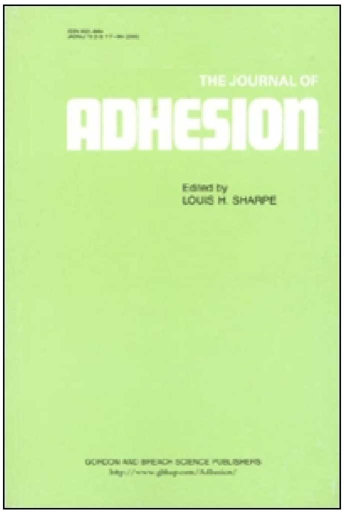

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Alami, M. , Charbonnier, M. and Romand, M.(1996) 'Plasma Chemical Modification of Polycarbonate Surfaces for Electroless Plating', The Journal of Adhesion, 57: 1, 77 — 90
To link to this Article: DOI: 10.1080/00218469608013645
URL: http://dx.doi.org/10.1080/00218469608013645

J. Adhesion, 1996, Vol. 57, pp. 77–90·
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Plasma Chemical Modification of Polycarbonate Surfaces for Electroless Plating*

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(Received December 2, 1995; in final form March 16, 1996)

The preliminary steps of the "electroless" metallization of polycarbonate are investigated by XPS. They consist of the chemisorption of a catalyst (Pd) on the surface to be metallized. The corresponding surface can be activated either by chemical etching or by reactive or non-reactive gas plasma treatment. Therefore, the surface treatment of polycarbonate determines the palladium adsorption. It is shown here that a surface carrying oxygenated functions adsorbs palladium through Sn^{2+} ions which are themselves bonded to oxygen atoms. On the other hand, a surface on which nitrogenated groups have been grafted (by NH_3 or N_2 plasma treatment) chemisorbs palladium directly on these nitrogen atoms. Reaction mechanisms are proposed in both cases and a new and simplified process for making the surfaces catalytic is proposed.

KEY WORDS: polycarbonate; polymer metallization; surface modification; low-pressure plasma; plasma surface treatment; palladium chemisorption; "electroless" metallization; XPS characterization

INTRODUCTION

Polymer metallization is generally performed under secondary vacuum either by ion sputtering or by thermal evaporation from a metallic source. Metallization by the electroless process is not widespread despite its numerous advantages (low cost and rapidity of the process, as well as uniformity of the film thickness deposited on substrates whose geometry may be complex). It must be recalled that this process consists of a redox reaction in aqueous solution between the ions of the metal to be deposited (Ni^{2+} or Cu^{2+} in most cases) and the reducing ions (hypophosphite or borohydride ions). Such a solution is in a metastable state and the redox reaction takes place on contact with a catalyst (Pd). While the latter is adsorbed on the polymer surface the reaction itself is initiated on the catalyst islands and then continues by itself, the metal deposited playing the role of catalyst in place of palladium which is now masked.

The catalyst adsorption is conventionally carried out either by a two-step process[1-7] which consists of immersing the substrate successively in an $SnCl_2$ solution

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* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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(sensitization step) then in a $PdCl_2$ solution (activation step) or by a one-step process[3, 8–11] which consists of immersing the substrate in a mixed solution of $SnCl_2$ and $PdCl_2$.

However, these treatments, to be efficient, must be performed on previously-treated surfaces in order to activate the functional groups of the polymer or to graft new chemical functionalities. The most efficient surface treatments of polymers are reactive or non-reactive gas plasma treatments.[12–15]

In this work, various surface treatments (chemical or plasma treatments) were performed on polycarbonate substrates prior to making them catalytic for nickel deposition, by the two-step process. XPS analyses were carried out after each of the different steps of the whole procedure in order to understand the role and the effects of each step and the chemical mechanisms involved. This systematic study has shown how it is possible to simplify and to improve the process by using an appropriate surface treatment.

EXPERIMENTAL

The plasma treatments of polycarbonate were performed in a reactor working in the radio-frequency mode (13.56 MHz). This reactor (RIE 80 from Plasma Technology) is equipped with two parallel electrodes. The sample to be treated lies on the cathode which is connected to the R.F. generator through an impedance-matching network. Various gases (Ar, O_2, NH_3, N_2...) are available for surface treatments. The experimental conditions used in this work were the following: treatment gas flow (100 sccm), pressure inside the reactor (100 mTorr), generator power density ($0.5\,W\cdot cm^{-2}$), treatment duration (variable).

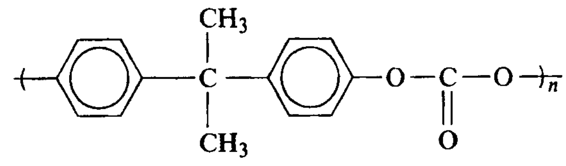
The chemical treatments of polycarbonate consisted of immersing the substrate in a sulfo-chromic bath ($K_2Cr_2O_7$:79 g/l, H_2SO_4:868 ml/l) at 75°C for 1 min.

The conventional sensitization/activation treatments were carried out successively, the first one by immersing the sample for 3 min in a solution containing $0.1\,g.l^{-1}$ of $SnCl_2$ and $0.1\,ml.l^{-1}$ of HCl, the second by immersing the sensitized sample for 3 min in a solution containing $0.1\,g.l^{-1}$ of $PdCl_2$ and $3.5\,ml.l^{-1}$ of HCl. Each step of sensitization and activation was followed by rinsing carefully with water.

Immediately after each treatment, the samples were analysed by XPS in a RIBER SIA 200 spectrometer equipped with a non-monochromatic MgK_α excitation source and a MAC 2 analyser. Spectra were recorded at a take-off angle of 25° with respect to the sample surface. Survey scans were recorded at overall resolution of 2.3 eV and core level spectra at 0.9 eV. All XPS peaks were referenced to the Cls signal, at a binding energy of 285 eV representative of the C—C and C—H environment of the polymer. It must be noted that the use of a non-monochromatic source involves the presence of small satellite peaks due to $MgK_{\alpha 3,4}$ and K_β radiation excitation. Such satellites, which appear approximatively 9 and 11 eV on the low-binding-energy side of the main photoelectron peaks, obviously need not be considered in the present study.

RESULTS AND DISCUSSION

All the experiments presented in this work were performed on 2 mm thick polycarbonate sheets of industrial quality, whose surface was protected by a peelable film. On removing this film, the samples were cleaned in an ultrasonic bath of ethanol. The polycarbonate formula is the following:



Effects of Surface Treatments

The effects of surface treatments were evaluated by XPS. Within the five minutes following their treatment, the samples were introduced in the "preparation" chamber of the spectrometer and kept under high vacuum (10^{-9} Torr) before analysis. The results presented in Figures 1 and 2, respectively, show the characteristic part of the XPS survey spectra and the curve-fitted Cls spectra of polycarbonate samples subjected to the following treatments: (a) ethanol cleaning in an ultrasonic bath, (b) sulfo-chromic

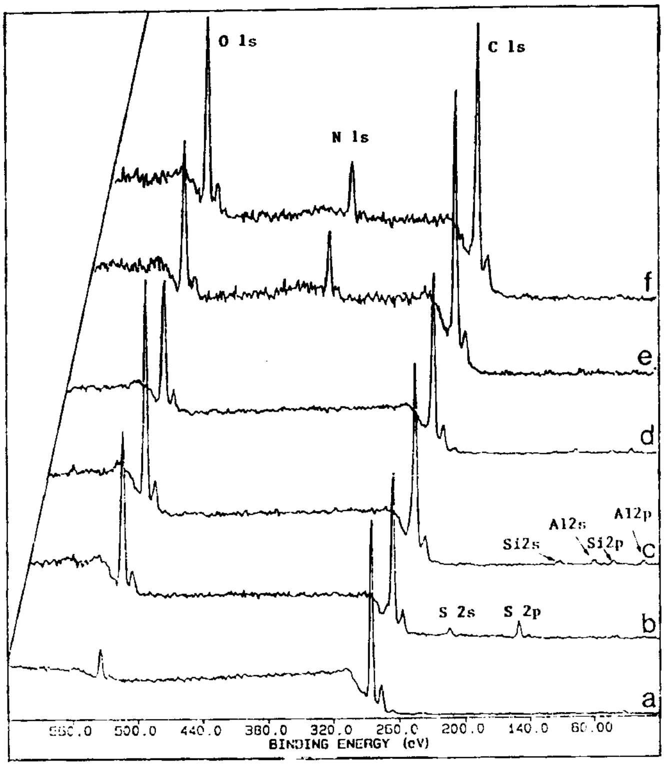


FIGURE 1 XPS survey spectra of polycarbonate cleaned with ethanol (a), chemically etched (b), plasma treated by O_2(c), Ar(d), NH_3(e), N_2(f).

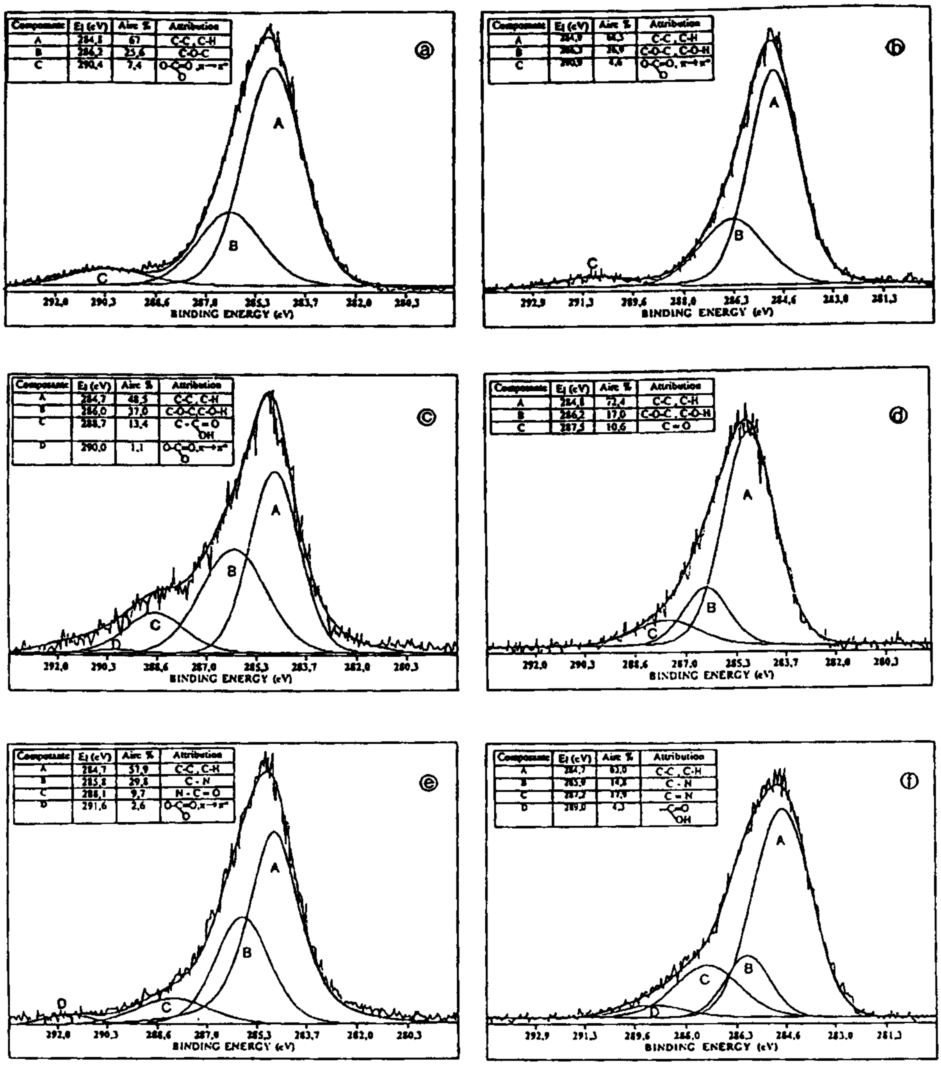


FIGURE 2 Curve-fitted Cls spectra of polycarbonate cleaned with ethanol (a), chemically etched (b), plasma treated by O_2 (c), Ar(d), NH_3(e), N_2(f).

treatment, (c) to (f) O_2, Ar, NH_3 and N_2 plasma treatments. Despite the relatively poor resolution obtained when using a non-monochromatic X-ray source it is possible to identify, in a reasonable manner, through the Cls peak curve fitting, the functional groups created on a surface.

Figure 1 shows, after surface treatment, a significant increase of the Ols signal on all the spectra and the appearance of the N1s electron peak characteristic of nitrogenated function grafting ((e) and (f) spectra). The chemical treatment (spectrum (b)) adds some sulfur to the sample surface but does not modify the nature of the functional groups present on the surface (Fig. 2b). It may seem surprising that the Ar plasma treatment which has, in principle, only a role of mechanical erosion, increases the oxygen surface concentration. This is due to the fact that a plasma treatment of any kind renders the surface highly reactive[12] so that it oxidizes on contact with ambient atmosphere. This effect of post-oxidation is seen in Figure 2c where C = O groups are identified. It can also be seen in Figure 1 that the Ar plasma treatment (spectrum (d)) and, to a lesser extent, the oxygen one (spectrum (c)), bring silicon and aluminium to the sample surface. Silicon comes from the polycarbonate surface. Its origin is unknown but could probably be attributed to the manufacturing process of the polymer sheet. It does not appear on the only-degreased sample (Fig. 1a) because it is masked by surface contamination. There is not much more present on the chemically-treated sample (Fig. 1b) probably because this treatment has a very mild effect on the polycarbonate surface. Indeed, a SEM observation does not show any topographic changes compared with the only-degreased sample. On the other hand, silicon is seen on the samples treated by Ar and O_2 plasmas which are known for their erosion power[12] and can, for short treatment times, suppress the surface contamination and make the underlying elements appear. Furthermore, the O_2 plasma treatment leads to significant widening of the Cls peak (Fig. 2c) on which O = C—OH groups can now be identified.

The NH_3 and N_2 plasma treatments, which present a weak erosion power,[16] do not reveal "buried" elements. On the other hand, as they have strong grafting power they bring nitrogenated functions to the polycarbonate surface, *viz.* amine groups for NH_3 plasma, amine and imine groups for N_2 plasma (Figs. 2(e) and (f)).

Figure 1 shows the presence of aluminium on the samples treated by O_2 and Ar plasmas. This results from the erosion of the plasma reactor Al cathode on which the samples lie during the treatments and from the partial redeposition of the sputtered atoms.

Let us note finally that the different plasma treatments modify the polycarbonate surface by opening up the aromatic rings which results in the disappearance (for Ar and N_2 plasmas) or weakening (for O_2 and NH_3 plasmas) of the $\pi \rightarrow \pi^*$ shake up satellite characteristic of the aromatic rings. On the other hand, the chemical surface treatment has no effect on these rings since the $\pi \rightarrow \pi^*$ satellite remains unchanged.

Palladium Adsorption by the Conventional Two-step Process

Main results highlighted by XPS survey spectra

The two-step process was chosen in this work in an attempt to understand the reaction mechanisms involved at the time of the sensitization/activation of the surface and, more particularly, the role of Sn^{2+} ions towards Pd adsorption.

Just after their surface treatment, the polycarbonate, samples, previously designed by (a) to (f) according to their surface treatment, were subjected to the sensitization treatment by $SnCl_2$, then to the activation treatment by $PdCl_2$. After rinsing and drying under nitrogen flow, their surface composition was determined by XPS. The corresponding results are gathered in Table I and the results of the "electroless" metallization are also indicated.

Table I shows that the sample (a), only degreased by ethanol, is not sufficiently reactive to adsorb chemical species on its surface or to allow electroless metallization of the polymer. It shows, too, that the Sn^{2+} ions do not adsorb on surfaces carrying nitrogenated groups ((e) and (f) samples) and that palladium adsorbs on these same

TABLE I
Atomic surface composition of polycarbonate subjected to various surface treatments before the sensitization/activation process and results concerning the electroless plating

Surface treatment before sensitization/activation	C%	O%	N%	Sn%	Pd%	Metallization
(a) ethanol cleaning	88.4	11.6				No
(b) sulfo-chromic etching	64.0	32.9		2.6	0.6	acceptable
(c)O_2 plasma	63.3	30.6		5.2	0.9	acceptable
(d) Ar plasma	77.9	20.2		1.5	0.4	acceptable
(e)NH_3 plasma	71.0	16.8	9.9		2.2	excellent
(f)N_2 plasma	68.9	16.5	12.9		1.6	excellent

surfaces in relatively large proportions mainly after NH_3 plasma treatment. On the other hand, the samples whose surfaces were activated by chemical etching (b) or by O_2 (c) or Ar (d) plasma adsorb the Sn^{2+} ions easily, mainly so in the case of the O_2 plasma. They also adsorb palladium but in lower proportion than the samples treated by NH_3 or N_2 plasma. The surface concentration of Pd plays a key role in the initiation of the metallization process. Indeed, the higher the Pd concentration the higher the adsorption site density and, therefore, the stronger will be the Pd-Ni alloy interface.

These results, somewhat surprising, have led us to study the sample surface after each of the process steps, *viz.* after the $SnCl_2$ treatment, and after the whole treatment ($SnCl_2/PdCl_2$) and to try out a treatment solely by $PdCl_2$. This study was performed on two substrates which were previously subjected to O_2 or NH_3 plasma, these treatments being considered as representative of the different surface treatments as a whole. Indeed, the former grafts oxygenated species on the surface while the latter mainly grafts nitrogenated functions. Figure 3 is characteristic of a polycarbonate substrate treated by O_2 plasma (a), the same treated by $SnCl_2$ (b), by $SnCl_2/PdCl_2$ (c), or by $PdCl_2$ (d). After the O_2 plasma treatment, the Sn^{2+} ions adsorb easily on the surface. The $PdCl_2$ treatment carried out just after the sensitization step brings forth some palladium and lowers the Sn surface concentration. Finally, $PdCl_2$ alone treatment is inefficient towards palladium adsorption.

Figure 4 represents the spectra characteristic of a polycarbonate substrate treated by O_2 plasma for 30 s then by NH_3 plasma for 1 min (a), the same treated by $SnCl_2$ (b) by $SnCl_2/PdCl_2$ (c), or by $PdCl_2$ (d). The $SnCl_2$ treatment (b) does not bring any Sn^{2+} ions to the surface, but the whole treatment ($SnCl_2/PdCl_2$) causes palladium adsorption (c) just as the $PdCl_2$ treatment alone does (d).

These results clearly show that Sn^{2+} ions adsorb on oxygen, but never on nitrogen. It agrees with the well-known affinity of Sn for oxygen. Conversely, Sn is not known for having the least affinity for nitrogen. Indeed, no tin nitrogenated compound is mentioned in the literature. This partly explains the absence of Sn on a polycarbonate surface carrying nitrogenated groups and sensitized by $SnCl_2$. However, a question remains. Why do the Sn^{2+} ions not adsorb on the polycarbonate surface on which oxygenated groups are present, together with nitrogenated ones? It seems that, in the possible reactive competition between oxygen and nitrogen atoms, both capable of giving an electron pair to an acceptor, it is the nitrogen ones which, because of their

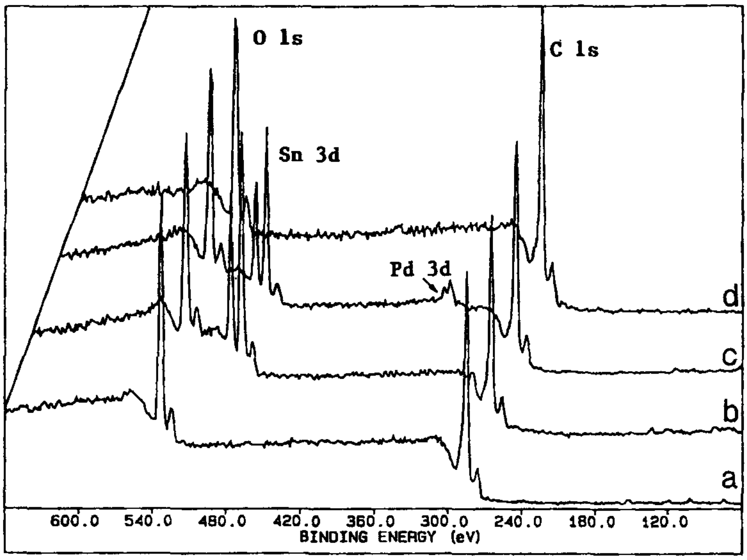


FIGURE 3 XPS survey spectra of polycarbonate O_2 plasma treated (a), the same as (a) treated by $SnCl_2$ (b), $SnCl_2/PdCl_2$(c), $PdCl_2$(d).

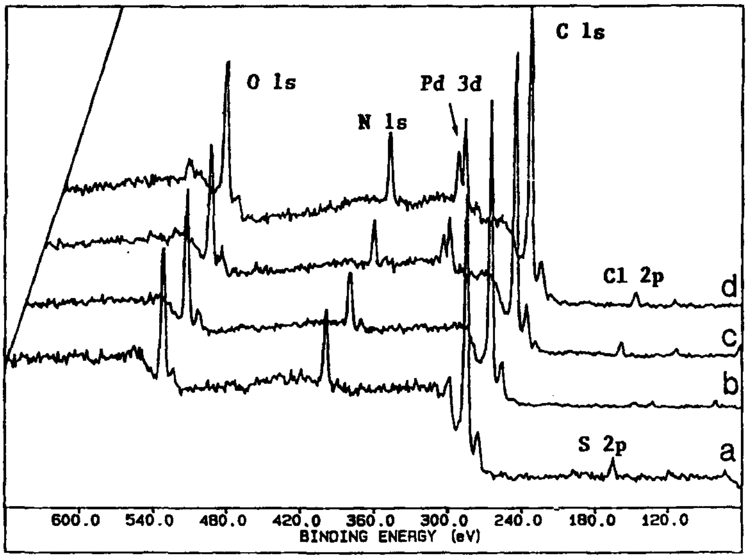


FIGURE 4 XPS survey spectra of polycarbonate, first O_2 then NH_3 plasma treated (a), the same as (a) treated by $SnCl_2$ (b), $SnCl_2/PdCl_2$(c), $PdCl_2$(d).

lower electronegativity, thus retaining their electrons less strongly than the oxygen ones, control the reaction and inhibit Sn^{2+} adsorption on the neighbouring oxygen atoms. Such an interpretation is supported by studies concerning other polymers containing, in particular, amide groups.[17]

On the other hand, these results show that palladium adsorbs either onto tin, with which it is likely to form intermetallic compounds or complexes, or onto nitrogen atoms, for which it presents a strong affinity. Indeed, many complexes of palladium II with 2 or 4 ammonia ligands are mentioned in the literature.

Chemical bond study from XPS core level spectra

To determine the nature of the chemical bonds formed at the time of tin and palladium adsorption, Cls, Ols and Nls XPS core-level spectra were recorded for 4 samples which were subjected to the following treatments: (b) sulfo-chromic etching, (c), (e), (f) O_2, NH_3 and N_2 plasma, respectively, then sensitization/activation by $SnCl_2/PdCl_2$ for (b) and (c), and activation only by $PdCl_2$ for (e) and (f). Cls spectra (not shown here) do not present any change after palladium adsorption compared with spectra recorded just after the different surface treatments of the polymer. Under these conditions, no chemical bonding between the carbon atoms of the polymer chain and the species adsorbed on the surface need be considered. On the other hand, Ols spectra show an increase of the full-width-at-half-maximum (FWHM) after the sensitization/activation step. The latter is particularly pronounced after O_2, NH_3 and N_2 plasma treatments as shown in Figure 5 which groups Ols spectra of the previously-mentioned samples, before (Fig. 5A) and after (Fig. 5B) the sensitization/activation or the activation step. After O_2 plasma treatment, the adsorption of tin, then palladium, leads to a dissymetry of the Ols peak which is widened on the low-binding-energy side. This widening can be attributed to the O—Sn bond formation in which oxygen strongly attracts the bonding electrons. It results in the modification of its electronic environment and in the creation of a component which is not resolved in the spectrum but which leads to peak broadening on the low-binding-energy side. After NH_3 and N_2 plasma treatments followed by Pd adsorption, the Ols peak is widened on the high-binding-energy side. In the previous section we have stated, on the basis of chemical considerations, that palladium adsorbed on nitrogen atoms. It is a quite likely hypothesis which, however, is not directly supported by the Nls spectra. Indeed, no change is noticed between Nls spectra (not shown here) recorded before and after the activation step. This is not really surprising if one considers the electronegativity (χ) of the atoms susceptible of bonding to nitrogen, *viz.* carbon ($\chi = 2.5$) and palladium ($\chi = 2.2$). These values, which are nearly the same, give rise to bonds which cannot be distinguished because their energy is too close. However, the Ols spectra widening on the high-binding-energy side is indirect evidence of the N-Pd bond. Indeed, nitrogen atoms transfer their free pair of electrons to palladium which results in a charge transfer that can be represented as follows:

$$O \rightarrow\!\!-\!C \rightarrow\!\!-\!C \rightarrow\!\!-\!N\!: \rightarrow Pd \quad \text{or} \quad O \rightarrow\!\!-\!C \rightarrow\!\!-\!N\!: \rightarrow Pd$$

Under these conditions, the electron density around oxygen is modified and the oxygen atoms attract the electrons of the O—C bond less strongly. As a consequence, an increasing of the binding energy of oxygen atoms located near by nitrogen ones is observed. This results in a widening of the Ols peak FWHM on the high-binding-energy side. Such an interpretation is supported by that used by some authors to interpret XPS spectra characteristic of the metal/polyimide interface. For example, Ohuchi *et al.*,[18] Bartha *et al.*,[19] and Clabes[20] have studied polyimide metallization by

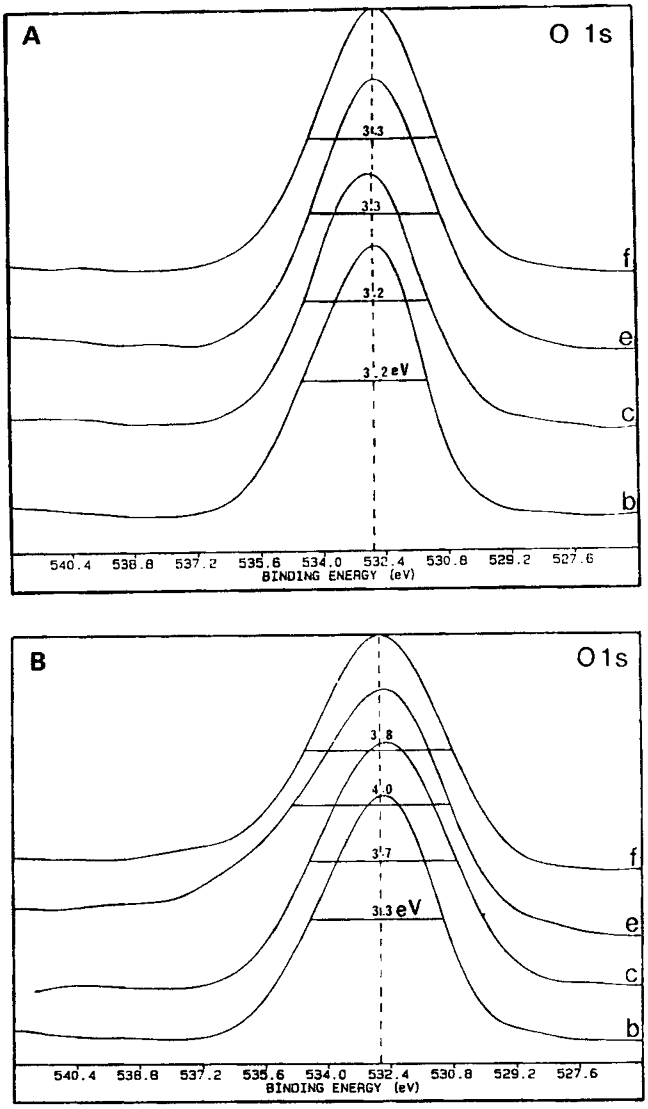


FIGURE 5 (A) Ols spectra of polycarbonate chemically etched (b), plasma treated by O_2 (c), NH_3 (e), N_2 (f). (B) Ols spectra of the same samples as in Figure 5 A, treated by $SnCl_2/PdCl_2$ ((b) and (c)), treated by $PdCl_2$ ((e) and (f)).

evaporation under high vacuum and have shown, by XPS, the formation of a metal-oxygen-carbon complex through a mechanism involving initial electron transfer from metal to carbon *via* oxygen atoms of carbonyl groups. This charge redistribution results in a shift of the corresponding Ols and Cls peaks to lower binding energies which is indicative of increased electron density at these atoms. The charge transfer hypothesis, whatever the electron transfer direction, is therefore able to explain chemical shifts or broadenings of XPS spectra of atoms not directly involved in the bond concerned (N: → Pd in the present study).

Reaction mechanisms involved at the time of the different chemisorption steps

Tin is chemisorbed on the polymer surface in the Sn^{2+} oxidized form as shown in Figure 6 which represents the Sn 3d 3/2, 5/2 spectra of Sn (a), $SnCl_2$ (b), Sn adsorbed on polycarbonate after O_2 plasma treatment. As mentioned above, the Sn^{2+} ions fix selectively on the oxygen atoms. The latter, which are strongly electronegative, attract the Sn^{2+} ions of the solution forming a polar bond (Fig. 7a). When the available sites are all occupied, other Sn^{2+} ions can physisorb on the Sn^{2+} ions already present, or

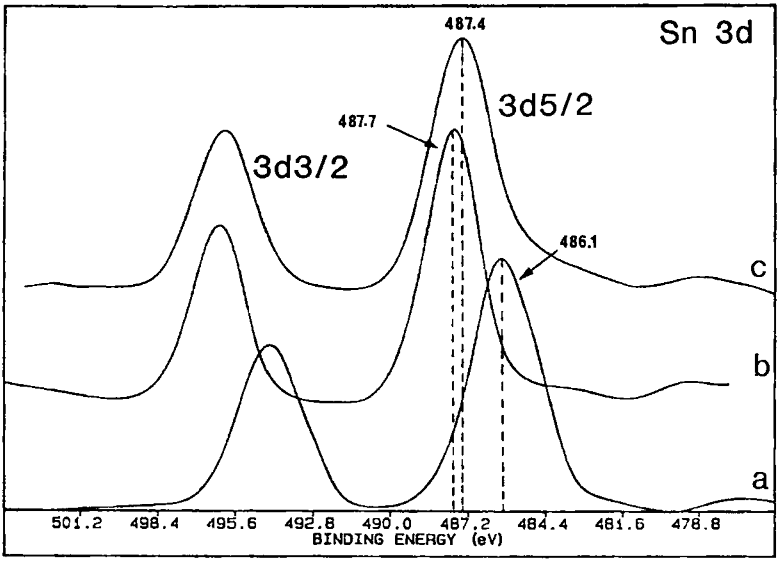


FIGURE 6 Sn 3d 3/2, 5/2 spectra of Sn in the metal form (a), $SnCl_2$ (b), Sn adsorbed on polycarbonate after O_2 plasma treatment (c).

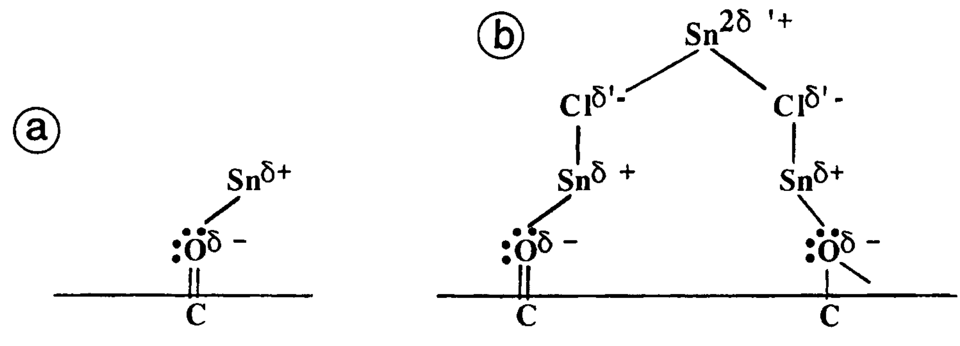


FIGURE 7 Schematic of the reaction mechanism proposed for tin chemisorption on polycarbonate carrying oxygenated functions.

better, chemisorb through Cl^- ions (Fig. 7b). However, if this second type of chemisorption takes place, it is probably of reduced importance, insofar as only immeasurable traces of chlorine are detected on the overall XPS spectra. Let us note, however, that the ionisation cross-section of Cl L-level by MgK_α is weak and, as a consequence, the method is relatively insensitive to chlorine.

Figure 8 represents the Pd 3d 3/2, 5/2 spectra characteristic of (a) Pd, (b) $PdCl_2$, (c) Pd chemisorbed on the substrate previously sensitized by $SnCl_2$. It clearly shows that palladium is adsorbed on tin in the Pd^{2+} oxidized form. This result agrees with those of de Minjer *et al.*,[2] Feldstein *et al.*,[6] and Tsukahara.[7] These authors have shown that the palladium adsorbed on a glass substrate forms complexes with tin and chlorine. On the other hand, Sard,[4] D'Amico *et al.*,[5] Meek,[3] and Cohen *et al.*,[8] consider that, during the activation step by $PdCl_2$, palladium fixes on the surface in the Pd(0) form. On the basis of purely thermodynamic considerations concerning the reactions in solution, the reduction of Pd^{2+} by Sn^{2+} must be taken into account: $Pd^{2+} + Sn^{2+} \rightarrow Pd(0) + Sn^{4+}$. However, the reactivity of the Sn^{2+} ions bonded to oxygen atoms is probably different from that of ions in solution and we have not retained this possibility of redox reaction. From our XPS results, we suggest that Pd^{2+} ions chemisorb on Sn^{2+} ions through Cl^- ions according to the scheme in Figure 9. Although chlorine quantities detected by XPS after the activation step are low and hardly measurable, the mechanism proposed is quite likely. Indeed, the detection limit of chlorine is estimated at about 1% in the experimental conditions used while that for palladium is about 0.1%. The palladium quantity adsorbed by the two-step process is about 1%. Insofar as the chlorine quantity adsorbed would be similar, the corresponding Cl 2p peak would not be observable.

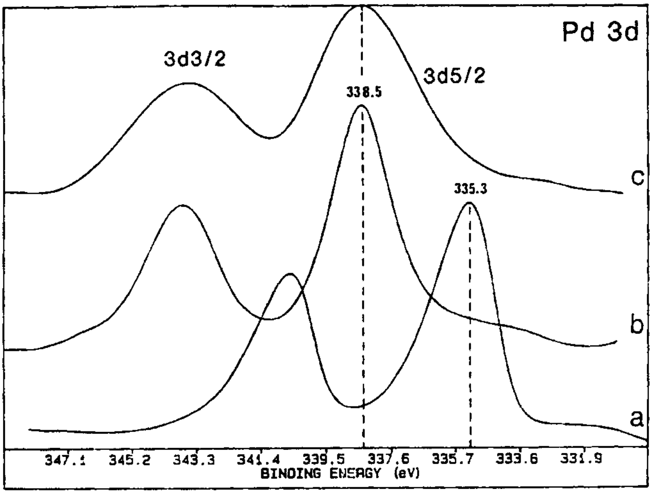


FIGURE 8 Pd 3d 3/2, 5/2 spectra of Pd in the metal form (a), $PdCl_2$ (b), Pd adsorbed on polycarbonate sensitized by $SnCl_2$(c).

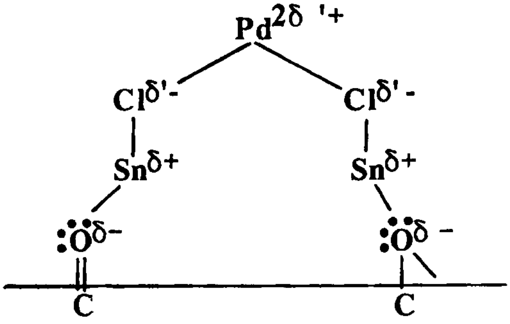


FIGURE 9 Schematic of the chemisorption mechanism of palladium onto tin according to the hypothesis of the chlorinated complex formation.

Palladium Adsorption by the Simplified One-step Process

The previous results have clearly shown that it is possible to simplify the palladium adsorption process on a surface, provided that nitrogenated groups are grafted on this surface. Under these conditions, a mere treatment by $PdCl_2$ allows the adsorption of palladium in relatively high proportion with a dense lateral distribution. This possibility of direct adsorption of palladium on nitrogen atoms has been shown on polyetherimide by Horn *et al.*,[21] and by Burrell *et al.*[11] Furthermore, Hamaya *et al.*,[22] have performed a direct adsorption of palladium on a glass previously coated with an aminosilane film. However, the grafting of nitrogenated groups by NH_3 and N_2 plasma treatments has not been used until now for obtaining "electroless" deposits by the process that we denote" the simplified process".

Some systematic studies performed by varying the experimental conditions of the NH_3 plasma treatment have shown that the grafting of nitrogenated functions is very rapid and that 5 s of treatment with a power density of $0.5\,W \cdot cm^{-2}$ is sufficient for obtaining the maximal percentage of nitrogen on the polycarbonate surface. This means that dynamic equilibrium between etching and grafting is quickly reached. However, in order to avoid grafting on weak boundary layers that may be present on insufficiently treated surfaces, we have chosen a duration of 30 s and a power density of $0.5\,W \cdot cm^{-2}$ for the NH_3 and N_2 plasma treatments.

The chemical state of the palladium adsorbed on the substrate was determined from Pd 3d 3/2, 5/2 spectra. Figure 10 represents the spectra characteristic of Pd (a), $PdCl_2$ (b), Pd adsorbed on a surface treated by NH_3 plasma and then by $PdCl_2$(c). Here, too, the catalyst is present in the Pd^{2+} form. This result agrees with those of Hamaya *et al.*,[22] and Burrell *et al.*,[11] but disagrees with those of Horn *et al.*[21]

The above-mentioned results have shown that Pd^{2+} ions chemisorb onto nitrogen atoms. The reaction mechanism proposed for this adsorption is the following: the nitrogen atoms give up their free electron pair to the Pd^{2+} ions to which they become bonded. Under these conditions, the latter gain a complete 4d electronic level which tends to stabilize the bond. The sites available for chemisorption are probably occupied from the very begining of the sample immersion into the $PdCl_2$ solution. If the

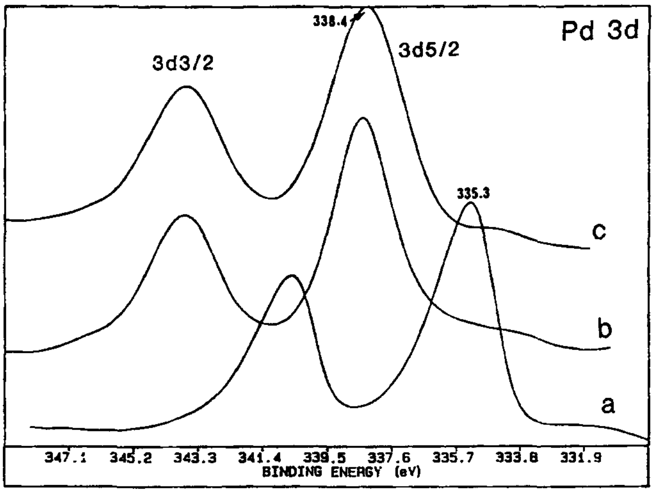


FIGURE 10 Pd 3d 3/2, 5/2 spectra of Pd in the metal form (a), $PdCl_2$ (b), Pd chemisorbed on polycarbonate treated by NH_3 plasma then activated by $PdCl_2$ (simplified process) (c).

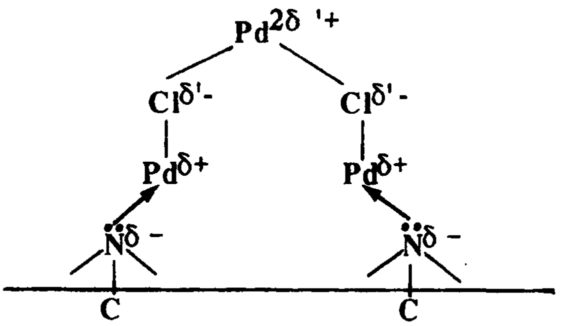


FIGURE 11 Schematic of the palladium chemisorption mechanism on nitrogen atoms grafted on polycarbonate.

immersion is prolonged, other Pd^{2+} ions can adsorb on the first ones either by mere physisorption or, according to the scheme proposed in Figure 11, through Cl^- ions which would be attracted by the $+\delta$ charge of the Pd^{2+} ions already chemisorbed. This mechanism would explain the presence of chlorine detected on XPS survey spectra (Fig. 4c, d).

CONCLUSION

This work highlights the interest in reactive gas plasmas for modifying polymer surfaces before making them catalytic for the redox reaction involved in the "electroless" process of polymer metallization.

An oxidizing surface treatment (chemical or O_2 plasma treatment) grafts oxygenated functions on the surface and the catalytic ions (Pd^{2+}) can adsorb only through Sn^{2+} ions which are themselves bonded to oxygen atoms.

Plasma treatments by NH_3 and N_2 bring nitrogenated groups to the polycarbonate surface on which Pd^{2+} ions adsorb directly. We have shown that the simultaneous presence of oxygenated and nitrogenated groups on polycarbonate does not lead to a reaction competition between oxygen and nitrogen atoms, but to an inhibition of oxygen reactivity. Indeed, it is nitrogen which governs the chemisorption reaction. It gives up its free electron pair to Pd^{2+} ions which results in a charge transfer along the carbon chain.

A simplified operating process is proposed for making a surface catalytic towards the "electroless" reaction which needs a previous grafting of nitrogenated functions that can be obtained by NH_3 or N_2 plasma treatment. This method is interesting because the operation consists of only a one-step process using an acidic $PdCl_2$ solution which is stable and does not oxidize in air. Since nitrogen grafting on the surface is sufficiently dense the palladium adsorption rate is high and the lateral distribution homogeneous. As the palladium islands constitute many nucleation sites on which the reaction initiates, the metal/polymer interface obtained in these conditions is low-stress and one can obtain thick and adhering metal films.

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