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Experimental evidence of a relationship between monomer plasma residence time and carboxyl group retention in acrylic acid plasma polymers

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Abstract

Decreasing carboxyl retention in deposits from the glow region of an acrylic acid plasma was measured by X-ray photoelectron spectroscopy and chemical derivatisation as the collection distance from the monomer vapour inlet was increased. Volatilisation of plasma polymerised acrylic acid was detected after trifluoroethanol derivatisation; this is correlated with evaporation of low molecular weight components observed previously.

Keywords: Plasma polymerisation; Acrylic acid; Carboxylic acid

Radio-frequency (RF) plasmas may be used to deposit organic thin films with a combination of structures and properties not achievable through conventional methods of polymerisation [1]. A reasonable degree of control over the nature of the deposit can be exercised by choice of compound for polymerisation (termed monomer) and by regulation of key plasma parameters (input power, pressure and flow rate). Thin film deposits retaining a high degree of the monomer functionality and structure can be obtained when low to very low plasma input powers are employed; this has been well demonstrated in the plasma polymerisation of acrylic acid [2,3]. Surface chemical studies of acrylic acid plasma polymers are relevant because these thin films have been proposed for application as interfacial bonding layers in structural adhesive joints [4] and as biomaterial surface coatings, where amount and type of surface oxygen functional groups in plasma polymers has a significant affect upon cell attachment [5,6].

X-ray photoelectron spectroscopy (XPS) lends itself to surface chemical analysis of thin film organic materials, yet distinguishing between certain chemical functional groups in polymers can be difficult. For example in the C1s core line carboxyl and ester groups share approximately the same chemical shift with respect to hydrocarbon, likewise hydroxyl and ether groups. In such cases to distinguish between and quantify the amounts of each surface chemical functionality, it may be beneficial to derivatise the functional group of interest by the introduction of a molecule containing a unique element. Molecules containing a number of halogen atoms are useful because of the relatively high photoemission cross section of the halogens and large chemical shift that facilitates accurate curve fitting of the C1s core level. Determination of the concentration of this element or group (e.g. $-CF_3$), allows the concentration of the derivatised functional group of interest to be calculated.

Although derivatisation has some drawbacks and limitations which have been documented [7] a number of derivatisation reactions have been used to label carboxyl groups, the most successful of which has been trifluoroethanol (TFE) vapour, which introduces OCH_2CF_3 at room temperature in the presence of pyridine and di-tert-butylcarbodiimide (Di-*t*BuC) ($COOH + CF_3CH_2OH \rightarrow C(OH)OCH_2CF_3 + H_2O$). There is a reasonable degree of confidence in this derivatisation scheme: it has been shown to label carboxyl groups in poly(acrylic acid) approximately

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stoichiometrically [8] and, further it has been used to show the effects of varying plasma power on the retention of carboxyl functional groups in acrylic acid plasma polymers formed downstream of the plasma glow [9].

Plasma conditions have previously been characterised by the ratio ($W/[F \times M_{\mathrm{W}}]$) of plasma power ($W$) to the product of monomer flow rate (F) and molecular weight (M_{W}), where monomer flow rate is related to the residence time of monomer in the reactor [10]. Here, where one monomer only is considered, the M_{W} term is a constant.

In the present study we present evidence that the level of carboxyl group retention is dependent on the distance along the plasma reactor vessel at which the deposited plasma polymer of acrylic acid (ppAAc) is collected.

As shown in Fig. 1 the plasma deposition apparatus consisted of a cylindrical glass reactor vessel of 10 cm internal diameter by 50 cm length closed at each end with aluminium flanges and sealed with PTFE gaskets. Aluminium foil substrates were placed at three positions: immediately adjacent the monomer inlet (ppAAc (inlet)), halfway along the vessel (ppAAc (mid.)) and adjacent the vacuum outlet (ppAAc (vac.)). The chamber was evacuated by a rotary pump via a nitrogen cold trap to a base pressure of 5×10^{-3} mbar. A RF power source with manual power matching was coupled via a copper wire wound with 8 turns along the cylinder. Input power was excited and subsequently regulated at 1 W and power matching was tuned to minimise the reflected power ($\ll 1$ W). The plasma glow region filled the glass vessel. Acrylic acid (Aldrich, UK) was degassed with a number of freeze-pump-thaw cycles. A constant vapour flow rate of acrylic acid of 2 $\mathrm{cm^3_{STP}\,min^{-1}}$ was controlled by manually operated needle valves at an operating pressure of approximately 5×10^{-2} mbar.

For TFE derivatisation, samples were placed on a microscope slide in a boiling tube, angled a few degrees from horizontal and sealed with a PTFE stopper. Reagents were introduced at 15 min intervals in the following order and amounts: TFE, 0.9 ml; Di-*t*BuC, 0.4 ml; pyridine, 0.3 ml. The tube was sealed and left at room temperature for 18 h allowing the reaction to run to completion [9]. As a control, polyacrylic acid (PAA) (Aldrich, UK), spin cast from a 2% w/w solution in methanol was included and used to measure reaction yield.

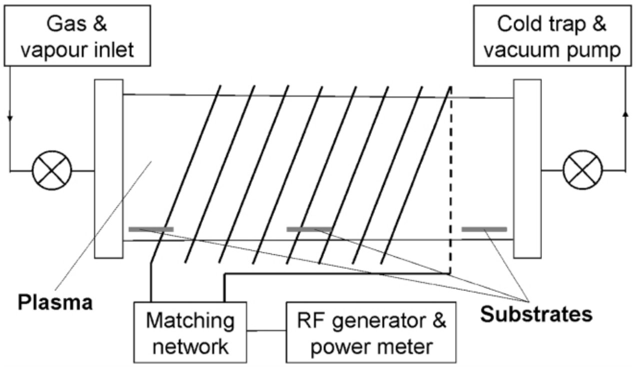


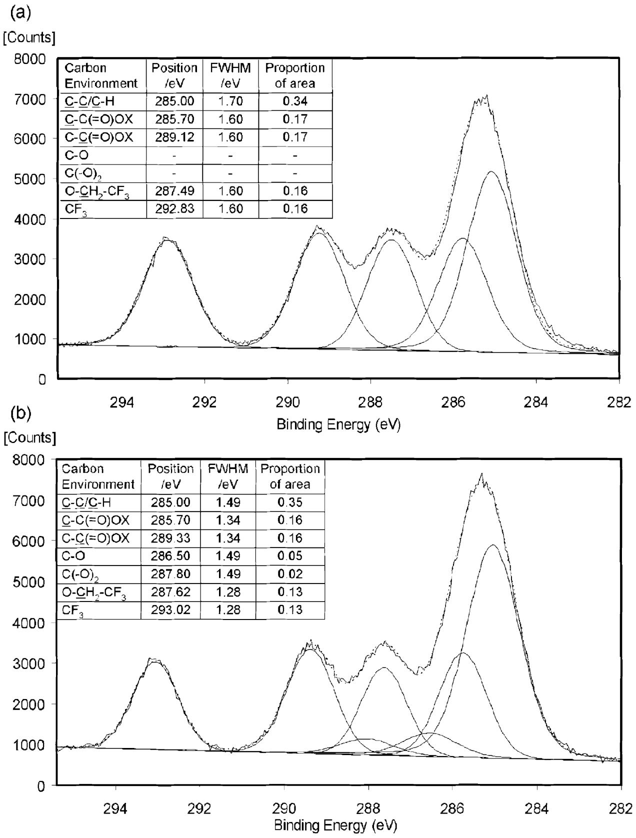
Fig. 1. Schematic of the plasma deposition apparatus.

All surfaces were analysed using a VG CLAM II photoelectron spectrometer, with Mg Kα X-rays ($h\nu = 1253.6$ eV), operated at 100 W, and a take off angle of 30° with respect to the surface normal. Peak fitting and elemental quantification using empirically derived sensitivity factors were performed with Scienta software (Uppsala, Sweden). The C1s core level spectrum was charge corrected by positioning the hydrocarbon (C–C) peak at 285.0 eV using the software. A linear background was applied to the C1s envelope and peaks were included for each functionality component. Chemical shifts were used as quoted in reference literature [11]. The mixing ratio of Gaussian/Lorentzian (G/L) character of each peak was restricted to values between 0.7 and 1.0 and the full width half maximum (FWHM) was restricted to values below 1.70 eV. G/L ratio and FWHM were kept constant in any one fit. The position of each peak was fixed according to its chemical shift and area equivalences set where appropriate, i.e. [C–$\underline{\mathrm{C}}$(=O)OX]=[$\underline{\mathrm{C}}$–C(=O)OX] and [O–$\mathrm{CH_2}$–$\underline{\mathrm{C}}\mathrm{F_3}$]=[$\underline{\mathrm{O}}$–$\mathrm{CH_2}$–$\mathrm{CF_3}$]. Oxygen to carbon (O/C) ratios from wide scans were determined by the relative areas of the sensitivity factor adjusted O1s and C1s peaks. Oxygen to carbon ratios from the peak fit were determined by the relative concentration of carbon–oxygen functionalities (hydroxyl, carbonyl, carboxyl) to hydrocarbon in non-derivatised samples.

The peak fits of C1s envelopes from PAA and ppAAc (inlet) after TFE derivatisation are presented in Fig. 2. Using the ratio of area under the peaks [$\mathrm{CF_3}$]/[C–$\underline{\mathrm{C}}$(=O)OX], the proportion of C–$\underline{\mathrm{C}}$(=O)OX carbons which correspond to carboxyl groups (C–$\underline{\mathrm{C}}$(=O)OH) was determined and is shown in Fig. 3. On PAA, the TFE derivatisation reaction reached near completion with a yield [$\mathrm{CF_3}$]/[C–$\underline{\mathrm{C}}$(=O)OX] of 97%. From the [$\mathrm{CF_3}$]/[C–$\underline{\mathrm{C}}$(=O)OX] ratio, it was calculated that in the ppAAc collected at the inlet, 80% of the C–$\underline{\mathrm{C}}$(=O)OX functionalities were carboxyls. In deposits collected at the mid point and vacuum outlet the contribution of carboxyl to the C–$\underline{\mathrm{C}}$(=O)OX peak was calculated to be less: 67% in the ppAAc (mid.) and 60% in the ppAAc (vac.), respectively. Given that 80% of the C–$\underline{\mathrm{C}}$(=O)OX signal is carboxyl in the ppAAc (inlet) this equates to 19.7 carboxyl groups per 100 carbons in the surface.

The retention of functionality can also be calculated by dividing the carboxyl concentration in the ppAAc (inlet) deposit (19.7%) by the carboxyl content of the monomer (33%) giving a value of 59%. In the same way, the ppAAc (mid.) deposit retained 53% of the monomeric carboxyl groups and the ppAAc (vac.) deposit retained 43% thus, the carboxyl retention decreases along the reactor length.

Increased plasma power leads to more cross-linking in plasma polymer deposits [2,3,9] and with power, the deposition rate increases up to a maximum, at the boundary between two deposition conditions, which have been termed



(a)

Carbon Environment	Position /eV	FWHM /eV	Proportion of area
$\underline{C}$-$\underline{C}$/$\underline{C}$-H	285.00	1.70	0.34
$\underline{C}$-C(=O)OX	285.70	1.60	0.17
C-$\underline{C}$(=O)OX	289.12	1.60	0.17
C-O	-	-	-
C(-O)$_2$	-	-	-
O-$\underline{C}$H$_2$-CF$_3$	287.49	1.60	0.16
CF$_3$	292.83	1.60	0.16

(b)

Carbon Environment	Position /eV	FWHM /eV	Proportion of area
$\underline{C}$-$\underline{C}$/$\underline{C}$-H	285.00	1.49	0.35
$\underline{C}$-C(=O)OX	285.70	1.34	0.16
C-$\underline{C}$(=O)OX	289.33	1.34	0.16
C-O	286.50	1.49	0.05
C(-O)$_2$	287.80	1.49	0.02
O-$\underline{C}$H$_2$-CF$_3$	287.62	1.28	0.13
CF$_3$	293.02	1.28	0.13

Fig. 2. XPS narrow scan of the C1s core line in trifluoroethanol derivatised samples: (a) polyacrylic acid and (b) plasma polymerised acrylic acid, collected from the near monomer inlet position (ppAAc (inlet)). Spectra have been charge corrected to C–C at a binding energy of 285.0 eV. The peak C–$\underline{C}$(=O)OX represents both carboxyl and ester which share the same chemical shift with respect to hydrocarbon while $\underline{C}$–C(=O)OX represents β-shifted carbon adjacent to carboxyl/ester groups.

the *energy deficient regime* at low power, and the *monomer deficient regime* at high power [1]. Power density and plasma density were not directly measured in this study however, we estimate plasma density to be around $1 \times 10^{15}\ \mathrm{m}^{-3}$ based on measurements in argon plasmas with similar pressure, input power and reactor geometry [12].

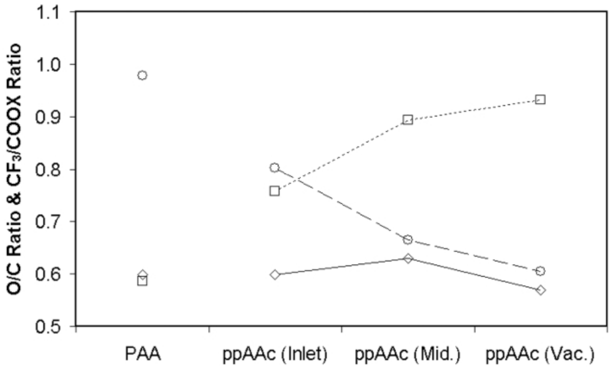


Fig. 3. Surface chemical composition of polyacrylic acid and acrylic acid plasma polymers showing the effect of substrate distance from monomer inlet to vacuum outlet in the plasma chamber on: (◇) O/C ratio from widescan of non-derivatised samples; (□) O/C ratio from C1s core-line peak fits in non-derivatised samples; (○) CF_3/C–$\underline{C}$(=O)OR ratio from C1s core-line peak fits in TFE derivatised samples.

We would expect that the low power (1 W) used in this study is well within the energy deficient regime [9]. However, from the results it appears that the increasing monomer residence time along the length of the reactor vessel is significant and we calculate a period of 4.3 s for a particle to travel the full length of the reactor.[1] Although we do not anticipate significant changes in the key plasma parameters (density, electron temperature etc.) along the reactor vessel, a longer monomer residence time in the vessel increases the opportunity for collision with an electron and fragmentation. Hence it seems reasonable to expect the degree of fragmentation of the monomer to increase along the reactor vessel and to be greatest adjacent to the vacuum outlet. We have no evidence of an etching mechanism operating under these plasma conditions.

It is notable in Fig. 3 that the O/C ratio measured from the widescan for conventional PAA is consistent with that calculated from the peak fit of the C1s core level assuming each carbon environment to equate to one (C–OX) or two (C(=O)OX) environments, i.e. O/C approx = 0.6 (Fig. 3). However, for each of the ppAAcs, the O/C ratio calculated from the peak fit is far greater than the widescan or elemental O/C. This disparity arises because the O/C ratio calculated from the peak fit does not take into account the possibility of ester C–$\underline{C}$(=O)OR or ether C–O–C environments, and therefore over-estimates the oxygen concentration when these groups are present, as in ppAAc but not PAA. The increase in this disparity with residence time (or reactor position) is indicative of the increase of ether and ester formation as the deposit incorporated more fragmented monomer and this is consistent with the derivatisation results.

This result is clearly power and flow rate dependent as, in an earlier study with a similar set up, but performed at higher plasma power and monomer flow rate, the oxygen content determined from the XPS widescan decreased with distance from monomer inlet for acrylic acid plasma polymers [10].

Thinning of the ppAAc (inlet) layer as a result of the TFE derivatisation was apparent through observation of the substrate Al signal after derivatisation. The ppAAc (mid.) and ppAAc (vac.) end deposits and PAA were not sufficiently thinned by the TFE reaction to reveal the Al 2p peak (data not shown). The thickness of the derivatised ppAAc (inlet) sample was estimated at ~8 nm by attenuation of substrate aluminium peaks using the Beer–Lambert law that describes the attenuation of photoelectron emission normal to the surface of a solid; $t = -\lambda \ln(I/I_0) \cos\theta$, where t is the emission depth or sample thickness, λ is

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[1] Monomer residence time was calculated from the gas flow rate corrected for room temperature and plasma pressure. Relating this to the volume of the vessel gave the time for replenishment.

the electron inelastic mean free path (2.75 nm [13]), I is signal intensity, I_0 signal intensity without the overlayer and θ is the take off angle with respect to the surface normal. Adventitious hydrocarbon present on the aluminium foil (at the Al/ppAAc interface) constitutes only a small fraction of the analysis since it was calculated that the thinned polymer was 8 nm thick. Thus, the XPS peak-fit analysis in Fig. 2 is considered to be a valid measurement of the plasma polymer alone.

Though only observed on the ppAAc (inlet) deposit, thinning may have occurred in the other samples by loss of plasma polymer as a result of derivatisation, which is most probably through evaporation. Previously, we have seen that high carboxyl retention ppAAcs are less cross-linked than ppAAcs produced at higher power (with lower carboxyl retention), indeed high retention ppAAcs contain significant amounts of volatile (non-bound or loosely bound) material [14]. It seems that material evaporation may be exacerbated by TFE derivatisation and observed to varying extents in the range of chemistries obtained along the reactor vessel. While we do not currently have data to conclusively describe the mechanism responsible for this effect, it should be noted that if derivatised material is lost from the surface, and therefore the analysis, an underestimation of the deposit's carboxylic acid concentration may result. Any such effect is considered insignificant here on the basis of the consistent widescan O/C levels of PAA and the ppAAcs.

In conclusion, this work shows for the first time that in these low plasma power conditions used to deposit ppAAcs, the collection position affects the degree of carboxyl retention. The use of TFE derivatisation with XPS analysis facilitated clear and unambiguous identification of carboxyl groups in the ppAAcs. Retention of carboxyl groups was reduced along the reactor length due to increasing residence time of molecules in the reactor vessel.

The likelihood of fragmentation of a molecule increases with residence time, in the plasma glow, and the effect is to reduce carboxyl retention in the ppAAc.

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