitting of the carbon (C 1s) peak was undertaken. Figure 8 shows curve fitting of coating deposited at precursor flow rate of 5 and 9 μl/m. Each spectrum deconvoluted into five peaks. Which are assigned as follows: C-C at 284.8 eV, C-O at 286.3 eV, C=O at 287.8 eV, CF₂ at 290.1 eV and CF₃ at 292.3 eV.

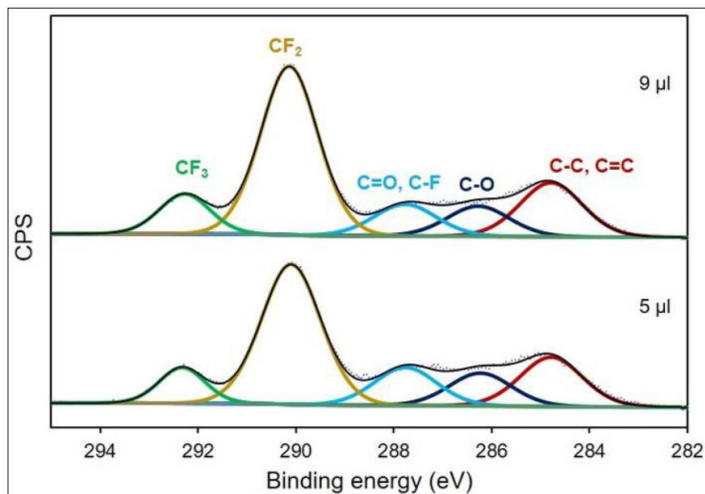


Figure 8: Curve fitting of the C 1s XPS spectrum of fluorocarbon coating deposited onto Si wafer at precursor flow rate of 5 and 9 μl

The percentages of the various functional groups present in a deposited film are listed in Table 2. The CF₂:CF₃ ratios were determined for comparison with the theoretical ratio of 7:1 for the precursor monomer. These values are lower than expected from the starting monomer indicating that some degradation of the monomer has occurred, as is typical plasma polymerisation processes [22]. The results also showed that the oxygen was decreased with increasing the precursor flow rate. In contrast, the ratio of CF₂:CF₃ was decreased.

Table 2: % concentration of species and ratio of CF₂ to CF₃ groups as determined via curve fitting of the C 1s XPS data

	% C-C	% C-O	% C=O	% CF ₂	% CF ₃	CF ₂ :CF ₃
Theoretical						7:1
5 μ l/m	7.6	5.0	5.8	20.5	4	5.1:1
9 μ l/m	7.6	4.3	4.5	22.1	4.6	4.8:1

Surface Morphology of Deposited Coating

The morphology of the coating deposited onto the silicone particle surface was examined using SEM and despite the relatively high macro surface roughness the visual examination indicated that the fluorocarbon polymer coating surface is smoother, compared with that obtained for the uncoated polymer. Figure 9 shows the surface of silicone particle before and after coating.

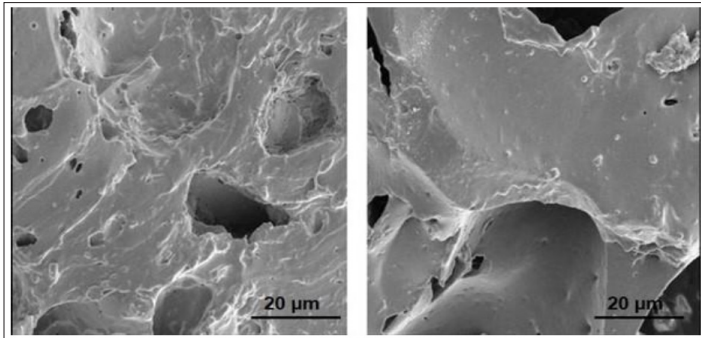


Figure 9: SEM images of a silicone particle before coating (left) and after coating (right)

Optical profilometry analysis showed as expected that coating deposited on the silicon wafer exhibits a higher roughness at the wafer edges and there are no significant differences between the roughness of samples before and after coating at the middle of the sample as shown in Figure 10.

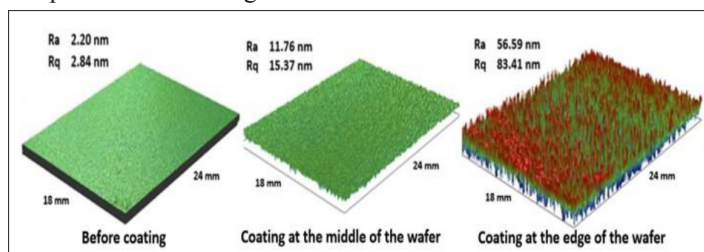


Figure 10: Optical profilometry image of coating deposited on silicon wafer (Precursor flow rate 5 μ l/m)

Conclusion

A barrel reactor was used to successfully deposit a fluoro polymer coating onto the silicone particles from a 1H, 1H, 2H-Perfluoro-1-Decene precursor. XPS and FTIR analysis of the deposited

coatings showed that the chemical functionality and structure of the precursor molecule was retained in the deposited coatings. At a precursor flow rate of 10 μ l/min, coating deposition rates of up to 25 nm/min were obtained. This study successfully demonstrated the ability of the barrel reactor system for the deposition of plasma polymerised coatings onto polymer particles.

Acknowledgement

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