

A Comparison between Gas and Atomised Liquid Precursor States in the Deposition of Functional Coatings by Pin Corona Plasma

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ABSTRACT

This work directly compares vapour and liquid aerosol states for the deposition of perfluorocarbon coatings using an atmospheric pressure, non-thermal equilibrium plasma jet system. The objective of the study is to evaluate how the physical state of the precursor (gas or liquid), influences the fragmentation of the monomer molecules in the plasma and the subsequent coating properties. Specifically the effect of gas or liquid aerosol precursor feed on the ability to achieve a soft plasma polymerisation (SPP) is assessed with a view to producing a coating that exhibits minimal fragmentation, while being well cross-linked. The precursor (Perfluoro-1-Decene) was introduced into a helium plasma and coatings deposited at rates of up to 50 nm/min. The deposited coatings were examined using XPS, FTIR, contact angle and ellipsometric measurements. These indicated that a controlled polymerization reaction through the vinyl group of the monomer had taken place in the case of the gas deposited samples with only minor fragmentation of the functional perfluoro chain. Furthermore, a high level of cross-linking was achieved and the perfluorocarbon coatings were stable to a toluene wash. In contrast, while

coatings deposited using the liquid deposition technique showed good retention of monomer molecular structure, they exhibited poor stability when immersed in toluene. This is attributed to lower levels of cross-linking of the liquid precursor in the plasma, compared with coatings deposited using the gaseous precursor technique.

KEYWORDS

Soft plasma polymerization; pin corona; non-equilibrium, atmospheric pressure plasma; functional coatings; gas vs. liquid precursor deposition

INTRODUCTION

Plasma enhanced chemical vapour deposition (PECVD) is a well established technique for the deposition of thin films across a wide variety of substrates and has been applied across numerous industries¹. Early PECVD systems were limited to the deposition of relatively simple coating chemistries due to fragmentation of the vaporised precursors² and coating functionality remained limited to materials such as SiO_x, SiN or TiO₂ deposited under vacuum conditions.

In the mid 1990s, a significant step forward occurred through the development of pulsed PECVD systems. The use of pulsed power supplies allowed the power coupled to the plasma to be pulsed on and off in a manner that still created the active species in the plasma, but did not contain enough energy to fragment all of the bonds within a precursor molecule. The resulting active species interacted with gas phase monomers and produced a controlled polymerization reaction which deposited coatings with complex functional chemistry^{3, 4}. Forch et al⁵ described this as a “soft plasma assisted modification” in which the precursor molecules do not fragment, but are activated predominantly at particular reaction sites, which then undergo polymerization reactions during the plasma “off period”. It is therefore possible to differentiate “polymerization sites” in the monomer molecule from “functional sites” containing the key molecular properties to be replicated in the polymer⁶. This led to the identification of

“soft plasma conditions” in which it is possible to carry out polymerization with the least damage to the functional chemistry. Thus, control of substrate temperature⁷, reactant pressure and flow rate, absorbed continuous wave power⁸ and location of substrates at varying distance from the plasma region² have all been used to bring greater levels of control to the polymerization process.

The soft plasma polymerised (SPP) coatings were confined to vacuum systems and were thus limited to batch coating applications. However, Badyal et al subsequently developed a controlled polymerization process at atmospheric pressure by combining a low energy helium atmospheric pressure glow discharge plasma with a liquid aerosol precursor delivery system^{9,10}. This combination of a liquid aerosol precursor and a low energy plasma was thought to produce a soft polymerization process due to the encapsulation of the monomer inside a protective liquid droplet which minimised the interaction with the aggressive plasma species. Helium glow discharges were chosen as the preferred plasma option as they provide a non-thermal, homogeneous plasma that can be readily produced under ambient pressure¹¹. This technology has received considerable interest and a number of groups have explored this area^{12, 13, 14,15,16,17} as it offers a convenient route to deposit functional coatings under ambient conditions in a continuous in-line process.

Laser imaging studies have shown that many volatile precursors actually evaporate when introduced into the plasma through pneumatic nebulizers and may actually be deposited onto substrates by a standard PECVD process¹⁸. In 2009, Herbert et al¹⁹ attempted to decouple the droplet and power factors by introducing precursor as a vapour rather than aerosol into a non-thermal pin corona plasma previously used for liquid deposition experiments. A standard vapour generating bubbler system was combined with a helium pin corona plasma to produce coatings using 1H, 1H, 2H, 2H-Heptadecafluorodecyl acrylate as the precursor monomer. Such coatings were shown to have similar functional chemistry retention and deposition rate as previously reported for an aerosol assisted plasma coatings, so that the PECVD process could be characterised as being compliant with SPP. It could be deduced that control

of the reaction mechanism cannot be predominantly dependent upon the presence of the monomer as an aerosol droplet but that the key control parameter is the low plasma power coupled per unit of monomer, resulting in coatings being deposited in the power deficient regime described by Yasuda in vacuum polymerization systems². It was concluded that the pin corona plasma is inherently predisposed to deliver low specific energy into the reaction zone and, hence, to give rise to a SPP process, even when gaseous precursors are used, which raises further questions about the necessity to use an aerosol based precursor.

The objective of this study is to examine the effect of using either the gaseous or liquid phase of the precursor monomer 1H, 1H, 2H-Perfluoro-1-Decene on the properties of the deposited coating. In particular, the aim is to determine if an atmospheric PECVD coating process can produce coatings with equivalent SPP performance to those delivered by an aerosol assisted plasma process by analysing the coatings for two performance parameters, namely the degree of polymerisation/cross-linking and the retention of molecular structure and functionality.. The precursor was chosen as it contains a polymerisable alkene group and fluorocarbon chain that can be readily characterized: $\text{CH}_2=\text{CH}-(\text{CF}_2)_7-\text{CF}_3$. The deposition studies were carried out using a pin corona plasma system operating at atmospheric pressure, as it delivers a low specific energy into the reaction zone. Maintaining a low plasma power coupled per unit of monomer, enables coatings to be deposited under the “soft plasma conditions” similar to the power deficient regime described by Yasuda in vacuum polymerization systems².

EXPERIMENTAL

The 1H, 1H, 2H-Perfluoro-1-Decene (HDFD) precursor was obtained from Fluorochem. The coating deposition studies were carried out using the PlasmaStreamTM atmospheric plasma jet deposition system which has been described previously²⁰. The source of this system incorporates a dielectric head housing two tungsten needle pointed electrodes to which are applied in parallel an alternating current voltage as shown schematically in Figure 1. The helium precursor mix exited the source through a 75 mm long x

16 mm diameter dielectric tube (Teflon) in which the corona plasma was struck. Low frequency electrical power was delivered to both electrodes from a modified Plasma Technic Inc 100W rf power supply at a frequency of approximately 19 kHz and a peak-to-peak voltage of approximately 23 kV. Essentially, the configuration was a conventional point-to-plane type corona configuration in which a high voltage was applied to generate plasma from the tip of vertically positioned sharp tungsten needles.

In the event, the system was run quasi-‘open circuit’, i.e. no physical counter-electrode in the form of a conductive plane needed to be placed to oppose the needles as the high electric fields at the pin tips saw the surrounding ambient as the ‘ground plane’ and discharged freely from the needle tips into the tube in the well known corona discharge. However, some return to ground was provided through the high voltage probe and toroidal current probe described below.

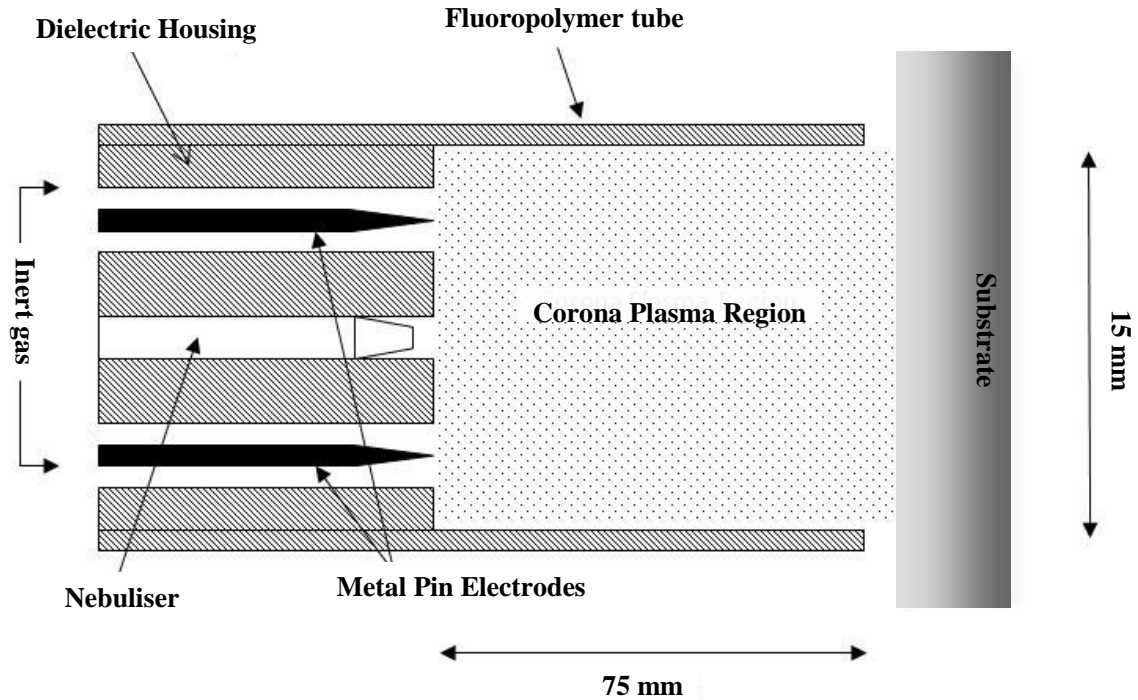


Figure 1: Schematic of 2-pin Electrode Head of a Pin Corona Discharge Coating System

A space around each electrode allows a 5 L/minute flow of helium ballast gas to enter the device. Between the two needle electrodes is a port for insertion of a pneumatic nebulizer (Burgener Ari Mist) through which liquid state precursor in the form of an aerosol is introduced directly into the plasma

region if the system is to be run in liquid deposition mode. A flow of 2 L/minute of helium was input into the pneumatic gas feed port and a flow of 5 μ L/minute of liquid precursor delivered by syringe pump was input to the liquid feed port.

Alternatively for gaseous precursor deposition studies, the nebulizer was configured to discharge into a heated flask, with the output of said flask fed through a heated line directly into the zone previously occupied by the nebulizer within the electrode head. The flask was immersed in an oil bath at 200°C in order that the HDFD precursor (boiling point of 146°C) vaporises upon emerging from the nebuliser nozzle. The plastic tubing connecting the flask to the plasma was 1 mm in internal diameter and approximately 300 mm long. The ~2 L/minute flow rate of precursor plus helium carrier gas ensured that the time between leaving the working nebulizer and reaching the plasma region was estimated as <1 second, reducing the time available for cooling and condensation of the precursor. No evidence of such condensation was observed either during the experiments or via the laser droplet measurement technique (described below).

Unless otherwise stated, all the perfluorocarbon coatings were deposited onto one-side polished P-type silicon wafers (450 μ m thick). These substrates were ultrasonically cleaned in acetone and methanol for 10 minutes respectively and dried in air prior to coating. The wafer substrates were placed onto an alumina support and positioned at a distance of 2 to 3 mm from the plasma jet outlet at the end of the Teflon tube. Samples were generated in both vapour and liquid deposition modes at the following power supply set powers, which are expressed as a percentage of generator full power: 2%, 5%, 10%, 20%, 40%. All deposition experiments were 180 seconds duration. Coating thickness was measured using a J.A. Woollam M2000 variable angle ellipsometer using multiple angle measurements (65°, 70° and 75°) over a wavelength of 250 to 1690 nm. In order to determine the degree of polymerization/cross-linking a toluene wash was carried out by immersion of the coated substrates in the solvent at room temperature for 5 minutes. Subsequent to this wash, the coating thickness was again determined using ellipsometry.

Fourier Transform Infra-Red (FTIR) data was collected on a Bruker Vertex - 70 system. Coatings were deposited directly onto either specially thinned polished silicon substrates or KBr substrates and spectra were collected using 64 scans at 4 cm^{-1} resolution. Water contact angle measurements were obtained using the sessile drop technique using an OCA 20 video capture apparatus from Dataphysics Instruments. Drop volumes of $1.5\ \mu\text{l}$ were used and images were collected 30 seconds after placing the droplet on the surface.

XPS analysis was performed using an Axis Ultra spectrometer (Kratos Analytical). Samples were irradiated with monochromated X-rays ($\text{Al K}\alpha$, 1486.6 eV) with photoelectrons analysed from a selected area $700\ \mu\text{m} \times 500\ \mu\text{m}$, with a take-off-angle of 90° . Approximately $1 \times 1\text{ cm}^2$ pieces of the composite were taken for analysis. Each position was analysed in the survey mode (Pass Energy 160 eV) to determine the elements present at the surface and their relative concentrations. CasaXPS (Casa Software Ltd) data processing software was used to calculate the area under peaks representative of elements detected, which were then normalized to take into account relative sensitivity to provide relative concentrations. The elemental composition is presented as the average of three ($700 \times 500\ \mu\text{m}^2$) areas, with 99.5% accuracy (2 SD).

Droplet size distribution of liquid precursor nebulized through a Burgener Ari mist nebulizer was examined using the HELOS particle size analyser from Sympatec GmbH. The software parameters set up of the system were defined as gradis (manual) for the dispenser and jet spray for the trigger condition. The feeder and the vacuum level were set as unknown and none respectively. The data were acquired with 10 seconds acquisition time. Before each measurement a reference data were taken with only the atomizing gas (helium) flowing through the nebulizer.

The applied voltage was measured using a North Star PVM-5 high voltage probe with a ratio of 1 V per kV directly connected to the pin electrodes. The current measurements were obtained with a Bergoz Instrumentation France, toroidal current transformer (CT-E5.0) with an output of 5 V per Ampere positioned around the Teflon tube of Figure 1 and 10 mm along the tube from the needle tips to capture the plasma discharge. The applied power to the PlasmaStream™ source is given on the system as a percentage of generator full power. The recent work of Nwankire et al²¹ demonstrated a large difference between plasma power and input circuit power in this type of system, with approximately 25% of the high voltage input line power being transferred to the plasma. It is therefore important to measure discharge power at the plasma rather than using the applied power measured at the input circuit. The current and voltage waveforms were therefore monitored using a National Instruments 2 channel digitizer (-3dB 100 MHz bandwidth) and LabVIEW 8.2 software. The drive frequency was determined from the voltage waveform as the output exhibited the least distortion and gave the highest signal-to-noise-ratio. As both current and voltage waveforms are highly distorted the use of peak and average values are inappropriate to characterize the discharge. In this study the RMS of the voltage and current waveforms were obtained over a time period of approximately 0.1 seconds using LabVIEW 8.2 software. This procedure yields an estimate of the average DC power of the non-sinusoidal waveforms from $V_{\text{rms}} \times I_{\text{rms}} = P_{\text{average}}$ in Watts.

RESULTS

Physical characterisation of both the plasma (electrical properties) and the precursor physical state (laser particle size) measurements were undertaken. Figure 2 shows the plasma discharge power as a function of percentage of full set power for both the gas and liquid deposition conditions.

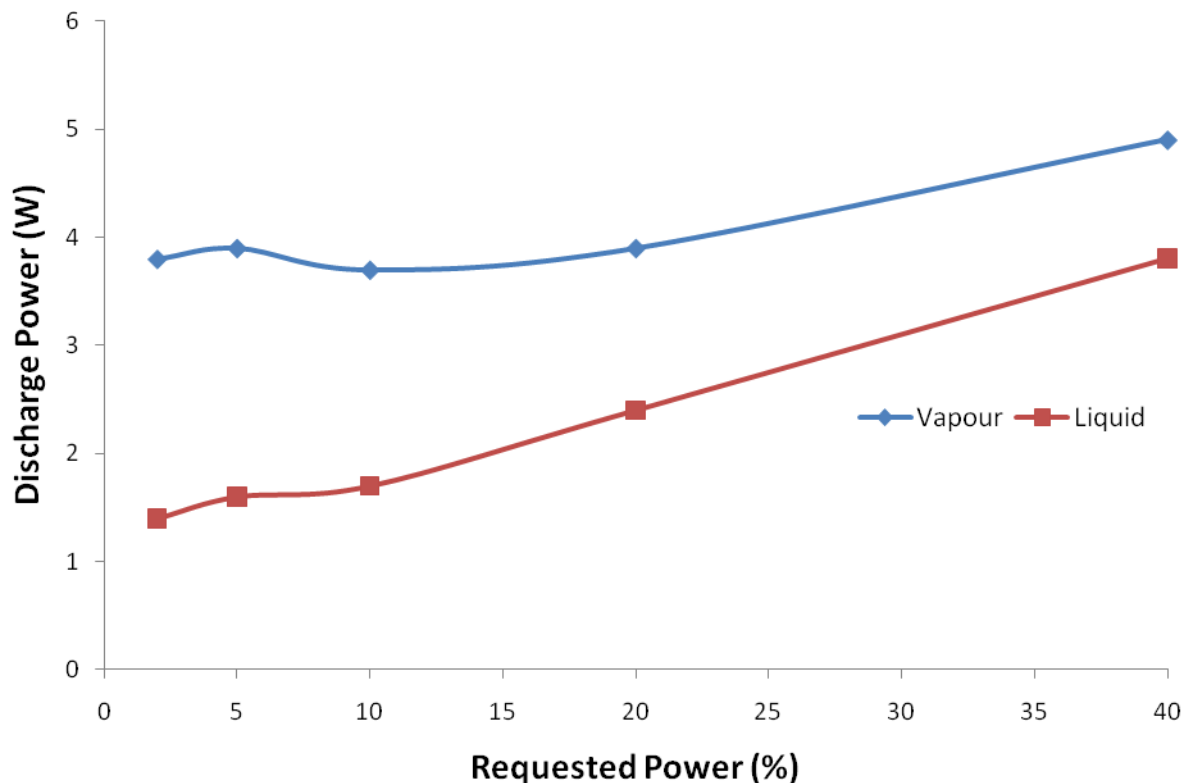


Figure 2: Plasma discharge power vs. percentage of full set power for gas and liquid deposition

In the vapour deposition case the power levels are similar to values reported previously for the PlasmaStream™ system²¹. The independence of discharge power from set power for this plasma system is an artefact of the power supply due to the non-linearity of the opto-coupler interface between the power supply and PLC control. From Figure 2 it is shown that the discharge power is almost independent of set power up to 20% of full set power. There is a significant difference in the plasma power observed with the use of the liquid compared with that of the vapour precursor. The latter exhibits power levels of 35% to 65% of that observed for the vapour containing plasma over the power range studied. It should be noted that the 40% (3.8 W) set power liquid deposition samples were equivalent in terms of discharge power to the 2% - 20% (3.8 - 3.9 W) set power vapour deposition samples. In all cases a relatively low energy discharge was created.

Figure 3 plots the liquid droplet size distribution with HDFD flow rate through the nebulizer (in the absence of a plasma) as obtained using the laser particle size analyzer. The particle size data shows that the liquid spray system introduces droplets into the plasma region with a mean particle size of less than 10 μm in all cases. Increases in the precursor flow rate were found to produce larger droplet sizes and a wider distribution of particle sizes. The larger nebulized droplets observed at higher precursor flow rates, are due to the fixed nebulising gas flow rate of the atomizer being distributed over a larger volume per second of liquid. Attempts were made to measure the particle size of the vapour derived precursor. However, no droplets were observed confirming that the vapour system is effectively evaporating all the introduced perfluorocarbon precursor and indicated that no re-condensation of the vapour occurred within the system.

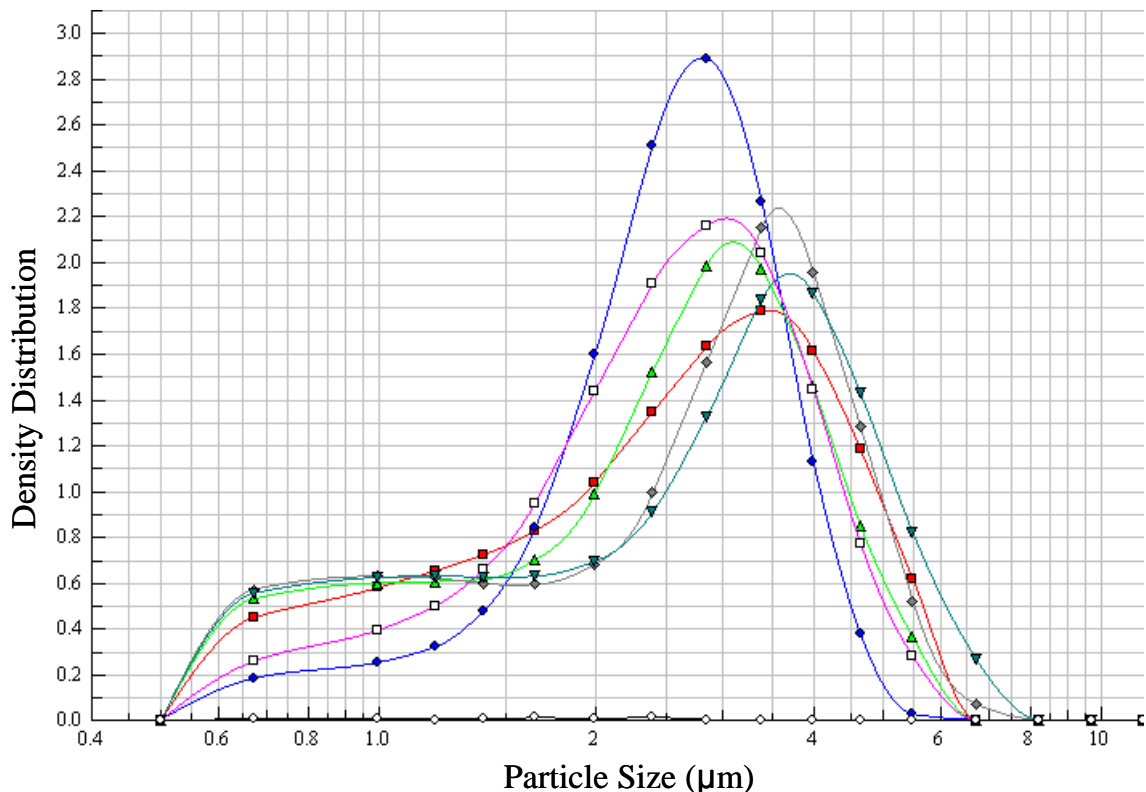


Figure 3: Liquid droplet size distribution for different liquid flow rates for the system in the liquid deposition mode (● 10 $\mu\text{l}/\text{min}$, □ 15 $\mu\text{l}/\text{min}$, ■ 25 $\mu\text{l}/\text{min}$, ◆ 50 $\mu\text{l}/\text{min}$, ▲ 75 $\mu\text{l}/\text{min}$ and ▼ 100 $\mu\text{l}/\text{min}$)

Water contact angle measurements were taken for coatings deposited at the 5 power settings of 2, 5, 10, 20 and 40%, in both vapour and liquid deposition modes. It was found that in the case of the liquid aerosol deposition samples the perfluorocarbon coatings were not well cured, being liquid in appearance and were readily removed by wiping. No reproducible contact angle data could be obtained from such samples. In contrast, the vapour deposition samples were well cured, stable and exhibited a homogeneous morphology. The coating contact angle was found to be homogeneous across the individual coatings and was in the range 107° to 122° (Table 1). These values are typical of vapour deposited plasma polymerized perfluoro compounds^{19, 22}.

% Set Power	Water Contact angle (°)		Coating Thickness (nm)	
	Liquid	Vapour	Liquid	Vapour
2	Not obtainable	107	32	160
5	Not obtainable	122	10	130
10	Not obtainable	108	42	160
20	Not obtainable	118	120	90
40	Not obtainable	109	85	92

Table 1: Water contact angle and ellipsometry thickness data for sample coated at the 5 power settings evaluated for liquid and vapour deposition modes

Figure 4 shows the FTIR spectra of 1H, 1H, 2H-Perfluoro-1-Decene monomer, liquid deposition plasma coating and vapour deposition plasma coating at 2% set power on KBr substrates. Similar features were observed at all power settings.

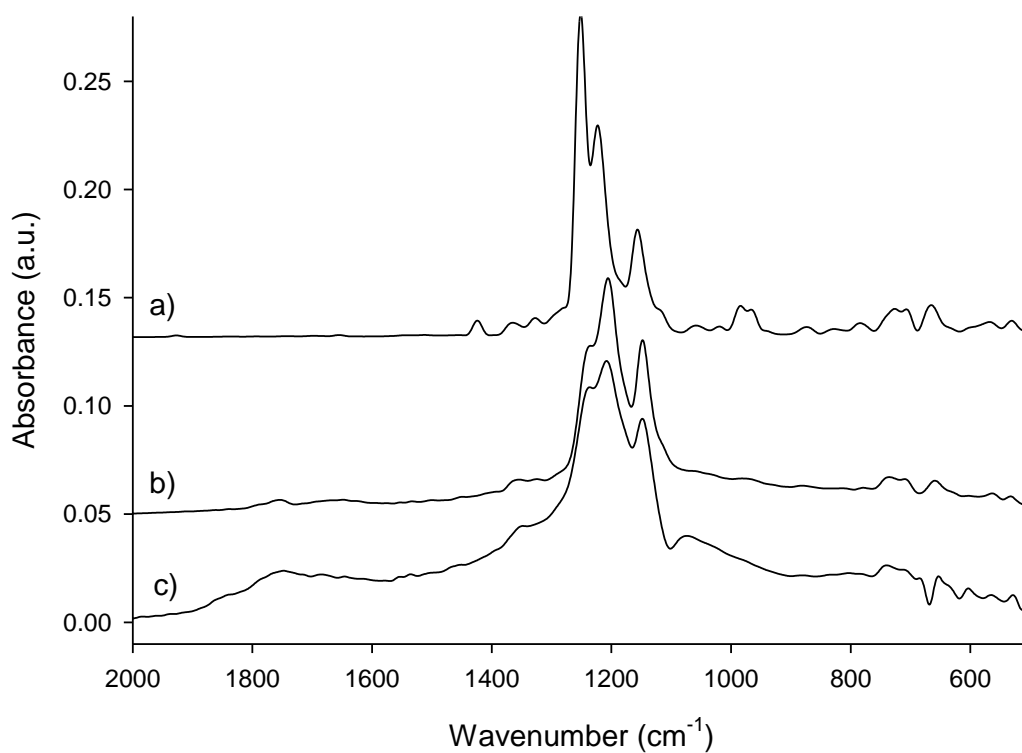


Figure 4: FTIR spectrum of a) 1H, 1H, 2H-Perfluoro-1-Decene monomer, b) liquid deposition plasma polymerization and c) vapour deposition plasma polymerization

The HDFD monomer shows major peaks at 1253, 1222 and 1155 cm^{-1} which are attributed to the various stretching modes of the CF_3 and CF_2 groups of the perfluoro chain. Both the vapour and liquid deposited films also contain peaks around 1240, 1210 and 1145 cm^{-1} , reflecting the shift to lower wavenumbers typically reported in plasma deposited fluorocarbon films and sometimes ascribed to the reduction of fluorine content in the film or to the formation of a disordered and cross-linked coating²³. As both fluorocarbon peaks are still well resolved in the coatings from both deposition processes, it can be deduced that the fluorocarbon chain has not undergone significant levels of fragmentation and degradation in either the vapour or aerosol assisted plasma processes. Inspection of the as-deposited spectra shows loss of the monomer peaks at 1425, 967 and 990 cm^{-1} corresponding to loss of the C=C bonds of the vinyl group. Both vapour and liquid deposited samples show slight peaks in the region 1700 – 1800 cm^{-1} which may suggest some C=O formation^{24, 25}. The small peak at 1350 cm^{-1} observed in all coated samples may be due to the C-F vibration²⁵. The vapour deposited samples also showed low intensity peaks below 3000 cm^{-1} indicative of saturated alkane chemistry and confirming polymerization has occurred through the vinyl group. Although these hydrocarbon features were not clearly defined in the liquid deposition mode samples, previous studies suggest that a similar polymerization mechanism can occur in these aerosol assisted plasmas^{12-17, 20}.

XPS analysis was undertaken to determine the elemental composition of the coatings. The theoretical elemental composition, based on the relative concentration of the elements in the HDFD molecule (excepting hydrogen, which is not detected by XPS) is 37% carbon, 63% fluorine giving an F:C ratio of 1.7:1. Table 2 shows the experimental values for the elemental composition of the analysed samples:

Precursor form	Plasma power	Thickness (nm)	Elemental Composition (%)					F:C ratio
			C 1s	F 1s	N 1s	O 1s	Si 2p	
liquid	2%	32	31.8	61.4	0.5	5.8	0.5	1.9
vapour	2%	156	37.0	50.1	1.7	11.2	0	1.4
vapour	40%	98	37.7	57.4	0.5	3.9	0.5	1.5

Table 2: XPS and coating thickness data for coatings deposited with liquid and gaseous HDFD precursors at the set powers shown

The elemental composition was found to be primarily composed of carbon and fluorine. Some oxidation is evident in both vapour and liquid deposited samples as is typical in such systems. Traces of nitrogen and silicon were also detected. In the case of silicon detected in two of the samples, the binding energy corresponded to that of elemental silicon, indicating that the substrate was being detected. The absence of a silicon signal from the 2% vapour sample is consistent with the ellipsometry data, which showed that this coating at 156 nm was significantly thicker than either the 40% vapour coating or the 2% liquid coating. It was noted that the vapour sample deposited at 40% power produced broadly similar XPS data to that obtained for the coating deposited at 2% power, indicating that both plasma powers are in the SPP regime.

Both deposition processes result in a small deviation in the chemistry of the starting monomer. The F:C ratio was less than that expected from an ideal polymerization reaction, but is in line with previous results reported for vacuum^{22,25} and atmospheric pressure^{23,24} plasma deposited long chain perfluoro compounds. To further investigate the chemistry of the coatings, high resolution curve-fitting of the carbon (C 1s) peak was undertaken. Figure 5 shows curve fitting for the 2% set power vapour deposition sample. Along with the expected hydrocarbon and fluorocarbon features, additional features were added to the curve fitting model to reflect the formation of oxidized species within the coating. Similar features were added to the liquid plasma model to achieve adequate curve fitting.

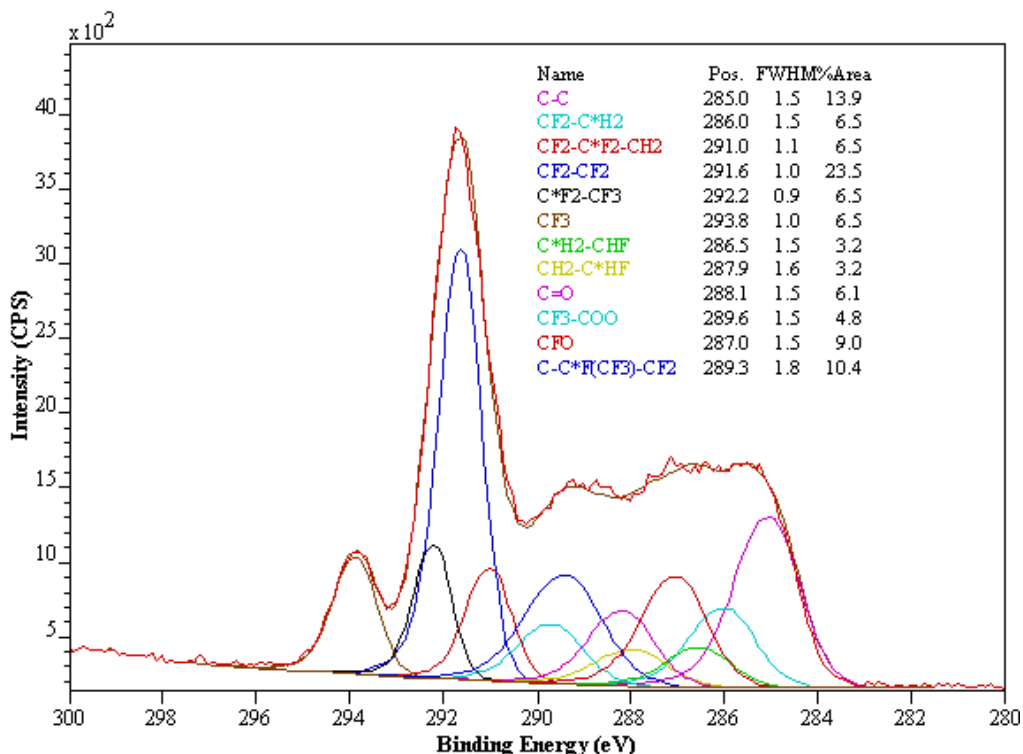


Figure 5: Curve fitting of the C 1s XPS spectrum of HDFD plasma vapour deposited on Si wafer

The CF₂:CF₃ ratios were determined for comparison with the ratio of 7:1 for the theoretical molecule and the values are shown in Table 3. These values are lower than expected from the starting monomer indicating that some degradation of the monomer has occurred, as is typical of all such plasma processes^{19-22, 24}. The vapour and liquid samples deposited at 2% power both produced similar CF₂:CF₃ peak ratios, suggesting that approximately 80% of the perfluoro chain has been retained intact, which compares favourably with previously reported soft plasma polymerization processes²⁶.

Sample	Ratio of CF ₂ to CF ₃
Monomer (idealised value)	7
2% Power Liquid Deposition	5.8
2% Power Vapour Deposition	5.6
40% Power Vapour deposition	4.8

Table 3: Ratio of CF₂ to CF₃ groups as determined via curve fitting of the high resolution C 1s XPS data.

The C 1s high resolution curve fitting suggests some cross-linking in the vapour samples, which is not seen in the liquid sample. A shift in binding energy position of the peak assigned to CF₃ from 292.9 eV in the liquid deposition sample to 293.8 eV in the vapour deposition samples is significant. Care was taken to ensure that this is a real effect, and not simply related to sample charging. This shift suggests the presence of the CF₃ species in a pendant position in the vapour samples, rather than at the end of a linear chain. This may indicate scission and reformation of the molecule in the vapour phase and confirms that the fluorocarbon chain has undergone a cross-linking reaction.

A toluene wash study was carried out as a semi-quantitative measure of the degree of polymerization and bulk stability of the Perfluoro-1-Decene coatings. Coating stability was determined by immersing the samples in toluene for 5 minutes and re-evaluating the coating thickness using ellipsometry. Figure 6 demonstrates the changes in coating thickness observed for the vapour and liquid deposition coatings, both before and after the toluene wash. For the vapour samples, the thickness of the as deposited coatings drops off slightly with increasing plasma power which may be related to higher cross-linking producing a denser film at high power. For liquid samples, deposition rates were highly variable and did not correlate well with discharge power. This may be related to the unstable contact angle data reported earlier, confirming that a durable coating was not formed using the aerosol assisted process. It was generally observed that the vapour phase coatings produced significantly higher deposition rates for most power settings. The vapour samples all exhibited a minor loss of coating thickness after washing, possibly due to removal of residual poorly polymerised material. The cross-linking detected in the high resolution curve fitting of the XPS spectra appears to be sufficient to stabilise the film and provides for significant toluene wash resistance. In contrast, the liquid precursor deposited coatings exhibited very poor wash resistance with complete removal of the coating in all cases. This would indicate that the samples appear to exhibit very low levels of cross-linking.

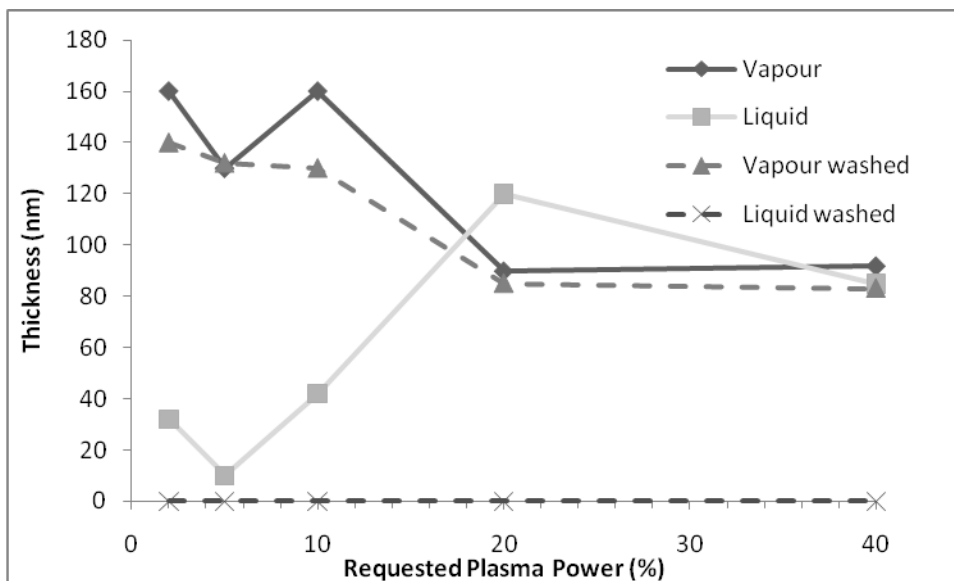


Figure 6: Coating thickness measurements for vapour and liquid deposited HDFD samples at 5 set powers before and after toluene wash

DISCUSSION

A low power, non-isothermal equilibrium, atmospheric pressure corona plasma has been generated from a pin electrode geometry and used to deposit plasma polymerized coatings from 1H, 1H, 2H- Perfluoro-1-Decene monomer precursor in both the gas state and in the liquid aerosol state.

A large reduction was seen in discharge power arising from introduction of the aerosol and it is hypothesised that this is due to the nebulized droplets acting as a sink for free electrons. Because of their small mass and mobility relative to ions, free electrons acquire kinetic energy from applied electric fields easily and rapidly and constitute the first instance sink for the applied power. Thereafter, the free electrons transmit energy to all other plasma microscopic species such as neutrals and ions through collisional processes including ionisation, excitation, dissociation, etc. Ionisation by high energy electrons is generally, therefore, the principle mechanism by which the plasma sinks power and is thereby generated and sustained. The rate of ionisation depends on the number of electrons with kinetic energy above the energy threshold required to initiate the process which, in turn, is determined by the

electron energy distribution function (EEDF). It is anticipated that the addition of liquid droplets into the plasma will significantly reduce the time averaged density of free electrons in the plasma. In particular due to their increased speed and collision rates, there will be a significant reduction in the density of fast electrons in the important high energy end of the EEDF. The fast electrons will also be preferentially lost as their higher kinetic energy more easily overcomes the negative potential barrier of the plasma sheath (the floating potential) set up by the droplet to ensure that the droplet is bombarded by equal fluxes of slow ions and fast electrons thus maintaining overall charge neutrality. Essentially, the liquid droplets act as a cold boundary surface to the plasma sinking charged species and imposing an overall cooling effect on the plasma. They almost certainly substantially change the EEDF by reducing both the mean electron energy and the high energy end or tail of the distribution. This reduction in electron density reduces the number of free electrons available to sink power directly resulting in the decrease in plasma power seen.

This work appears to be the first direct comparison of the coating performance of precursors in the conventional gas state and in the so-called liquid deposition state applied via a pin corona plasma of low specific energy $\sim 0.1 \text{ J/cm}^3$. Previous work¹⁹ confirmed that in non-isothermal plasma chemistry the specific energy [J/cm^3] is the decisive parameter in achieving soft plasma polymerisation (SPP) and that low specific energy, an intrinsic attribute of this corona plasma type, can be an essential condition for SPP. The work also confirmed that, because of the low specific energy offered by this plasma type, SPP could be achieved using precursor in the conventional gas state, i.e. in standard PECVD mode, and that it was not necessary to use precursor in the liquid aerosol state in the so-called 'liquid deposition' process as had been proposed^{12-17, 27}. This work was aimed at assessing the relative performance of the gas and liquid precursor states in a specific corona plasma and the resulting coatings were analysed for the two key SPP performance parameters, namely the degree of polymerization/cross-linking and retention of molecular structure.

The vapour deposited samples showed that it was possible to deposit cured polymeric coatings which substantially retained the chemical structure of the HDFD precursor monomer so that the process could be characterised as SPP. Analysis of the coatings clearly shows that the precursor has undergone a controlled polymerization through the vinyl component of the molecule with low fragmentation of the functional fluorocarbon chemistry of the monomer. Some levels of, but not complete, oxidation of the coatings were evidenced by carbonyl and water peaks detected by FTIR and oxygen detected by XPS, as might be expected in this open perimeter system with the substrate exposed to ambient air. The absence of complete oxidation is consistent with the low specific power levels generated by this plasma type. The resultant coatings, however, produced XPS and FTIR spectra fully comparable to those produced by pulsed vacuum plasma or by liquid aerosol plasma processing. Furthermore, wash tests and FTIR and XPS data showed clear evidence of a high level of cross-linking, an essential attribute of a viable functional coating.

In contrast, although the liquid droplet deposited HDFD coatings showed good chemistry retention, the XPS data suggested that cross-linking within the deposited coatings was negligible and they exhibited no significant toluene wash resistance, even at plasma power levels equal to those of vapour deposition processes. From this study it was concluded that both deposition rate and the extent of cross-linking of the deposited coatings are dependent on the degree of monomer interaction with the plasma at the molecular level. It is self-evident that monomer molecules in the vapour phase will be fully exposed to the interaction with plasma species from entry into the plasma region, throughout their flight and on the substrate surface. In contrast, most monomer in the liquid state will be shielded from the plasma, certainly during flight and probably to a significant extent on the substrate surface when the droplet wets out to spread across an area, leaving only the surface available to interact directly with the plasma. Previous studies have however also highlighted the difficulty in obtaining adequate levels of polymerization and wash stability of liquid state atomised precursors^{12, 28, 29}. Vapour phase monomer molecules will have a much higher probability of engaging in plasma induced chemical reactions than

liquid phase molecules so that the vapour phase reaction rate will be substantially higher generating more cross-linking and thicker coatings at low plasma power. The greatly enhanced deposition rate and wash resistance of the vapour derived coatings reported herein clearly support this assumption.

Despite the results obtained with the HDFD precursor it is important to note that that previous deposition studies carried out with aerosol assisted plasma systems have demonstrated the capability to deposit stable coatings¹³⁻¹⁷ It is therefore concluded that the ability to deposit adherent highly cross-linked plasma polymerized coatings using liquid precursors is likely to dependent on the precursor type (i.e. lability of functional groups), flow rate and plasma power density.

CONCLUSIONS

This paper compares the degree of soft plasma polymerization (SPP) coatings deposited from 1H, 1H, 2H-Perfluoro-1-Decene (HDFD) in which the precursor was passed into a non-thermal equilibrium, atmospheric pressure plasma jet in both the gas and liquid aerosol states. The work confirmed that, with this type of corona discharge, largely damage-free polymerization of monomer molecules to deposit a functional coating can be readily achieved with precursor in the conventional gas state, i.e. operating in standard PECVD mode. This suggests that the use of precursor in the liquid state as nebulized droplets is not required to achieve SPP, as has been suggested elsewhere^{9, 10, 12-17}. Vapour deposition showed high retention of monomer molecular structure in the coating combined with excellent cross-linking and durability, the two key SPP parameters of merit.

Previous deposition studies however with other precursors have demonstrated that stable coatings can be achieved using liquid precursors in atmospheric pressure plasmas^{9,10,21} and the perfluoro alkenes have been effectively deposited in vacuum plasma devices²⁵. Despite this, introducing the perfluoro decene precursor into the plasma as a liquid aerosol in the so-called liquid deposition mode was unable to achieve a coating that was comparable to the vapour system. Good retention of monomer molecular

structure was seen in the liquid coatings, but cross-linking within the coating was negligible and the coatings were not stable to physical wiping or to solvent washing.

Under the conditions explored within this study, a standard vapour deposition process appears to offer a superior alternative to aerosol assisted plasma processing of the HDFD precursor for the experimental range investigated herein.

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