Differences in the Aging of Allyl Alcohol, Acrylic Acid, Allylamine, and Octa-1,7-diene Plasma Polymers As Studied by X-ray Photoelectron Spectroscopy

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Thin organic films were deposited from plasmas of allyl alcohol, acrylic acid, allylamine, and octa-1,7-diene onto aluminum substrates. These plasma polymerized films were analyzed by X-ray photoelectron spectroscopy (XPS) before and after prolonged periods of storage under laboratory atmosphere to attempt to quantify changes in surface chemistry as a result of aging over 400 days. Plasma polymers produced from octa-1,7-diene and allylamine showed a distinct uptake of oxygen during the first 30 days post-polymerization, gradually leveling off but not appearing to reach a stable level. In addition, the allylamine plasma polymers showed a loss of nitrogen. Those polymers produced from allyl alcohol and acrylic acid plasmas did not show any changes with time in their oxygen content, or in the composition of their C 1s core levels. While the aging seen in the hydrocarbon plasma polymer and the nitrogen-containing plasma polymer is broadly consistent with what has been previously reported in the literature for similar materials, the aging of plasma-polymerized allyl alcohol and acrylic acid is quite different. The data highlight the differences in aging between different monomers plasma polymerized under the same reactor conditions, and "alike" plasma polymers deposited using very different experimental setups (reactor geometry, power coupling, and frequency).

Introduction

Plasma polymerization has proved popular as a means of modifying the surface chemistry of materials. Depositing ultrathin films with a specific chemical functionality without the need for solvents has found use in a wide range of applications. Plasma polymers have been used as dielectric films[1,2] and protective coatings[3,4] and are being utilized in applications where a clean processing environment is necessary. Plasma polymers may be used to modify the surface properties of materials without compromising the bulk characteristics, leading to improvements in composite material properties.[5] Plasma polymers have been used even more extensively in the field of biomaterials,[6−9] both in vitro as substrates for cell culture,[10,11] surfaces to promote or prevent protein adsorption[12,13] and as membranes for biosensors,[14] and in vivo as coatings for contact lenses[15] and biocompatible implants.[10,16] In all of these applica-

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tions, particularly those in the medical devices field, it is often necessary to store samples for extended periods before they are used. Therefore, it is important to examine how these materials change as a function of time.

Plasma polymers may differ markedly from conventional polymers. Rather than consisting of regular repeat units, a plasma polymer may contain a wide range of functional groups introduced as a result of fragmentation of the precursor in the plasma. It is often stated that plasma polymers are highly cross-linked rigid structures;[17] however, this is not always the case. Ward and Short[18] and Alexander and Duc[19] have both demonstrated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) that polymers deposited from methyl methacrylate and acrylic acid plasmas, respectively, can be structurally and chemically very similar to their conventional counterparts. In both these studies, plasma polymerization was carried out under low power conditions at an rf frequency of 13.56 MHz.

Plasma polymers have been produced and analyzed from a wide variety of different monomers.[20−34] In addition, workers have utilized different excitation regimes for their plasmas, and investigated the effect of deposition parameters upon the chemistry of the final product. It has been demonstrated that the chemistry of the final product can be significantly altered by controlling several deposition parameters. Plasma power,[35] substrate temperature,[36] substrate position,[37] reactor pressure and geometry,[38] plasma on−off times[39,33] (in pulsed experiments), and monomer flow rate[35] have all been shown to have an effect. Although these effects have been well-described, the subsequent changes in surface chemistries with time have not.

The aging of plasma polymers has been investigated by Gengenbach et al., who studied the postdeposition properties of ethylenediamine,[40] diaminopropane,[41] *n*-heptylamine,[42] methyl methacryate,[24] and *n*-hexane[17] plasma polymers. These plasma polymers were produced in a parallel plate radio frequency system operated at a frequency between 100 and 225 kHz and powers of 5−20 W. They observed an increase in oxygen content of their ethylaminediamine plasma polymer films over a period of 100 days, and in the same period a slight loss of nitrogen. Initially the films had an O/C ratio of less than 0.05 but by 100 days this had increased to 0.2. At the same time, the N/C ratio fell from around 0.42 to 0.35. The presence of nitrogen and oxygen functionalities together makes it difficult to be specific about the surface chemistry when analyzed by XPS. By measuring the position of the N 1s photoelectron peak relative to that of the C 1s, using the method of Wagner et al.,[46] they demonstrate that the freshly prepared surfaces contain mostly amine and imine functional groups, which appear to hydrolyze over time, leading to a shift in the mean N 1s binding energy toward higher binding energy. This N 1s binding energy shift is indicative of the presence of amide groups in aged surfaces, and this shift is also observed in the *n*-heptylamine and diaminopropane plasma polymers. In the aging of methyl methacrylate surfaces, an uptake of oxygen was observed, with surfaces produced using a higher power exhibiting more marked changes in surface chemistry. This uptake of oxygen is mirrored in the aging of *n*-hexane surfaces.

Candan et al.[37] examined the aging of acrylic acid plasma polymers over a period of 90 days; however, the aging of these films manifests a loss of oxygen. The loss of oxygen is fairly rapid, appearing to reach a stable level after approximately 30 days. This is also observed by Alexander and Duc[28] who suggest that the changes are caused by the evaporation of physisorbed oligomeric species.

This paper aims to examine the changes with sample age in the surface chemistry of plasma-polymerized allyl alcohol, acrylic acid, allylamine and octa-1,7-diene produced under nominally identical deposition conditions (power, flow rate, reactor pressure) over a period of around 400 days.

These particular materials were chosen for several reasons. Octa-1,7-diene was used to give a hydrocarbon control surface comparable to other hydrocarbons used by other workers.[17] Plasma polymers of acrylic acid have been used with considerable success as substrate materials for in vitro cell culture,[7] and allyl alcohol and allylamine[47] plasma polymers have both been used extensively in protein adsorption studies. Additionally, these four materials provide surfaces which differ substantially from each other in terms of their functionality when polymerized under indentical plasma conditions.

Experimental Section

1. Plasma Polymerization. Allyl alcohol, acrylic acid, allylamine, and octa-1,7-diene were obtained from Aldrich (Gillingham, UK). They were used as received, save several freeze−thaw cycles to remove dissolved gases prior to use. The substrate for plasma polymerization was aluminum foil, which was cleaned with acetone and isopropyl alcohol immediately before use.

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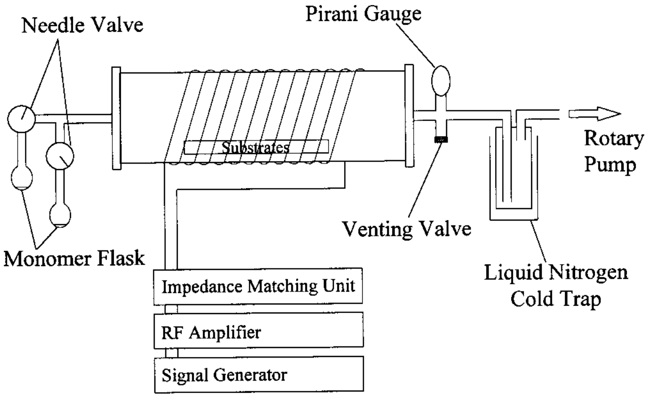

Figure 1. Schematic diagram of the plasma polymerization apparatus.

A diagram of the reactor is show in Figure 1. Plasma polymerization took place in a cylindrical (10 cm internal diameter and 50 cm length) glass reactor capped with two earthed brass flanges. The reactor was connected to a vacuum pump and liquid nitrogen cold trap. Radio frequency power (13.56 MHz) was coupled to the reactor via an impedance matching unit and a copper coil wound externally. The substrates were placed in the "in-coil" region of the reactor and the vessel was pumped down to a base pressure of 3 × 10^{-3} mbar.

Monomer flow rates were controlled by a needle valve and estimated by measuring the increase of pressure in the reactor when isolated from the vacuum line. This pressure change is converted to a flow rate using the method described by Yasuda[38] which assumes idea gas behavior and gives an estimate of monomer flow rate in $\mathrm{cm^3_{(stp)}\ min^{-1}}$.

All of the plasma polymers produced for this experiment used a constant monomer flow rate of 1.5 $\mathrm{cm^3_{(stp)}\ min^{-1}}$ at a pressure of approximately 1.5×10^{-1} mbar and a plasma power of 5 W. Depositions took place for a period of 15 min, which has been found to be enough time to provide deposits of sufficient thickness to obscure all substrate signals from the XPS spectrum.

2. X-ray Photoelectron Spectroscopy. XPS was performed using a VG Clam 2 X-ray photoelectron spectrometer operating in constant analyzer energy mode with a dual anode utilizing Mg Kα X-rays at a power of 100 W. The spectrometer has a base pressure better than 10^{-9} mbar and a normal operating pressure of better than 10^{-8} mbar. The instrument is calibrated monthly using a clean gold sample to measure the resolution of the instrument. (At 20 eV pass energy the Au $4f_{7/2}$ peak has a width of ~1.1 eV.) Relative sensitivity factors are measured monthly using a variety of standard polymeric samples. This allows us to quantify the elemental composition of the plasma polymer surfaces.

A constant take off angle of 30° with respect to the sample surface, was used for all the samples. A survey spectrum was recorded using a pass energy of 100 eV to determine the elemental composition of the plasma polymer surfaces. Core level scans were then taken of all regions of interest (carbon, oxygen and nitrogen core levels where appropriate) at a pass energy of 20 eV.

The data were analyzed using Scienta software (Uppsala, Sweden), and Gaussian–Lorenzian component peaks were fitted to the C 1s core level spectrum using well-established chemical shifts.[43] The hydrocarbon component peak was set at 285.0 eV to correct for any sample charging (typically 4–5 eV).

Results

XPS survey scans of all the plasma polymer surfaces show only the presence of carbon and oxygen (and nitrogen for the allylamine plasma polymers), illustrating the conformal nature of the films. It is worth noting that plasma polymers deposited from octa-1,7-diene still contain a significant (up to 5%) amount of oxygen. This oxygen is incorporated into the film immediately upon exposure of the films to the atmosphere before they can be analyzed by XPS. Also, the presence of H_2O and residual O_2 in the reactor during polymerization could lead to the formation of oxygen-containing groups during plasma deposition. It is reasonable to assume that the similar amount of oxygen also incorporated into the allylamine plasma polymer came from the same sources. The widescans were used to determine the surface O/C ratio of the plasma polymers and the C 1s core level scans were fitted to obtain functional group information.

A peak-fitted C 1s core level spectrum from an allyl alcohol plasma polymer is shown in Figure 2. The scan has been corrected for charging by setting the hydrocarbon component (*C*–C) peak to 285.0 eV. The peak fitting procedure used chemical shifts from the literature to guide the iterative routine to a chemically meaningful solution rather than a mathematically cor-

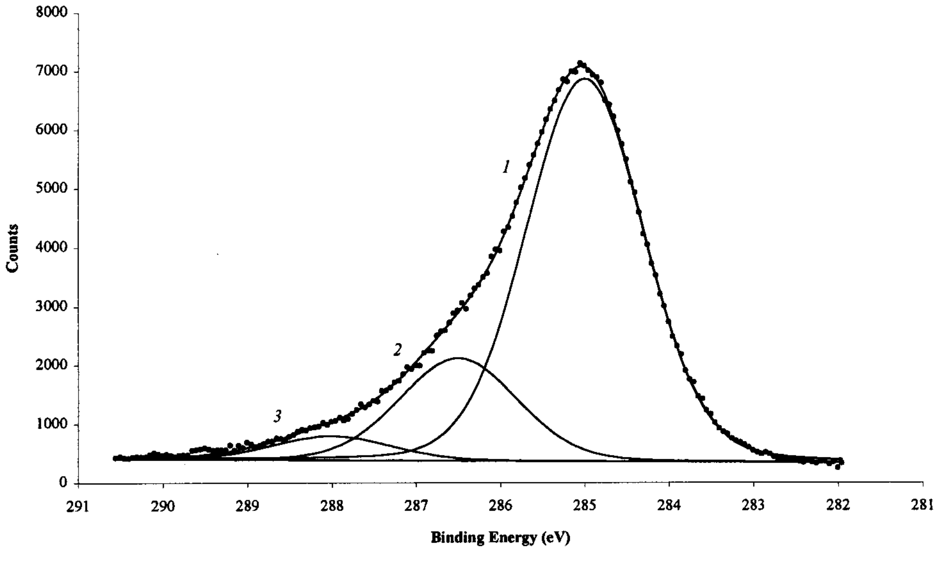

Figure 2. C 1s core level of an allyl alcohol plasma polymer.

Table 1. Results from Curve Fitting the C 1s Region of As-Prepared Plasma Polymers[a]

monomer	C−C, %	C−O, %	C=O, %	COO, %	% retention
allyl alcohol	74.2 ± 1.9	21.0 ± 1.6	4.9 ± 0.3		64
acrylic acid	53.8 ± 2.7	11.4 ± 1.8	5.7 ± 1.7	14.6 ± 1.2	44
octa-1,7-diene	94.1 ± 1.0	5.9 ± 1.0			

[a] Data given as mean ± SD ($n = 8$).

rect one. For the allyl alcohol plasma polymers, three component peaks were fitted to the data; peak *1* at 285.0 eV represents *C*−C, or hydrocarbon environments, peak *2* at 287.5 eV (a chemical shift of 1.5 eV) represents *C*−OH/R functional groups, and peak *3* at 288.0 eV (3.0 eV shift) represents *C*=O groups. The results of curve fitting the C 1s regions of the acrylic acid, allyl alcohol, and octa-1,7-diene plasma polymers are summarized in Table 1.

The exact form of the C−OH/R peak is not clear from XPS data. Theoretically, this chemically shifted peak could originate from hydroxyl or ether functional groups. Work by Ameen et al.[20] and later Rinsch et al.[39] used trifluoroacetic anhydride labeling to show that the majority of −OH/R groups present under these mild deposition conditions are not ether groups, and hence are most likely hydroxyls retained from the monomer structure. However, it is not possible to comment on the similarly assigned peak in the octa-1,7-diene C 1s core level. For the acrylic acid C 1s regions, an additional two peaks were used; *C*OOH/R at a shift of 4.4 eV and a β-shift corresponding to *C*−COOH/R at an energy of 0.7 eV. On the basis of labeling experiments using trifluoroethanol, Alexander and Duc[28] suggest that the majority of these groups are carboxyl in nature.

Figures 3−6 show the O/C ratios or allyl alcohol, octa-1,7-diene samples, acrylic acid, and allylamine aged under laboratory atmosphere. Included in Figure 5 are the changes in the N/C ratio with time. For all figures, the first data point represents an average of eight different samples produced at different times, but under identical deposition conditions, to give some indication of the repeatability of the polymer deposition. The errors bars represent one standard deviation taken from the first data point.

Figures 7−9 show the C 1s component peaks present in the aged allyl alcohol, acrylic acid, and octa-1,7-diene plasma polymers, respectively. The hydrocarbon con-

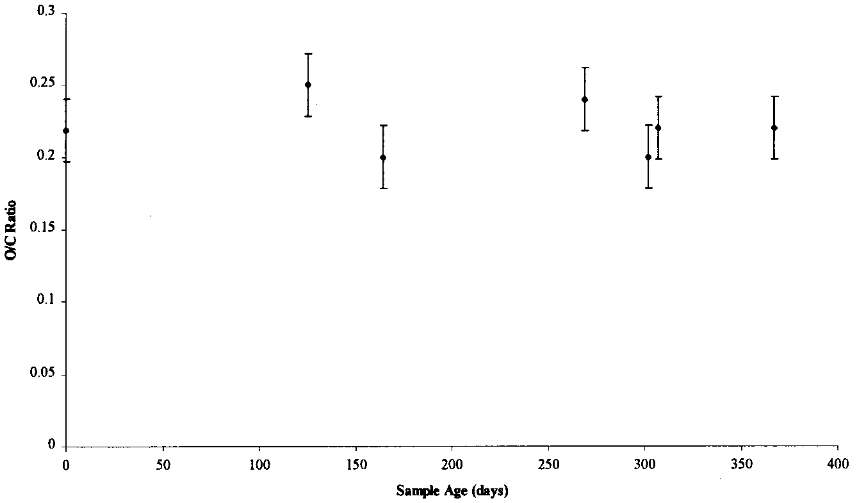

Figure 3. O/C ratio of allyl alcohol plasma polymers as a function of sample age.

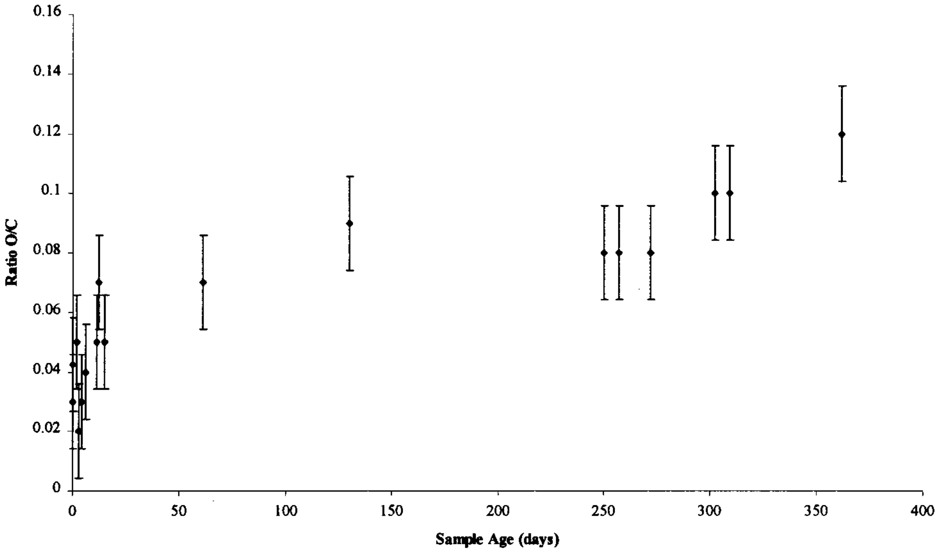

Figure 4. O/C ratio of octa-1,7-diene plasma polymers as a function of sample age.

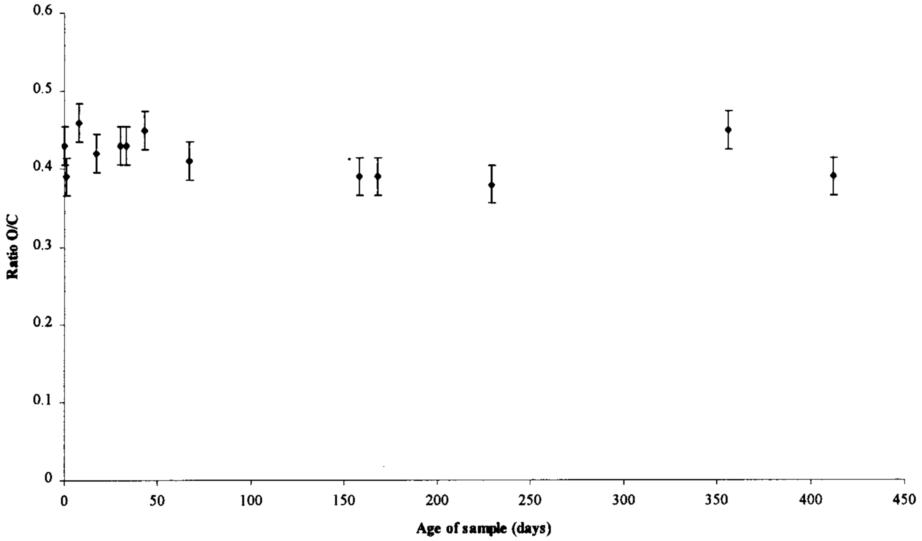

Figure 5. O/C ratio of acrylic acid plasma polymers as a function of sample age.

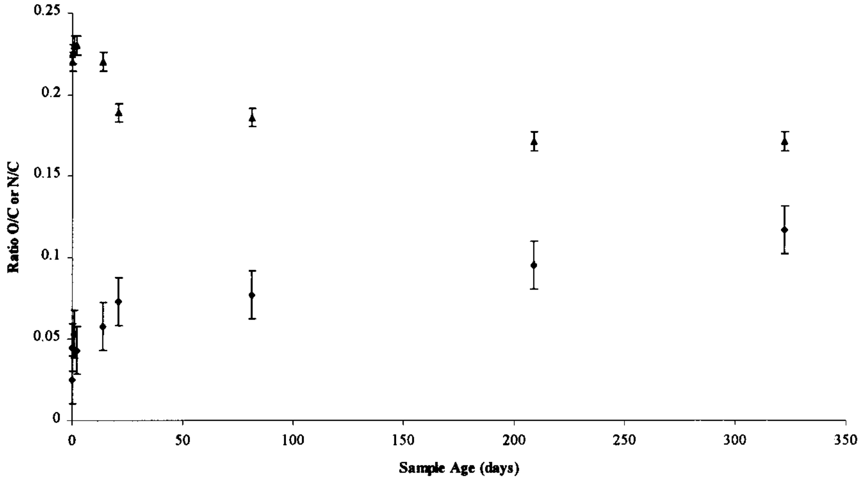

Figure 6. O/C ratio (diamonds) and N/C ratio (triangles) of allylamine plasma polymers as a function of sample age.

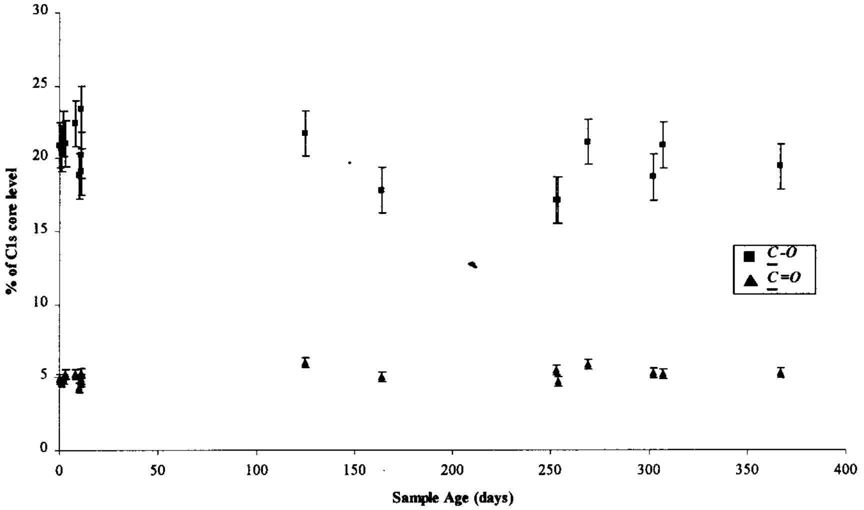

Figure 7. C 1s component peaks in allyl alcohol plasma polymers as a function of sample age.

tribution has been removed for clarity, since it constitutes the remainder of the core level peak area.

Since allylamine plasma polymers contained both nitrogen and oxygen functional groups there was considerable overlap between probable peaks in the C 1s region making curve fitting difficult. The position of the N 1s photoelectron peak relative to that of the C 1s has been used by other workers[40] as an indicator of the functional groups present. We measured the separation of the C 1s and N 1s peaks by fitting Gaussian–Lorentzian curves to each region by an nonlinear least-squares method. Measurements of the relative position

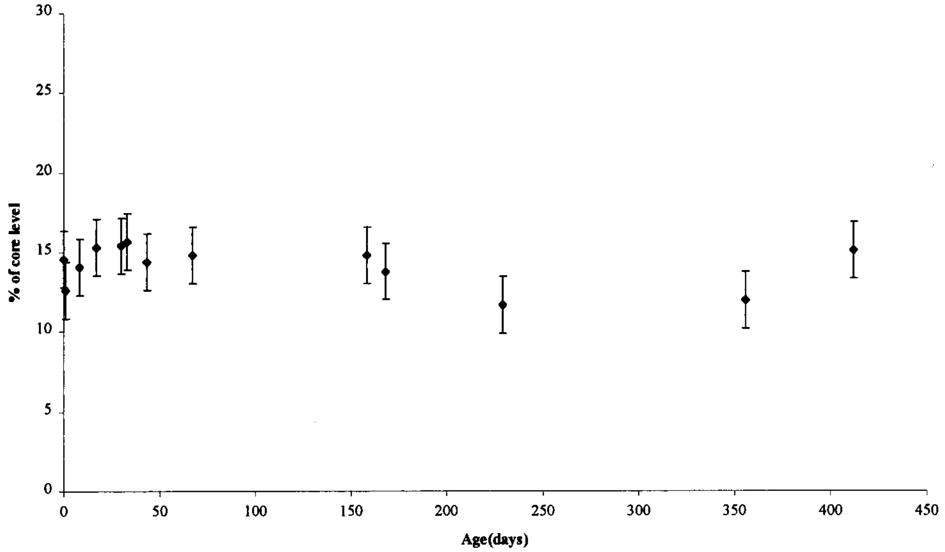

Figure 8. −*C*OOR component of the C 1s region of acrylic acid plasma polymers as a function of age. The other components have been removed for clarity, but follow the same trend.

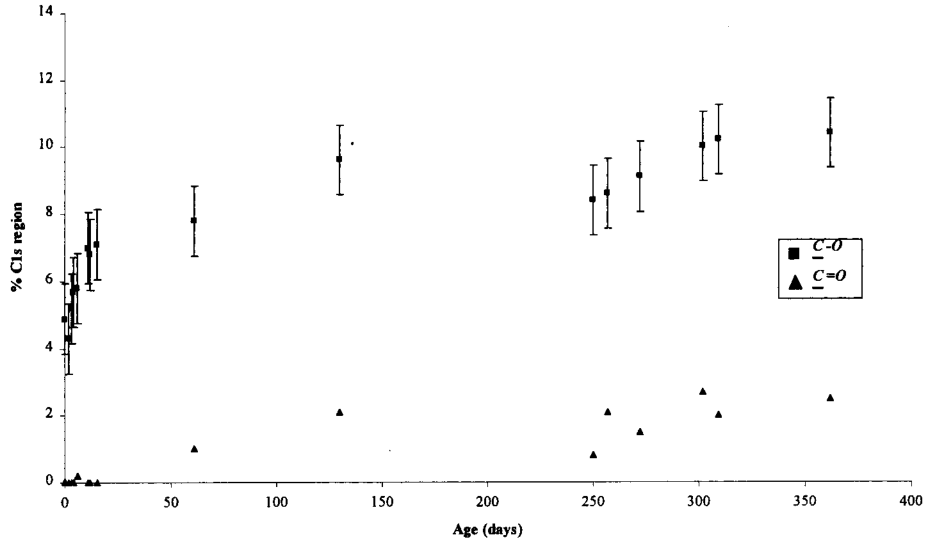

Figure 9. C 1s component peaks in octa-1,7-diene plasma polymers as a function of sample age.

of the N 1s and C 1s peaks by this method show a definite change over time. The mean binding energy of the N 1s region increases by around 0.19 eV from an initial 399.37 eV (±0.08 eV) over the aging period (322 days). This represents a change in the chemical environment of the nitrogen in the surface, from being dominated by amine/imine functionalities toward amide.

Discussion

No significant change was observed in the O/C ratios of allyl alcohol or acrylic acid plasma polymers with sample aging (up to 350 days). It may be that any actual changes are too slight in comparison with the experimental variations. These variations are mostly due to the fact that each data point represents a different sample, produced under the same conditions but at a different time. A further possibility is that any changes in the surface chemistry occur extremely quickly upon exposure to the atmosphere, before the initial analysis can take place. Examination of the C 1s regions of the allyl alcohol and acrylic acid plasma polymers show that there are no changes in the relative amounts of the various functional groups, supporting the idea that the surface chemistries of these products remain constant with aging. It does not rule out, however unlikely, the possibility of several competing processes (e.g., loss of volatiles, oxidation) effectively balancing each other in these plasma polymers. This result is in contrast with the results presented by Candan et al.[37] for pp(acrylic acid) and with those of Gengenbach et al.[42] for pp(methyl methacrylate).

The apparent loss of oxygen from the plasma polymers of Candan et al. is relatively small (the change in O/C ratio is less than 0.05 over 30 days) and may be caused by the desorption of low molecular weight oligomers from the surface. The evaporation of low molecular weight material from similar acrylic acid plasma polymers has been observed by variable-temperature ellipsometry.[44]

In the post-plasma oxidation of pp(methyl methacrylate) produced at 5 W input power and a frequency of 200 kHz, Gengenbach et al.[24] reports an increase in O/C from 0.25 to 0.34 over 300 days. Although we have not undertaken a systematic study of pp(methyl methacry-

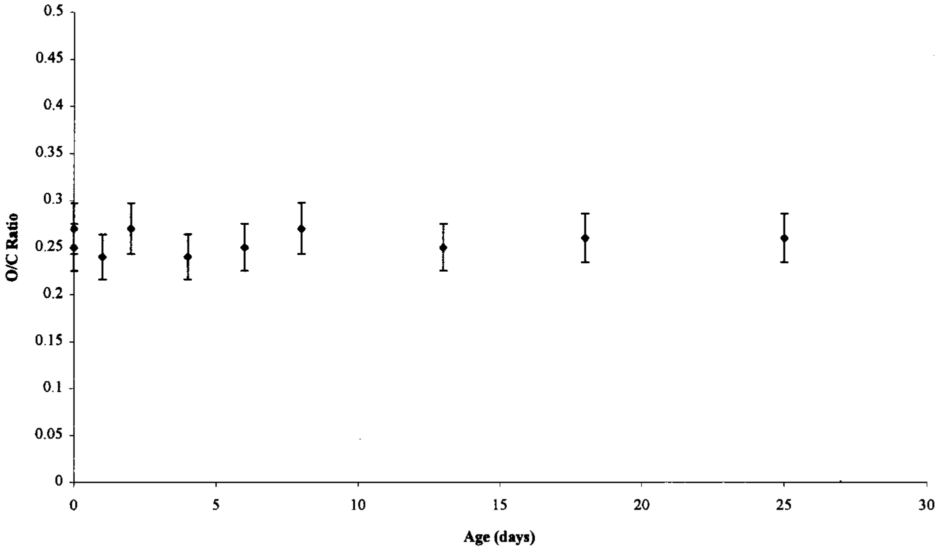

Figure 10. O/C ratio of methyl methacrylate plasma polymers as a function of sample age.

late), over short periods of time (<30 days) no noticeable aging has been observed.[45] In this respect, pp(methyl methacrylate) produced in our laboratory (at a frequency of 13.56 MHz and <5 W input power) would appear to behave similarly to the pp(acrylic acid) and pp(allyl alcohol) reported in this study. The O/C ratio of methyl methacrylate plasma polymers over a period of 30 days is shown in Figure 10. Analysis of the C 1s region of this plasma polymer show that it consists of around 8.5% −*C*OOR character.

Although the plasma polymers produced for this study and those described by Gengenbach et al. are produced under comparable W/F conditions, they are quite dissimilar in their aging, suggesting that the W/F parameter is not as useful in comparing deposits from different systems as has been previously thought. Our results show that it is possible to produce plasma polymers under these mild conditions that do not age significantly. It is generally inappropriate, therefore, to compare samples produced in systems where there are differences in the deposition plasma environment. The effects of even small differences in reactor geometry, plasma frequency, power coupling, etc. on the ion fluxes and energies, UV and VUV fluxes and the composition of various species within the plasma, are difficult to predict and probably need to be measured before comparisons can be made between separate systems.

The polymers deposited from non-oxygen-containing precursors do show a very clear change in elemental composition with time. Both show a sharp uptake of oxygen over the first 30 days post-polymerization, with the O/C ratio continuing to rise more slowly after that time. In the case of the allylamine plasma polymer this is accompanied by a loss of nitrogen from the surface, indicating an exchange of nitrogen with atmospheric oxygen. The position of the N 1s photoelectron peak relative to that of the C 1s peak changes as the samples age, increasing from a mean position of 399.37 eV to around 399.56 eV. This shift indicates a fall in the number of amine (399.0 eV) and imine (399.1 eV) functional groups relative to the number of amide groups (399.9 eV) over time. These results are in agreement with those previously published by Gengenbach et al.[40−42] for other amine-containing plasma polymers. The C 1s region of the octadiene plasma polymer shows oxygen initially incorporated in the form of C−O groups, but with C=O groups beginning to appear after longer times (50 days).

There are clear differences then between the behavior of allyl alcohol and acrylic acid plasma polymers and that of the allylamine and octadiene films with respect to aging.

The mechanism by which we would expect oxygen to be incorporated over time is by the reaction of atmospheric oxygen with long-lived reactive species within the surface. The most likely form of these are radicals trapped in the plasma polymer during the treatment. An excellent description of these oxidative processes is given by Gengenbach et al.[17,41]

The reason for the different aging behavior in the plasma polymers of acrylic acid and allyl alcohol and plasma polymers of 1,7-octadiene and allylamine is not known. It might arise from differences in the plasma-phase chemistry (e.g., oxygen quenching of free radicals in plasmas of acrylic acid and allyl alcohol) or differences at the plasma boundaries (e.g., higher ion and/or energy fluxes at depositing surfaces in the case of 1,7-octadiene and allylamine plasmas). The data are not yet available to determine which of these possibilities is in fact the case.

Conclusions

The wider application of plasma polymers relies on their long-term properties. While in research it may be practical to produce surfaces as required, it is manifestly impractical on a larger scale. For this reason it is important that the changes in surface chemistry with time are more fully understood, particularly in application where specific surface functionalities are required.

The aging characteristics of a particular plasma polymer surface depends heavily on the conditions employed during its deposition. We have shown that for allyl alcohol and acrylic acid plasma polymers under typical deposition conditions in our laboratory there is little detectable change over time. Allylamine and octadiene plasma polymers in contrast demonstrate an initial sharp uptake of oxygen, which levels off after 30 days, but does not appear to reach a stable level. Allyl amine surfaces also manifest a loss of nitrogen over the same period. Our results for some monomers are not consistent with those previously described in the literature, hence, the aging characteristics of a particular plasma polymer are not constant, but vary depending on the apparatus used to deposit them. The parameters which dictate the aging properties of these deposits are not yet known.

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