

7. Aging of plasma deposited polymer films

7.1. Introduction

Plasma deposited polymer films have a significant amount of active surface species, radicals and non-radicals, that play a role in the development of the chemistry of the polymers when they are exposed to air. This process is normally described as “aging”. For most of the technological applications of plasma deposited films, the films are not expected to be under vacuum but would be exposed to ambient air. It is therefore necessary to monitor the changes in the film chemistry with time of exposure. This section deals with the aging phenomena of plasma deposited organic films using the analytical procedures that were used for “in-situ” characterization of the films in chapters 5 and 6. The same plasma deposited polymer films described in chapters 5 and 6 were analyzed at different intervals of exposure time for this study.

7.2. Aging of plasma deposited homopolymers

7.2.1. Aging of plasma deposited ethylene films

On exposure to air the plasma deposited ethylene films were found to uptake oxygen. This was monitored using the O/C atomic ratio obtained from XPS survey scans of the samples analyzed at different intervals of exposure time. As an example Figure 7.1a shows the survey scans of sample X-PDE2 prepared at “mild” plasma conditions and air-exposed over periods of time. Figure 7.1b displays the change in the O/C atomic ratio with time. The slope of the curve plotted in Figure 7.1b is large for the first week (first three data points) and then it decreases indicating saturation in the oxygen uptake. This reflects the kinetics of the consumption of the surface radicals with time. The oxygen uptake by the films can also be followed from the valence band spectra as shown in Figure 7.1c for X-PDE2. The O2s feature is found to increase in intensity as the oxygen content in the films increases with time. It is known that the reaction of molecular oxygen from the air with C radical sites would result in the formation of peroxy radicals (Equation.7.1) and subsequently, hydroperoxides (Equation.7.2).



Hydroperoxides may then decay or rearrange to form many kinds of oxygen functionalities for example C-O, C=O, COOR species, etc. This process is known as “auto-oxidation”. A

more detailed reaction scheme of the oxygen uptake and auto-oxidation process is given in Figure 7.2.

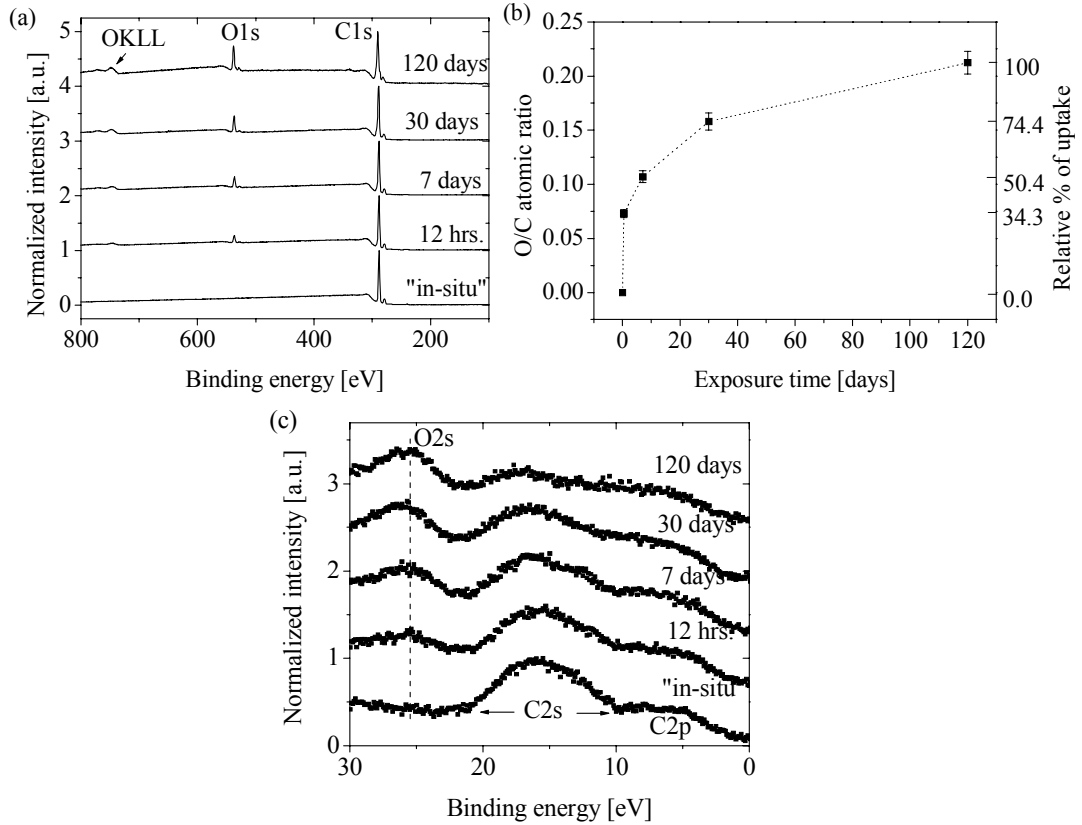


Figure 7.1: XPS of aged plasma deposited ethylene film X-PDE2 (cf. Table 3.1 for deposition parameters). (a) XP survey scans for the plasma deposited ethylene film X-PDE2 (20W, 5 Pa, 0.25 duty cycle) (b) XPS O/C atomic ratio vs. exposure time for X-PDE2. (c) XPS valence band spectra for X-PDE2.

The extent of oxygen uptake by each sample considered in chapter 5 (section 5.2.1) was monitored. The saturated O/C atomic ratio (after 120 days of exposure) is plotted in Figure 7.3. It can be observed that this ratio was found to depend on the deposition parameter employed during the preparation of the plasma deposited ethylene films. The samples prepared at "hard" plasma conditions such as high duty cycle and high power show a large change in O/C ratio or a large uptake of oxygen. This is due to a higher concentration of surface radicals on the films prepared at "hard" plasma conditions.

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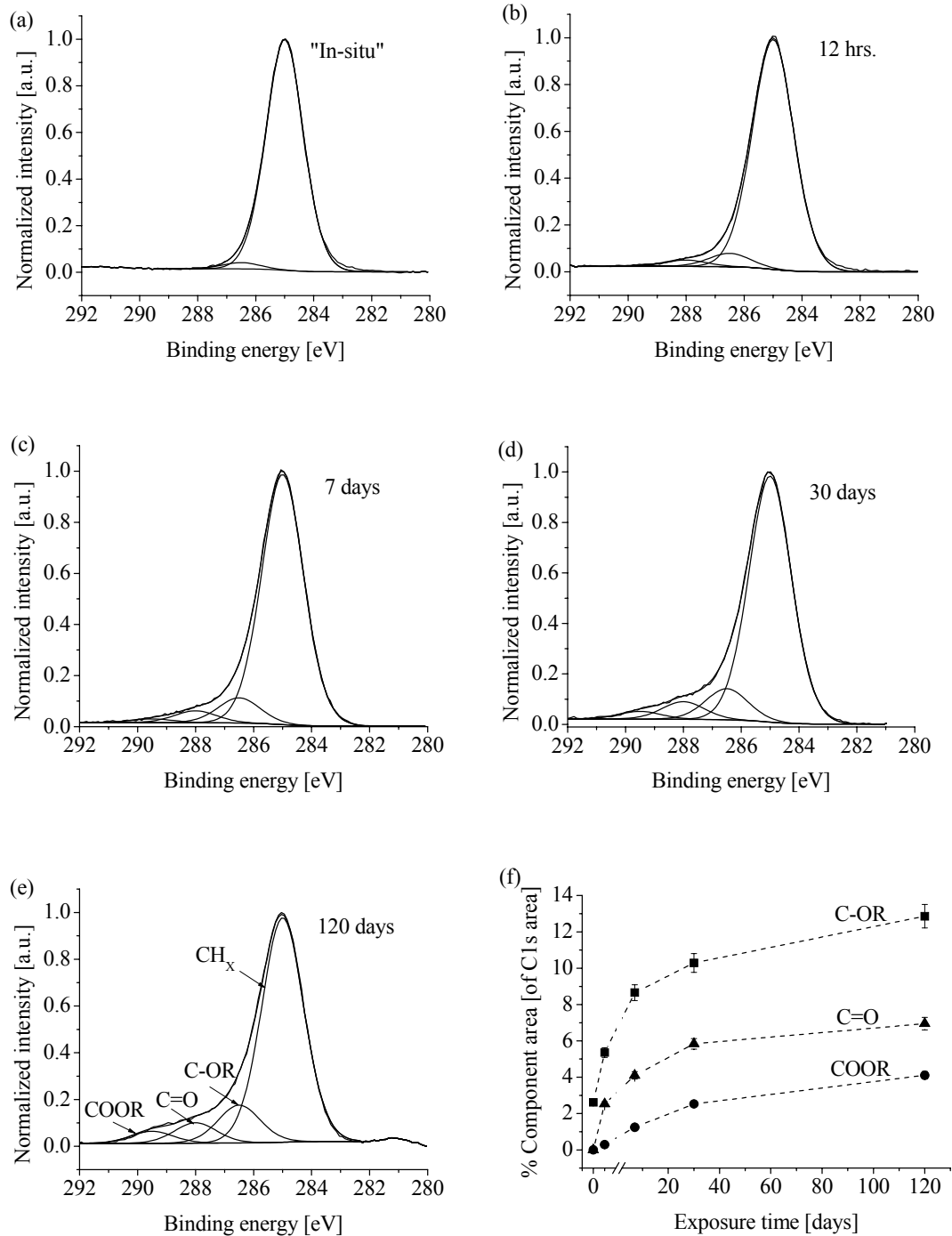


Figure 7.4: (a)-(e) XPS C1s spectra for the plasma deposited ethylene film X-PDE2 (20W, 5 Pa, 0.25 duty cycle) measured “in-situ” and at different intervals of air exposure time. (f) Component areas of the C1s spectra of X-PDE2 vs. exposure time.

The formation of oxygen functionalities as depicted in Figure 7.2 was monitored for the films from the XPS C1s spectra after peak fitting. Figure 7.4 shows the formation of such oxygen functionalities in the case of X-PDE2 with time. It also gives the change in the area of various component curves of the C1s photoemission spectrum of X-PDE2 with the

increase in exposure time. In the first weeks the rate of formation ($\Delta\text{COR}/\Delta t$) of C-OR species is higher than the rate of formation of other functionalities (the respective slopes of the plots). Later the rate of formation of all the functionalities decreases and then levels off. This behavior is in accordance with the O/C atomic ratio which also levels off after long exposure to air (Figure 7.1b). This reflects the kinetics of simultaneous oxygen uptake and auto-oxidation by the film.

The branching and cross-linking condition of the film was followed by comparing the FWHM of the CH_X component at different intervals of exposure time. Figure 7.5 shows a high increase of the FWHM of X-PDE2 during the first few weeks and then it tends to level off. Along with the formation of various oxygen functionalities this might also be because of a higher degree of branching and cross-linking of the films occurring during the first few weeks when the number of available radicals is high. The fact that branching and/or cross-linking of the samples is increased on exposure to air, is also emphasized in Figure 7.6 that shows the change in FWHM for all the plasma deposited ethylene samples. The FWHM of the CH_X component of all the plasma deposited samples increases on exposure to air. However, a definite conclusion about any branching or cross-linking cannot be derived from this data alone.

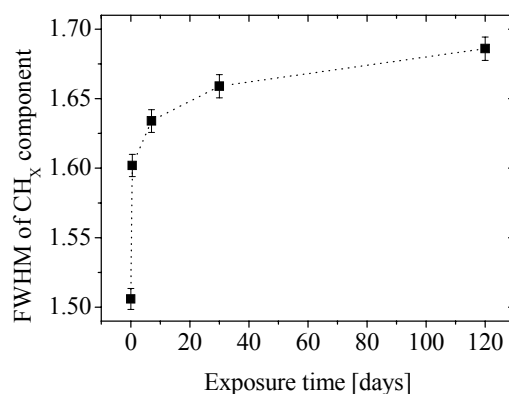


Figure 7.5: FWHM of the CH_X component of C1s XP spectra of the plasma deposited ethylene films X-PDE2 (20W, 5 Pa, 0.25 duty cycle) vs. aging time in air.

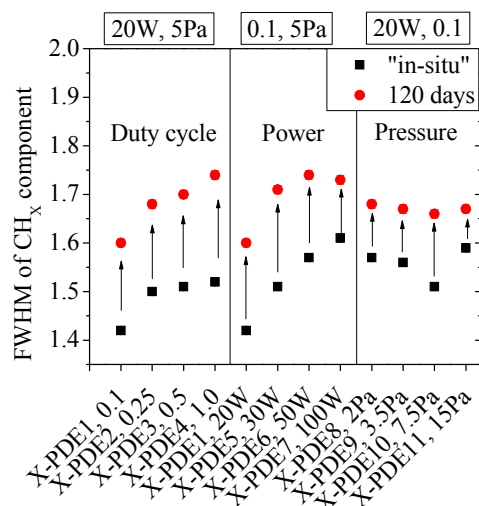


Figure 7.6: FWHM of CH_x component for all the plasma deposited ethylene (X-PDE) films studied for aging in air for 120 days (cf. Table 3.1 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

The changes in the degrees of unsaturation of the films was monitored by following the change in the area of C1s $\rightarrow\pi^*_{(C=C)}$ resonance, over a period of 30 days, in the NEXAFS spectrum for all the samples. Figure 7.7 gives the concentration of C=C bonds in terms of the area of C1s $\rightarrow\pi^*_{(C=C)}$ resonance for the “in-situ” state and after exposure to air for 30 days.

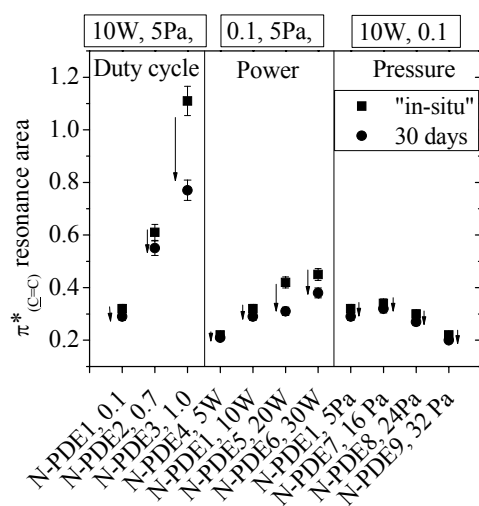


Figure 7.7: NEXAFS C1s $\rightarrow\pi^*_{(C=C)}$ resonance area for the “in-situ” and 30 days aged state of all the plasma deposited ethylene films (N-PDE) (cf. Table 3.1 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

It can be observed that the loss of C=C bonds is high (as high as 30%) in case of samples prepared at "hard" plasma conditions. This points to the fact that the number of radicals which also involves C=C radicals is high in the samples prepared at "hard" plasma conditions. For the case of samples prepared to study the variation in pressure (N-PDE1, 7, 8 & 9) the loss in the unsaturated character of the films was found to be as small as ~1%.

7.2.2. Aging of plasma deposited styrene films

Similar to the aging of plasma deposited ethylene samples, plasma deposited styrene samples were also found to uptake oxygen on exposure to air. This uptake was also followed at different intervals of exposure time by XPS.

A comparison between the oxygen uptake of X-PDS2, prepared under "mild" plasma conditions and X-PDS6, prepared under "hard" plasma conditions, is shown in Figure 7.8. The oxygen uptake of X-PDS6 is much higher compared to that of X-PDS2. The oxygen uptake of the X-PDS2 can also be followed from the valence band spectra as shown in Figure 7.8b. The O2s feature is observed to increase in intensity with exposure time.

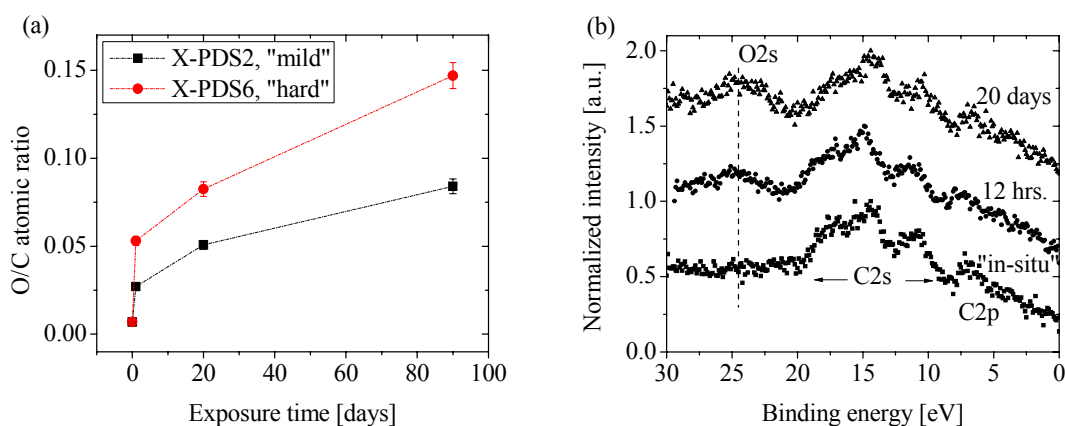


Figure 7.8: (a) XPS O/C atomic ratio of the plasma deposited styrene film X-PDS2 (20W, 0.1 duty cycle, 5 Pa) and X-PDS6 (50W, 1 duty cycle, 5 Pa) vs. aging time. (b) XPS valence band spectra of X-PDS2 at different intervals of exposure time.

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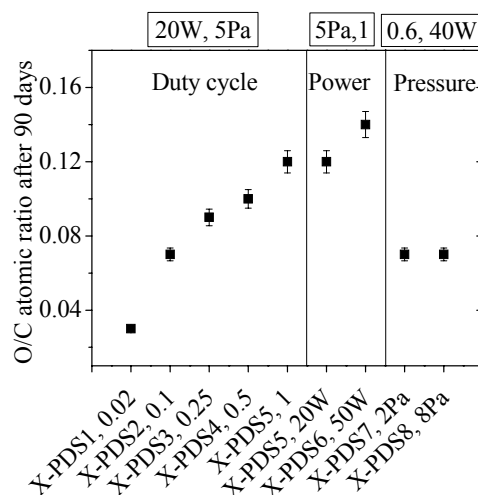


Figure 7.9: XPS O/C atomic ratio after 90 days of aging time for all the plasma deposited styrene (X-PDS) films (“in-situ” O/C \cong 0) (cf. Table 3.2 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

The O/C atomic ratio after 90 days of exposure to air is plotted in Figure 7.9. A high uptake of oxygen was once again observed in the case of samples prepared at “hard” plasma conditions. In addition to the uptake of oxygen, a loss in the shake-up area in the C1s spectra was also observed (Figure 7.10). This implies a loss in the aromatic content of the films on exposure to air.

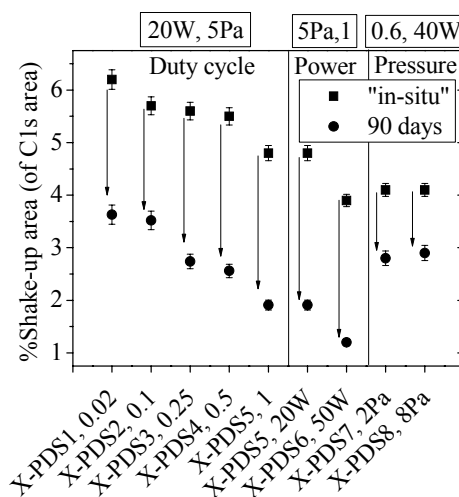


Figure 7.10: Shake-up area in percentage of the total XPS C1s area for the plasma deposited styrene (X-PDS) films for “in-situ” and 90 days aged states (cf. Table 3.2 for deposition parameters). Boxes on the top of the figure gives the constraints of the deposition conditions.

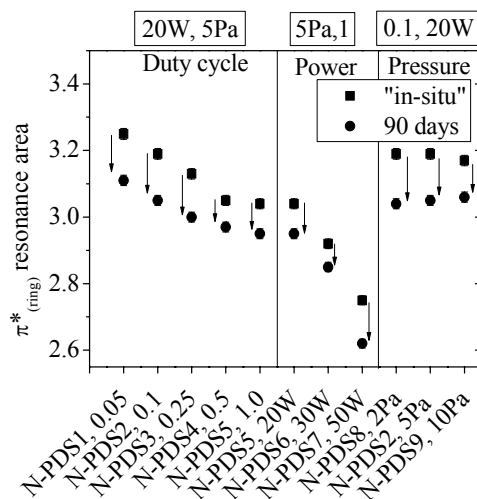


Figure 7.11: NEXAFS $C1s \rightarrow \pi^*_{(ring)}$ resonance area of the plasma deposited styrene (N-PDS) samples for “in-situ” and 90 days aged states (cf. Table 3.2 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

This loss in the aromatic content of the films was also cross-checked by NEXAFS measurements. The area under the $C1s \rightarrow \pi^*_{(ring)}$ resonance area in the C K-edge NEXAFS spectra was found to decrease on exposure to air (Figure 7.11). Similar to the loss in shake-up area for the samples studied for duty cycle variation in XPS studies, the relative loss in the $C1s \rightarrow \pi^*_{(ring)}$ resonance area was not found to vary to a large extent for the samples studied for duty cycle variations in NEXAFS studies (minimum 3% to maximum 4%). It is assumed that the aging behavior is governed by the concentration as well as the nature of radicals present on the surface of the films. The radicals which take part in the aging of the plasma deposited styrene films are the aromatic radicals as well as C=C radicals. Compared to the C=C radicals the aromatic radicals are stable. This leads to only a limited loss of aromatic character by all the films on exposure to air as detected by these two methods. However, in the case of N-PDS7 a slightly higher loss (5%) in the aromatic content can be observed compared to samples with lower powers (N-PDS5 & N-PDS6). A high power applied in this case leads to a high number of surface radicals (including aromatic radicals) which are consumed on exposure to air

The loss in the $C1s \rightarrow \pi^*_{(ring)}$ resonance area for the samples prepared at various pressures was around 4% on an average and did not vary to a large extent. The loss of shake-up feature was around 30% and did not vary significantly to draw any conclusions.

7.2.3. Aging of plasma deposited allyl alcohol films

The case of aging of plasma deposited allyl alcohol is rather different to that of plasma deposited ethylene or styrene. Figure 7.12 displays the aging in terms of XPS O/C atomic ratios for three different plasma deposited allyl alcohol films. They represent the cases of “mild” (X-PDA1) and “hard” (X-PDA6) plasma conditions together with a “medium” one (X-PDA3). It is striking that a decrease of the O/C atomic ratio vs. time of aging in air has to be stated. It depends on the deposition parameters used during deposition of the film. The samples prepared at “mild” plasma conditions show a higher decrease in the O/C atomic ratio than the samples prepared at “hard” plasma conditions.

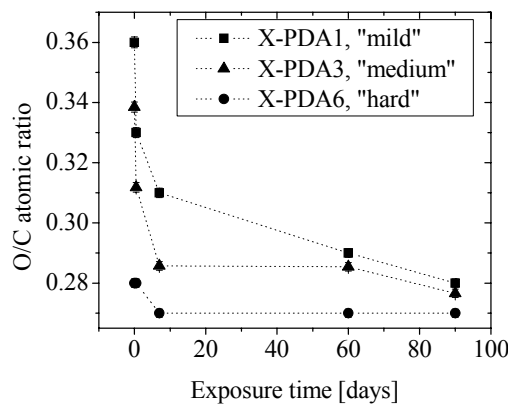


Figure 7.12: XPS O/C atomic ratio vs. aging time for the plasma deposited allyl alcohol films X-PDA1, X-PDA3 and X-PDA6 (cf. Table 3.3 for deposition parameters).

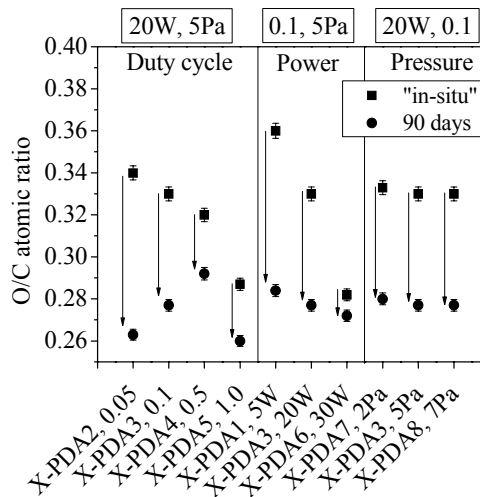


Figure 7.13: XPS “in-situ” and 90 days aged state O/C atomic ratio for all the plasma deposited allyl alcohol (X-PDA) films (cf. Table 3.3 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

Figure 7.13 displays a survey of the O/C atomic ratios measured by “in-situ” XPS and again by XPS after saturation of the aging phenomena. The effect of the deposition parameters applied during deposition of the films on the extent of the decrease of the XPS O/C atomic ratio is clearly displayed again. This decrease in the oxygen surface concentration of plasma deposited allyl alcohol films was also found by other authors. Fallyl et al. [71] reported that with aging the alcohol functions tend to point inside the bulk of the sample. In a different study on aging effects of oxygen plasma modified polyethylene surfaces, [126] the decrease in surface oxygen with time was attributed to the diffusion of low molecular weight oxidized species into the bulk of the polymer. Obviously, the capability of the oxygen moieties to move into the bulk must be different for different deposition parameters applied during the deposition of the investigated plasma deposited allyl alcohol films. The main reason for that is probably the difference in the cross-linking in the plasma allyl alcohol films which was also studied by ToF-SSIMS [127]. In this study, the cross-linking and branching in these films was found to increase vs. harder plasma conditions. The samples prepared at "mild" deposition conditions were found to be less cross-linked compared to the samples prepared at "hard" deposition conditions and the diffusion of low molecular weight oxidized species is hindered by a more cross-linked structure. Hence it follows that the decrease in the O/C atomic ratio in the samples prepared at “hard” plasma conditions must be lower. This interpretation is successfully proved by the data given in Figure 7.13.

The cross-linking and branching in these films were also monitored by following the change in the FWHM of the CH_x component in the fitted C1s spectra of the films. Figure 7.14 gives the change in this FWHM after 90 days of aging. All the samples show an increase in the FWHM. Along with the variation in the O/C atomic ratio, the variation in the fitted component areas in the C1s spectrum was also studied. Figure 7.15 showing the variation in the fitted component area in the C1s spectra of a selected sample (X-PDA3) vs. aging time. These set of spectra also represent the aging phenomena of all the other plasma deposited allyl alcohol samples. A decrease in the C-OR intensity can be observed, while the other components show an increase in the intensity. The decrease in C-OR intensity is attributed to diffusion and reorganization while the increase in the intensity of other components is attributed to the auto-oxidation process that follows the oxygen uptake by the sample.

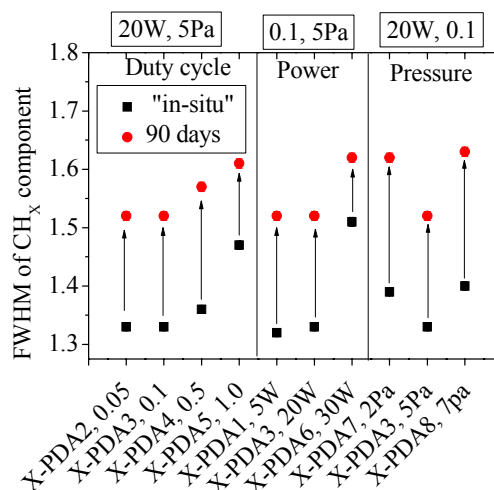


Figure 7.14: XPS “in-situ” and 90 days aged state O/C atomic ratio for all the plasma deposited allyl alcohol (X-PDA) films (cf. Table 3.3 for deposition parameter). Boxes on the top of the figure give the constraints of the deposition conditions.

By means of NEXAFS spectroscopy the behavior of the C=C and C=O bonds upon aging can be studied more in detail. Here the area under the $C1s \rightarrow \pi^*_{(C=C)}$ spectral feature decreased in each sample but the extent of decrease was found again to depend on the plasma deposition conditions employed (Figure 7.16). Among the various radicals which can be produced during the plasma polymerization process, C=C radicals are also present in the films and on exposure to air these radicals react with oxygen and form other oxygenated species in course of a auto-oxidation process. The samples prepared at “hard” plasma conditions show a large decrease in $C1s \rightarrow \pi^*_{(C=C)}$ area. A higher concentration of surface radicals in the case of these samples make them more susceptible to oxygen uptake and subsequent formation of oxygenated species. The formation of radicals in the films is mainly attributed to the fragmentation of the monomer molecules and the recombination of these fragments in the plasma.

The increase in the area under the $C1s \rightarrow \pi^*_{(C=O)}$ spectral feature after exposure to air (Figure 7.16) can also be correlated to the concentration of surface radicals and the subsequent auto-oxidation reactions. An increase of the carbonyl concentration due to aging time was already observed in the respective XPS spectra (see Figure 7.15). The increase is found to be higher in the case of samples prepared at “hard” plasma conditions. The samples prepared at “hard” plasma conditions have a higher concentration of surface radicals and hence the uptake of oxygen and the formation of C=O bonds is higher in their

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case. The samples N-PDA2 and N-PDA6 studied for pressure effects did not show any significant changes in the $C1s \rightarrow \pi^*$ resonance area even though there was an increase in pressure by more than 100% from N-PDA2 to N-PDA6.

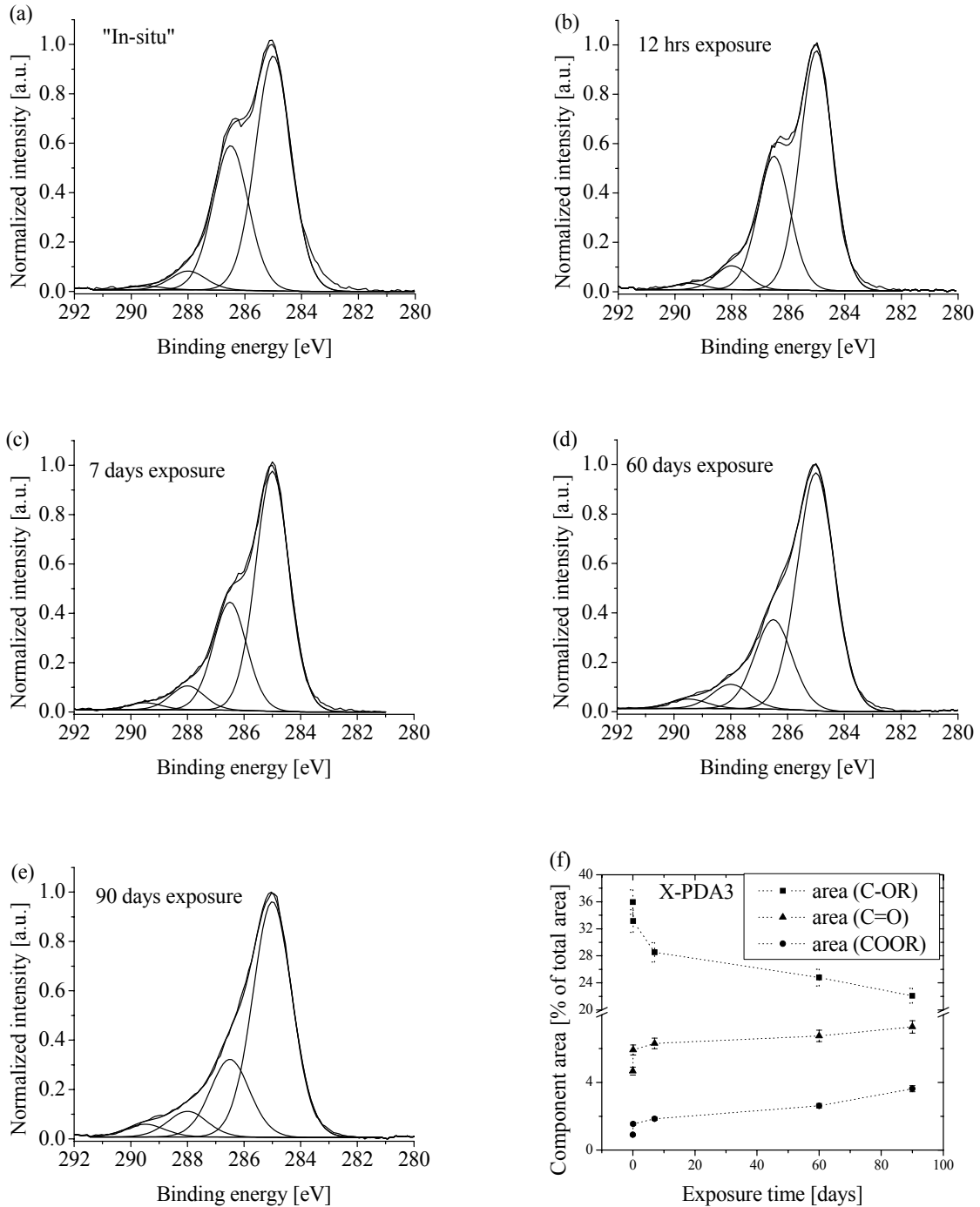


Figure 7.15: (a)-(e) XPS C1s spectra of the plasma deposited allyl alcohol X-PDA3 film after different aging times. (f) Fitted component area of the XPS C1s spectra vs. aging time.

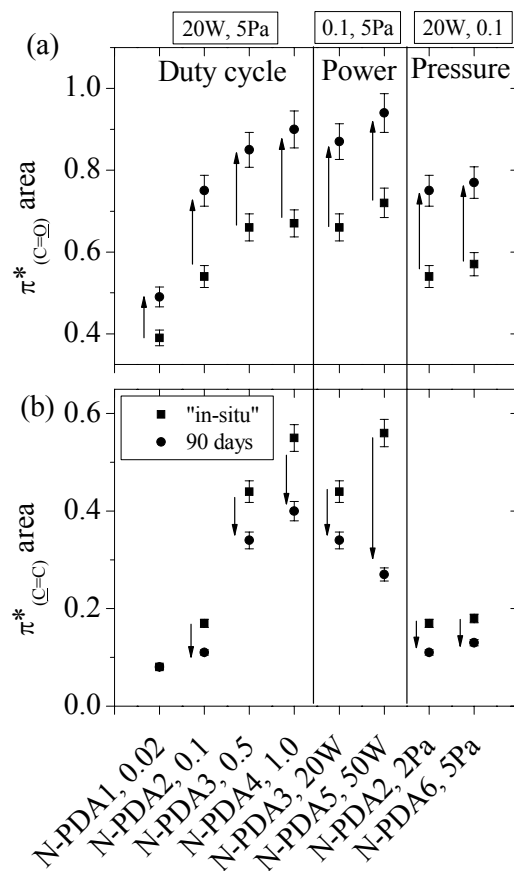


Figure 7.16: (a) NEXAFS $C1s \rightarrow \pi^*_{(C=O)}$ resonance area and (b) $C1s \rightarrow \pi^*_{(C=C)}$ resonance area for “in-situ” and 90 days of aged states for the plasma deposited allyl alcohol (N-PDA) films (cf. Table 3.3 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

7.2.4. Aging of plasma deposited allylamine films

In the case of plasma deposited allylamine films a loss of nitrogen surface concentration of the films was observed along with an increase in the oxygen content on exposure to air. Figure 7.17a shows the change in XPS O/C atomic ratios of three different plasma deposited allylamine films prepared at “mild” (X-PDAm1), “medium” (X-PDAm4) and “hard” (X-PDAm6) plasma conditions measured at different aging time. It can be observed that oxygen uptake by these three very different films is very similar. It seems that in addition to external plasma parameters the nature of the monomer also plays an important role in the formation of radicals in the plasma deposited film.

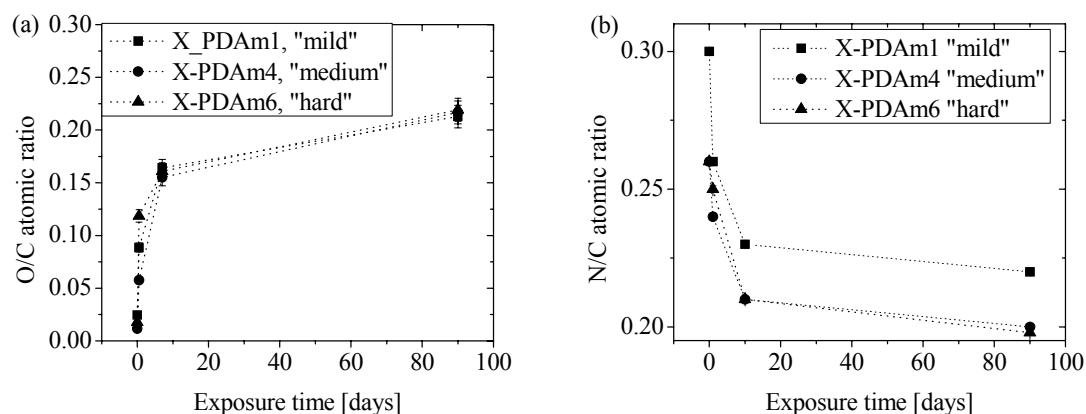


Figure 7.17: (a) XPS O/C atomic ratio vs. aging time (b) XPS N/C atomic ratio vs. aging time for the plasma deposited allylamine films, X-PDAm1, X-PDAm4 and X-PDAm6 (cf. Table 3.4 for deposition parameters).

Figure 7.17b shows the change in the N/C atomic ratio with time for these three samples. The rate of loss of nitrogen from the surface of the films, which can arise due to loss of nitrogen in the form of NH_3 or due to diffusion of low molecular weight nitrogen species into the bulk of the sample, was high during the first few days and then it saturates with time. The possibility of such a loss of nitrogen after absorption of humidity (H_2O) from the air in the form of NH_3 has been discussed by Gerenser [128] and Förch [129]. A proposed reaction pathway is given in Equation 7.3.



In the Figure 7.17b the saturation level of the samples prepared at “mild” conditions are rather different from the samples prepared at “medium” or “hard” plasma conditions. The difference arises from the fact that these samples are prepared at difference plasma conditions and for the “mild” conditions the surface of the film has a high concentration of nitrogen containing species such as amine groups. Additionally valence bands for all the samples were also measured (not shown) and the $\text{O}2\text{s}$ feature was found to increase in intensity with aging of the samples. This provided additional support to the data presented in Figure 7.17a.

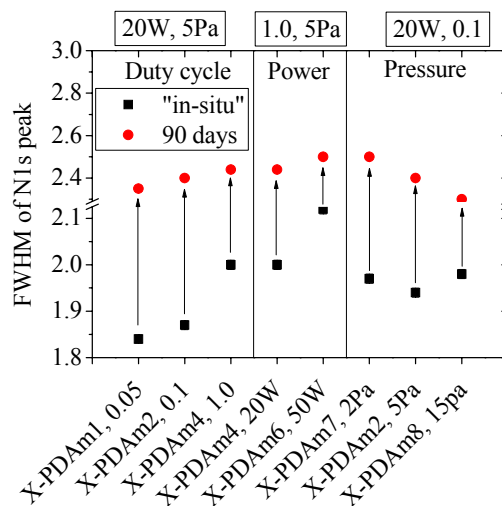


Figure 7.18: FWHM of the XPS N1s spectra for all the plasma deposited allylamine (X-PDAm) films after “in-situ” and 90 days aging (cf. Table 3.4 for deposition parameters). Boxes on the top of the figure give the constraints of the deposition conditions.

The change in the FWHM of the N1s XP spectra was also monitored after exposure to air (Figure 7.18). It was found to increase with aging time. This increase is due to the formation of new species involving nitrogen and oxygen with slightly shifted binding energies. The extent of the increase was similar in almost all the cases except for the samples studied vs. pressure variation.

In similar studies by Geganbach et al. [130, 131], where the authors investigated the aging of plasma polymers made by n-heptylamine and 1, 3-diaminopropane, it was also found that the oxygen incorporated due to aging is fixed at sites adjacent to nitrogen containing functional groups. This might be the reason for an increase in the FWHM of the N1s XPS spectra as shown in Figure 7.18. The various reaction pathways proposed by the authors of reference [130, 131] are given in Figure 7.19. The formation of amide and similar groups during the aging of amino group bearing plasma polymers has been concluded also in other studies by XPS, NEXAFS and FTIR methods [116, 132-134].

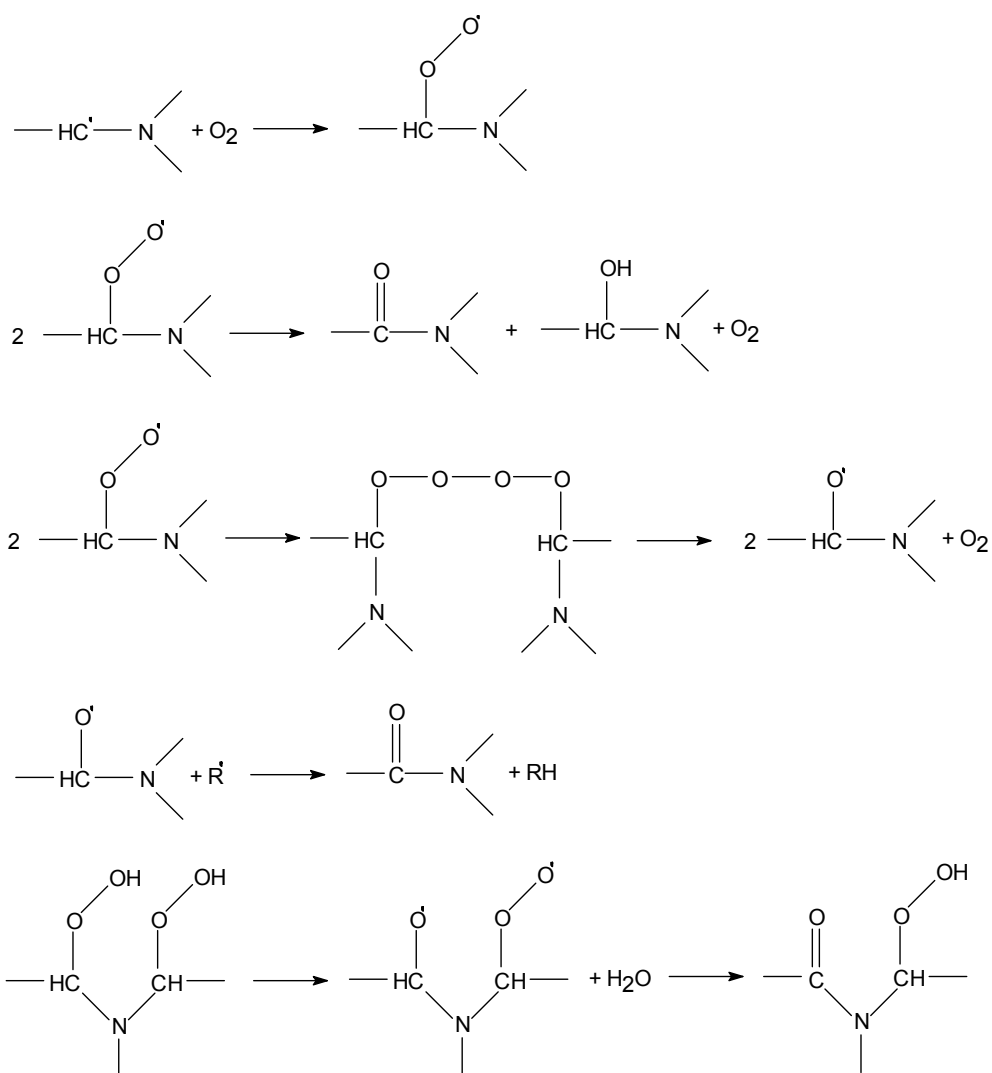


Figure 7.19: Reaction scheme of the oxygen uptake and auto-oxidation reactions for plasma deposited 1,3-diaminopropane film (adapted from ref. [130]).

The change in the extent of unsaturation was monitored for these films with the help of NEXAFS N K-edge spectra. The unsaturation in terms of the presence of C=N and C≡N bonds was monitored by considering the sum of the N1s→π*(C=N) and N1s→π*(C≡N) maximum intensities in the N K-edge spectra. Figure 7.20 displays the sum of these maximum intensities for "in-situ" and 120 days aged films. A loss of unsaturation can be concluded from this data. The loss of these bonds was found to be high in the samples prepared at "hard" plasma conditions. It is suggested that a high concentration of radicals on the surface of the films include nitrogen containing unsaturated radicals. These radicals along with some non-radical species are oxidized on exposure to air. This is observed as a decrease in the sum of maximum intensities of N1s→π*(C=N) (cf. Equation 7.3) and

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$N1s \rightarrow \pi^*_{(C \equiv N)}$ resonances. For samples prepared for a study of variation in monomer pressure, it was found that for the samples prepared at low pressure the uptake of oxygen was higher. At low pressures when the electron energy in the plasma is high, there exists a high number of surface radicals available for oxygen uptake.

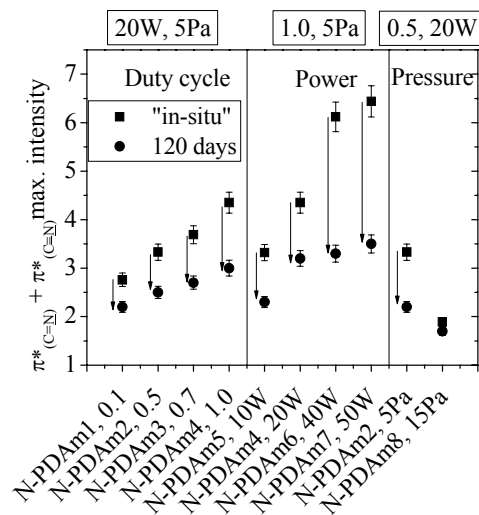


Figure 7.20: NEXAFS results of aged plasma deposited allylamine films. Sum of NEXAFS $N1s \rightarrow \pi^*_{(C \equiv N)}$ and $N1s \rightarrow \pi^*_{(C=N)}$ maximum intensities for all the plasma deposited allylamine (N-PDAm) films after “in-situ” and 120 days aged states (cf. Table 3.4 for deposition parameters). Boxes on the top of the figure gives the constraints of the deposition conditions.

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7.3. Summary of aging of plasma deposited homopolymers

The following table summarizes the results and general trends obtained in the case of aging of the plasma deposited homopolymers investigated in this study.

Table 7.1: Summary of the effect of the plasma deposition parameters on the aging of the plasma deposited films.

Monomer	Duty cycle	Power	Pressure
Ethylene	<ul style="list-style-type: none"> • Oxygen uptake \propto duty cycle • Loss of C=C \propto duty cycle 	<ul style="list-style-type: none"> • Oxygen uptake \propto power • Loss of C=C \propto power 	<ul style="list-style-type: none"> • Oxygen uptake \propto pressure • Loss of C=C without trend
Styrene	<ul style="list-style-type: none"> • Oxygen uptake \propto duty cycle • Loss of rings without trend 	<ul style="list-style-type: none"> • Oxygen uptake \propto power • Loss of rings without trend 	<ul style="list-style-type: none"> • Oxygen uptake without trend • Loss of rings without trend
Allyl alcohol	<ul style="list-style-type: none"> • Oxygen loss \propto 1/duty cycle • Loss of C=C \propto duty cycle • Gain in C=O \propto duty cycle 	<ul style="list-style-type: none"> • Oxygen loss \propto 1/power • Loss of C=C \propto power • Gain in C=O without trend 	<ul style="list-style-type: none"> • Oxygen loss \propto without trend • Loss of C=C \propto without trend • Gain in C=O \propto without trend
Allylamine	<ul style="list-style-type: none"> • Oxygen uptake without trend • Nitrogen loss \propto 1/duty cycle • Increase in concentration of multiple N species without trend. • Loss of C=N& C\equivN \propto duty cycle 	<ul style="list-style-type: none"> • Oxygen uptake without trend • Nitrogen loss \propto 1/power • Increase in concentration of multiple N species without trend. • Loss of C=N& C\equivN \propto power 	<ul style="list-style-type: none"> • Oxygen uptake without trend • Nitrogen loss \propto 1/pressure • Increase in concentration of multiple species \propto 1/pressure • Loss of C=N& C\equivN \propto 1/pressure

7.4. Aging of plasma deposited copolymers

The aging of the plasma deposited copolymer films was similar to the aging of the respective plasma deposited homopolymer films with respect to the

- (a) Gain or loss in surface concentration of oxygen,
- (b) Loss in surface concentration of nitrogen and
- (c) Changes in the unsaturated and aromatic character.

These three aspects of the aging phenomenon with respect to all the copolymer films are dealt within this section.

7.4.1. Gain or loss in surface concentration of oxygen

Figure 7.21 displays the change in the XPS O/C atomic ratio of ethylene-allyl alcohol (Etal) and styrene-allyl alcohol (Stal) samples after 60 days of aging. The copolymer films prepared at a high PFR of ethylene or styrene are observed to uptake oxygen shown as an increase in O/C atomic ratio. The samples prepared at a high PFR of allyl alcohol showed a decrease in oxygen surface concentration. A significant difference between the plots in Figures 7.21a & b is the PFR of allyl alcohol at which the oxygen gain changes to oxygen loss by the films. For ethylene-allyl alcohol copolymer films this inflexion point is at 10% PFR of allyl alcohol while for the styrene-allyl alcohol copolymer films the inflexion point is at 90% PFR of allyl alcohol. In both these cases the inflexion point was the PFR of allyl

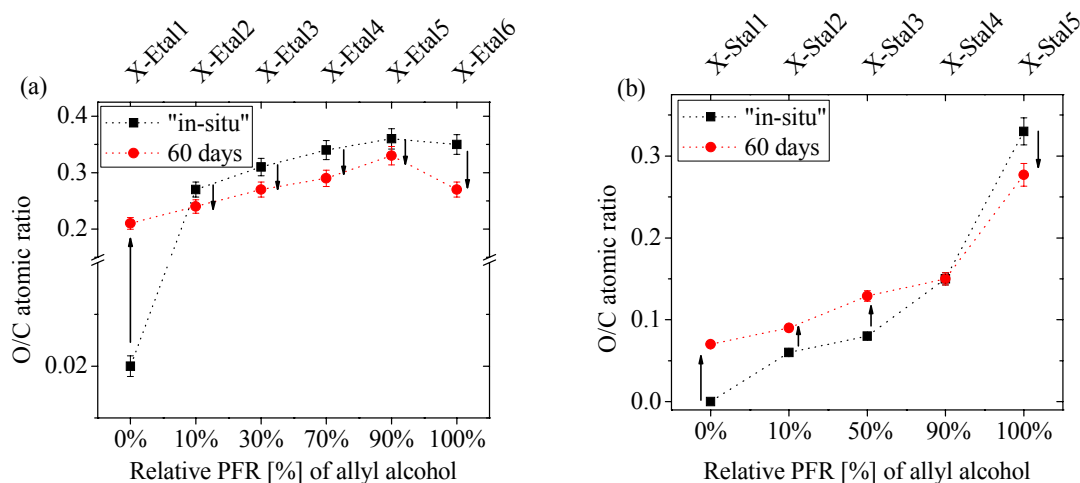


Figure 7.21: XPS O/C atomic ratio over a period of 60 days of aging in air for (a) Ethylene-allyl alcohol [Etal] copolymer films, (b) Styrene-allyl alcohol [Stal] copolymer films. (cf. Table 3.5 for deposition parameters).

alcohol at which it takes over the chemical character of the copolymer film as observed in Figure 6.2a and Figure 6.4a. The difference in the case of ethylene-allyl alcohol and styrene-allyl alcohol copolymers arises due to the difference in reactivity of the respective comonomers (cf. Table 6.1).

The change in the area of C-OR species in the fitted XP C1s spectra was also monitored with time and the behavior was found to be the same as that of the O/C atomic ratio (Figure 7.22).

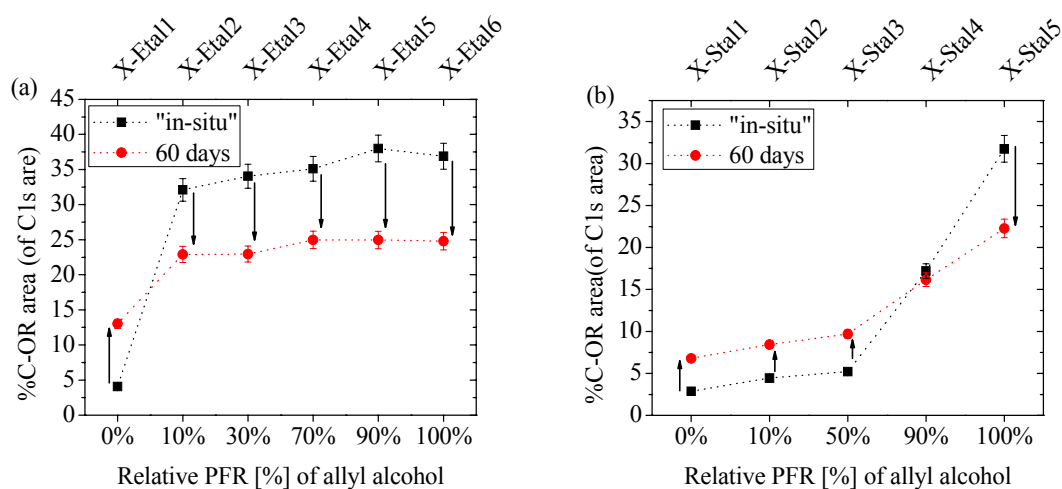


Figure 7.22: C-OR component area of the fitted XP C1s spectra over a period of 60 days for (a) Ethylene-allyl alcohol [Etal] copolymer films, (b) Styrene-allyl alcohol [Stal] copolymer films. (cf. Table 3.5 for deposition parameters).

The gain in the surface concentration of oxygen for the case of ethylene-allylamine and styrene-allylamine copolymer films is given in Figures 7.23a & b. It was found that the uptake of oxygen was higher in the case of films prepared at a high PFR of allylamine. As already discussed in section 7.2.4 there are various reaction pathways for uptake of oxygen by nitrogen containing species and a high concentration of these species, such as in the case of films prepared at a high PFR of allylamine, the probability of oxygen uptake is higher.

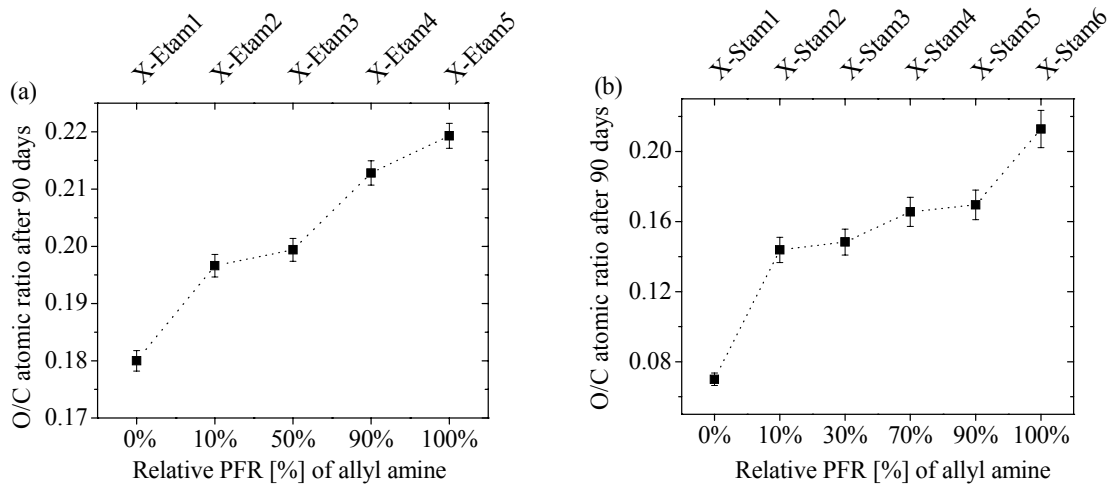


Figure 7.23: XPS O/C atomic ratio over a period of 90 days of aging in air ("in-situ" O/C atomic ratio ~ 0) for (a) Ethylene-allylamine [Etam] copolymer films, (b) Styrene-allylamine [Stam] copolymer films. (cf. Table 3.5 for deposition parameters).

7.4.2. Loss in surface concentration of nitrogen

Figure 7.24 displays the change in the XPS N/C atomic ratio of ethylene-allylamine (Etam) and styrene-allylamine (Stam) samples after 90 days of aging. Both the copolymer films show a decrease in nitrogen surface concentration on aging. The loss of nitrogen was slightly higher in the case of samples prepared at high PFR of allylamine.

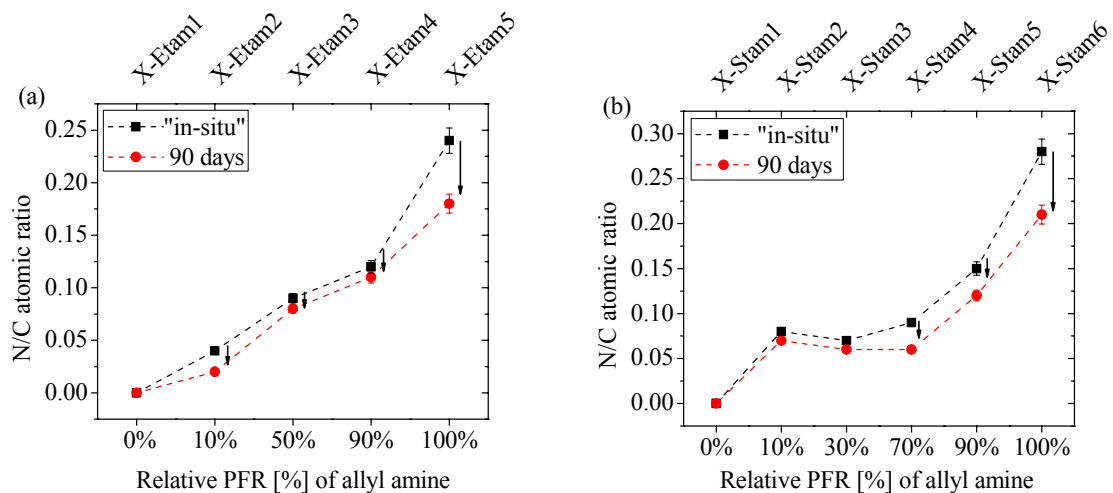


Figure 7.24: XPS N/C atomic ratio for "in-situ" and 90 days aged states for (a) Ethylene-allylamine [Etam] copolymer films, (b) Styrene-allylamine [Stam] copolymer films. (cf. Table 3.5 for deposition parameters).

This loss of nitrogen is probably in the form of NH_3 or due to diffusion of low molecular weight nitrogen species into the bulk of the sample and is similar to the case of plasma deposited allylamine samples as already discussed in the section 7.2.4.

7.4.3. Changes in unsaturated and aromatic character

Changes in the unsaturated and aromatic character of the copolymer films are monitored by observing the changes in the area of the shake-up feature in the XP C1s spectra (as in the case of styrene-allyl alcohol and styrene-allylamine copolymers) as well as the changes in the area of the π^* resonance features in the NEXAFS C, O or N K-edge spectra.

The change in the shake-up area implying a change in the aromatic content for the styrene-allyl alcohol and styrene-allylamine copolymer films is given in Figure 7.25. In both the cases there was a loss of shake-up area on aging of the films. In the case of styrene-allyl alcohol copolymer films this loss was found to be higher in the case of samples prepared at high PFR of styrene while in the case of styrene-allylamine films this loss was found to be almost constant in all the cases.

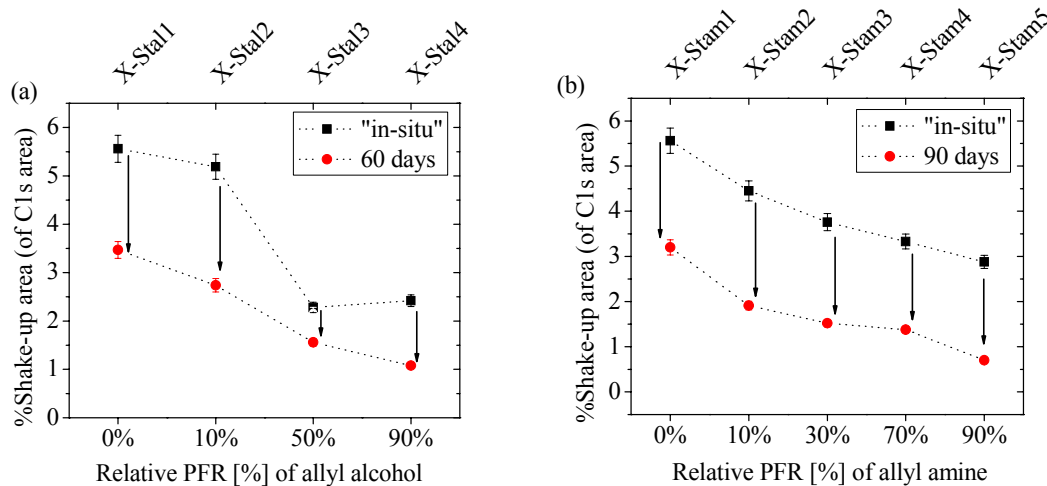


Figure 7.25: Shake-up in percentage of the XPS C1s area after (a) 60 days of aging in air for styrene-allyl alcohol [Stal] copolymer films, (b) 90 days aging in air for styrene-allylamine [Stam] copolymer films. (cf. Table 3.5 for deposition parameters).

The change in the unsaturated character of the ethylene-allyl alcohol films, investigated through the changes in the $\text{C1s} \rightarrow \pi^*_{(\text{C}=\text{C})}$ and $\text{O1s} \rightarrow \pi^*_{(\text{C}=\text{O})}$ resonance areas after aging times of 30 days and 60 days is shown in Figure 7.26. A high loss of $\text{C}=\text{C}$

bonds was observed with samples prepared at high PFR of ethylene (Figure 7.26a). This loss was less for samples prepared at PFR of allyl alcohol >10%. During the plasma deposition of ethylene-allyl alcohol copolymer films, two different processes effecting the surface concentration of C=C bonds and radicals simultaneously should be considered. Firstly the efficient formation of C=C bonds and radicals from the co-monomers and secondly the consumption of these bonds and radicals by the oxygen provided by the allyl alcohol monomer. For samples prepared at high PFR of allyl alcohol a majority of these C=C radicals and bonds are consumed even before the exposure to air. This could be the reason why a lower loss of C=C bonds is observed for samples prepared at high PFR of allyl alcohol.

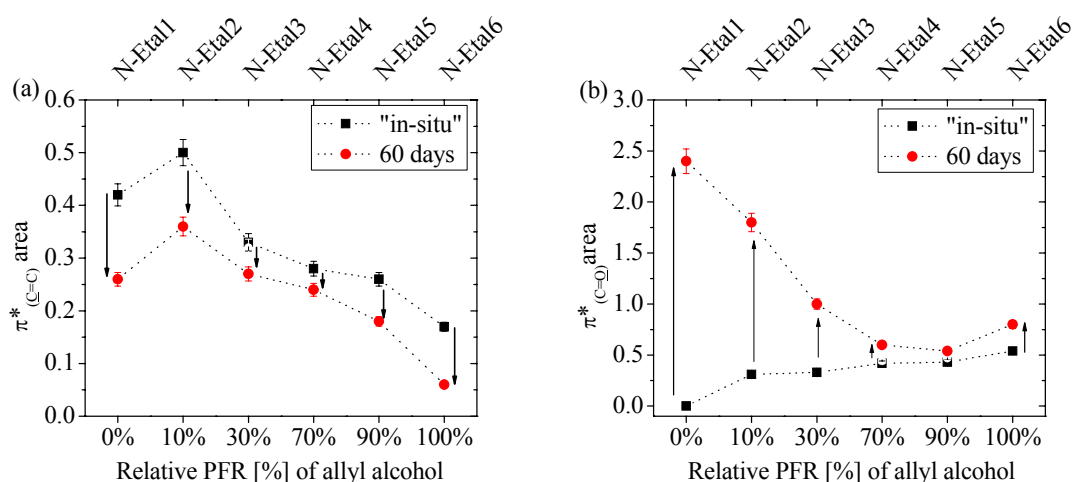


Figure 7.26: (a) NEXAFS C1s $\rightarrow\pi^*_{(C=C)}$ resonance area and (b) C1s $\rightarrow\pi^*_{(C=O)}$ resonance area after "in-situ" and 60 days of aging in air for ethylene-allyl alcohol [Etal] copolymer films. (cf. Table 3.5 for deposition parameters).

A gain of C=O bonds can be observed for all the samples in Figure 7.26b. A relatively high gain was observed for samples prepared at high PFR of ethylene. This gain was found to decrease with increase in the PFR of allyl alcohol and for PFR of allyl alcohol >30% this gain was almost constant. For samples prepared at high PFR of ethylene the surface radicals are probably less consumed or minimally consumed during the plasma deposition process because of a relatively small amount of oxygen available from the allyl alcohol monomer fragmentation. On exposure to air these surface radicals uptake oxygen and subsequently form the C=O bonds in course of auto-oxidation process.

The change in the aromatic character of the styrene-allyl alcohol and styrene-allylamine films is monitored by following the change in the NEXAFS C1s $\rightarrow\pi^*_{(ring)}$

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resonance area (Figure 7.27). In each case a loss of the aromatic character of the films was observed with aging. In general this loss was found to be high for samples prepared at high PFR of styrene. In the case of styrene-allyl alcohol samples the loss in this area was constant for samples prepared at PFR of styrene > 50% while in the case of styrene-allylamine samples this loss was almost constant.

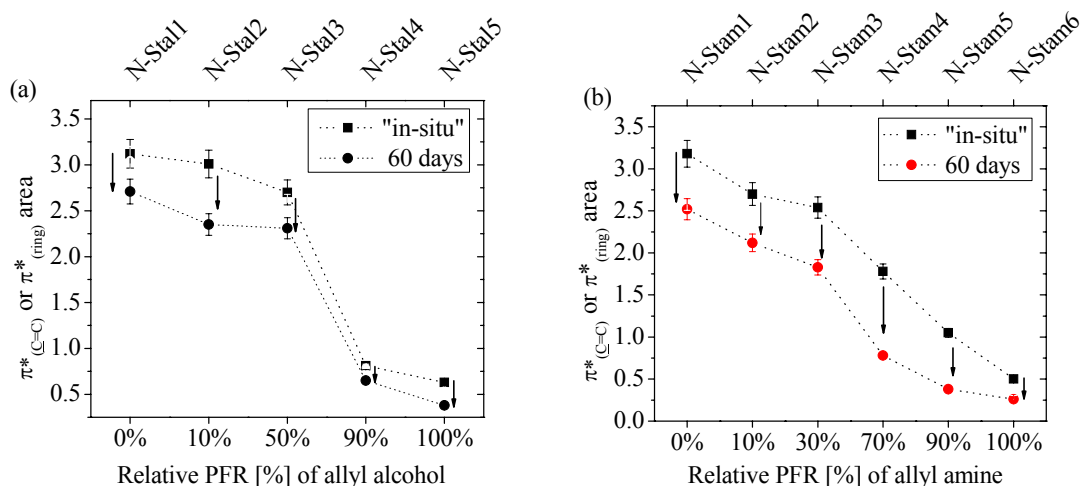


Figure 7.27: NEXAFS $C1s \rightarrow \pi^*_{(C=C)}$ or $C1s \rightarrow \pi^*_{(ring)}$ resonance areas for “in-situ” and 60 days of aging for (a) styrene-allyl alcohol [Stal] and (b) styrene-allylamine [Stam] copolymer films. (cf. Table 3.5 for deposition parameters).

In the case of copolymer films prepared by using allyl amine as one of the co-monomers the loss in the unsaturated character was reflected in the loss of maximum intensities of the $N1s \rightarrow \pi^*_{(C=N)}$ and $N1s \rightarrow \pi^*_{(C \equiv N)}$ resonances of the N K-edge NEXAFS spectra (Figure 7.28a & b). In the case of ethylene-allylamine copolymer films all the samples were found to reach the same minimum unsaturation in terms of C=N and C≡N bonds. Similarly in the case of styrene-allylamine films the unsaturation was once again reduced to low values. This loss can be related to the loss of nitrogen species in the form of ammonia on reaction with water in the air as already discussed in section 7.2.4.

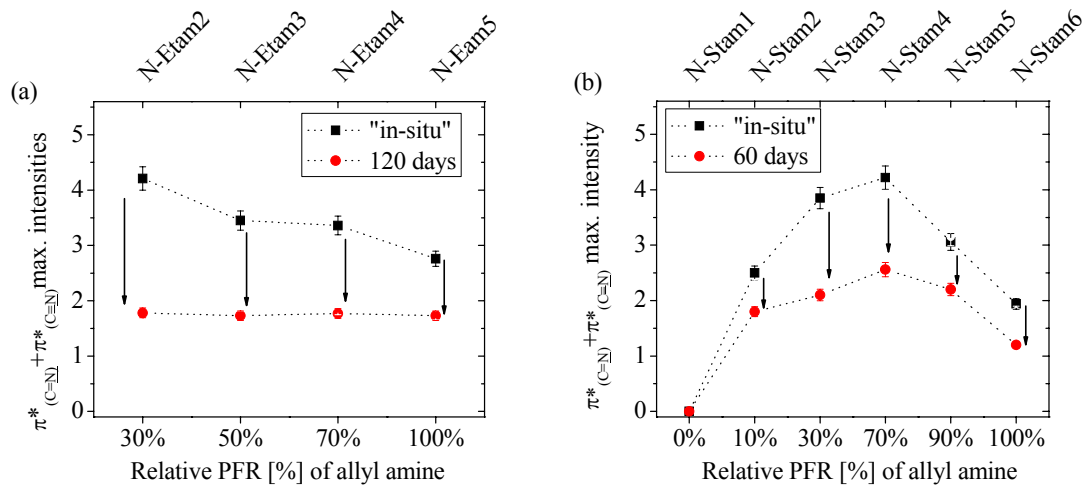


Figure 7.28: Sum of NEXAFS $N1s \rightarrow \pi^*_{(C=N)}$ and $N1s \rightarrow \pi^*_{(C\equiv N)}$ maximum intensities for (a) ethylene-allylamine [Etam] copolymer films (b) styrene-allylamine [Stam] copolymer films (cf. Table 3.5 for deposition parameters).

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7.5. Summary of aging of plasma deposited copolymers

The following table summarizes the results and general trends obtained in the case of aging of the plasma deposited copolymers investigated in this study.

Table 7.2: Summary of the effect of the comonomers on the aging of the plasma deposited copolymers.

Copolymer	Monomer 1	Monomer 2	Effects of monomer 1	Effects of monomer 2
Ethylene-Allyl alcohol	Ethylene	Allyl alcohol	<ul style="list-style-type: none">• Promotes oxygen uptake• Promotes concentration of C-OR species• Promotes loss of C=C bonds• Promotes gain of C=O bonds	<ul style="list-style-type: none">• Promotes oxygen loss• Promotes loss of C-OR species
Styrene-Allyl alcohol	Styrene	Allyl alcohol	<ul style="list-style-type: none">• Promotes oxygen uptake• Promotes concentration of C-OR species	<ul style="list-style-type: none">• Promotes oxygen loss• Promotes loss of C-OR species
Ethylene-Allylamine	Ethylene	Allylamine	<ul style="list-style-type: none">• Induces lower degree of oxygen uptake	<ul style="list-style-type: none">• Promotes oxygen uptake
Styrene-Allylamine	Styrene	Allylamine	<ul style="list-style-type: none">• Induces lower degree of oxygen uptake	<ul style="list-style-type: none">• Promotes oxygen uptake