

Grafting of a thin layer of poly(organophosphazene) containing succinic anhydride groups onto poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol)

L. Pemberton^a, R. De Jaeger^{a,*} and L. Gengembre^b

^aLaboratoire de Spectrochimie Infrarouge et Raman CNRS UPR 2631L Bât. C5, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

^bLaboratoire de Catalyse Hétérogène et Homogène, CNRS URA 402, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France
 (Received 12 August 1996; revised 7 May 1997)

A poly(organophosphazene) functionalized with succinic anhydride groups was bonded to the surfaces of poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol) films. The starting materials and the resultant surfaces were studied by XPS and ATR-i.r. spectroscopies and contact angle measurements. The comparison of XPS results obtained for the two grafted surfaces gave a clear indication of the protonation of the nitrogen atoms in the phosphazene backbone by the hydroxyl groups of the substrates. The extent of this protonation is greater in the case of the hydroxylated copolymer. The variations of the calculated atomic ratio and the deposited layer thickness *versus* polyphosphazene concentration demonstrated that the grafting yield is higher in the case of poly(vinyl alcohol). The poly(vinyl alcohol) modified surfaces showed a marked decrease in hydrophilic character. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: PVA; EVOH; films)

INTRODUCTION

The chemical modification of polymeric materials provides one approach in not only inducing important variations in their bulk properties, such as flame retardancy or thermal stability, but also modifying their surface properties, for example by introducing functional groups for the linkage with other oligomers or polymers. Poly(vinyl alcohol) (CH₂CH(OH))_n (PVA) is one of the water-soluble resins which has the greatest world-wide production. It is synthesized by the direct hydrolysis or the catalysed alcoholysis of the poly(vinyl acetate) copolymer. The ethylene-vinyl alcohol copolymer ((CH₂CH(OH))_x(CH₂CH₂)_y)_n (EVOH) is formed by hydrolyzing ethylene-vinyl acetate. The corresponding films of these products have excellent barrier performances against gases such as oxygen, carbon dioxide and nitrogen, as well as good mechanical properties. Thus, PVA and EVOH films are excellent materials, particularly in food packaging or in other industrial fields such as electronics, pharmaceutical, etc.^{1,2} The presence of hydroxyl groups on their surface suggests that these polymers have the potential for forming covalent linkages with other polymers containing chemical functions with which they are reactive. Because of their extreme versatility in applications, poly(organophosphazenes) (N = P(X)(X'))_n (POPZ) are relatively unique in macromolecular chemistry. Indeed, although the structure of an organic polymer is generally determined by its

monomer, in the case of POPZ an almost unlimited variety of structures can be obtained from the same chlorinated precursor (N = PCl₂)_n. Thus, very diverse physical and chemical properties can be obtained, depending on the nature and the number of the substituents X and X'. These polymers may be hydrophobic or hydrosoluble, photoresistant or photodegradable, resistant or not to solvents and to chemical attacks³⁻⁶. Therefore, one of the objectives of this work was to obtain organic polymer film surfaces with some of the properties of the POPZ polymers, while preserving their bulk performances.

The study by Allcock *et al.*⁷ concerning the thin-layer grafts of poly(bis(methoxyethoxy)ethoxyphosphazene) on surfaces of polypropylene, poly(vinyl chloride), poly(ethylene terephthalate) or poly(methyl methacrylate) provides a good example of the approach described above. In a previous paper it was reported that the radical grafting of a POPZ containing (2-methoxy 4-allyl)phenoxy substituents onto PVA films resulted in the transformation of their hydrophilic surface into an hydrophobic one⁸. The present work describes an alternative to this process which involves the reaction between a POPZ containing succinic anhydride groups with the hydroxylated PVA film surface. The grafting process and the characterization by XPS analysis, ATR-i.r. spectroscopy and contact angle measurements of the POPZ polymers and the ungrafted and grafted films are presented in detail. For the XPS analysis, a comparison is made between the results obtained with poly(vinyl alcohol) and those with poly(ethylene-co-vinyl alcohol). The latter has a lower surface density of hydroxyl groups, but probably a greater

*To whom correspondence should be addressed

ability for intermolecular hydrogen bonding with other polymers⁹.

EXPERIMENTAL SECTION

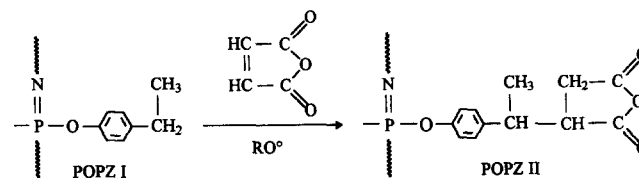
Materials

Poly(vinyl alcohol) (PVA) films manufactured by Nippon Gohsei Film Co. Limited (Japan) under the trademark 'BOVLON' were supplied by the Castel Fils Society (France). The melting point was 227°C and the heat resistance 220°C. The films were characterized by infrared spectroscopy (ATR). Absorbance bands are as follows: 3292 cm⁻¹ ν (O-H); 2938 cm⁻¹, 2905 cm⁻¹ ν (C-H); 1450 cm⁻¹ δ (C-H + O-H); 1419 cm⁻¹ δ (CH₂); 1373 cm⁻¹ γ_w (CH₂); 1321 cm⁻¹ δ (C-H + O-H); 1235 cm⁻¹ γ_w (C-H); 1142 cm⁻¹ ν (C-O + C-C); 1085 cm⁻¹ ν (C-OH) + δ (O-H); 913 cm⁻¹ γ_r (CH₂); 844 cm⁻¹ ν (C-C). The films of 14 mm thickness were cut to 2 × 4.5 cm size.

Poly(ethylene-co-vinyl alcohol) (EVOH) films manufactured under the trademark 'SOARNOL A' were supplied by Atochem Society (France). The melting point was 165°C. They were characterized by infrared spectroscopy (ATR). Absorbance bands are as follows: 3318 cm⁻¹ ν (O-H); 2929 cm⁻¹, 2854 cm⁻¹ ν (C-H); 1462 cm⁻¹ δ (C-H + O-H); 1436 cm⁻¹ δ (CH₂); 1328 cm⁻¹ δ (C-H + O-H); 1142 cm⁻¹ ν (C-O + C-C); 1089 cm⁻¹ ν (C-OH) + δ (O-H); 893 cm⁻¹ γ_r (CH₂); 845 cm⁻¹ ν (C-C). Films of 100 mm thickness were cut to 2 × 4.5 cm size. Just before use, PVA and EVOH films were dried at 100°C for 3 h.

Poly[(phenoxy)(4-ethylphenoxy)phosphazene] (POPZ I), supplied by the Atochem Company, was synthesized by the reaction of poly(dichlorophosphazene) (PCPZ) (previously obtained by polycondensation of P,P,P-trichloro-N(dichlorophosphoryl) monophosphazene)¹⁰ with the sodium salts of phenol and pethylphenol. Elemental analysis calculated from ¹H n.m.r. data: C, 64.26%; H, 5.15 N%, 5.56%; P, 12.31%. Found: C, 64.09%; H, 4.96%; N, 5.70%; P, 12.34%. The molecular weight, determined by light scattering, was 347 000, and the polydispersity index, determined by gel permeation chromatography, was $M_w/M_n = 7$. POPZ I was modified by solution grafting of maleic anhydride molecules (promoted by radical initiators) as reported by Gleria and co-workers¹¹ and Fontana¹² to give the polymer POPZ-g-SA (POPZ II) according to the

following structure:



This grafting is favoured by the low tendency of maleic anhydride to homopolymerize¹³. POPZ I and II were characterized by ¹H, ³¹P, ¹³C n.m.r. and infrared spectroscopies. Proton n.m.r. spectroscopy was used to estimate the percentage of the different side groups (phenoxy 63%, p-ethylphenoxy 37%) that formed the basis of the calculated elemental microanalysis for POPZ I. The amount of grafted SA in POPZ II being low (< 5% w/w according to Fontana¹²), the n.m.r. spectra of modified and unmodified POPZ were superimposable, and only i.r. data unequivocally support the grafting of SA onto the POPZ matrix. A summary of these data is presented in Table 1.

The formation of POPZ II is confirmed by the appearance of two i.r. bands at $\nu = 1785$ and 1861 cm⁻¹, which are assigned to the carbonyl stretching vibrations in the anhydride groups¹⁴.

Xylene (Aldrich) was used after drying on molecular sieves. Benzoyl peroxide and maleic anhydride were obtained from Fluka and used as received.

Grafting process

The film samples were supported in teflon frames for treatment. After drying, PVA and EVOH films were dip-coated at room temperature with xylenic POPZ II solutions, the phosphazene concentrations varying between 0.1 and 40 g l⁻¹ for PVA and between 0.5 and 10 g l⁻¹ for EVOH. After a few hours they were treated at 110°C for 7 h. The grafted films were then washed with xylene to remove the ungrafted polymer and finally dried at 110°C for 2 h. Control films were also prepared following the same procedure, but with POPZ I.

Equipment

The ³¹P, ¹H and ¹³C n.m.r. spectra of CDCl₃ solutions were recorded with a Bruker WP 300 n.m.r. spectrometer. Chemical shifts are given in parts per million from TMS

Table 1 N.m.r. and i.r. data for POPZ I

¹ H n.m.r. (ppm)	¹³ C n.m.r. (ppm)	³¹ P n.m.r. (ppm)	Infrared (cm ⁻¹)
0.91 (t, CH ₃ (6))	151.8 (s, aromatic(7))	- 19.3	3050 w ν (C-H) aromatic
2.23 (q, CH ₂ (5))	150 (s, aromatic(1))		2963 m, 2870 w ν (C-H) aliphatic
6.55-6.87 (m, aromatic)	139 (s, aromatic(4))		1592 m, 1507 s ν (C-C) aromatic
	128.7 (s, aromatic(9,9'))		1454 w δ (C-H) aliphatic
	127.9 (s, aromatic(3,3'))		1201 vs (br) ν_{as} (P=N)
	123.2 (s, aromatic(10))		1024 w δ (C-H) aromatic
	121.2 (s, aromatic(8,8'))		941 vs(br) ν (P-O-Ph), ν (P-N)
	121 (s, aromatic(2,2'))		835 s δ (C-H) aromatic
	28 (s, CH ₂ (5))		756 m δ (C-H) aromatic
	15.5 (s, CH ₃ (6))		688 m δ (C-C) aromatic
			509 s(br) δ (PNP), δ (NPN)

(^1H , ^{13}C) or 85% H_3PO_4 (^{31}P) as external standards. Elemental analyses were carried out at the Service Central d'Analyse (CNRS), France.

Contact angle measurements were made with a Face (Kyowa) contact angle goniometer at ambient humidity and temperature. The volume of the applied drop was 1 ml. All reported values are the average of at least eight measurements taken at different locations on the film surface.

Infrared spectra were recorded with a Bruker IFS 48 spectrometer. For the POPZ polymer, the spectra were obtained from films between KBr windows. For PVA films, a Graseby Specac, continuously variable-angle ATR accessory equipped with a KRS-5 crystal was used to obtain all ATR-i.r. spectra.

Size exclusion chromatography was carried out at the ATOCHEM Company on a water 150 ALC/GPC instrument. The columns used were a set of two similar Shodex 80M, with styrene-divinylbenzene organic micropacking as the stationary phase and THF with added LiBr (0.1 mol l^{-1}) as the eluent. A chromatix CMX 100 low-angle laser light scattering (LALLS) detector was inserted on line between the outlet of the columns and the inlet of the refractometer¹⁵.

The XPS analyses were performed in a LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 20 mA using $\text{AlK}\alpha$ radiation (1486.6 eV). The binding-energy scale calibration was based on Au $4f_{7/2}$ at 84 eV, Ag $3d_{5/2}$ at 368.2 eV, Cu $2p_{3/2}$ at 932.7 eV and C_{1s} ($-\text{CH}_2-$ -like species) at 285 eV. The analyser was operated in the FRR (fixed retarding ratio) mode. The vacuum was in the 10^{-8} mb range. The atomic ratios were determined by using the following empirical equation:

$$\frac{n_A}{n_B} = \frac{I_A}{I_B} \times \frac{K_B}{K_A}$$

where I_A , I_B are the intensities (areas) of the peaks of interest and K_A , K_B the sensitivity factors. These quantities depend on the electronic level cross-sections¹⁶, on the attenuation length¹⁷ and on the transmission of the analyser of the spectrometer¹⁸, the latter two being kinetic energy dependent. The fitting of the Tamuna's computed IMFs for 14 organic compounds¹⁷ with the equations proposed by Wagner *et al.*¹⁹ for describing the dependence of measured Al_s on electron energy,

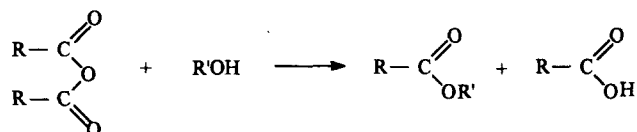
$$\lambda_{\text{Al}} = kE^m$$

gives values of k ranging from 0.107 to 0.149 Å while values of m vary between 0.781 and 0.795. For the calculation of P_{2p} and C_{1s} electrons attenuation lengths (38.8 and 35.3 Å, respectively) the average values of k (0.1315 Å) and m (0.789) have been considered (the overlayers calculated in Table 7 may seem to be very large, but their relative

variations must be considered rather than the absolute ones). Peak synthesis of the XPS spectra were performed with the software Peakfit (Jandel Scientific). The curve-fitting algorithm permitted the operator to synthesize peaks with the use of four parameters (position, height, width and shape), in addition to the background slope and intercept.

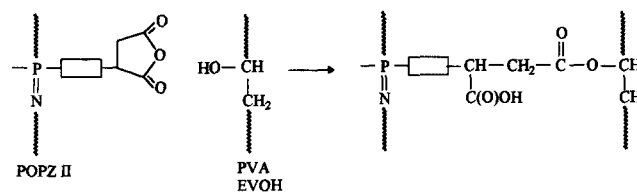
RESULTS AND DISCUSSION

The grafting process is based on the reaction between anhydrides and alcohols according to the structure depicted



below:

The generality of this reaction allowed it to be applied to poly((phenoxy)(p-ethylphenoxy)phosphazene)(POPZ I) functionalized with succinic anhydride groups (POPZ II), in order to obtain a grafting with the hydroxylated polymers poly(vinyl alcohol) (PVA) and poly(ethylene-co-vinyl



Where $\text{---}\square\text{---}$ is the spacer $\text{---OC}_6\text{H}_4\text{CH}_2\text{---}$

alcohol) (EVOH) according to

XPS characterization

EVOH, PVA and POPZ films. The XPS data for the EVOH copolymer and the PVA polymer before grafting are given in Table 2, while the respective C_{1s} photopeaks are reported on Figures 1 and 2. In both cases, four components were observed in the C_{1s} spectrum from 285 to 289.2 eV. The two components at the lower binding energies are representative of the $-\text{CH}_2-$ (285 eV)²⁰ and $-\text{CHOH}-$ (286.5 eV)²⁰ groups. Their relative intensities show that the EVOH copolymer composition is not far from 50 mol.% vinyl alcohol 50 mol.% ethylene, and that the PVA formulation corresponds to the $(\text{CH}_2-\text{CHOH})$ unit.

The two other components at 287.9–289.2 eV (EVOH) and 287.7–289 eV (PVA) are representative of the $\text{C}=\text{O}$ and

Table 2 XPS data for EVOH and PVA

Peak	EVOH BE ($\pm 0.2\text{eV}$)	Area (%)	nO/nC	PVA BE ($\pm 0.2\text{eV}$)	Area (%)	nO/nC
$\text{C}(1s)$	$-\text{CH}_2-$ 285	68	0.22	285	44	0.49
	$-\text{C}-\text{O}$ 286.5	24		286.5	45	
	$\text{C}=\text{O}$ 287.9	6		287.7	7	
	$-\text{C}(=\text{O})-\text{O}-$ 289.2	2		289	4	
$\text{O}(1s)$	532.8			532.8		

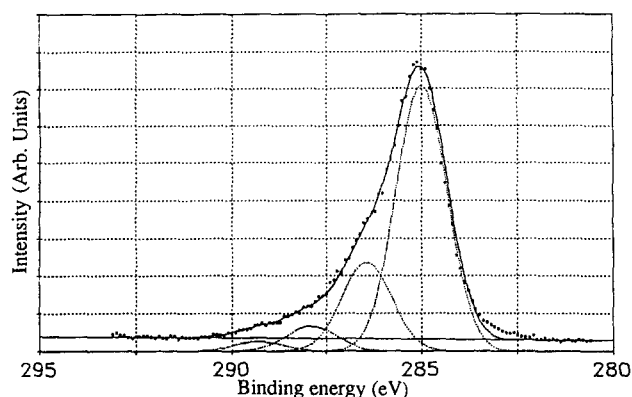


Figure 1 C(1s) XPS spectrum of EVOH.

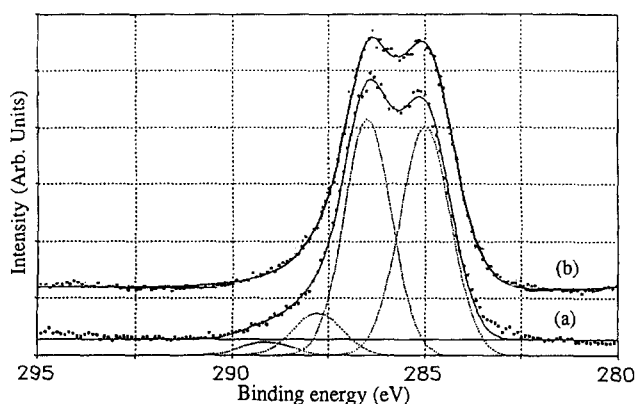


Figure 2 C(1s) XPS spectrum of PVA: (a) fresh PVA (5 mn mean exposure duration); (b) X-ray exposed PVA (30 mn mean exposure duration).

the X-ray source²¹, but more probably from the residual vinylacetate functions (EVOH and PVA being commercial materials derived from the parent vinylacetate polymers). Indeed, a very slight decrease in the C–OH component intensity is observed in the case of PVA with an exposure duration (between 5 and 30 min) to the X-ray source (Figure 2). There is no significant increase in the number of C=O and O–C=O-like species, as previously observed by Akhter *et al.*²¹ after a 90 min exposure at 15 kV, 20 mA. The nO/nC surface atomic ratios are 0.22 and 0.49 for EVOH and PVA, respectively; they are close to the theoretical values.

The photoelectronic features of POPZ I and POPZ II are quite similar (Table 3 and Figure 3). The C_{1s} photopeak reveals four components: (1) 285 eV (75%) due to the C–H species of the POPZ substituents; (2) 286.7 eV (18%) due to the C–O–P chemical environment; (3) 288.9 eV related to

species with relative intensity less than 2%; and (4) 291.5 eV (5%) representative of the Π – Π^* shake-up satellite of the aromatic rings. Due to their very low percentage in POPZ II, the succinic anhydride groups cannot be directly detected by XPS.

The binding energies of the P_{2p} and N_{1s} levels of the P=N chain are 134.1 and 398 eV, respectively. The P_{2p} profile shows a very slight asymmetry towards high binding energy that can be attributed to a more oxygenated terminal phosphorus, such as the =P–(OR)₃-species. This hypothesis is in accordance with the formation of low molecular weight oligomers during the polycondensation of P,P,P-trichloro-N(dichlorophosphoryl)monophosphazene. The N_{1s} profile presents a component at 400 eV with a relative intensity of approximately 15%. This shift to higher binding energy can be attributed to a loss of charge density on the nitrogen atom²². The O_{1s} binding energy of the P–O–X species is 533.5 eV; a slight asymmetry towards lower binding energy is also observed.

The O and P surface atomic stoichiometries (*versus* C) are close to the bulk atomic stoichiometries (Table 3). Only a slight lack of N is observed in the superficial layers analysed by XPS, leading to a ratio nP/nN which is higher than the bulk one.

EVOH and PVA grafted films. As the percentage of the succinic groups is very low (< 5%), a straightforward proof of the esterification cannot be obtained. The EVOH, PVA and POPZ polymers exhibit C_{1s} profiles containing components at equivalent binding-energy positions²³, but with different ratios. Therefore, the grafting process gives rise to a mixture of two C_{1s} profiles, depending on its extent. Fortunately, the heteroatoms N and P can be used as probes to check the effectiveness of the POPZ coating.

Following the grafting process described above, a series of EVOH and PVA films were treated with xylene solutions of the unmodified POPZ I and POPZ-g-SA II polymers (0.5 g l⁻¹ for POPZ I, 0.5 and 0.1 g l⁻¹ for POPZ II). The data from the XPS analyses are reported in Table 4 and Table 5. For the EVOH/POPZ II system the nN/nC and nP/nC atomic ratios of 5.2×10^{-2} and 4.8×10^{-2} , respectively, lead to $nP/nN = 0.93$, a slightly lower value than that for POPZ-g-SA II alone (Table 3).

In the case of the EVOH/POPZ I system, these atomic ratios are consistently lower, 2.34×10^{-2} for nN/nC and 0.95×10^{-2} for nP/nC , leading to $nP/nN = 0.4$. In addition, these variations are accompanied by a very noticeable modification of the N_{1s} peak (Table 5 and Figure 4).

The component at 398 eV, which represents 84% of the N_{1s} signal in POPZ I, decreases to 70 and 28% for the EVOH/POPZ II and EVOH/POPZ I systems, respectively; the 400 eV component increasing in the inverse sense.

Table 3 XPS data for POPZ I and POPZ II

Peak	POPZ I		POPZ II		Surface atomic stoichiometry	Bulk atomic stoichiometry POPZ I
	BE (± 0.2eV)	Area (%)	BE (± 0.2eV)	Area (%)		
C(1s)	285 ^a		285 ^a		nO/nC	17×10^{-2}
O(1s)	533.6		533.5		nN/nC	16×10^{-2}
N(1s)	398	84	398	85	nP/nC	6.5×10^{-2}
	399.8	16	400	15		7.3×10^{-2}
P(2p)	134.5		134.1		nP/nN	0.97

^aMain peak, for others see text

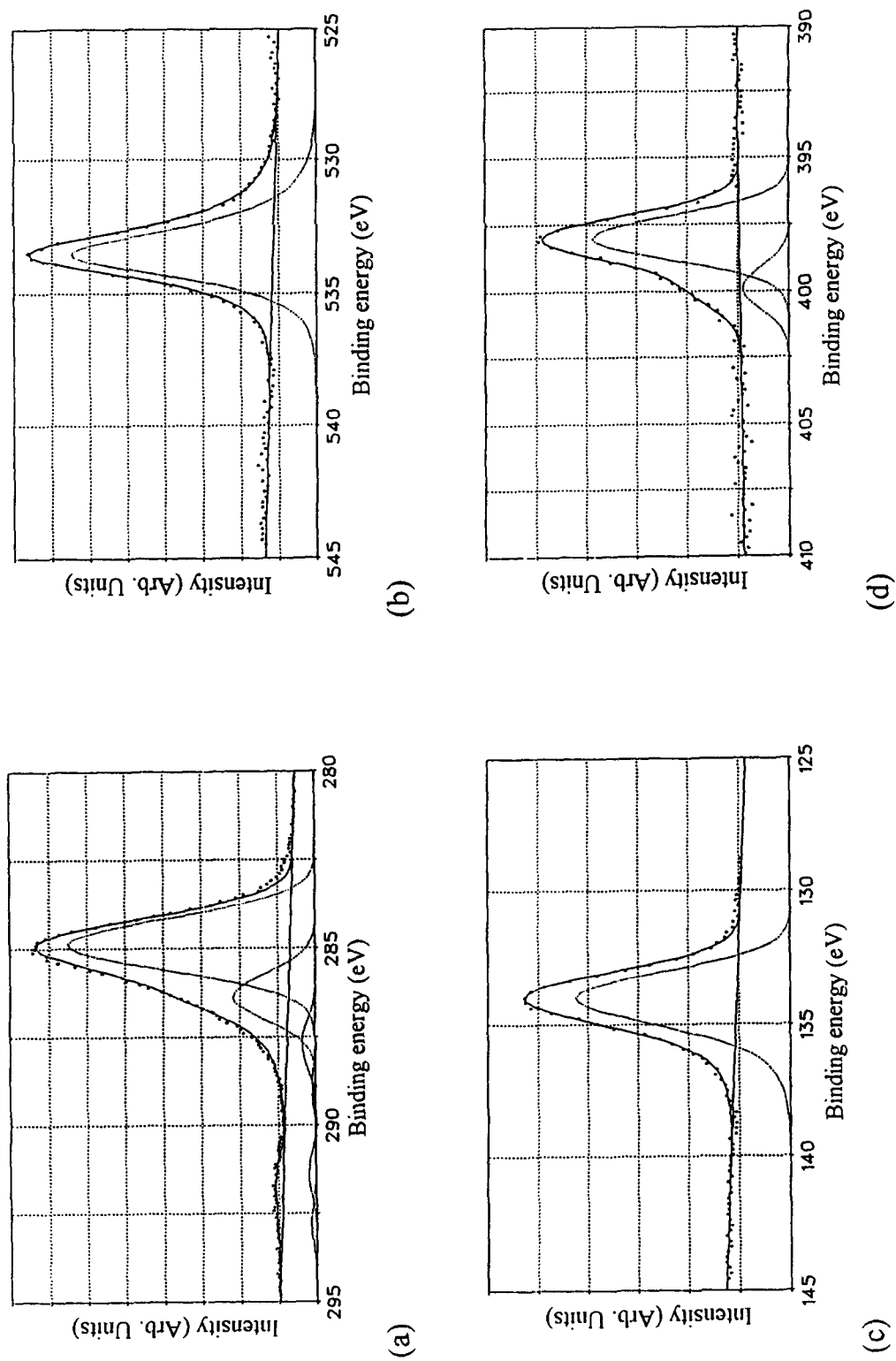


Figure 3 C(1s) (a), O(1s) (b), P(2p) (c), and N(1s) (d) XPS spectra of POPZ II.

Table 4 Surface atomic stoichiometry of EVOH/POPZ I, II and PVA/POPZ I, II systems

Surface atomic stoichiometry				
	EVOH/POPZ I 0.5 g l ⁻¹	EVOH/POPZ II 0.5 g l ⁻¹	PVA/POPZ I 0.5 g l ⁻¹	PVA/POPZ II 0.1 g l ⁻¹
<i>nO/nC</i>	0.19	0.19	0.38	0.31
<i>nN/nC</i>	2.34×10^{-2}	5.2×10^{-2}	2.5×10^{-2}	5.7×10^{-2}
<i>nP/nC</i>	0.95×10^{-2}	4.8×10^{-2}	2.5×10^{-2}	5.9×10^{-2}
<i>nP/nN</i>	0.40	0.93	1	1.03

Table 5 EVOH/POPZ I, II and PVA/POPZ I, II systems. Binding energies of the O(1s), N(1s) and P(2p) levels and evolution of the two N(1s) species

Peak	EVOH/POPZ		EVOH/POPZ II		PVA/POPZ I		PVA/POPZ II	
	BE (± 0.2eV)	Area (%)	BE (± 0.2eV)	Area (%)	BE (± 0.2eV)	Area (%)	BE (± 0.2eV)	Area (%)
O(1s)	532.7		533.5		532.8		533.6	
N(1s)	398	28	398	70	397.8	78	398	86
	400	72	400	30	399.7	22	400.1	14
P(2p)	134.1		133.8		134.1		134	

These variations are not observed in the PVA/POPZ I, II systems. In the latter systems, the ratio *nP/nN* and the 398–400 eV component proportions are in the same order of magnitude as for a thick film of POPZ I or II. Moreover, the P_{2p} binding energy and profile remain unchanged as compared to those of POPZ. These results indicate that the nitrogen atoms in the POPZ I polymer are protonated by interaction with the hydroxyl groups on the surfaces of EVOH and PVA, the extent of protonation being greatest on

EVOH. This result seems to be a consequence of the fact that PVA must be more strongly self-associated than the EVOH copolymer. Indeed, in PVA the hydroxyl functions are in closer proximity to one another in the chain, than in EVOH⁹. Intramolecular hydrogen bonding is therefore more important in the first case, interassociations of the hydroxyl groups with the nitrogen atoms in POPZ prevailing in the second. Identical variations for the N_{1s} band were also observed in the case of films formed by aminosilanes onto

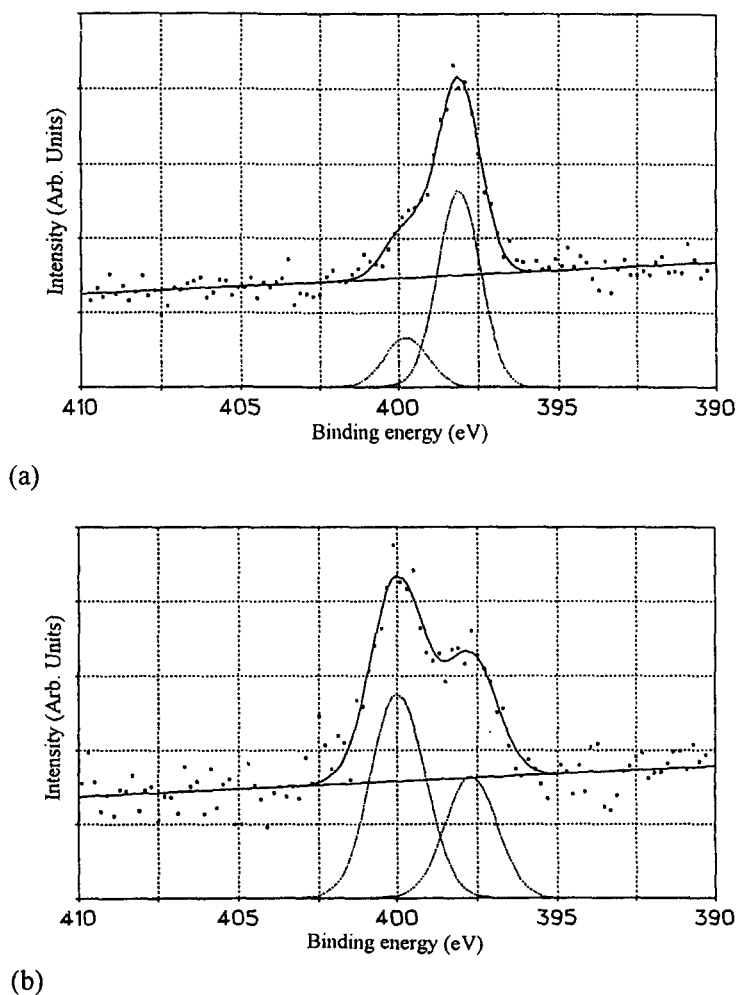
**Figure 4** N(1s) XPS spectra of PVA/POPZ I (a) and EVOH/POPZ I (b).

Table 6 EVOH and PVA/POPZ II systems. Surface atomic stoichiometry as a function of POPZ concentration

POPZ II Concentration (g l ⁻¹)	nO/nC		nN/nC × 10 ²		nP/nC × 10 ²		nP/nN	
	EVOH	PVA	EVOH	PVA	EVOH	PVA	EVOH	PVA
0	0.22	0.49	—	—	—	—	—	—
0.1	—	0.31	—	5.7	—	5.9	—	1.03
0.5	0.19	—	5.2	—	4.8	—	0.93	—
1	0.16	0.20	5.8	6.7	5.5	7.1	0.95	1.06
3	0.16	0.18	6.7	6.7	6.5	7.5	0.98	1.11
10	0.16	0.18	6.8	7.1	7.0	8.3	1.03	1.16
POPZ II	0.16	—	6.5	—	7.3	—	1.12	—

metal substrates or acidic glass. The component at lower energy was assigned to the free amino groups and the one at higher energy to amino groups protonated by the superficial hydroxyl functions^{24,25}. The assignment according to Fewell²⁶ of the 400 eV component to -N=N- bonds resulting from branching in the polymer during substitution reactions seems not to be plausible here. Indeed, in this case the results should be the same for PVA and EVOH. This nitrogen protonation seems to be responsible for the coupling of POPZ I with the PVA surface. On the other hand, in the case of EVOH, the decrease of the nP/nN atomic ratio indicates that the coupling does not concern POPZ I, but its degradation products. No satisfactory explanation has been found for this degradation, although it could be compared to the cleavage of the N protonated polyalkyl-phosphazenes chains²⁷ and of the poly(methoxy-alkoxyphosphazene) in their reactions with BBr₃/H₂O²⁸.

For the two systems EVOH and PVA/POPZ I, the binding energies for the maximum of the O_{1s} peak are the same as for O_{1s} in EVOH or PVA, and the transitions II-II* in the C_{1s} peak are not observed, suggesting that only very little coating occurs in these cases. This interpretation is also corroborated by the nN/nC values. In addition, the atomic ratio nN/nC that is 2.5 × 10⁻² for the system PVA/POPZ I ([POPZ I] = 0.5 g l⁻¹), increase to 5.7 × 10⁻² in the system POPZ II/PVA ([POPZ II] = 0.1 g l⁻¹). This result clearly demonstrates that the yield of the grafting reaction is dependent on the number of succinic anhydride functions introduced into POPZ matrix.

Influence of the POPZ concentration. The influence of POPZ II concentration was checked by carrying out a series of experiments with the use of xylene solutions with concentrations varying from 0.1 to 40 g l⁻¹. 'POPZ II-like' XPS spectra were obtained with the more diluted solutions 0.1 g l⁻¹ for PVA and 0.5 g l⁻¹ for EVOH. The variation of the calculated atomic ratios with POPZ II concentration shown in Table 6 demonstrates that it is easier to graft PVA-POPZ II than EVOH-POPZ II. Indeed, the POPZ ratios nN/nC and nP/nC are reached for a 1 g l⁻¹ POPZ II concentration in the first case, and 3 g l⁻¹ in the second.

Table 7 EVOH and PVA/POPZ II systems. Evolution of the calculated POPZ layer thickness with POPZ concentration

POPZ II concentration (g l ⁻¹)	Thickness (Å)	
	EVOH	PVA
0.1	—	60
0.5	39	—
1	52	130
3	85	130
10	120	130

This result was corroborated by the calculation of the deposited POPZ layer thickness. It was made by assuming that the covering of the substrate surfaces was by a homogeneous film of POPZ, disregarding its possible diffusion into the EVOH or PVA matrix. As long as the substrate remains accessible to the XPS analysis, the thickness can be evaluated from the ratio

$$\frac{I(P)}{I(C)} = \frac{I(P)_{\text{POPZ}}^{\infty} \left(1 - e^{-\frac{d}{\lambda_P^{\text{POPZ}}}} \right)}{I(C)_{\text{POPZ}}^{\infty} \left(1 - e^{-\frac{d}{\lambda_C^{\text{POPZ}}}} \right) + I(C)_{\text{EVOH (PVA)}}^{\infty} e^{-\frac{d}{\lambda_C^{\text{POPZ}}}}}$$

In this expression the numerator represents the intensity of the P_{2p} peak obtained from a deposited POPZ film having thickness *d*, and the denominator the intensity of the C_{1s} peak due to the POPZ film and the substrate. The symbols I[∞] represent the intensities obtained from thick films of POPZ, EVOH and PVA; and λ_p, λ_c represent the attenuation lengths of the phosphorus and carbon photoelectrons in the polymers¹⁷. The values obtained are reported in Table 7. The higher grafting yield observed for PVA compared to EVOH correlates with its higher surface density of hydroxyl groups. In fact, similar overlayer thicknesses (60 Å for PVA and 52 Å for EVOH) are obtained for a 10-times lower POPZ II concentration in the case of PVA. In the same way, an infinite overlayer seems to be obtained with a 1 g l⁻¹ POPZ II concentration for PVA, whereas a 10 g l⁻¹ POPZ II concentration is required for EVOH.

ATR-i.r. spectroscopy

A comparison of the ATR-i.r. spectra of an original PVA film and those of POPZ II treated films (the concentration of the POPZ solution varying from 5 to 40 g l⁻¹) is made in Figure 5. The variation of these spectra is characterized by the appearance of principal absorption bands at 1592.5, 1490, 1198 and 934.5 cm⁻¹, which can be assigned, respectively, to the C-C (aromatic) (1592.5 and 1490 cm⁻¹), and the P=N and P-O-(C) stretching vibrations in POPZ^{14,29}. Their intensities increase with POPZ concentration. The progressive disappearance of the broad band at 3280 cm⁻¹ representative of the hydroxyl groups in PVA can also be noted.

It was also possible to follow the evolution of the grafting reaction by measuring the ratio of the intensities of the bands at 1592.5 and 836.4 cm⁻¹, the latter being assigned to the aromatic δ(C-H) vibrations in POPZ and ν(C-C) in PVA. The variation in their intensity ratio as a function of

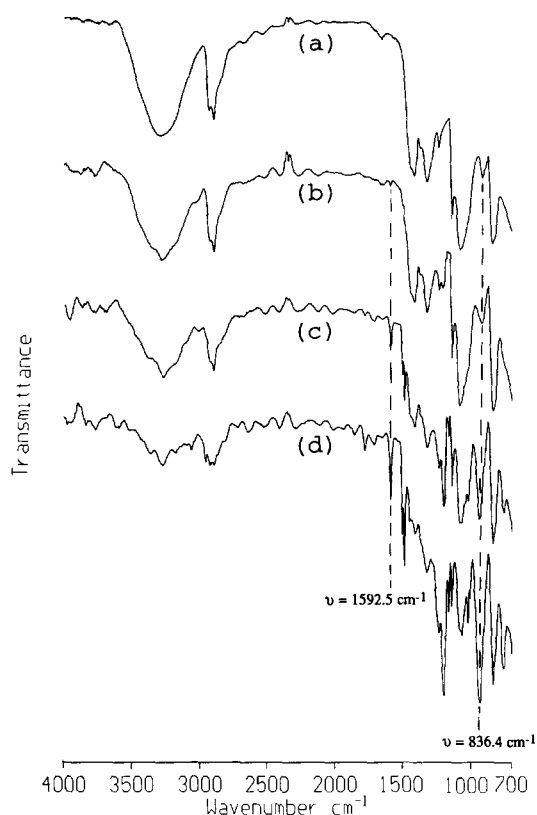


Figure 5 ATR-i.r. spectra of grafted PVA films as a function of POPZ II concentration: (a) virgin PVA; (b) POPZ II 5 g l⁻¹; (c) POPZ II 25 g l⁻¹; (d) POPZ II 40 g l⁻¹.

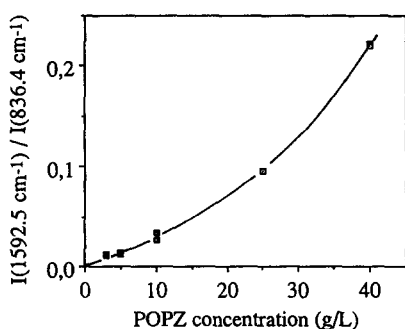


Figure 6 Variations of the intensity ratio of i.r. bands at $\nu = 1592.5$ and 836.4 cm^{-1} versus POPZ concentration.

POPZ concentration, is shown in *Figure 6*. In addition to the effect of covalent grafting, the continuous increase of this ratio can be explained by the intervention of a cross-linking reaction of POPZ, which occurs with time at room temperature in xylene solutions of POPZ-g-SA.

Contact-angle measurements

The occurrence of the grafting reaction at the PVA film surface can also be evidenced by the change in contact angle. Thus, a series of films treated with POPZ II solutions of various concentrations (between 0.1 and 40 g l⁻¹) were studied by contact angle measurements with water droplets. Their variations are represented in *Figure 7* as a function of POPZ concentration. The curve shows a rapid and noticeable increase in the contact angle from $\theta = 35^\circ$ for PVA to $\theta = 70$ and 86° for 0.3 and 40 g l⁻¹ POPZ concentrations, respectively. In addition, for each concentration the contact angles are identical to within $\pm 4^\circ$ across the PVA film

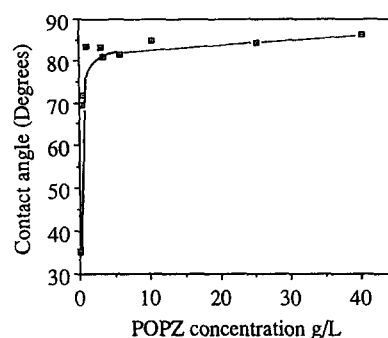


Figure 7 Variations of contact angle measurements versus POPZ concentration.

surface, suggesting an uniform grafting of POPZ. These results corroborate those obtained with the XPS analysis, which showed that the thickness of the POPZ layer deposited on the PVA surface was already of the order of 100 Å for a POPZ concentration of 1 g l⁻¹.

CONCLUSION

In conclusion, the results reported here show that the grafting reaction of succinic anhydride functionalized polyorganophosphazenes onto poly(vinyl alcohol) or poly(ethylene-co-vinyl alcohol) films can be obtained with the application of a very simple procedure.

A comparison is made, with the use of XPS analysis, of the results obtained by changing the substrate (EVOH or PVA) or the concentration of the POPZ solution. It clearly demonstrates the influence of the hydroxyl group surface density on the substrate and the concentration of succinic anhydride functions. In the present case the grafting results in significant modifications in the surface properties of the hydroxylated polymers, inducing a decrease in the degree of hydrophilicity of the PVA films. However, considering the large diversity of potential structures of the POPZ polymers, it should be possible to infer many other properties, e.g. electrical conductivity, resistance to solvents and other chemicals, to any carbon backboned polymer bearing hydroxyl groups.

REFERENCES

1. Pritchard, J. G., *Poly(vinyl alcohol) Basic Properties and Uses*. MacDonald Technical and Scientific, London, 1970.
2. Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G., *Encyclopedia of Polymer Science and Engineering*, Vol. 17. Wiley, New York, 1989, p. 173.
3. Allcock, H. R. *Phosphorus-Nitrogen Compounds*. Academic Press, New York, 1972.
4. Mark, J. E., Allcock, H. R. and West, R. *Inorganic Polymers*. Prentice Hall, Englewood Cliffs, NJ, 1992.
5. Wisian-Neilson, P., *Encyclopedia of Inorganic Chemistry*, Vol. 6. Wiley, Chichester, 1994, p. 3371.
6. Potin, Ph. and De Jaeger, R., *European Polymer Journal*, 1991, **27**, 341.
7. Allcock, H. R., Fitzpatrick, R. J. and Salvati, L., *Chemistry of Materials*, 1992, **4**, 775.
8. Pemberton, L. and De Jaeger, R., *Chemistry of Materials*, 1996, **8**, 1391.
9. Coleman, M. M., Yang, X., Zhang, H. and Painter, P. C., *Journal of Macromolecular Science and Physics*, 1993, **B32**(3), 295.
10. D'Halluin, G., De Jaeger, R., Chambrette, J. P. and Potin, Ph., *Macromolecules*, 1992, **25**, 1254.
11. Gleria, M., Minto, F., Scoponi, M., Pradella, F. and Carassiti, Y., *Chemistry of Materials*, 1992, **4**, 1027.
12. Fontana, G., Thesis, Università degli studi di Padova, 1994.

13. Datta, S. and Lohse, D. J., *Macromolecules*, 1993, **26**, 2064.
14. Silverstein, R. M., Bassler, C. G. and Morrill, T. C., *Spectrophotometric Identification of Organic Compounds*. Wiley, New York, 1974, p. 86.
15. De Jaeger, R., Lecacheux, D. and Potin, Ph., *Journal of Applied Polymer Science*, 1990, **39**, 1793.
16. Scofield, J. H., *Journal of Electron Spectroscopy and Related Phenomena*, 1976, **8**, 129.
17. Tamuna, S., Powell, C.J. and Penn, D.R., *Surface Interface Analysis*, 1994, **21**, 165. (and previous papers in the series).
18. Van Eenbergen, A. and Brunninx, E., *Journal of Electron Spectroscopy and Related Phenomena*, 1984, **33**, 51.
19. Wagner, C. D., Davis, L. E. and Riggs, W. M., *Surface Interface Analysis*, 1980, **2**, 53.
20. Lopez, G. P., Castner, D. G. and Ratner, B. D., *Surface Interface Analysis*, 1991, **17**, 267.
21. Akhter, S., Allan, K., Buchanan, D., Cook, J. A., Campion, A. and White, J. M., *Applied Surface Science*, 1988, **35**, 241.
22. Hiraoka, H. and Lee, W., *Macromolecules*, 1978, **11**, 622.
23. Briggs, D. and Beamson, G., *Analytical Chemistry*, 1992, **64**, 1729.
24. K. L. Mittal, *Silanes and Other Coupling Agents*. VSP ED, 1992.
25. Fowkes, F. M., Dwight, D. W., Cole, D. A. and Huang, T. C., *Journal of Non-Crystalline Solids*, 1990, **120**, 47.
26. Fewell, L. L., *Journal of Applied Polymer Science*, 1990, **41**, 391.
27. Neilson, R. H. and Wisian-Neilson, P., *Chemical Reviews*, 1988, **88**, 541.
28. Medici, A., Fantin, G., Pedrini, P., Gleria, M. and Minto, F., *Macromolecules*, 1992, **25**, 2569.
29. Thomas, L. C., *Interpretation of the Infrared Spectra of Organophosphorus Compounds*. Heyden, London, 1974.