A study of the interaction of acrylic acid/1,7-octadiene plasma deposits with water and other solvents

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Abstract

Plasma polymerised acrylic acid (ppAAc) coatings were deposited on aluminium substrates from acrylic acid plasmas at various plasma powers (P). The chemistry of the ppAAc deposit was characterised using X-ray photoelectron spectroscopy (XPS) and trifluoroethanol derivatisation of the carboxylic acid functionalities. The absorption of atmospheric moisture by ppAAc was quantified using a vibrating quartz crystal microbalance. The solubility in ethanol, water and hexane of ppAAc deposited on aluminium was investigated using substrate signal attenuation in XPS. The high carboxylic acid concentrations retained in the low P deposits correlates with a hydrophilic ppAAc coating, i.e. they are readily soluble in water and absorb moisture from the atmosphere. The lower carboxylic acid content and greater crosslinking of coatings produced at higher P result in less hydrophobic deposits which are resistant to rinsing with water.

Addition of 1,7-octadiene vapour to a $P = 2$ W acrylic acid plasma produces insoluble plasma polymerised acrylic acid-co-1,7-octadiene (ppAAc-co-Oct) deposits. A carboxylic acid containing fraction of these insoluble coatings is removed by hexane rinsing which we propose is physisorbed oligomer. We propose that slow evaporation of these oligomers is responsible for the decrease in the acidity of the coatings observed over time under atmospheric storage.

The contact angle of water insoluble coatings is measured as a function of time after a water drop is placed on the surface. An initial fast decrease of the contact angle was observed which is consistent with a rapid absorption of water into the plasma polymer. A low contact angle/high wettability correlates with coatings determined to have high carboxylic acid concentrations. By changing the ppAAc-co-Oct chemistry a change in the contact angle of 40° can be achieved. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Plasma polymerisation; Acrylic acid; X-ray photoelectron spectroscopy

1. Introduction

The plasma polymerisation of organic compounds to produce thin polymeric coatings has been an active area of research since the early seventies [1–4]. Much of the interest in plasma deposition has been concerned with the physical properties of the deposits that may be obtained, such as "anti-scratch" coatings [5]. However, recently it has been established that through control of the plasma parameters it is possible to produce plasma polymers (PP) with high concentrations of a specific chemical functionality retained from the monomer e.g. hydroxyl from allyl alcohol [6] and carboxylic acid from acrylic acid [7–10]. Subsequently, control of the deposit chemistry using plasma copolymerisation has been investigated where the plasma is sustained in a mixture of a functional and a non-functional hydrocarbon monomer [11]. These coatings offer the

potential to alter the surface chemistry of solids in a controlled manner with a thin and highly adherent plasma polymer while having a negligible influence upon the bulk properties of the substrate material.

In a recent publication we used X-ray photoelectron spectroscopy (XPS) combined with derivatisation and time-of-flight secondary ion mass spectrometry (TOF-SIMS) in an investigation of the chemistry of plasma polymerised acrylic acid (ppAAc) and its dependence on plasma power (P) [12]. Acrylic acid was chosen for its retention of carboxylic acid functionalities which have potential in the application of adhesion promotion. [9,13–16]. TFE derivatisation enabled the differentiation of acid and ester functionalities by XPS, thus providing a quantitative description of the functional composition of ppAAc [17]. We identified that deposits formed at low P had a functional composition similar to conventional poly(acrylic acid) (PAA) whereas the chemistry of deposits formed at high P were dominated by ester functionalities and were more cross-linked.

In the work presented here we extend our study of the structure of ppAAc, to its absorption of atmospheric

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moisture and to its solubility in a range of solvents. The solubility is an important consideration when these materials are used in contact with liquids, e.g. adhesion promotion coatings where the resin may dissolve the deposit [16] and in biomedical coatings where body fluids interact with the coating [9,18]. There is very little work in the literature on the solubility of plasma polymers [2,3], possibly because of the difficulties involved in carrying out measurements on a thin coating. In order to determine whether the coatings were soluble we analysed coatings after rinsing in a fixed volume of solvent using XPS. If the rinsing process removed sufficient coating to reveal the substrate we used the intensity of a substrate core-level to estimate the remaining overlayer thickness, otherwise the XPS spectra acquired from samples before and after rinsing were compared to assess the effect of the solvent on the coating. This approach provides a measure of solubility specific to the rinsing conditions used, which is sufficient to determine the effect of deposition parameter on deposit solubility. To reduce the water solubility of ppAAc coatings we use the technique of plasma copolymerisation, i.e. adding 1,7-octadiene to the acrylic acid plasma to form plasma polymerised (acrylic acid-co-1,7-octadiene), ppAAc-co-Oct [11,19].

A few publications have already investigated some of the physical properties of ppAAc [7–9]. The *dissolution of hydrophilic molecules* from ppAAc has been noted by Cho et al. during adhesion measurement made under water [7]. However, only recently was the solubility in water of ppAAc deposits explicitly detailed by Candan et al. [19]. None of these authors have quantified the exact change in the surface chemistry from their XPS data because of the omission of TFE derivatisation in their approach. Thus, we apply this technique herein to fully characterise the effect of water and other solvents on ppAAc and ppAAc-co-Oct.

The wettability of polymeric surfaces is often related to their adhesion performance [4]. The wettability of water insoluble ppAAc-co-Oct deposits was investigated by measuring the contact angle of a drop of water placed on the surface of the deposits. This was compared to the behaviour of the conventional polymers; poly(tetrafluoro ethylene) (PTFE) and PAA.

2. Experimental

2.1. Plasma deposition apparatus

The plasma deposition system, which has previously been illustrated elsewhere [12], comprised of a radio frequency power source (13.56 kHz) with manual power matching which was tuned to minimise the reflected power (<1 W). This was capacitively coupled via two copper bands to a deposition chamber evacuated to a base pressure of approximately 1 Pa. The deposition chamber comprised a cylindrical borosilicate glass T-piece sealed with stainless steel

end-plates using PTFE o-rings. An alumina and a liquid nitrogen trap were used to prevent fowling of the rotary pump with condensable plasma products and contamination of the reaction chamber by pump oil (Fomblin™). The acrylic acid and 1,7-octadiene monomers, both supplied by Aldrich, were degassed using three freeze–thaw cycles. The flow of monomer vapour into the reaction vessel was regulated through the use of manually operated needle valves. The monomer flow rate was monitored before and after deposition, and found to remain constant for a fixed leak-valve setting.

The pressure in the chamber, before the plasma was initiated, was kept constant (40 Pa) using a valve on the pumping line. All ppAAc samples in this paper were produced at an acrylic acid flow rate, $\phi_{AAc} = 5\ cm^3_{STP}min^{-1}$ (sccm). Plasma copolymerisation of acrylic acid and 1,7-octadiene was carried out by introducing the two vapours into a volume prior to the main reactor volume to encourage mixing. We describe the mixture using the ratio of the acrylic acid pressure (p_{AAc}) and the pressure of the 1,7-octadiene (p_{oct}) vapours prior to plasma ignition. The sum of p_{oct} and p_{AAc} was maintained at a total pressure of 40 Pa using the needle valves to restrict the flow of the individual vapours prior to mixing. Assuming ideal gas behaviour, where $[X] \propto p_X$, it is possible to estimate the molar ratio of the gases in the mixture (R) using the expression $R = p_{oct}/(p_{oct} + p_{AAc})$.

Deposit weight measurements were made using an STM-100/MF vibrating quartz crystal microbalance (QCMB) (Sycon Instruments New York) which utilised a gold coated quartz crystal with an exposed area of diameter 8 mm. The mass of deposit was determined by measurement of the resonance frequency of the exposed quartz crystal which was recorded by computer once a second. The coating thickness was calculated assuming a deposit density, $\rho = 1\ g\ cm^{-3}$. This apparatus was calibrated by comparison with the deposit thickness determined using the Au 4f XPS signal attenuation (using $\lambda = 28\ Å$ [20]) by a coating analysed on the gold plated quartz crystal. This method assumes that the plasma is of a sufficiently low power not to etch and redeposit the gold coating.

For XPS and contact angle measurements, ppAAc was deposited on aluminium foil positioned downstream of the electrodes, although the plasma is formed throughout the reactor. Samples were stored in aluminium foil envelopes at ambient conditions. Rinsing, to remove soluble material, was carried out using 80 ml of solvent which was poured over a sample of approx. 1 cm × 1 cm, whilst supported above a container to collect the flow off the sample.

2.2. XPS

The XPS spectra were acquired on a Scienta ESCA200 spectrometer. A monochromated Al Kα X-ray beam (4 mm × 1 mm, source power 500 W) was used to generate the emission of photoelectrons from the surface of the sample,
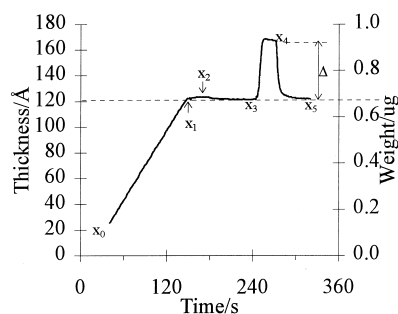
Fig. 1. QCMB measurements made every second during the ppAAc deposition process ($P = 2$ W); while the plasma was ignited (x_0–x_1), monomer flow in the chamber after the power was cut (x_1–x_2), evacuation of the chamber (x_2–x_3), venting to air of 30% RH (x_3) and evacuation of the chamber to the base pressure (x_4–x_5).

analysed at a take-off angle (θ) of 90°. Thus, the analysis depth (d), from which 95% of the photoelectrons contributing to the spectra emanate, may be estimated to be 70 Å for carbon and 80 Å for Al 2p electrons ($d = 3\lambda \sin\theta$ where $\lambda = 24$ Å for C 1s and 28 Å for Al 2p electrons) [20].

Curve fitting of all C 1s peaks was carried out using the same initial conditions and inter-peak constraints for each spectra. The C 1s envelope from ppAAc was fitted with component peaks of equal full width at half maximum (FWHM) values, except for the β-shifted carbon which was constrained to be 10% greater. This procedure was adopted on the basis of the C 1s curve fit of PAA [12,21]. The shape of the peaks was also kept equal, and varied between a Gausssian to Lorentzian (G/L) mix of 0.8–1. Again, the β-shifted carbon was an exception to this with a G/L mix of 10% less than the other components. The total intensity of the β-shift was constrained to equal to that of the well defined carboxylic acid component. The position of the C(–O) and C(–O)$_2$ components were fixed at 1.4–1.5 eV and 2.7–2.8 eV from the CH/C–C component respectively. Curve fitting of TFE-labelled ppAAc was conducted using the same procedures for the pre-labelled polymer. The position and FWHM of the two peaks from the TFE molecule (CF$_3$ and –O–CH$_2$–CF$_3$) were optimised while their areas were constrained to be equal.

XPS overlayer thickness estimate

Analysis of samples taken from different positions in the roll of aluminium foil, which was used as a substrate, indicated that for a given acquisition conditions the total counts in the Al 2p core-level were reproducible to 3%. This uniformity of signal from the foil allowed us to use the mean value ($I_0 = 543 \pm 16$) and the Al 2p signal intensity through an overlayer (I) to calculate the overlayer thickness (t) using the Beer–Lambert approach for analysis of photoelectrons emitted perpendicular to the surface where $\lambda = 28$ Å for Al 2p.[20]:

$$t = -\lambda \ln(I/I_0).$$

For rough surfaces, such as the conformal plasma

polymer on aluminium foil, the XPS spectra include a range of take-off angles and a corresponding range of analysis depths. It has been shown theoretically that for analysis normal to the sample plane ($\theta = 90°$) that t was overestimated by an amount proportional to the increase in roughness relative to a planar surface [22]. Thus, while the value of t is relatively precise, by virtue of the good counting statistics of the instrument, it may only be regarded as an estimate. The actual overlayer thickness is likely to be less than t.

2.3. Derivatisation

Trifluoroethanol (TFE) labelling of acid functionalities was carried out according to the protocol detailed in Ref. [17]. This involved exposure of the samples to TFE vapour in the presence of a volatile catalyst, pyridine, and a drying agent, di-*tert*-butylcarbodiimide (Di-*t*BuC) at room temperature. All reagents were supplied by Aldrich. The samples were placed on a microscope slide in a boiling tube which was sealed with a PTFE coated stopper. The reagents were introduced below the samples at 15 min intervals in the quantities 0.09, 0.04 and 0.03 ml respectively and left in the sealed container for 5 h. These conditions have previously been determined to provide stoichiometric reaction of TFE with the carboxylic acid functionality in this class of material [12]. By fitting peaks to the carbon functionalities in the C 1s core-level we can determine the ratio of the CF$_3$ and COOX environments in the TFE labelled deposit. Thus, we calculate the acid and ester concentration relative to the total carbon signal.

2.4. Contact angle apparatus

The contact angle was measured using a goniometer supplied by NFT communication S.A, France. This apparatus comprises a CCD camera to record an image of a water drop (volume of 0.2 μl) placed on the sample surface using a micro-syringe. Image processing software (WinGoutte for Windows 95) was used to determine the contact angle at the intercept of a circle representing the drop (calculated from the image) with a line positioned manually by the user at the substrate–drop interface. The equation for the circle is a best-fit calculated from all combinations of three pixels at the circumference of the circle.

3. Results

3.1. Interaction of acrylic acid vapour and atmospheric moisture with ppAAc

We used a QCMB, located in the deposition chamber, to measure the change in deposit weight on exposure of the plasma polymer to acrylic acid vapour and on venting to the atmosphere immediately after deposition. The thickness and the weight of a ppAAc deposit ($P = 2$ W) are plotted against
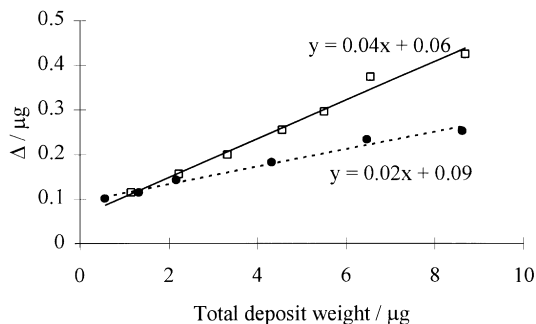
Fig. 2. The weight increase, Δ, measured by QCMB upon venting with ambient air (RH = 30%) for plasma polymers deposited at $P = 2$ W($\square$) and $P = 20$ W($\bullet$).

time (x) in Fig. 1. Shortly after supplying power to the coils, the plasma ignited at x_0 and deposited on the crystal at a constant rate of 0.9 Å s^{-1} until the power was turned off at x_1. Immediately after the plasma was extinguished, a slight adsorption and/or absorption of monomer vapour was observed. This weight gain was completely removed when the monomer flow was stopped at x_2, and the system was evacuated to the base pressure. At x_3 the system was vented to atmosphere with a relative humidity (RH) of 30% which resulted in the large weight increase, Δ. Upon evacuation of the system to the base pressure, between x_4 and x_5, this weight gain was fully removed and thus we assign it to water vapour pick-up. In order that the entire process may be clearly presented on the same diagram the deposition illustrated was made on a crystal already coated with 1000 Å of identical ppAAc.

To identify the origin of Δ, ppAAc was deposited incrementally on a virgin crystal and the magnitude of the weight increase upon venting to air was monitored over a range of deposit weights. In Fig. 2, Δ is plotted against the total deposit weight for $P = 2$ and 20 W ppAAc deposits. It is apparent that Δ is linearly related to the deposit weight, i.e. $\Delta = k$(deposit weight) $+ C$. Thus, there are two components to the water pick-up, (i) water adsorption on the surface, as represented by C, and (ii) water absorption into the bulk of the deposit. In Fig. 1 it can be seen that this latter process
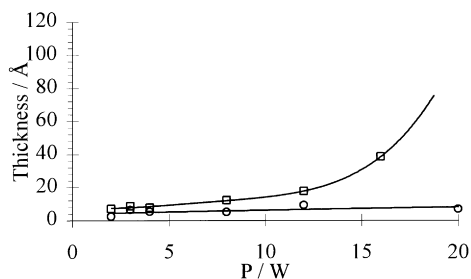

Fig. 3. Thickness of ppAAc remaining on aluminium after rinsing with water ($\square$) and ethanol ($\bigcirc$) versus plasma deposition power, P. Note: No aluminium signal was present after rinsing the $P = 20$ W sample with water indicating that the remaining materials is of a thickness greater than the analysis depth of XPS.

occurs very rapidly reaching an equilibrium value almost instantaneously, upon venting to atmosphere at x_3. Absorption proceeds more rapidly than the time it takes to fully vent the deposition chamber to atmospheric pressure and thus the kinetics of this process cannot be measured using our apparatus.

The water absorption reached an equilibrium concentration, $k = 4$ wt% for $P = 2$ W. No significant divergence from linearity was observed indicating that there was no barrier to diffusion of the water through the entire coating thickness. The ppAAc deposited from a $P = 20$ W plasma (onto a new crystal) showed that the water pick-up of this material was of the same form as the $P = 2$ W material, presented in Fig. 2. The equilibrium concentration of absorbed water, $k = 2$ wt%, was half that of the 2 W deposit. The linearity of the data again indicate that in this material the diffusion was uninhibited through the full coating thickness (0.2 μm). Thus, although k was reduced by increasing P, water still diffused through the entire coating thickness. The data contained in Fig. 2 were acquired at a RH = 30%. Venting with air of higher RH resulted in an increase in the equilibrium water content of the coatings (not shown) indicating that these data do not represent saturation of the plasma polymer.

It is apparent in Fig. 2 that the intercept with the y-axis, C was different for $P = 2$ and 20 W where $C = 0.06$ and 0.09 μg respectively. This indicates different amounts of surface adsorption which is probably influenced by different surface morphologies of the two quartz crystals used for each P, and the resultant PP topography and surface chemistry.

3.2. Assessment of PP solubility

To determine the relative solubility of ppAAc deposited from a range of plasma powers ($P = 2$–20 W) we analysed samples by XPS before and after rinsing in hexane, ethanol and water. Plasma polymers of approximately equal thickness were deposited on aluminium foil such that the aluminium core-levels were fully attenuated by the plasma polymer. Using the attenuation of the substrate Al 2p signal it was possible to determine the thickness of PP remaining on the surface after rinsing as presented in Fig. 3 for water and ethanol. After rinsing in ethanol, only a thin overlayer of less than 10 Å remained for deposits formed at all values of P. When rinsed in water, ppAAc formed below $P = 5$ W also left a strongly adsorbed layer of similar thickness. Deposits corresponding to higher values of P were less soluble in water as indicated by the increased thickness of material remaining on the substrate. At $P = 20$ W the deposits were sufficiently insoluble that the substrate signal was not observed after rinsing.

The functional composition of as-deposited ppAAc-co-Oct was determined from curve fitting of the XPS C 1s core-level and plotted in Fig. 4 against the proportion of 1,7-octadiene in the plasma, R. It is apparent that the
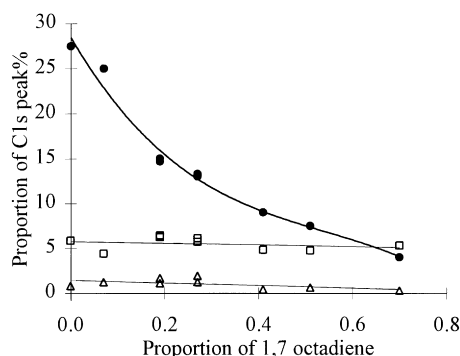
Fig. 4. The functional composition, C–OX($\square$), C=O($\triangle$) and C(=O)OX($\bullet$), of deposits formed from a $P = 2$ W acrylic acid/1,7 octadiene plasma determined from the XPS C 1s peak shape versus the proportion of 1,7 octadiene (R).

concentration of the C–OX and C=O functionalities did not change significantly with 1,7-octadiene addition while acid/ester functionality (C(=O)OX) decreased in relative intensity.

The XPS analysis of a number of water rinsed ppAAc-co-Oct which had been deposited over a range of R indicated that the addition of $> 20\%$ 1,7-octadiene to the acrylic acid plasma was sufficient to produce relatively insoluble deposits, i.e. the substrate signal was not present in the XPS spectra. The C 1s core-level of such a coating, which was deposited at $R = 0.2$, before and after water rinsing is presented in Fig. 5a. Comparison of these two spectra indicates that while the coating was mainly insoluble, the relative intensity of the C(=O)OX component was reduced after rinsing. This indicates that a soluble fraction has been removed by the rinsing process. No discernible change in the relative concentration of the C–C, C–OX and C=O functionalities occurred as indicated by the concurrence of the data below the binding energy of 286 eV (Fig. 5a).

To quantify the concentration of the carboxylic acid functionalities deposits were labelled with TFE using a vapour phase derivatisation protocol described previously. The curve fit of a C 1s core-level acquired from a representative derivatised specimen is presented in Fig. 5b. Using the CF$_3$/C(=O)OX ratio, we calculated the proportion of the C(=O)OX functionality which is carboxylic acid. This is plotted against R for coatings before and after rinsing in water and hexane in Fig. 6. These data illustrate that rinsing in water reduces the carboxylic acid concentration of deposits formed at plasma octadiene introduction levels of $0.2 < R < 0.4$. At values of $R \geq 0.4$ the carboxylic acid concentration of the deposit was unaffected by water rinsing. Rinsing in hexane removed a portion of the deposit which was characterised by a reduction in acid functionality for $R < 0.27$. We interpret this to represent the removal of polar material that was sufficiently loosely bound to the deposit surface to be removed by the rinsing action of the non-polar hexane. The greater reduction in the carboxylic acid concentration resulting from water rinsing indicates the greater

solubility of the polar deposit in this polar solvent. Deposits at all values of R were highly soluble in ethanol, leaving only 5–10 Å of strongly bound deposit at the aluminium surface (not shown).

3.3. Contact angle

We measured the contact angle of a drop of water on ppAAc-co-Oct samples that had been rinsed in water and determined to be insoluble in Section 3.2. Our data indicate that this rinsing procedure has removed all readily soluble material at the deposit surface which may introduce artefacts in the measurement. The contact angle experiment is known to be very sensitive to low levels of surface contamination and therefore PTFE (Goodfellow Ltd) was used to verify the purity of the water and the sample handling procedure. Over the period of time considered (0–20 s) the contact angle (ϑ) on PTFE was well represented by a straight line; $\vartheta = -0.05 \times \text{time} + 119$. This high value of ϑ for PTFE, 119 at $t = 0$, gave us confidence that the water and the handling procedures do not introduce contamination which would reduce ϑ [4]. The contact angle of water on PAA (MW $= 1.08 \times 10^6$, Scientific Polymer Products Inc.) was measured to determine the response of a conventional linear carboxylic acid containing polymer.

To monitor dynamic changes at the surface in response to the aqueous environment the contact angle was measured at 2 s intervals after the water drop was placed on the surface. The data from the range of insoluble ppAAc-co-Oct deposits and PAA are presented in Fig. 7. For all samples a decrease in the contact angle with time was observed. Drop volume was varied on a PAA surface and determined not to influence the measured contact angle. Thus, we assume that evaporation is not the cause of the decrease with time. Moreover, the decrease in contact angle with time measured for PTFE was very much less ($m = -0.05° \text{ s}^{-1}$) than that determined on PAA ($m = -0.2° \text{ s}^{-1}$) indicating that the structure of the polymer influences the rate of decrease of ϑ with time. Therefore, we assign this linear decrease in contact angle to reorientation of functionalities at the water–near surface interface in response to the aqueous environment. Thus, the greater decrease in the contact angle for PAA, cf. PTFE, reflects the interactions of the water with the polar carboxylic acid functionalities. Such interactions do not exist at the hydrophobic PTFE–water interface, hence the almost constant contact angle with time.

In Fig. 7, the contact angle measured on the plasma-co-polymers was observed to decrease with time, however, in contrast to the conventional linear polymers the PP deposits exhibited two distinct regimes. An initial sudden non-linear decrease in ϑ was observed which eventually reached the same linear rate as determined for PAA, i.e. $-0.2° \text{ s}^{-1}$.
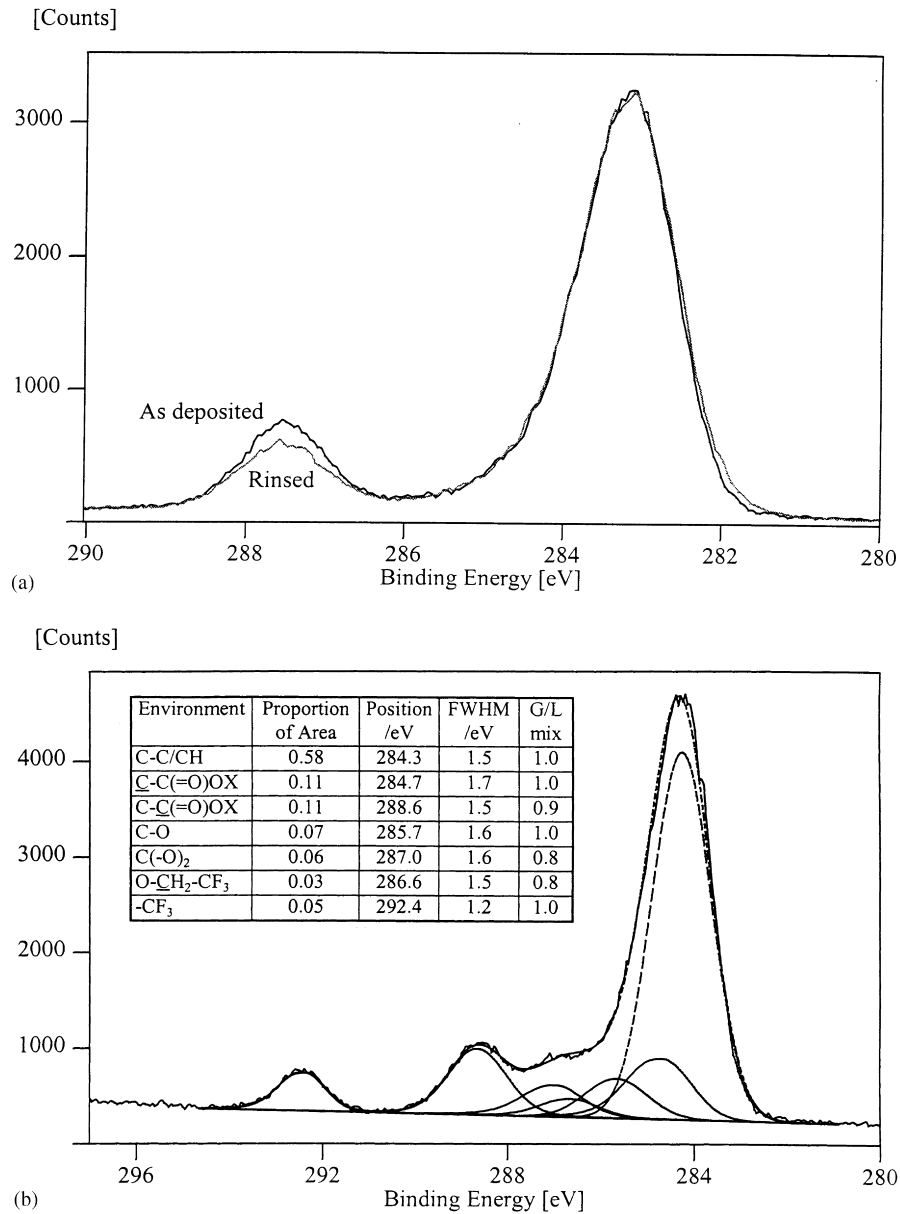
[Counts]

(a)

Environment	Proportion of Area	Position /eV	FWHM /eV	G/L mix
C-C/CH	0.58	284.3	1.5	1.0
C-C(=O)OX	0.11	284.7	1.7	1.0
C-C(=O)OX	0.11	288.6	1.5	0.9
C-O	0.07	285.7	1.6	1.0
C(-O)₂	0.06	287.0	1.6	0.8
O-CH₂-CF₃	0.03	286.6	1.5	0.8
-CF₃	0.05	292.4	1.2	1.0

[Counts]

(b)

Fig. 5. (a): C 1s core level of plasma-co-polymer deposited from an acrylic acid and octadiene plasma ($R = 0.19$) before and after rinsing in water. (b): Curve fitted C 1s core level after TFE derivatisation of rinsed deposit.
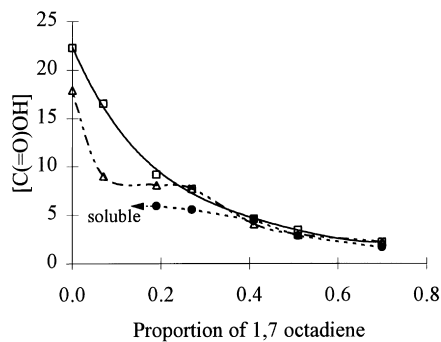
Fig. 6. Carboxulic acid concentration determined by TFE deivatisation and XPS analysis of as-deposited (□), water rinsed (●) and hexane rinsed (△) polymers deposited from acrylic acid/1,7 octadiene plasmas.
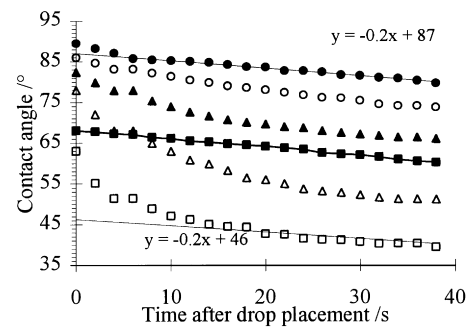
Fig. 7. Water contact angle against time for poly(acrylic acid) (■) and plasma-co-polymers of acrylic acid and octadiene over a range of monomer flow rates, $R = 0.19$ (□), 0.27 (△), 0.41 (▲), 0.51 (○), 0.7 (●).

4. Discussion

4.1. Absorption of water by ppAAc

Monitoring the deposit weight changes upon incremental deposition and venting with the QCMB enabled the water absorption from the atmosphere (RH = 30%) to be delineated from surface adsorption, illustrated in Fig. 2. The concentration of water absorbed by ppAAc produced at $P = 2$ W (4 wt%) was determined to be double that for deposits made at $P = 20$ W (2 wt%). Two factors may contribute to this significantly greater water vapour absorption by the 2 W deposit; (i) the greater concentration of oxygen functionalities in the $P = 2$ W deposit, and/or (ii) the lower degree of crosslinking known to exist in low P deposits [12]. However, our data does not allow us to determine which of these is the dominant factor. The weight increase, Δ, was almost instantaneous indicating very rapid diffusion though the full thickness of the polymer, suggesting that these coatings are highly permeable to water at both $P = 2$ and 20 W.

4.2. Interaction of ppAAc with the atmosphere immediately after deposition

In the literature on deposition of plasma polymers it is often stated that a period of exposure to the monomer vapour (soaking) is used after the plasma is extinguished and prior to exposure to atmosphere. This is intended to encourage reaction of radicals at the plasma polymer surface with monomer molecules rather than with atmospheric oxygen upon venting of the deposition chamber. This approach probably originates from the adsorption of atmospheric species with polymers after plasma ion etching [23]. In Fig. 1, a weight gain was observed after the plasma was extinguished, during exposure to acrylic acid vapour which was assigned to pick-up of monomer, (x_1-x_2). However, this pick-up was determined to be completely reversible upon evacuation of the chamber, i.e. the species were not chemisorbed. The same fully reversible physisorption was observed after deposition at $P = 20$ W (not shown). This indicates that significant reaction of radicals in the PP with adsorbed monomer does not occur under the conditions used in our reactor. Therefore, we propose that considerable etching of the polymer surface, which would be expected to generate highly reactive radical species, has not taken place. Moreover, the fully reversible nature of Δ, indicates that no reaction with atmospheric species occurs.

4.3. Solubility of ppAAc

The removal of virtually all of the ppAAc coating by ethanol rinsing is apparent in Fig. 3. However, there still remains a sub-nanometre coverage of PP. By XPS and FTIR analysis of this strongly adsorbed monolayer, we have identified interfacial complex formation between the carboxylic acid functionalities and hydroxyl functionalities at the aluminium surface, i.e.:
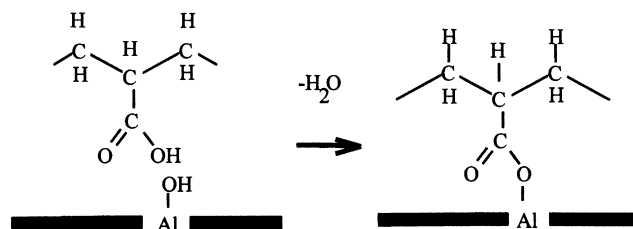
The characterisation of this reaction is reported in detail for poly(acrylic acid) and ppAAc on AlO(OH) within Ref. [15]. We propose that it is these bonds which cause this material to remain at the surface after rinsing with a solvent in which the bulk of the deposit is readily soluble.

Hence, we consider a coverage of less than 10 Å as a *baseline* representing a sample which is readily soluble. Using this criterium we class low P ppAAc to be readily soluble in water (Fig. 3). Increasing P produces less soluble ppAAc up to the point that the deposit withstands the water rinsing procedure to such a degree that no substrate signal was detected, $P = 20$ W. Although this indicates that we can obtain deposits which are relatively insoluble in water, we know that high P ppAAc coatings are dominated by ester functionalities [12]. Carboxylic acid functional deposits are potentially the most interesting because the acid functionality allows further chemical reactions, e.g. reaction with epoxy functionalities in adhesives to form interfacial covalent bonds [13,14,16]. Thus, we investigated the use of 1,7-octadiene as a co-monomer in the plasma to retain the carboxylic acid functionality.

4.4. Solubility of pp(AAc-co-Oct)

The 1,7-octadiene molecule may be considered as a diluent of carboxylic functionalities as it does not contribute carbon–oxygen functionalities to the deposit. This is consistent with decrease in the concentration of COOX functionalities in the deposits with the increase in R, presented in Fig. 4. The XPS analysis of the rinsed deposits, presented in Fig. 6 illustrates that addition of the 1,7-octadiene renders the deposits less soluble. This may be through the introduction of cross-links by the 1,7-octadiene as proposed by Canden et al. [19]. The inclusion of more hydrocarbon in the deposit, and the associated increase in the hydrophobic nature of the deposits may also contribute to the reduced solubility of ppAAc-co-Oct relative to ppAAc.

4.5. Mechanism of pp(AAc-co-Oct) deposition

We have previously determined that increasing P in acrylic acid plasmas results in a high concentration of ester functionalities in the deposit, i.e. the importance of esterification in deposit formation increases with increasing P [12]. Calculating the concentration of ester functionalities, from the TFE labelling data, for as-deposited samples

Table 1
The effect on the functional chemistry of a 2 W ppAAc deposit determined by TFE derivatisation and XPS. All concentrations are presented as a percentage of the total carbon concentration

Time in atmosphere before analysis	[CF$_3$/C(=O)OX]	[C(=O)OH]	[$\underline{C}$(=O)OC]	[C(=O)OH]/[$\underline{C}$(=O)OC]
4 minutes	0.82	23.1	5.0	4.6
1 month	0.78	20.3	5.7	3.5
2 month	0.71	19.1	7.6	2.5

we determined that it varied little for $R < 0.7$, i.e. [C(=O)O–R] = 5.5 + 1.4%. Thus, the mechanism of 1,7-octadiene incorporation does not appear to result in the formation of ester linkages in the deposit. Therefore, we conclude that the copolymerisation of the acrylic acid and 1,7-octadiene molecules occurs through the double bond present in both these molecules. Such a mechanism may easily be incorporated in the ion-molecule plasma-phase polymerisation mechanism proposed by O'Toole et al. where polymerisation through the double bonds of the acrylic acid molecule was detailed [10].

The concentration of the C–OX and C=O functionalities in the deposit was constant over the range of R as shown in Fig. 4. It was originally proposed that at $P = 2$ W these functionalities formed from the fragmentation of the acrylic acid molecule. However, should this be the case one would expect their concentration to decrease at greater plasma octadiene concentrations (R), when acrylic acid is more dilute in the plasma, which they do not. A significant amount of water has been detected by mass spectrometry in similar deposition apparatus to ours [10]. This was assigned to continuously water desorption from the PP coated walls of the chamber. Thus, we propose that these functionalities arise from incorporation in the deposit of oxygen originating from water in the plasma. Deposits with lower concentrations of these functionalities might therefore be obtained by reducing the residual water content of the deposition chamber.

Elsewhere we report the decrease in the ppAAc carboxylic acid concentration over a period of months exposure to the atmosphere [16]. These results are summarised in Table 1 which contains the carboxylic acid concentration, determined from TFE derivatisation, immediately after

production and after 1 and 2 month storage in ambient conditions. It is apparent that a 4% decrease in the carboxylic acid concentration occurs over 2 months for ppAAc ($P = 2$ W). An aroma, similar to that of acetic acid, is given off by ppAAc deposits suggesting that an acidic component of the PP is lost to the atmosphere. The reduction in the carboxylic acid concentration of a pure ppAAc plasma ($R = 0$) upon rinsing with a non-polar solvent (hexane) was also measured as 4%, see Fig. 6. This correlation with the reduction in carboxylic acid concentration of 4% measured over 2 months exposure of air is in agreement with our proposal that hexane, a non-solvent for polar species, removes loosely bound physisorbed material from the deposit surface. We propose that these are physisorbed oligomeric species. Species have been observed in the positive mass spectrum of low power acrylic acid plasmas containing up to 3 acrylic acid repeat units [10] and also in the SIMS spectra from such low P deposits [12]. By virtue of their low molecular weight such physisorbed species may evaporate over the long periods of time considered in Table 1. This is consistent with the observation that the carboxylic acid content of similar deposits was dependant on the PP surface area/roughness, reported recently in Ref. [19].

4.6. Response of pp(AAc-co-Oct) on contact with water

The method we have used to measure the contact angle normally provides a measure of the *equilibrium* contact angle, as distinct from either the advancing or receding contact angle where the vapour–water–solid point is intentionally moved. The data in Fig. 7 clearly indicate the term equilibrium may only be used if we consider that the surface changes with time, and therefore the equilibrium at the PP–water interface also changes with time. Such phenomena are not uncommon in polymeric materials. Thus we will consider the contact angles that we have measured to be at an instantaneous equilibrium with the surface, and thus characteristic of the surface at that point in time. For the purpose of comparison we have arbitrarily chosen contact angles data at time = 0 and 30 s. To illustrate the effect of surface acid functionality on contact angle we combine the data determined by XPS and derivatisation (Fig. 6) with the contact angles and present them in Fig. 8. The trends for both the initial and 30s measurements illustrate that a higher concentration of carboxylic acid (lower R) is associated with a low contact angle.
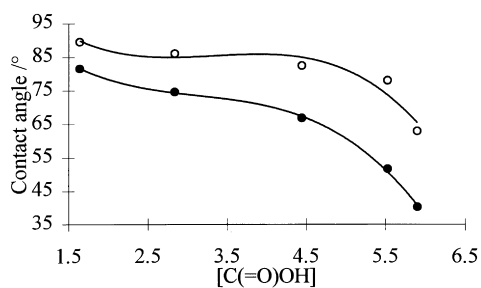

Fig. 8. The water plasma-co-polymer contact angle measured immediately after the drop was placed on the sample (○) and 30 s after (●) plotted against the carboxylic acid concentration determined by XPS and TFE derivatisation.

The initial rapid drop in contact angle observed for all ppAAc-co-Oct samples may be caused by reorientation of polar groups at the PP–water interface and/or the absorption of water into the deposit, in the same way that water vapour absorption occurred upon exposure of ppAAc to air. We favour the latter explanation because the rotational freedom of the carboxylic acid functionalities in ppAAc should be of the same order as those in PAA (where a purely linear decrease in ϑ is observed). This interpretation is consistent with the observation that the initial decrease in ϑ, before a linear decrease is attained, becomes smaller as the acrylic acid content, and therefore the water absorption capability, decreases at higher values of R in Fig. 7.

It is apparent from Fig. 8 that the ϑ is lower for higher carboxylic acid concentration on the ppAAc-co-Oct samples. Given that the concentration of C–OX and C=O change little in the rinsed deposits, as determined in Section 3.2, we can assign the decrease in ϑ primarily to the effect of the carboxylic acid functionalities, i.e. a decrease of ϑ from $80°$ to $40°$ was achieved for an increase in [COOH] of 4%.

The concentration of carboxylic acid functionalities at $R = 0.19$ (with the lowest contact angle in Fig. 7) is 1/5 that of PAA, yet it exhibits a lower initial contact angle than PAA. The lower concentration of acid at the ppAAc surface would be expected to be associated with an initial ϑ than that of PAA. This discrepancy suggests that a very rapid initial water absorption into the PP occurs, i.e. our time $= 0$ s measurement is in error, with the actual value significantly higher but not measurable using this method. Additionally, absorption of atmospheric water vapour may contribute to this effect by reducing the contact angle through its presence in the near surface region.

The contact angle experiment provides an assessment of the wettability of a surface. The wettability of a surface is often related to the adhesion between the surface and material deposited on them [4]. This ability to control the wettability of surfaces using ppAAc-co-Oct coatings will make these coatings applicable in adhesion promotion and to the investigation of adhesion. Mechanical testing of joints fabricated using ppAAc-co-Oct coatings is to be carried out to investigate the relationship between contact angle measurements, functional composition of the PP and adhesive bond strength.

5. Conclusions

Upon exposure to atmosphere (RH = 30%) after deposition, deposits of ppAAc were observed to absorb up to 4 wt% of water. The equilibrium concentration of absorbed water depended on the chemistry of the deposit and the RH of the air. High water absorption correlated with a high concentration of carboxylic acid functionalities (determined by XPS) and low crosslinking (estimated by SIMS). Adsorption of water and acrylic acid vapour immediately after deposition was found to be fully reversible. Thus, we conclude that the concentration of radicals at the deposit surface is not significant in our system, and that soaking of the deposit prior to venting of the chamber is not necessary.

Two means of reducing the solubility of ppAAc in water were identified; increasing the deposition power, and by using a 1,7-octadiene co-monomer. The former approach correlated with an increase in cross linking and ester formation in the deposits coincident with a reduction in the concentration of carboxylic acid functionalities. Co-plasma polymerisation to form ppAAc-co-Oct resulted in deposits with [C(=O)OH] $\leq$ 6% (determined by TFE derivatisation) but no increase in the concentration of ester functionalities. Based on the change in the deposit functional composition with increasing octadiene content of the plasma, we propose that copolymerisation occurs through the unsaturation in the acrylic acid and 1,7-octadiene molecules.

The loss of carboxylic acid functionality from ppAAc, over a period of 2 months exposure to atmosphere after deposition, was correlated with the polar material removed upon rinsing in a non-polar solvent. We propose that physisorbed oligomeric species are the species which evaporate in the former process and that in the latter process it is the same species that are removed by rinsing.

A rapid initial contact angle reduction occurred immediately after a water drop was placed on ppAAc-co-Oct surface. From comparison with the atmospheric moisture absorption of these materials we attributed this phenomena to rapid absorption of water from the drop. By varying R, initial contact angles greater and less than that of PAA were obtained on ppAAc-co-Oct.

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