# Surface Grafting of a Poly(organophosphazene) onto Poly(vinyl alcohol) and Poly(ethylene-*co*-vinyl alcohol) Using Triethoxysilane as a Coupling Agent

LYDIE PEMBERTON,[1] ROGER DE JAEGER,[1] L. GENGEMBRE[2]

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

[2] Laboratoire de Catalyse Hétérogène et Homogène, CNRS URA 402, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

**ABSTRACT:** Triethoxysilane $HSi(OEt)_3$ was used as coupling agent to graft a poly(organophosphazene) (POPZ) containing allylic functions to the surface of poly(vinyl alcohol) or poly(ethylene-*co*-vinyl alcohol) films. Hydrolyzed $HSi(OEt)_3$, which contained both inorganic (Si—OH) and organic (Si—H) reactivities, acted at the interface between the hydroxylated substrates (via a condensation reaction) and the allylic functions in POPZ (via a hydrosilylation reaction). Starting materials and grafting surfaces were studied by ATR-IR and XPS spectroscopies and contact angle measurements. Data obtained indicated that different POPZ layers were produced, depending on whether the functionalization of materials with silane, and the grafting reaction were separately or simultaneously made. The POPZ layer thickness was higher when the grafting reaction was preceded by the POPZ functionalization. In each cases, the modified surfaces showed marked increases in hydrophobicity character. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1965–1974, 1998

**Key words:** poly(vinyl alcohol); triethoxysilane; poly(organophosphazene); films; grafting

## INTRODUCTION

Poly(ethylene-*co*-vinyl alcohol) (EVOH) and poly(vinyl alcohol) (PVA) are considered as the most efficient gas-barrier materials (to oxygen, carbon dioxide, etc.). They are macromolecules widely used in several different scientific and industrial domains like food packaging.[1,2] These polymers are, however, hydrophilic, and it is extremely important to protect them against inopportune moisture regain, which would substantially alter their barrier properties.

Surface chemistry provides one approach to solving this problem, and particularly the superficial grafting of thin layers of poly(organophosphazenes) (POPZ). Indeed, the very diverse physical and chemical properties of these phosphorus-nitrogen macromolecules[3–5] are able to completely change the nature of the surface of conventional polymers. For example, Allcock et al.[6] described the modification of different organic polymer surfaces (polypropylene, poly(vinyl chloride), poly(ethylene terephtalate), or poly(methyl methacrylate)) by radiation grafting of thin films of poly[bis((methoxyethoxy)ethoxy)phosphazene]. In this case, the grafted surfaces form hydrogels with high water content in the presence of aqueous media. In a previous article[7] we reported the radical grafting of a hydrophobic

POPZ containing (2-methoxy 4-allyl)phenoxy substituents onto PVA film surfaces. An interesting alternative, which was also applied to both poly(ethylene-*co*-vinyl alcohol) and poly(vinyl alcohol) polymer, involved the reaction between a POPZ containing succinic anhydride groups and the hydroxylated surfaces.[8]

The objective of this work was to investigate the possible use of organofunctional silanes as adhesion promoters between a POPZ containing allylic functions and EVOH or PVA. Silanes, which usually act at the interface between an inorganic substrate (glass, metal) and an organic substrate (polymer, adhesive), generally improve adhesion and give increased mechanical strength. Alkoxysilanes $(RO)_nSiR'_{(4-n)}$[9] containing hydrolysable siliconfunctional groups $(OCH_3, OC_2H_5)$ and organofunctional groups (vinyl, epoxy, methacrylate) were widely used as surface modifiers. As an example, we can report the adhesion of a polychlorotrifluoroethylene film containing alkyltriethoxysilane functionalities to the glass.[10] The silane selected for the present study was triethoxysilane $HSi(OEt)_3$. This choice was made because of the Si—H bonds, which allowed hydrosilylation reactions, and the Si—OEt groups, which can react after their hydrolysis with hydroxyl functionalities.

The surface modification of EVOH and PVA films with POPZ could be achieved in three ways: (1) the functionalization of POPZ by triethoxysilane was followed by its grafting onto the film surface; (2) the functionalization of PVA or EVOH by triethoxysilane was followed by the reaction of POPZ onto the modified substrates; and (3) functionalization and grafting reactions occurred simultaneously. The results obtained according to these three ways were reported in this article.

## EXPERIMENTAL

### 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$^{-1}$ $v$(O—H); 2938 cm$^{-1}$, 2905 cm$^{-1}$ $v$(C—H); 1450 cm$^{-1}$ $\delta$(C—H + O—H); 1419 cm$^{-1}$ $\delta$(CH$_2$); 1373 cm$^{-1}$ $\gamma_w$(CH$_2$); 1321 cm$^{-1}$ $\delta$(C—H + O—

H); 1235 cm$^{-1}$ $\gamma_w$(C—H); 1142 cm$^{-1}$ $v$(C—O + C—C); 1085 cm$^{-1}$ $v$(C—OH) + $\delta$(O—H); 913 cm$^{-1}$ $\gamma_r$(CH$_2$); 844 cm$^{-1}$ $v$(C—C). The films of 14 $\mu$m thickness were cut to $2 \times 4.5$ cm sizes.

Poly(ethylene-*co*-vinyl alcohol)(EVOH) films manufactured under the trademark "SOARNOL A" were supplied by the Atochem Society (France). The melting point was 165°C. They were characterized by infrared spectroscopy (ATR). Absorbance bands were as follows: 3318 cm$^{-1}$ $v$(O—H); 2929 cm$^{-1}$, 2854 cm$^{-1}$ $v$(C—H); 1462 cm$^{-1}$ $\delta$(C—H + O—H); 1436 cm$^{-1}$ $\delta$(CH$_2$); 1328 cm$^{-1}$ $\delta$(C—H + O—H); 1142 cm$^{-1}$ $v$(C—O + C—C); 1089 cm$^{-1}$ $v$(C—OH) + $\delta$(O—H); 893 cm$^{-1}$ $\gamma_r$(CH$_2$); 845 cm$^{-1}$ $v$(C—C). Films of 100 $\mu$m thickness were cut to $2 \times 4.5$ cm sizes. Just before using, PVA and EVOH films are dried at 100°C for 3 h.

Poly[(phenoxy)(4-ethylphenoxy)(2-methoxy-4-allylphenoxy)phosphazene] (POPZ), 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)[11] with the sodium salts of phenol, 4-ethylphenol and (2-methoxy-4-allyl)phenol in chlorobenzenic solution. Elemental analysis calculated from $^1$H-NMR data: C, 64.24%; H, 5.51%; N, 5.15%; P, 11.41%; Found: C, 65.42%; H, 5.49%; N, 5.09%; P, 10.91%. The molecular weight, determined by light scattering, was 1,240,000, and the polydispersity index, determined by gel permeation chromatography, was $M_w/M_n = 14$. It was characterized by infrared spectroscopy. Absorbance bands were as follow: 3050 $v$(C—H) arom; 2964,2871 $v$(C—H)aliph; 1593, 1507 $v$(C—C) arom; 1455 $\delta$(C—H)aliph; 1206 $v_{as}$(P═N); 1019 $\delta$(C—H) arom; 943 $v$(P—O—Ph), $v$(P—N); 835 $\delta$(C—H) arom; 756 $\delta$(C—H) arom; 688 $\delta$(C—C) arom; 526 $\delta$(PNP), $\delta$(NPN).

Toluene (Aldrich) was used after drying on molecular sieves. Triethoxysilane and platinum divinyltetramethyldisiloxane complex were obtained from ABCR and used as received.

### Functionalization of POPZ with Silane (Silane-*g*-POPZ)

To a solution of poly[(phenoxy)(4-ethylphenoxy)(2-methoxy-4-allylphenoxy)phosphazene] in toluene (100 g/L) under dry nitrogen flow, were added triethoxysilane and three drops of platinum divinyltetramethyldisiloxane complex. The triethoxysilane/(2-methoxy 4-allylphenoxy) molar ra-

tio was 1 : 5. The mixture was stirred and refluxed for times ranging between 1 and 20 h. The polymer was recovered by removal of the solvent under reduced pressure.

### Functionalization of PVA and EVOH with Silane (Silane-*g*-PVA and Silane-*g*-EVOH)

A mixture water/ethanol (5/95), with a pH adjusted to 5 by acetic acid, was prepared. Triethoxysilane (2 mass %) was added to the mixture. After 20 min, the hydrolysis of ethoxy groups was achieved.[12] The PVA and EVOH films (dried at 110°C for 4 h) were dip coated with this solution for 10 min, washed briefly with ethanol, and dried at 110°C for 1 h.

### Reaction of Silane-*g*-POPZ with PVA

PVA film samples (dried at 110°C for 4 h) were dip coated under anhydrous conditions with a refluxing solution of Silane-*g*-POPZ in toluene. The films were then treated in an oven at 60°C under humid atmosphere during 24 h; next they were washed with toluene for 15 h and finally dried at 110°C for 2 h.

### Reaction of Silane-*g*-PVA and Silane-*g*-EVOH with POPZ

Silane-*g*-PVA and Silane-*g*-EVOH film samples were immersed in a toluenic POPZ solution (50 g/L) containing 3 drops of platinum divinyltetramethyldisiloxane complex. The mixture was refluxed for 20 h. Then, the films were washed with toluene to remove ungrafted polymer, and finally dried at 110°C for 3 h.

### Simultaneous Reactions of PVA and POPZ with Silane

PVA film samples (dried at 110°C) were dip coated 5 min in a toluene solution containing POPZ (50 g/L), triethoxysilane (triethoxysilane/(2-methoxy 4-allylphenoxy) molar ratio 1 : 7) and platinum divinyltetramethyldisiloxane complex (3 drops). They were then heated at 110°C for 4 h, and treated under humid atmosphere at 60°C for 24 h. Finally, they were washed with toluene for 15 h and dried at 110°C for 2 h.

### Equipment

The ^{1}H-NMR spectra of CDCl$_3$ solutions were recorded with a Bruker WP 300 NMR spectrometer. Chemical shifts were given in parts per million from TMS 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 μL. All reported values were 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 and EVOH films, a Graseby Specac, continuously variable angle ATR accessory equipped with a KRS-5 crystal was used to obtain all ATR-IR 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) 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 intlet of the refractometer.[13]

The XPS analyses were performed in a LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 20 mA using Al$_{K\alpha}$ 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$_{1s}$ (—CH$_2$— like species) at 285 eV. The analyzer 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.
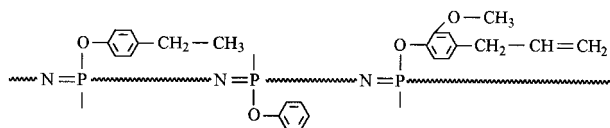
$$\frac{n_A}{n_B} = \frac{I_A}{I_B} \times \frac{K_B}{K_A}$$

where $I_A$, and $I_B$ are the intensities (areas) of the peaks of interest, and $K_A$, and $K_B$ the sensitivity factors.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of the Poly(organophosphazene)

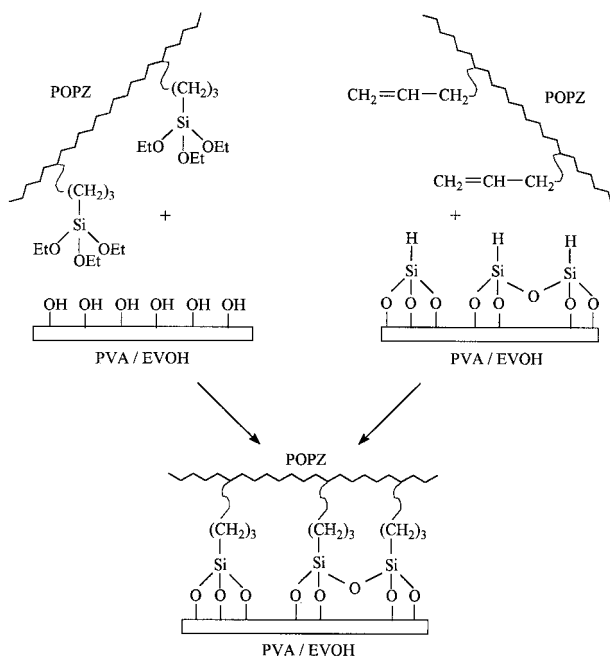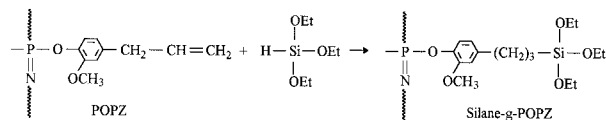The structure of the POPZ used was represented Scheme 1. It contained 38.5% of phenoxy, 60% of

**Scheme 1**



**Scheme 3**

4-ethyl phenoxy, and 1.5% of (2-methoxy 4-allyl-phenoxy) side groups. The molecular weight (light scattering) was $1.2 \times 10^6$ g·mol$^{-1}$, with a polydispersity index (gel permeation chromatography) $M_w/M_n = 14$. It was obtained from a two-step reaction: polycondensation of P,P,P-trichloro-N(dichlorophosphoryl)monophosphazene) $Cl_3P = N-P(O)Cl_2$ leading to the poly(dichlorophosphazene) $(N = PCl_2)n$ following a method described previously.[11] Substitution of chlorine atoms in $(N = PCl_2)_n$ by reaction with sodium salts of phenol, 4-ethylphenol, and (2-methoxy 4-allyl)phenoxy leading to POPZ. The choice of this POPZ was based on the hydrophobicity of corresponding films and on its ease of radical reaction due to the presence of allylic functions.[14]

### Grafting of POPZ onto PVA or EVOH Film Surface

A simplified picture of the two bonding mechanisms between POPZ and PVA or EVOH using triethoxysilane as a coupling agent was shown in Scheme 2. They involved the preliminary functionalization reactions of POPZ and PVA or EVOH with silane, respectively.

### Functionalization of POPZ with Silane (Silane-*g*-POPZ)

The functionalization process was based on the hydrosilylation reaction between the allylic functions in POPZ and the triethoxysilane HSi(OEt)$_3$, leading to the Silane-*g*-POPZ according to the Scheme 3.[15] The reaction was carried out in toluene at 110°C and catalyzed by the platinum divinyl tetramethyldisiloxane complex.
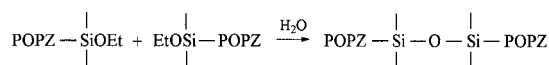
The formation of the Silane-*g*-POPZ from the parent polymer POPZ was distinguished in ^{1}H-NMR by the disappearance of the signals corresponding to the allylic groups at $\delta = 3.1$ ppm ($-CH_2-$), $\delta = 5.7$ ppm ($-CH=$), and $\delta = 4.9$ ppm ($=CH_2$), and by its hydrolytic crosslinking in contact with atmospheric moisture (Scheme 4).

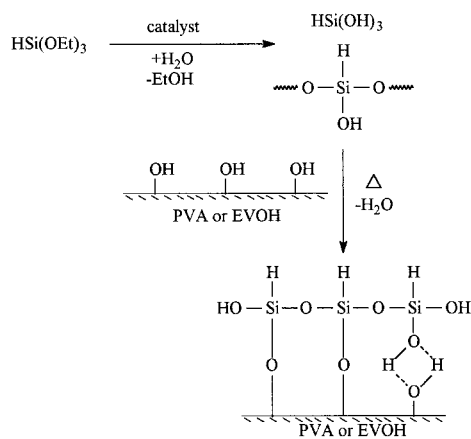### Functionalization of PVA and EVOH with Silane (Silane-*g*-PVA and Silane-*g*-EVOH)

The general mechanism for the $\equiv$Si$-$O$-$surface bond formation between the triethoxysilane and the hydroxylated substrates PVA and EVOH was depicted in Scheme 5.[16,17] Three stages were involved in this process: acid catalyzed hydrolysis and condensation of the triethoxysilane giving monomeric or oligomeric silanol; hydrogen bonding between them and the hydroxyl groups of the substrate; and covalent linkage formation.

After dip coating in the silanol oligomers solution, washing, and thermal treatment,[12] the PVA and EVOH films were studied by water contact angle measurements and XPS analysis.

The results obtained in water contact angle measurements were summarized in Table I. They showed a noticeable increase from $\theta = 35°$ for the uncoated PVA to $\theta = 58°$ for the coated PVA film. This increase was less in the case of EVOH copoly-



**Scheme 2**



**Scheme 4**

**Scheme 5**



**Figure 1** XPS spectra of Silane-*g*-PVA (a) and Silane-*g*-EVOH (b).

mer film, from 66° to 74°. The difference noted after treatment between the two coated films suggested a nonuniform grafting of the silanol monomers or oligomers on their surface.

The XPS spectra of treated samples of PVA and EVOH contained the expected $O_{1s}$, $C_{1s}$, $Si_{2s}$, and $Si_{2p}$ photopeaks [Fig. 1 (a) and (b), respectively]. The two peaks $Si_{2s}$ and $Si_{2p}$ were not present in the spectra of the uncoated films. The binding energies and the observed atomic ratios nO/nC and nSi/nC were reported in Table II. The nO/nC ratio for the starting PVA and EVOH films (0.49 and 0.22, respectively) increased to 1.2 and 0.33 for the coated films. This result clearly demonstrated that the yield of the grafting reaction was dependent of the number of hydroxyl functions on the substrate surface. For the coated PVA, the value nSi/nC = 0.44 was quite similar to that of nO/nC found for the uncoated film (0.49). That means that the number of grafted Si and the number of OH groups on the starting PVA film surface were of the same order. This result associated with the value found for nO/nC in the grafted PVA film (1.2) was in accordance with a covering

of the substrate surface by the silanol oligomers. That was not true for EVOH copolymer. Indeed, in this case the ratio nSi/nC (0.06) showed that only a third of the hydroxyl groups was concerned by the grafting. The different results obtained with PVA and EVOH could be attributed to the different surface density of hydroxyl groups, and consequently, to the different wettabilities. Indeed, the PVA surface, being more hydrophilic than EVOH surface, probably reacted more easily with silanol groups in the presence of the aqueous triethoxysilane solution.

### Reaction of Silane-*g*-POPZ with PVA. Factors Affecting the Grafting of Silane-*g*-POPZ onto PVA Film Surfaces

PVA films dip coated with toluenic Silane-*g*-POPZ solutions, were thermally treated under humid atmosphere.

Three reactions were possible during the thermal treatment: (1) the hydrolytic conversion of the $\equiv$Si—OEt groups into $\equiv$Si—OH groups (Scheme 6); (2) the condensation between silanol and hydroxyl functions in POPZ and PVA, respec-

**Table I  Contact Angle (with Water): Effect of Grafted Silane on PVA or EVOH, and of POPZ on Silane-*g*-PVA or EVOH**

| Polymers | Contact Angles (°) |
|---|---|
| PVA | 35 |
| Silane-*g*-PVA | 58 |
| POPZ-*g*-PVA | 86 |
| EVOH | 66 |
| Silane-*g*-EVOH | 74 |
| POPZ-*g*-EVOH | 82 |

**Table II  XPS Data of Ungrafted and Silane-Grafted-PVA and EVOH**

| | Binding Energy ± 0.2 eV | | | Surface Atomic Stoichiometry | |
| | $C_{1s}$ | $O_{1s}$ | $Si_{2p}$ | $nO/nC$ | $nSi/nC$ |
|---|---|---|---|---|---|
| PVA | 285 286.5 $\langle 3 \rangle$ | 532.8 $\langle 1.8 \rangle$ | | 0.49 | |
| Silane-$g$-PVA | 285 286.3 $\langle 3 \rangle$ | 532.9 $\langle 1.9 \rangle$ | 103.3 $\langle 2 \rangle$ | 1.2 | 0.44 |
| EVOH | 285 286.5 $\langle 1.8 \rangle$ | 532.8 $\langle 2 \rangle$ | | 0.22 | |
| Silane-$g$-EVOH | 285 286.5 $\langle 2 \rangle$ | 533 $\langle 2 \rangle$ | 103.4 $\langle 2.5 \rangle$ | 0.33 | 0.06 |

$\langle \rangle$ Full width at half-maximum (eV).

tively, leading to the coupling POPZ-PVA; and (3) the condensation of the silanol functions in POPZ leading to the crosslinking of POPZ (Scheme 7).

### Effect of the Silane

It was checked by studying two PVA films treated with toluenic solutions of ungrafted POPZ and Silane-$g$-POPZ (100 g/L) according to the procedure described in the experimental section. The films were studied by ATR-IR spectroscopy and water contact angle measurements.

The ATR-IR spectra of the original PVA and the two treated films were compared in Figure 2. The spectrum of the film treated with the ungrafted POPZ (b) was similar to the one of the starting PVA (a). On the other hand, new absorbance bands appeared in the spectrum of the film treated with Silane-$g$-POPZ principally at $\upsilon = 1592, 1505, 1180$, and $915$ cm$^{-1}$. These bands can be respectively attributed to the C—C (aromatic) ($\upsilon = 1592$ and $1505$ cm$^{-1}$), —P=N— and P—O—(C) stretching vibrations in POPZ. The disappearance of the broad band at $\upsilon = 3280$ cm$^{-1}$ representative of the OH stretching vibration in PVA could also be noted.
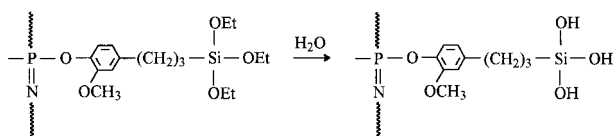
A noticeable increase of the contact angle from $\theta = 35°$ for the starting PVA film to $\theta = 103°$ for the Silane-$g$-POPZ coated PVA was observed, indicating a hydrophobic surface completely covered by the POPZ polymer.

### Effect of Extraction Time

After thermal treatment under humid atmosphere, grafted films were washed with toluene to remove unreacted POPZ. The effect of this extraction was followed by ATR-IR measurements.

For this purpose, a PVA film was first coated with the solution of Silane-$g$-POPZ at 110°C,
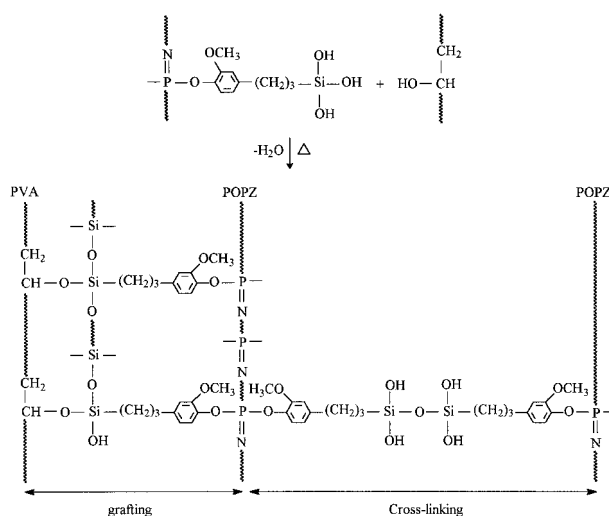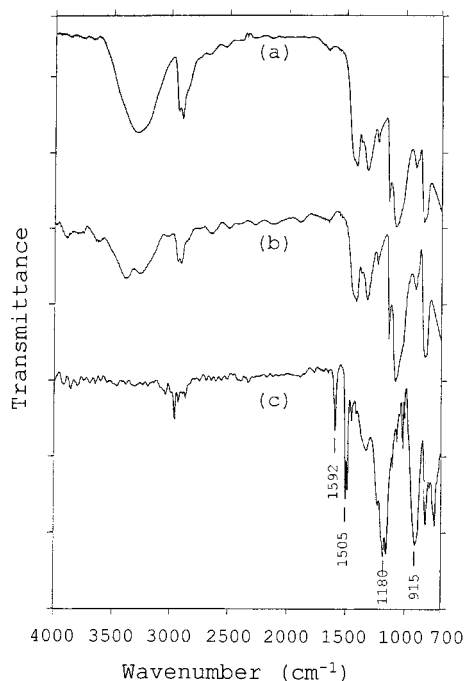
**Scheme 6**

**Scheme 7**

**Figure 2** Effect of silane: ATR-IR spectra of PVA (a), PVA coated with POPZ (b), and PVA-coated Silane-*g*-POPZ (c).

treated at 60°C under humid atmosphere and washed with toluene for 20 h. The same film was then extracted by soxhlet with toluene for an additional 20 h. ATR-IR spectra before (a) and after (b) soxhlet extraction were similar (Fig. 3). That resistance to washes provided additional evidence for the covalent grafting of POPZ onto the PVA film surface.
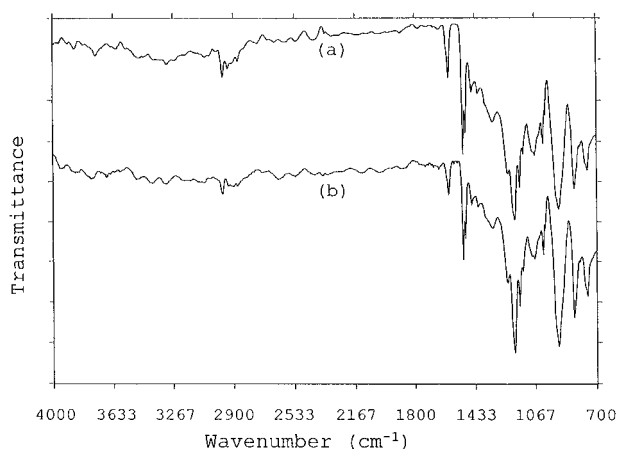
### Effect of Temperature

This effect was studied by ATR-IR measurements (Fig. 4) from two PVA films coated with the same solution of Silane-*g*-POPZ and thermally treated under humid atmosphere at 20 and 60°C. The two spectra showed the POPZ characteristic absorbances. Nevertheless, the band at $v = 1070$ cm$^{-1}$ representative of the (C—OH) stretching and (O—H) bending vibrations in PVA, which was present in the first case (20°C), disappeared in the second (60°C), showing an increase in the amount of grafted POPZ with temperature.

### Effect of POPZ Functionalization Time

The last factor to investigate was the amount of $\equiv$Si(OEt)$_3$ functions grafted on the POPZ matrix. For that, toluenic solutions of POPZ (concentration 50 g/L), triethoxysilane, and catalyst were heated at 110°C for periods of time from 1–4 h. After dip coating in these Silane-*g*-POPZ solutions and thermal treatments, the film samples were analyzed by ATR-IR spectroscopy and contact angle measurements.

All spectra exhibited the characteristic absorbances of POPZ. By measuring the intensity ratios of the bands at $v = 1593$ cm$^{-1}$ ($v$C—C aromatic) and $v = 831$ cm$^{-1}$ ($\delta$C—H aromatic in POPZ and $v$C—C in PVA), it was possible to follow the evolution of the grafting reaction. This ratio increased from 0.38 to 0.75 for, respectively, 1 and 4 h of reaction. This result clearly showed that the grafting yield was dependent on the number of $\equiv$Si(OEt)$_3$ functions introduced in POPZ.

Moreover, the absorbances at $v = 1070$ cm$^{-1}$



**Figure 3** Effect of extraction time: ATR-IR spectra of PVA coated with Silane-*g*-POPZ (a) before soxhlet extraction, and (b) after soxhlet extraction.
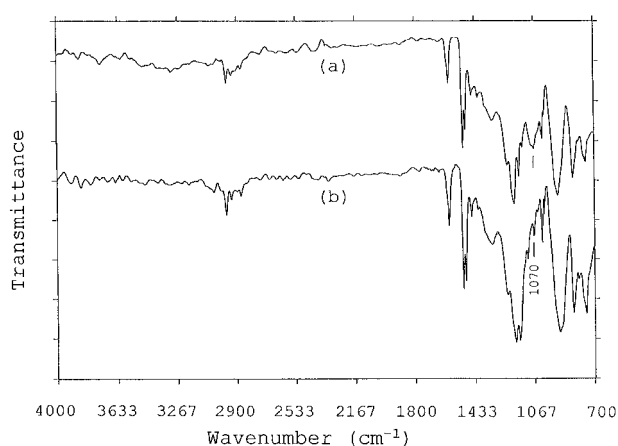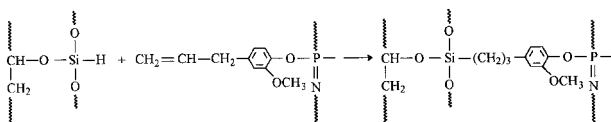


**Figure 4** Effect of temperature: ATR-IR spectra of PVA coated with Silane-*g*-POPZ at (a) 20°C, and (b) 60°C.

**Scheme 8**

characteristic of the (C—OH) stretching and (O—H) bending vibrations in PVA, disappeared completely for a four hours functionalization time. This proved that the thickness of the POPZ deposited layer was already superior to the penetration depth at the given wavelength, that is to say, in the order of 2 $\mu$m. This may be due to the intervention of the crosslinking reaction of POPZ, which occurs all the more easily as the number of $\equiv$Si-OEt bonds and so $\equiv$SiOH bonds, is important.

After treatment, the contact angles increased drastically (from 35° to 93–103°). A significant influence of different functionalization times on contact angles of PVA films could not be detected. However, a hydrophobic PVA surface completely covered by POPZ was already obtained from the weaker reaction time.

### Reaction of Silane-$g$-PVA and Silane-$g$-EVOH with POPZ

POPZ was bonded to the functionalized surfaces Silane-$g$-PVA and Silane-$g$-EVOH via the hydrosilylation reaction of its allylic groups in the presence of platinum divinyltetramethyldisiloxane complex in toluene at 110°C for 20 h (Scheme 8).

The XPS data for POPZ and for the POPZ-$g$-EVOH copolymer and POPZ-$g$-PVA polymer were reported in Table III. In these two latter cases, the presence of the photopeaks $P_{2p}$ and $N_{1s}$ that exhibited the same profiles with components at

equivalent binding energies positions than for POPZ alone, and the value founded for the ratio $nP/nN = 1$ proved the effectiveness of the POPZ grafting. The binding energies of the $P_{2p}$ and $N_{1s}$ levels of the P=N backbone are 134.5 eV and 398 eV, respectively, according to the work of Fewell.[18] The component at 399.8 eV in the $N_{1s}$ profile was previously attributed to a protonation of the nitrogen atom in POPZ.[8]

For the two systems POPZ-$g$-PVA and POPZ-$g$-EVOH, the binding energies and the profiles of the $C_{1s}$ and $O_{1s}$ peaks remained unchanged compared to those of PVA and EVOH before grafting. Moreover, the $Si_{2s}$ and $Si_{2p}$ peaks were still present in their spectra. This result suggested that only a very little coating occurred in these cases. In fact, the nN/nC atomic ratios were the same for PVA and EVOH, suggesting that the POPZ layer was similar in the two cases, the silylated layer alone being different.

The contact angle values with water droplets for the POPZ-$g$-PVA and POPZ-$g$-EVOH were reported in Table I. The films coated with POPZ were more hydrophobic compared to the Silane-$g$-PVA and Silane-$g$-EVOH, but less than for Silane-$g$-POPZ-coated PVA (103°). The angles were quite similar in the two cases, confirming the informations obtained from XPS analysis.

### Simultaneous Reactions of PVA and POPZ with Silane

The methods described previously showed some disadvantages: (1) based on the functionalization of POPZ with silane, leaded to the POPZ crosslinking. Thereby, the characterization of the functionalized POPZ and the dip coating of films were

**Table III   XPS Data of POPZ and Silane-$g$-PVA and EVOH Coated with POPZ**

| | Binding Energy $\pm$ 0.2 eV | | | | | Surface Atomic Stoichiometry | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{1s}$ | $O_{1s}$ | $Si_{2p}$ | $N_{1s}$ | $P_{2p}$ | $nO/nC$ | $nN/nC$ | $nP/nC$ | $nP/nN$ | $nSi/nC$ |
| POPZ-$g$-PVA | 285 $\langle 2.1 \rangle$ | 532.8 $\langle 2 \rangle$ | 103.4 $\langle 3 \rangle$ | 397.8 399.8 $\langle 1.6 \rangle$ | 134 $\langle 2.1 \rangle$ | 0.28 | 0.03 | 0.03 | 1.00 | 0.06 |
| POPZ-$g$-EVOH | 285 $\langle 2 \rangle$ | 533 $\langle 2.1 \rangle$ | 103 $\langle 3 \rangle$ | 397.9 399.9 $\langle 1.7 \rangle$ | 134.1 $\langle 2 \rangle$ | 0.226 | 0.03 | 0.03 | 1.00 | 0.01 |
| POPZ | 285 | 533.6 | | 398 399.8 | 134.5 | 0.17 | 0.06 | 0.08 | 1.2 | |

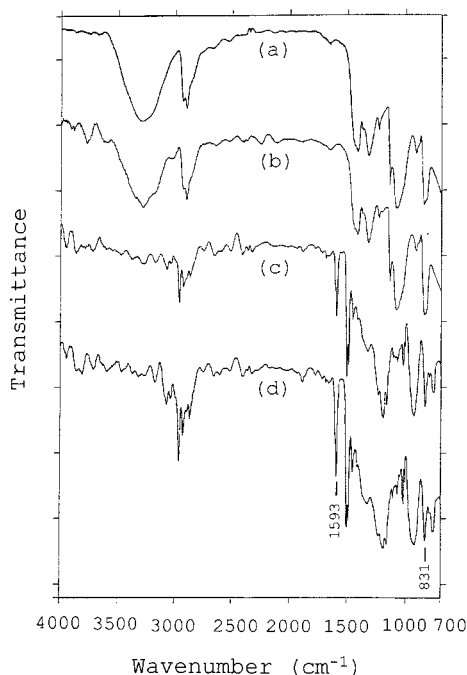$\langle \rangle$ Full width at half-maximum (eV).

**Figure 5** ATR-IR spectra of: (a) Virgin PVA; (b) Silane-*g*-PVA coated with POPZ; (c) Simultaneous functionalization and grafting reactions; (d) PVA coated with Silane-*g*-POPZ.

difficult. Moreover, the grafted surfaces were not homogeneous. Nevertheless, the POPZ deposited layers were important (in the order of a micrometer); and (2) based on the functionalization of the substrate PVA or EVOH, the crosslinking reaction of POPZ was impossible, leading to very thin POPZ-grafted layers. Thereby, X-ray photoelectron spectroscopy and contact angle measurement only provided a sensitive measure of changes to the polymer surface. Infrared (ATR) spectroscopy was not effective.

Therefore, an alternative to these processes involved the dip coating of the film samples with a solution containing at once POPZ, silane, and catalyst. In this procedure, the functionalizations of Schemes 3 and 5 and the grafting reaction occurred simultaneously during the thermal treatment.

A comparison between the ATR-IR spectra of PVA films coated according to these conditions and according to the two previous procedures was shown in Figure 5 (the POPZ concentration being the same 50 g/L). The evolution of the intensity ratio of bands at $v = 1593$ cm$^{-1}$ ($v$C—C aromatic) and $v = 831$ cm$^{-1}$ ($\delta$C—H aromatic in POPZ and $v$C—C in PVA) demonstrated that the amount

of grafted POPZ increased in the order Silane-*g*-PVA–coated POPZ (ratio $\approx 0$) < this procedure (ratio $\approx 0.4$) < Silane-*g*-POPZ-coated PVA (ratio $\approx 0.75$).

The contact angle obtained in this case was 99°.

## CONCLUSION

Three methods using triethoxysilane as a coupling agent for grafting poly(organophosphazenes) containing allylic functions onto the surface of poly(vinyl alcohol) or poly(ethylene-*co*-vinyl alcohol) films have been studied. It was shown that: (1) based on the previous functionalization of poly(phosphazene) with silane we were allowed to obtain thick deposited layers, because of its crosslinking reaction. However, in this case, the substrates surface was not homogeneous; (2) where the hydroxylated polymers were previously treated with silane, they gave thin poly(phosphazene) grafted layers; and XPS analysis and contact angle measurements only, provided sensitive measures of the surface changes; (3) simultaneous functionalization and grafting reactions improved the procedure, giving intermediate poly(phosphazene) layers thickness. In each case, this coating with poly(organophosphazene) conferred a hydrophobic character to the hydroxylated substrates. That could result in their greater resistance to attack of moisture, and consequently, in the preservation of their gas-barrier properties at humidity exposure.

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