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Radio Frequency-Induced Plasma Polymerization of Allyl Alcohol and 1-Propanol

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The effect of the composite parameters' plasma power (P)-to-monomer flow rate (ϕ) ratio (P/ϕ) in the plasma polymerization of allyl alcohol and 1-propanol was studied. The radio-frequency plasmas of deposits operated at low power (1-15 W) were investigated using deposition rate measurements. Detailed chemical information on the plasma polymers was obtained by X-ray photoelectron spectroscopy (XPS). The study of the surface chemistry of films created from allyl alcohol and 1-propanol demonstrates the importance of the double bond for good $\underline{C}$-O group retention. The deposition rates of both plasma polymers were found to increase with increasing P. The comparison of the deposition rates of plasma-deposited allyl alcohol and 1-propanol suggests that the double bond is involved in the deposition mechanism.

Key Words: Plasma Polymerization, Plasma Deposition, Allyl Alcohol, 1-Propanol, XPS.

Introduction

Radio-frequency (RF) plasmas of volatile organic compounds are used for depositing thin polymeric films, termed plasma polymerization or plasma deposition. Plasma deposition has been extensively studied and is gaining recognition as an important process for the formation of entirely new kinds of materials[1]. There are a number of features that make plasma deposition an attractive coating technology. The process does not involve the use of solvents; the plasma deposition process is often referred to as a "clean technology"[1]. Ultra-thin pinhole-free films may be deposited onto almost all substrates (polymer, metal, glass and ceramic). The processed substrate may be fully immersed and the high degree of diffusion of particles at low gas pressures enables objects of complicated geometry to be coated. Cross-linking within the plasma deposit and the level of adherence of the deposit to the substrate may be tailored through the manipulation of the plasma parameters: input power (P), the composition of the gas mixture (from single component "monomer" to complex mixture with added gases), the gas flow rate (ϕ) and pressure. The influence of the plasma parameters on film chemistry has been studied in a series of recent papers[2−12].

Plasma deposition of oxygen-containing monomers can be used to prepare hydrophilic thin films on solid substrates[13]. For example, plasma polymerization can be used to prepare thin hydrophilic coatings for contact lens applications[14]. Several potential applications of these films have been described in the literature[14−19] ranging from electronic devices to medical implants. Comprehensive studies of structure and chemistry on plasma deposition of alcohols have been reported[2,6,7,13,19−30].

This article reports plasma deposited films prepared from unsaturated and saturated alcohols in order to investigate the influence of molecular structure on plasma deposition and changes in the surface chemical composition with the ratio of P/ϕ on plasma deposits. The surface chemical composition of deposits were investigated by means of X-ray photoelectron spectroscopy (XPS). The rate of deposition of plasma polymerized allyl alcohol and 1-propanol was monitored using a quartz-crystal mass balance.

Experimental

Plasma Deposition

Allyl alcohol and 1-propanol of 99% purity or greater were purchased from Aldrich Chemical Co., UK. Plasma was sustained by an RF generator (13.56 MHz) signal generator and power amplifier which were inductively coupled to the plasma chamber. The substrates were placed in the coil region and apparatus pumped down to base pressure of about 1.5 x 10^{-2} mbar. To prepare samples for XPS analysis, a piece of Al foil was wrapped around a microscope cover slip and placed in the reactor. The details of the reactor and the procedure for film deposition have been reported previously[10,20]. Plasma polymers of allyl alcohol were deposited under a ranges of different P/ϕs (2.2→36). Plasma polymers of 1-propanol were prepared at three different P/ϕs (3, 18 and 36). Two different monomer flow rates (3.4 and 0.84 cm^3_{STP} min^{-1}) were used to get these range. P is the RF power (Watts or J s^{-1}) and ϕ is the flow rate of monomer which has the units cm^3_{STP} min^{-1}. P/ϕ thus, has the units J $\mathrm{s}^{-1}/\mathrm{cm}^3_{STP}$ min^{-1}. For simplicity, the units will not be stated each time P/ϕ is referred to.

Deposition Rate Measurements

Deposition rate measurements were obtained by using the Leybold XTM/2 package, which consists of a quartz crystal inserted into the glow discharge, an oscillator package and a deposition monitor. The quartz crystal probe and deposition rate monitor were mounted in the cruciform plasma rig. A schematic drawing of the experimental configuration is shown in Figure 1. The deposition monitor was set to give readout in ng s^{-1}. Taking into account the exposed surface area of the crystal (0.535 cm^2), and assuming its density is 1 g cm^{-3}, the deposition rate (ng s^{-1}) can be readily converted to coating thickness (nm).

XPS Measurements

The XP spectra were acquired on a VG Clam 2 instrument (Sheffield, UK), using Mg K(α) X-rays to excite spectra. A take-off angle of 30 ° with respect to the sample surface was used. For survey scan spectra, the 0-1100 eV binding energy region was analysed. Narrow scan spectra of the C 1s regions were acquired for each sample. The data were analysed using Scienta software. Peak fitting of the C 1s and O 1s core levels was carried out using a least squares iterative peak fitting routine. Elemental composition was determined by measuring the area under the peaks of the elements of interest in the sample. Experimentally derived sensitivity factors were used to calculate the concentrations of the elements.

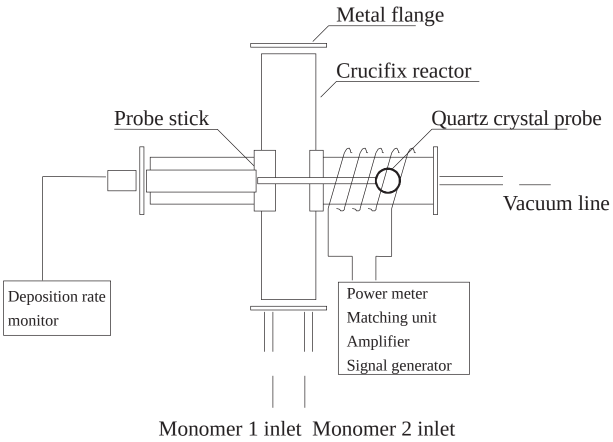


Figure 1. Schematic of cruciform plasma reactor with deposition rate monitor.

Results and Discussion

The C 1s peak-fitted core-level spectra of both plasma-deposited allyl alcohol and 1-propanol, which were prepared at a P/ϕ of 3, are shown in Figures 2a and 2b, respectively. The spectra are corrected for sample charging. The C 1s curve fit results are summarized in Table 1. A total of five chemical environments were fitted, of which four occurred at a characteristic chemical shift (ΔE_b) with respect to pure hydrocarbon (285.0 eV). The first peak is due to carbon atoms in a C-R environment. The second peak is due to the β-shift undergone by carbon atoms directly bonded to a carboxyl group. The third component is due to carbon atoms singly bonded to oxygen (alcohol functions, ether functions or epoxide groups), while the fourth component arises from carbonyl functions. The last component corresponds to carbon atoms from esters or carboxylic acid functions.

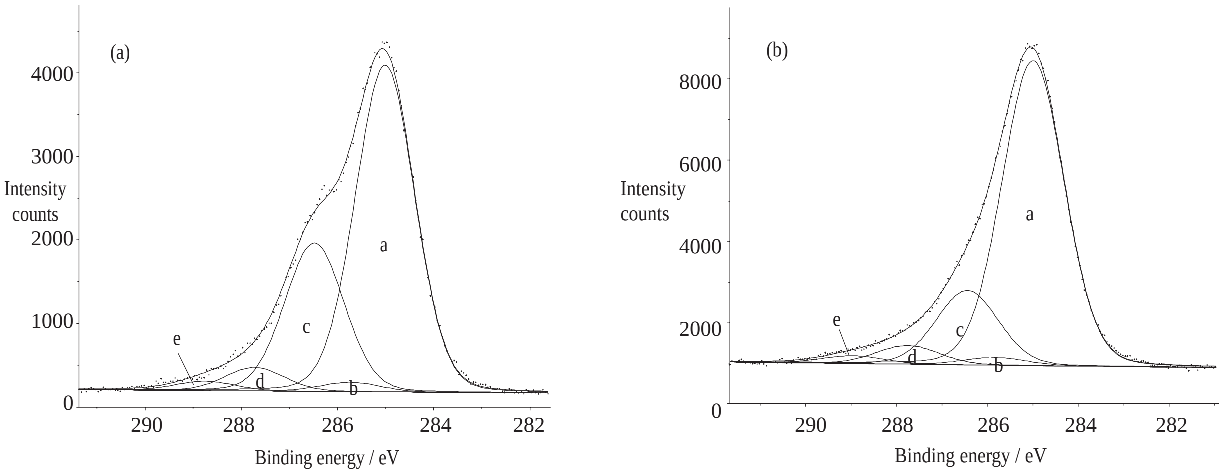


Figure 2. C 1s core level spectra of plasma-deposited (**a**) allyl alcohol and (**b**) 1-propanol at $P/\phi = 3$. a.$\underline{C}$-R; b. $\underline{C}$-CO_2R; c. $\underline{C}$-OR; d. $\underline{C}$=O; e. $\underline{C}O_2R$ (R represents hydrogen or an alkyl substituent).

It can be seen from Figures 2a and 2b that the tendency to produce films containing alcohol functionalities is not so great in the case of 1-propanol. That is, in contrast to allyl alcohol, plasma polymers of 1-propanol showed very little $\underline{C}$-O retention. Other functional groups were found to be present in very similar amounts. In the fit of plasma-deposited allyl alcohol the full width at half maximum (FWHM) used was 1.45 eV, whereas a larger FWHM of 1.61 was used for plasma-deposited 1-propanol.

Table 1. Results from curve-fitting the C 1s core-level XP spectrum of a plasma-deposited allyl alcohol and 1-propanol (in brackets) prepared at $P/\phi = 3$.

Environment Chemical	E/(eV)	D E_b/(eV)	% Area
C-R	285.0 (285.0)		63.0 (73.9)
C-CO_2R	285.72 (285.8)	0.72 (0.8)	1.8 (1.9)
C-OR	286.47 (286.45)	1.47 (1.45)	28.7 (18.0)
C=O	287.71 (287.76)	2.71 (2.76)	4.6 (4.5)
CO_2R	288.74 (288.97)	3.74 (3.97)	1.8 (1.9)

(FWHM = 1.45 for allyl alcohol and 1.61 for 1-propanol)

The variation in chemical composition of the plasma-deposited allyl alcohol films, with increasing P/ϕ, is displayed in Figure 3. The amount of C-O in the plasma-deposited allyl alcohol films decreased as P/ϕ increased. No significant difference in the C=O component can be seen between the plasma-deposited allyl alcohol samples. Note also the CO_2R component, in which the variation is very small over the P/ϕ range investigated indicating that only an extremely small quantity of esters or carboxylic acids is formed. A summary of the results of quantification for both allyl alcohol and 1-propanol is given in Table 2, from which the power-dependence of alcohol retention is clearly seen.

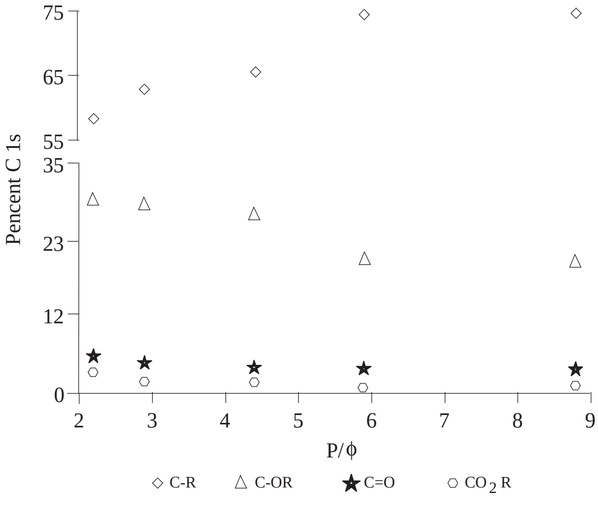


Figure 3. Contribution of component functional groups in plasma-deposited allyl alcohol as a function of P/ϕ.

Table 2. Retention of C-O groups and O/C ratios of the plasma-deposited allyl alcohol and 1-propanol obtained at different P/ϕs.

P/ϕ	Retention of C-O (%)		O/C	
	Allyl alcohol	1-propanol	Allyl alcohol	1-propanol
3	86.2	54.1	0.31	0.20
18	55.0	42.0	0.23	0.16
36	46	37.5	0.21	0.14

The hydroxyl group retention was calculated by dividing the percentage area of the C-OR component (the C-OR component was taken from the C 1s curve fit) by the theoretical value for poly(allyl alcohol), which is 33.3%. Implicit in this calculation is the assumption that all of the intensity of the C-OR component is due to the alcohol, to the exclusion of ether. The data show that the plasma-deposited allyl alcohol had retained a significant amount of C-O groups compared with plasma-deposited 1-propanol.

The atomic ratios of plasma-deposited films from allyl alcohol and 1-propanol showed strong variations with P/ϕ. In each case, allyl alcohol produced plasma polymers with a higher oxygen content than 1-propanol, as seen in Table 2. The O/C ratios of plasma-deposited films were calculated from a survey scan (0-1100 eV). These results reveal a decrease in the O/C ratio with increasing power for both saturated and unsaturated alcohol.

The polymer deposits from plasmas of allyl alcohol and 1-propanol have been studied by Ameen et al.[2,22], and Fally et al.[24,25]. Comparisons between the work of Ameen et al.[2,22] and Fally et al.[25] and the present work are summarized in Table 3. In the work of Ameen et al.[2,22], plasma polymers of allyl alcohol were prepared under conditions similar (P and ϕ) to those used in our work. It has been shown that the C-O functionality is readily derivatized using trifluoroacetic anhydride (TFAA). This result points to the involvement of the alkene in polymer formation, leaving the hydroxyl group unreacted and available for subsequent derivatization. The trends reported by Fally et al.[25] are in accordance with the observations by Ameen et al.[2,22] and those made in the present work (i.e. O/C ratio and retention of C-O groups decreased with increased power), although the reactor design (geometry) and experiment were different.

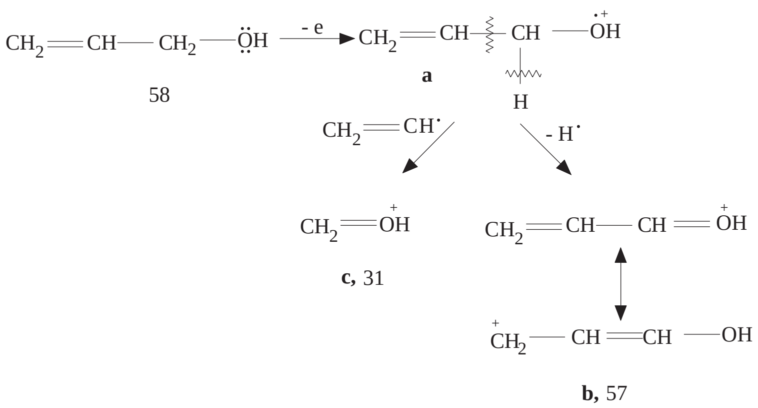
Table 3. Comparison of the work of Ameen et al., (1993 & 1994), Fally et al., (1996) and the present work. O/C ratio and retention of C-O groups for plasma-deposited allyl alcohol and 1-propanol.

P	allyl alcohol O/C	1-propanol O/C O/C	allyl alcohol % retention of C-O	1-propanol % retention of C-O
10^a ($\phi = 3.1$)	0.29	-	76.9 (56.8*)	-
10^a ($\phi = 0.8$)	-	54 (13*)	-	
10^a ($\phi = 3.0$)	-	-	-	14*
12^b ($\phi = 30$)	-	0.20	-	~ 63 (24*)
20^b ($\phi = 37$)	0.43	-	-	-
30^b	0.28	0.08	~ 80 (66*)	-
10^c ($\phi = 3.4$)	0.31	0.20	86.2	54.1
30^c ($\phi = 0.84$)	0.21	0.14	46	37.5

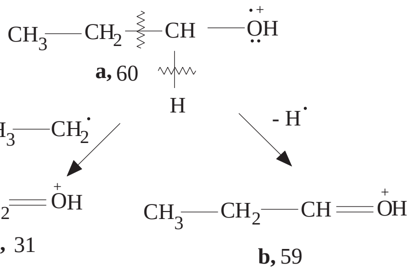
[a] Ameen et al.[2,22] [b] Fally et al.[25] [a] present work

*% retention of C-O groups after derivatization

XPS analysis revealed an inverse relationship between plasma power and the retention of C-O functionality. The same relationship between plasma-phase oligomers and functional group retention has also been previously reported for acrylic acid[3,8]. As reported elsewhere[6,7], a certain degree of fragmentation already occurs at $P/\phi = 1$, as observed with mass spectrometry. The mechanism of the plasma polymerization of allyl alcohol at low P/ϕ has been studied previously[6,7]. The first process to occur when an alcohol undergoes electron bombardment is the removal of the non-bonded electrons on oxygen to yield the cation, see **a**, in Scheme 1a for allyl alcohol: **a** decomposes further, and one of the energetically most favoured paths appears to be α-cleavage to furnish a stable oxinium ion **b** or **c**[31]. These are shown in Scheme 1a and Scheme 1b for both alcohols. For allyl alcohol and 1-propanol, two alternative decompositions of the molecular ion to an oxonium ion are possible, namely the loss of a hydrogen atom (radical) or ethyl radical, to yield **b** or **c,** respectively. The reaction in Scheme 2 was proposed by O'Toole and Short[6] and confirmed by means of a selected ion flow tube (SIFT)[7]. At low P, there is sufficient evidence to suggest that specific reactions between ions and molecules take place in the plasma gas phase leading to the formation of oligomeric species[3,6–9]. Major mechanisms initially involve the reaction of $(M\text{-}H)^+$ ion with M, where M represents a unit of the starting material, followed by a sequence of secondary ion-molecule reactions. These reactions could contribute to the formation of the plasma polymer deposit.

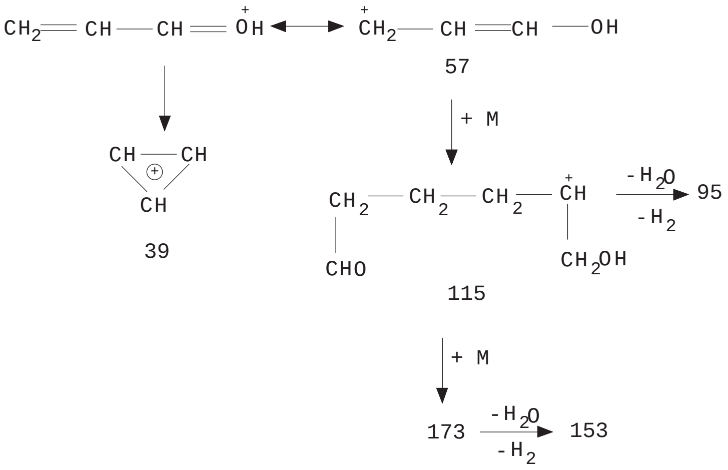


Scheme 1a.



Scheme 1b.

Turning to 1-propanol, the mechanism of polymerization may not be the same as in allyl alcohol due to the absence of the carbon carbon double bond. In the positive ion mass spectrometry, species of the form $(nM\text{-}H)^+$ were prevalent for allyl alcohol, whereas for 1-propanol the dominant species were of the form $(nM+H)^+$. The oligomeric species $(nM+H)^+$ probably corresponds to ion-neutral complexes, which are stabilized by the interaction of the component molecules with a shared proton. Similar behaviour has been reported by Beck and Short[29] in the mass spectrometric study of a mixture propanoic acid and 1-propanol. The possible ion-neutral complexes are shown in Table 4.



Scheme 2.

Table 4. Possible ion-neutral combinations in the positive ion mass spectra of 1-propanol.

m/z	Probable origin	Proposed structure
61	$(60n+H)^+$	$CH_3CH_2CH_2OH_2^+$
121	$(61+60n)^+$	$CH_3CH_2CH_2OH\cdots H^+\cdots HOCH_2CH_2CH_3$ Ion-neutral complex
181	$(121+60n)^+$	$CH_3CH_2CH_2OH\cdots H^+\cdots 2(HOCH_2CH_2CH_3)$ Ion-neutral complex

The degree of fragmentation continues to increase with P/ϕ, causing an increased loss of functional groups (distinguished by XPS). The general explanation for this kind of observation is that more energy per monomer is available at high P, leading to more severe monomer fragmentation. At high P, free-radical reactions are likely to assume greater importance. It is well known that plasma polymers can contain a high density of trapped free radicals (10^{17}-10^{20}spins per cubic centimetre)[1]. There are two pieces of information which support this assertion. First, a simple UV ageing experiment revealed that plasma-deposited allyl alcohol prepared at high P photo-oxidized rapidly[2,22], which suggests a higher concentration of trapped free radicals. Second, despite high oxygen retention, the high P products are less reactive to trifluoroacetic anhydride (TFAA)[2,22], which implies the incorporation of oxygen into the polymer network in the form of ether linkages. The decrease in hydroxyl functionality provides further evidence for the occurrence of rearrangement reactions.

Deposition-Rate Measurements

The deposition rates of allyl alcohol and 1-propanol are shown in Figure 4. These results demonstrate the difference in deposition rates between the unsaturated and saturated analogues. Allyl alcohol polymerizes more rapidly than 1-propanol. This trend was also observed in plasma polymers of saturated and unsaturated acrylic acids[3] and amines[20].

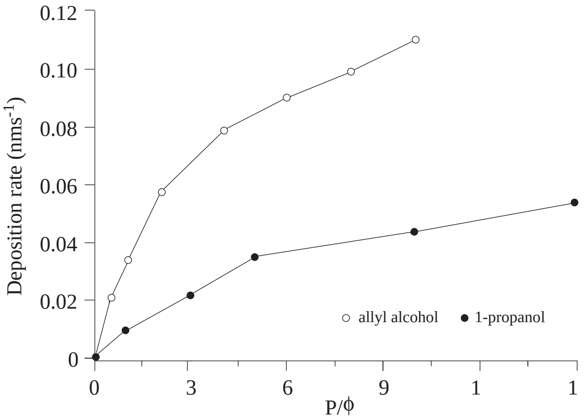


Figure 4. Deposition rate from plasmas of allyl alcohol and 1-propanol vs. P/ϕ.

Increased P/ϕ results in an increased ion flux[30] and greater ion energies[20] as well as an increased deposition rate. The importance of the effect of the double bond on the deposition rate can be seen in Figure 4. The comparison of the deposition rates of plasma-deposited allyl alcohol and 1-propanol suggests that the double bond is involved in the deposition mechanism: a higher deposition rate is observed for allyl alcohol than for 1-propanol. The opening of the double bonds probably plays a role in the deposition mechanism. Much bond breaking occurs during the polymerization of saturated monomer, which deposits very slowly. Moreover, plasma-deposit 1-propanol is probably highly crosslinked; they contain many unprotonated carbon atoms.

Conclusions

The effect of P/ϕs on thin-film properties was investigated by XPS analysis of plasma polymers from unsaturated and saturated alcohols. The study of the surface chemistry of films created from allyl alcohol and 1-propanol demonstrates the importance of the double bond for good C-O group retention. It has been shown that power has a pronounced influence of C-O group retention. At low P/ϕ, the double bond of allyl alcohol seems to be involved in the polymerization mechanism, leading to the formation of oxygen-rich polymers with a relatively low degree of crosslinking. In the absence of unsaturation, plasma polymers of 1-propanol contain lower amounts of C-O functionality. Opening of the double bond plays a role in the deposition mechanism: a higher deposition rate is observed for allyl alcohol.

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