

New Coating Capability by Pin Corona Plasma Soft Polymerisation

Abstract. Pin corona plasma jet operating at atmospheric pressure (AP) was used to deposit polymeric coatings from monomer precursor in both vapour and liquid aerosol states to enable a direct comparison of the coatings for soft plasma polymerisation (SPP). Vapour deposited samples showed polymerization with only minor fragmentation of the functional molecule and a high level of cross-linking. In contrast, while liquid deposition samples showed good retention of monomer structure, they exhibited negligible cross-linking rendering them functionally useless.

Streszczenie. Strumień plazmy ostrze-korona operujący w warunkach ciśnienia atmosferycznego został użyty w celu otrzymania powłoki polimeru z prekursora w stanie pary i aerozolu cieczy umożliwiając bezpośrednie porównanie nałożonych powłok w strefie "soft" polimeryzacji plazmowej (SPP). Próbki nałożone w fazie gazowej wykazały polimeryzację ze znikomą fragmentacją cząsteczek funkcjonalnych i wysoki poziom wiązania. Natomiast, próbki nakładane w fazie ciekłej wykazały się bardzo niskim poziomem związania, przez co były funkcjonalnie bezużyteczne. (Możliwości nowych powłok w wyniku łagodnej polimeryzacji ostrze-korona plazmy)

Keywords: plasma, soft polymerization, coatings

Słowa kluczowe: plazma, łagodna polimeryzacja, powłoki

Introduction

Conventional PECVD gas precursors are bombarded with aggressive plasma species which fragment the precursor monomers limiting coatings to simple materials such as SiO_x, SiN or TiO₂. Complex chemistry cannot be deposited using such systems. SPP is the ability to plasma deposit a cross-linked solid film with a very high degree of structural retention of the starting precursor molecule.

Around 2000, Badyal et al combined helium AP glow discharge plasma with liquid aerosol precursor delivery (called 'liquid deposition') to produce thin films with a high degree of monomer functionality retention [1, 2]. Aerosol was thought to protect the precursor from aggressive plasma species by encapsulating it in a droplet. The use of aerosol, however, produces complexities related to stability of the spray, control of droplet size, even precursor distribution over wide areas, dispensing low volumes of liquid at a constant rate and rapid build-up of unwanted deposits on reactor surfaces.

In 2009, Herbert et al [3] introduced vapour precursor into non-thermal pin corona plasma previously used for liquid deposition. The introduction of vapour allows for standard PECVD equipment to be used to generate a controlled, even flux of precursor onto a substrate. The coatings were shown to have the same functional chemistry retention and deposition rate as seen in liquid deposition coatings. 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 [4]. It was concluded that the pin corona is predisposed to deliver low specific energy into the reaction zone and, hence, to SPP, even using gas precursors.

This work directly compares the performance of coating precursor in the conventional gas and in the liquid deposition states applied via a pin corona plasma of low specific energy ~ 0.1 J/cm³. The precursor used was 1H, 1H, 2H-Perfluoro-1-Decene (HDFD). The coatings were analysed for the two key performance parameters, namely the degree of polymerisation/cross-linking and 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: CH₂=CH-(CF₂)₇-CF₃.

Experimental

A plasma jet was constructed based on the aerosol-plasma jet system described by O'Neill and O'Sullivan [5]. It consists of a dielectric head housing two tungsten needle pointed electrodes to which are applied in parallel an alternating current voltage. A space around each needle 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 nebuliser through which 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 ensuring aerosol is introduced directly into the plasma region.

Alternatively, if the system is to be run in gas deposition mode, the working nebuliser is replaced in the electrode head by a 'dummy' nebuliser in which the liquid input port is blanked and a precursor plus helium carrier gas flow is fed into the gas input port. This precursor plus helium flow is the flow output from the real, working nebuliser which was configured to discharge into a heated flask whose output fed directly into the dummy nebuliser. The flask was immersed in a 200°C oil bath to vaporise the precursor (boiling point 146°C) emerging from the working nebuliser nozzle.

Very Low Frequency electrical power was delivered to both electrodes at a frequency of c. 19 kHz and a peak-to-peak voltage of c. 23 kV. The helium-precursor mix exited through a 75 mm x 15 mm diameter fluoropolymer tube in which the corona plasma was generated from the tips of the vertical needles. Coatings were deposited for 180 seconds onto substrates placed 2 mm from the end of the tube. Samples were generated in both vapour and liquid deposition modes at the following set powers as a percentage of full power: 2%, 5%, 10%, 20% and 40%. The sample was then measured for coating thickness by ellipsometry. To determine cross-linking, a toluene wash was carried out on selected samples for 5 minutes. Coating thickness was again characterized by ellipsometry.

FTIR, contact angle and XPS measurements were taken. The droplet size distribution of atomised liquid and vapour phase precursor was examined using the laser diffraction technique. Electrical characterisation was by high voltage probe and toroidal current transformer.

Results

Discharge powers were in the range 1.4 to 4.9 W. The introduction of liquid droplets into the discharge at constant set power resulted in a fall in measured discharge power of from 19% to 63% depending on the setting. The laser particle size data showed the liquid deposition droplets to have a mean particle size of <10 microns. No droplets were observed in the vapour deposition mode confirming effective evaporation of all of the introduced HDFD and no re-condensation of the vapour.

Contact angle data was taken at all 5 power settings in both vapour and liquid deposition modes. For liquid deposition samples no reliable contact angle data could be obtained. Contact angles dropped from an initial value of approximately 120° to approximately 30° in 5 minutes. Coatings were not well cured being liquid in appearance and readily removed by wiping. For the vapour deposition samples the contact angle dropped by ~10° 5 minutes after deposition and then stabilised to give values between 107° and 122°, typical for plasma polymerised perfluoro compounds [6].

Figure 1 shows FTIR spectra of original monomer and as-deposited samples on KBr substrates

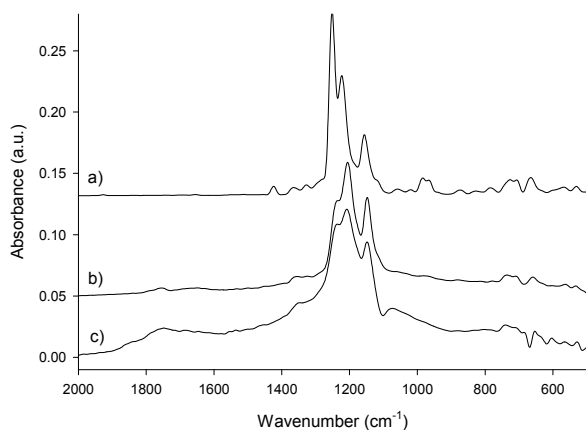


Fig.1. FTIR spectrum of a) 1H, 1H, 2H-Perfluoro-1-Decene monomer, b) liquid deposition plasma polymerisation 2% set power and c) vapour deposition plasma polymerisation 2% set power

The original monomer shows major peaks at 1253, 1222 and 1155 cm^{-1} attributed to 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 wave numbers reported in plasma deposited fluorocarbon films and sometimes ascribed to the reduction of fluorine content in the film or to formation of a disordered and cross-linked coating [7]. As both fluorocarbon peaks are still well resolved in both deposition processes, it can be deduced that the fluorocarbon chain has not undergone significant levels of fragmentation and degradation in either plasma process. The as-deposited spectra show 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 [6, 8] in agreement with the XPS analysis. The vapour deposited samples also showed peaks below 3000 cm^{-1} indicative of saturated alkane chemistry and confirming polymerisation through the vinyl group. These hydrocarbon features were not seen in the liquid deposition mode samples.

XPS analysis determined $\text{CF}_2:\text{CF}_3$ ratios for comparison with the ratio of 7:1 for the theoretical molecule: 2% set power liquid deposition sample = 5.8:1; 2% set power vapour deposition sample = 5.6:1. These values are lower than the monomer indicating that degradation of the monomer has occurred typical of such plasma processes [6, 10, 11, 14]. However, ~80% of the perfluoro chain has been retained intact, comparing favourably with previously reported SPP processes [9].

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 CF_3 from 292.9 eV in the liquid deposition sample to 293.8 eV in the vapour deposition samples suggests the presence of the CF_3 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.

Figure 2 shows the ellipsometric data from all ten vapour and liquid deposition samples before and after toluene wash. The wash test results appear to be highly significant. The vapour samples all show a minor loss of coating thickness after washing, probably due to removal of any residual poorly polymerised material. However, 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 wash resistance. In contrast, in the liquid samples almost no cross-linking has taken place so that wash resistance is non-existent and the entire coating is removed in all cases.

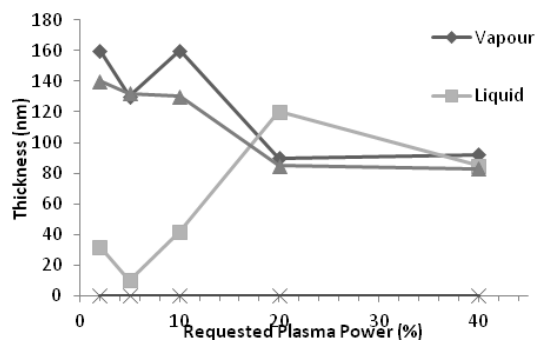


Fig.2. Ellipsometric coating thickness data from vapour and liquid deposited samples at 5 set powers before and after toluene wash

Discussion

A low power, atmospheric pressure pin corona plasma has been used to deposit plasma polymerised coatings from HDFD monomer precursor in both the gas state and in the liquid aerosol state.

The large reduction seen in discharge power on introduction of the aerosol appears due to the nebulised droplets acting as a sink for free electrons.

The vapour deposited samples showed cured polymeric coatings which substantially retained the chemical structure of the precursor monomer so that the process could be characterised as SPP. Analysis 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. The resultant coatings produced XPS and FTIR spectra fully comparable to those produced by pulsed vacuum plasma or by liquid aerosol plasma processing. Furthermore, wash tests, 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 deposition samples showed good chemistry retention, the XPS data suggested that cross-linking within the deposited coatings was negligible and the resultant wash tests rendered the coatings functionally useless, even at plasma power levels equal to those of vapour deposition processes. Difficulty in obtaining adequate levels of polymerisation of liquid state atomised precursors with pin corona has been seen in previous work [10].

Cross-linking of the deposited coating should be associated with 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 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 possibly to a significant extent on the substrate surface. Vapour phase monomer molecules will, therefore, have a much higher probability of engaging in plasma induced chemical reactions than liquid phase molecules so that the vapour phase reaction rate is likely to be substantially higher generating more cross-linking at low plasma power.

Conclusions

This paper reports a direct comparison of coatings targeting SPP from both gas and liquid aerosol state precursors using a cool, atmospheric pressure, highly non-isothermal equilibrium pin corona discharge with a low specific energy $\sim 0.1 \text{ J/cm}^3$.

The work confirmed that, with this type of corona discharge, largely damage-free polymerisation of monomer to deposit a functional coating can be readily achieved with precursor in the conventional gas state operating in standard PECVD mode. The use of precursor in the liquid state as nebulised droplets is, thus, not required to achieve SPP, as has been suggested elsewhere [1, 2, 11, 12]. 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.

In contrast, the same process but using precursor as liquid aerosol in the so-called liquid deposition mode was unable to achieve a comparable coating. Good retention of monomer molecular structure was seen in the liquid

coatings, but cross-linking within the coating was negligible thereby rendering the deposits functionally useless.

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