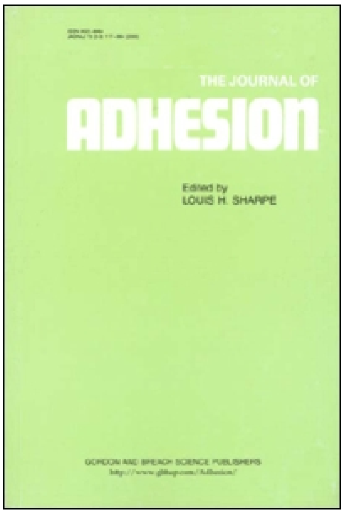

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Adhesion Improvement of Poly(Phenylene-Vinylene) Substrates Induced by Argon-Oxygen Plasma Treatment*

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Copper films evaporated on argon-oxygen plasma-treated poly(phenylene-vinylene) films have been studied by scratch test, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The adhesion of the metallic film to the polymer substrate was greatly enhanced after treatment and found to increase with the treatment time. SEM observation of the treated samples revealed that the morphology of the polymer surface was gradually changed with the treatment time as compared with that of the bare polymer film. On the other hand, XPS analysis of the polymer-metal interface showed that the bonding between carbon, oxygen and copper were subsequently modified as compared with those obtained in untreated samples. The high adhesion strength observed on these substrates was related to the modification in the surface morphology on the one hand and to the formation of new compounds at the polymer-metal interface on the other. The nature of the interfacial layer and its influence on the adhesion of the copper layer was discussed by comparing the results with those obtained in poly(phenylene-vinylene) (PPV)-Al systems.

Keywords: Adhesion; metal-polymer interface; XPS; scratch test; scanning electron microscopy; PPV; copper; plasma treatment

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1. INTRODUCTION

Among conjugated polymers, poly(phenylene-vinylene) or PPV is the most promising for electronic applications due to its optical properties. Light-emitting diodes (LED) fabricated with this polymer have shown remarkable electroluminescent characteristics with high quantum yields for photoluminescence (which may reach 8% [1] when high quality films are used). Possible improvement of the efficiency can further be achieved by using an intercalated layer between the electrode and the polymer which provides a better injection rate of the charge carriers from the electrode [2]. Actually, the PPV-metal contact plays a primary role in the transport mechanism in LED devices, and the use of adequate electrode materials can facilitate the injection mechanism and lead to better devices with improved performance. In addition, adhesion of the metal electrode to the polymer should be sufficiently good to insure the quality of the contact.

In the present study, we have investigated adhesion of the copper layer on the PPV substrates. The influence of the plasma treatment of the polymer surface was studied by comparing the adherence of the metal layer on treated and untreated layers of PPV. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were performed in order to arrive at an explanation of the results obtained.

2. EXPERIMENTAL

Thin films of PPV were cast on cleaned glass substrates from a polymer precursor synthesized by Wessling and Zimmerman's method [3]. The conversion of the precursor films were carried out under vacuum at 300°C for 3 h. Optical absorption measurements performed on probe films showed that the films obtained in these conditions are fully converted. The thickness of the films were controlled and kept constant (1 mm) in order to insure the homogeneity of the polymer substrates which is necessary for reliable mechanical testing.

Metallization of the polymer substrates was performed by RF planar sputtering of a pure copper target, at a power of 200 W, in an argon pressure of 0.15 Pa. The thickness of the copper layer was kept constant (30 nm) in order to achieve reliable comparison of the adhesion strength.

For plasma treatment of the PPV substrates, an Ar$-$O$_2$ mixture was used. The pressure of the etching gas was 5 Pa with a total gas flow rate of 80 sccm and the applied RF power was 100 W.

For the scratch test measurement, a tungsten carbide stylus with a tip radius of 17 mm was used at a speed of 3.7 mm min^{-1}. The adhesion failure was estimated by optical inspection of the channels from which the mean critical load (L_C) was determined.

The XPS analysis was performed on a Leybold LH ESCA analyser (Université de Nantes-CNRS) with Mg Kα radiation ($h\nu = 1253.6$ eV). The PPV films were deposited under the same conditions as described above on stainless steel to avoid charging effects. With the thickness used, no displacement of the spectra was observed and the absolute binding energy was referenced to the Au 4f$_{7/2}$ line (84 eV) from a gold spot evaporated on the surface of the sample. The data were processed using a computer program allowing background satellite subtraction, smoothing and integration. Decomposition of the spectra into components was performed by considering the bonding possibilities between the elements present and by using a spectra subtraction technique to identify the peak positions of the components. Gaussian and Lorentzian function combinations were used by varying parameters such as Gaussian/Lorentzian ratio, full width at half maximum (FWHM), intensity and position of each contribution to obtain the best fit of the experimental curves.

3. RESULTS AND DISCUSSION

a) Scratch Test Measurements

The critical load, L_C, is defined as the load applied to the stylus at which the loss of adhesion occurs. This can be determined by optical inspection of the channel; however, in some cases, there is no evidence of failure from the observation. A statistical technique based on the Weibull method [4] was then used. It consisted in determining the failure probability, P_f, corresponding to the load, Q, and then to plot the Weibull diagram (Fig. 1). The mean critical load was then evaluated from the slope of the straight line and the ordinate intercept. In Table I the mean L_C values obtained are shown from samples with different treatments. Previous results in PPV-Al systems are also given

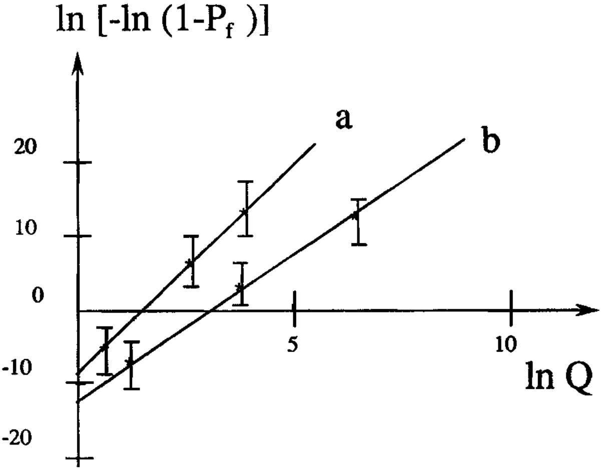


FIGURE 1 Weibull diagram for PPV-Cu system: a) untreated PPV substrate; b) 10 minutes AR—O_2 treated PPV substrate.

TABLE I Mean critical load, L_C, determined in PPV-Cu system with and without treatments. The parameters of the plasma treatments are: gas pressure, 5 Pa; total gas flow, 80 sccm; RF power, 100 W. Values of L_C from PPV-Al system are also given for comparison

Treatment time (minutes)	*0*	*2*	*5*	*10*	*15*
Critical loads (10^{-3}kg)					
PPV-Cu	2	3	20	25	35
PPV-Al	2	2	15	20	25

for the purpose of comparison. The adhesion strength is strongly enhanced by increasing treatment time. This result is in agreement with those reported earlier on oxygen-plasma-treated polymer [5–6]. The adhesion improvement due to the oxygen plasma treatment was explained by the change of the basic chemical nature on the polymer surface. For instance, in the case of polypropylene or PP [4], carbon-oxygen bonds were found to be formed on the surface of the polymer after the treatment. This then favored the attachment of the metallic atoms to the polymer substrate by forming a carbon-oxygen-metal complex at the interface. The chemical reaction between the polymer and the metal layer could also occur before the treatment as in the case of poly(ethylene terephtalate) covered by silver [6]. However, the reaction sites were found to be much less important than in the case of treated surface. Additional reaction sites induced by oxygen plasma were thought to cause the adhesion enhancement. These results indicate that the main cause of the adhesion improvement by the plasma treatment is the increase in degree of the chemical interaction between metallic atoms and the polymer backbone. It should be noted that in the cited examples, the polymers already contain oxygen which seems to be of prime importance for the reaction. In the case of PPV, pristine samples would be free of oxygen although spectroscopic analysis [7] showed that hydroxyl groups coming from the precursor solution could not be completely eliminated during the conversion, even in fully-converted films. Upon heating, the hydroxyl defects could react with traces of oxygen resulting in the formation of a ketone-based carbonyl impurity on the surface of the films [7]. Depending on the deposition conditions, the amount of carbonyl could be increased or decreased. These impurities can be reduced but not prevented [8]. In the case of our film, the atomic oxygen concentration found on pristine PPV films by XPS is less than 5%. Upon argon-oxygen plasma treatment, this concentration was expected to increase. Therefore, chemical reaction between metal layer and the polymer could occur upon metallization, leading to improvement of the copper adhesion to the polymer substrates.

b) XPS Analysis of the PPV-Copper Interface

In order to verify the possible chemical reaction between copper and PPV, we have analyzed the polymer-metal interface using XPS. The process was the following. Pristine and plasma-treated samples were first analyzed. The interface of copper-covered samples (untreated and treated) was then exposed for examination by successively removing the copper layer using argon bombardment. The accelerating voltage of the ion beam was kept at 1 kV in order to avoid damaging the polymer film. Under these conditions, the pristine PPV films were not affected by the bombardment (no change was observed in the C 1s line before and after each bombardment). The actual polymer-metal interface corresponds to the simultaneous observation of carbon, copper and oxygen lines. When reaching the bulk polymer, copper was no longer present showing that there is no metallic diffusion inside the polymer.

Figure 2 shows the core level spectra recorded in an oxygen-treated PPV sample. The C 1s line of pristine PPV is located at 284.4 eV with a full width at half maximum (FWHM) of 1.5 eV [9]. With oxygen treatment, the surface of the film is oxidized as revealed by both C 1s and O 1s lines. The decomposed C 1s spectrum shows three additional components with peaks at 286.1 eV (C—O) and 287.5 eV (—O—C—, ether group) and 289.1 eV (—C=O, carbonyl group). The oxygen spectrum also has two components with peaks at 532.5 eV (—O=C)

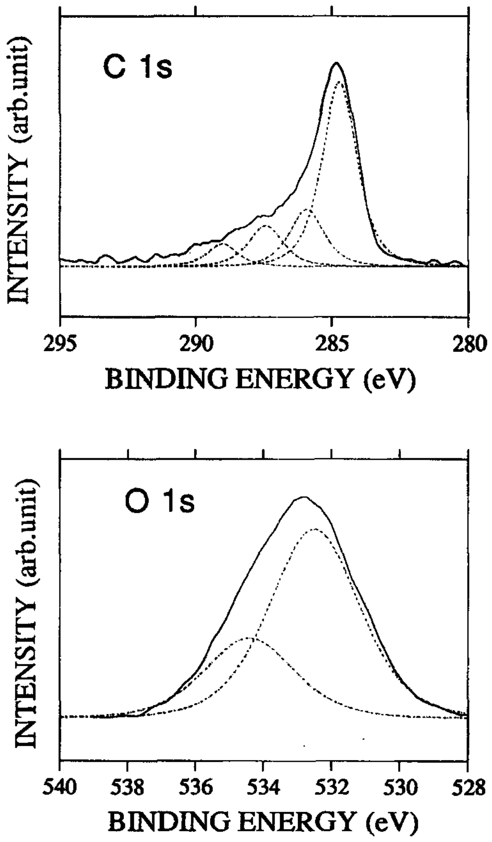


FIGURE 2 Core level spectra of: a) carbon; b) oxygen recorded on an argon-oxygen plasma-treated PPV sample.

and 534.5 eV (—O—C—) in accordance with findings in the carbon spectrum [10].

Figure 3 shows the spectra recorded in the interface of an untreated film covered by the copper layer. Some interesting features can be seen from these spectra. Firstly, the main peak of the C 1s line located at 284.5 eV is unchanged in position throughout the interface. Near the copper side (curve a), this line exhibits a small shoulder at lower binding energy (283 eV) together with features at higher energies which can be identified as oxygen-carbon bonding according to the different assignments in the previous section. Near the polymer side

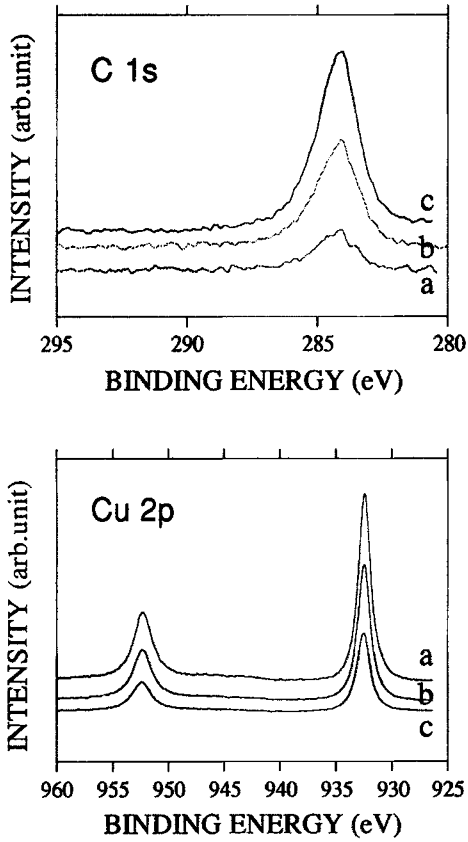


FIGURE 3 Core level spectra of: a) carbon; b) copper recorded in the untreated PPV-Cu interface by successive removals of the copper layer.

(curve c), these bondings are masked by a screening effect due to the dominant hydrocarbon peak but they can be evidenced by decomposition as shown in Figure 4. The component at 283 eV is found in some polymer-metal interfaces [11–13] and can be assigned to carbide bonding. It is noteworthy that oxygen is also present at the interface but its concentration is rather low ($<5\%$). The decomposed curve of the O 1s line presents two components, at 532.5 and 534.5 eV, which are in agreement with the chemical binding of carbon found in the interface. On the other hand, the Cu $2p_{3/2}$ line shows a peak at 932.4 eV which, apparently, corresponds to pure copper [12]. This peak remains approximately constant in position and in shape (FWHM ~1.2 eV) within the interface region. The possibility of copper oxide formation can be considered by examining the positions of both oxygen and copper peaks. The Cu $2p_{3/2}$ peak position suggests that CuO is not present since it would appear at higher binding energy (933.2 eV) [14]. For CuO_2, the Cu $2p_{3/2}$ peak is very close to that of pure copper and would not be distinguished from it. However, the low value of the FWHM of the Cu 2p line on the one hand and the absence of the O 1s component at low energy on the other [14], allow us to conclude that CuO_2 would not be formed in the untreated PPV-Cu interface.

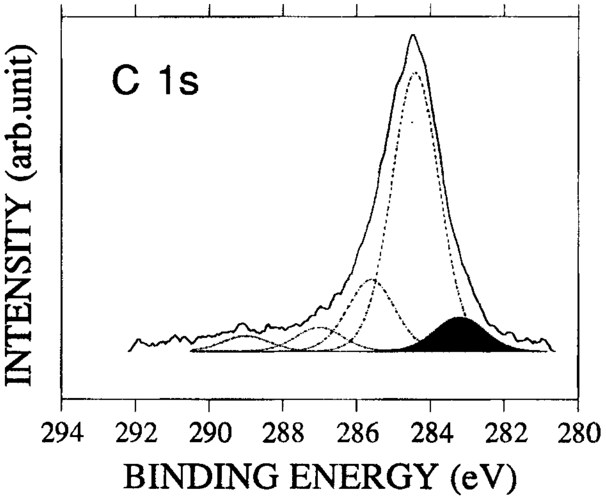


FIGURE 4 Decomposition analysis of C 1s spectrum recorded in the PPV-Cu interface of an untreated sample. New component due to the carbide is darkened.

From this analysis, the interface between PPV and copper is characterized by a reaction between copper and carbon to form a carbide. This reaction is, however, weak as compared with the PPV-aluminum system [9] where Al—O—C compounds are found in the interface. This may be explained by the fact that copper does not react as readily with oxygen as does aluminum. In addition, the concentration of the residual oxygen present on the surface of PPV film is low; therefore, one does not reasonably expect the formation of observable copper oxide as revealed by the O 1s and Cu 2p lines.

Figure 5 shows the spectra from the PPV-Cu interface treated in Ar—O_2 for 15 minutes. Comparing them with those obtained in the untreated sample, we notice the following differences. Firstly, oxygen is present throughout the interface and its concentration shows a maximum at approximately half the thickness of the interfacial layer. In the outermost layers, the peak position of the O 1s line is located at lower binding energy (531.5 eV) than that observed in the treated and uncovered sample. It shifts towards lower energy when approaching the polymer side and the final position is found at around 530.5 eV. Simultaneously, the Cu $2p_{3/2}$ line also shifts from 932.4 to 933 eV from the Cu side of the interface to the polymer side. The C 1s spectra are, on the whole, similar to those found in the untreated sample; the main peak of carbon is located at 284.5 eV which remains unchanged throughout the interface. It should be noticed, however, that the intensity of the curve at the high-energy side has decreased and the decomposed spectrum (Fig. 6) indicates that the components corresponding to C=O bonding have been drastically reduced or have practically disappeared. The resolved curve of the oxygen line taken in the middle part of the interface (Fig. 6) shows that: i) the 532.5 eV component has nearly disappeared; ii) new peaks appear at 531.5 and 530.4 eV with a strong intensity. The former peak is similar to that found in poly(3-octyloxy-methylthiophene)-copper [11] or poly(ethylene terephtalate)-copper systems [15] and can be assigned to oxygen bonding in a metal-oxygen-carbon complex. The latter one may be related to CuO_2 oxide [14]. It should be noted that the Cu $2p_{3/2}$ peak position is closer to that of CuO (933.2 eV) than CuO_2 (932.4 eV) [14]. However, the absence of the shake-up satellite at high binding energy as well as the position of the O 1s peak suggest that CuO could not be formed in this case. The observed Cu $2p_{3/2}$ peak in the innermost region of the

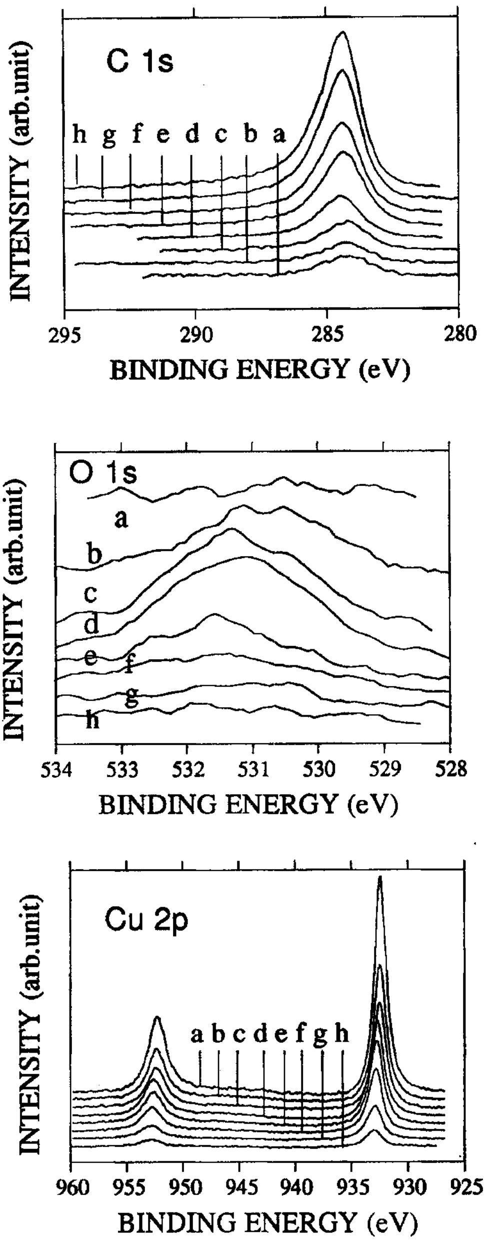


FIGURE 5 Core level spectra of: a) carbon; b) oxygen and c) copper recorded in the Ar—O_2 treated PPV-Cu interface by successive removals of the copper layer.

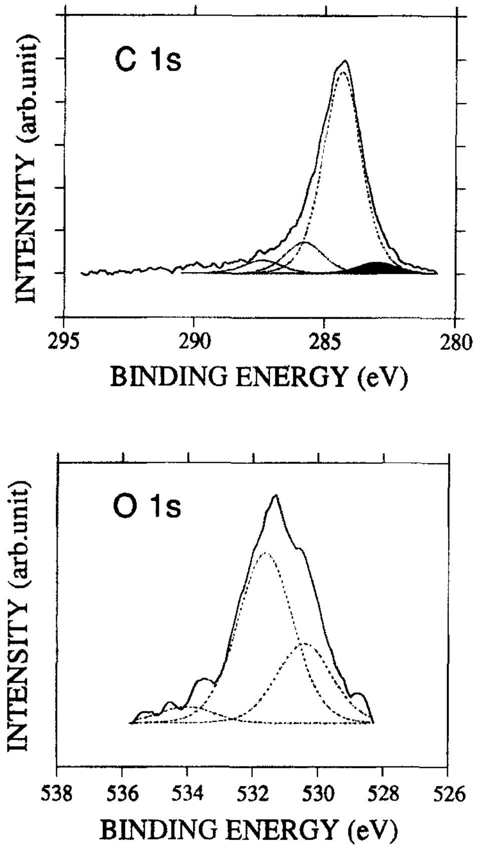


FIGURE 6 Decomposition analysis of C 1s and O 1s spectra recorded in the PPV-Cu interface of a treated sample.

PPV-Cu could correspond to copper in a metal-oxygen-carbon complex. It can be concluded, therefore, that, on the one hand, copper reacts with oxygen at the surface of the treated sample to form CuO_2 copper oxide. On the other hand, reaction with copper has also occurred at ether and carbonyl linkages leading to the formation of a new compound in the interfacial layer.

To complete the analysis of the polymer-metal interface, we show in Figure 7 the concentration profiles of C, O and Cu recorded along the interface layer as a function of time for both untreated and treated

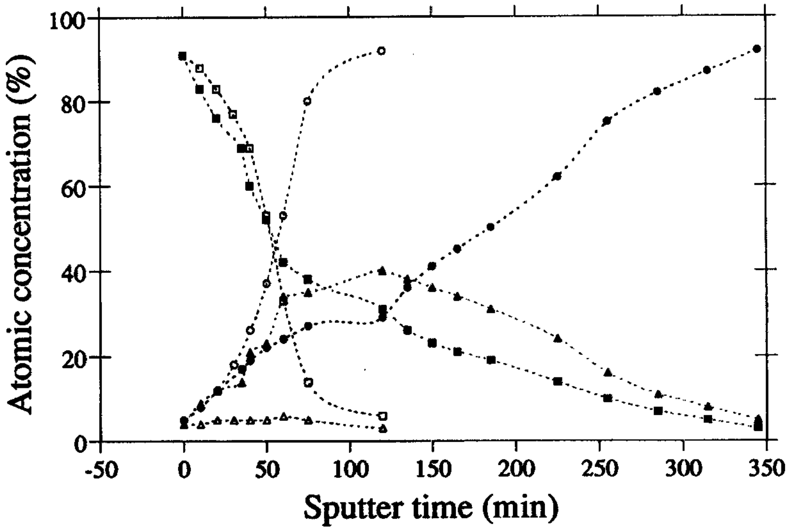
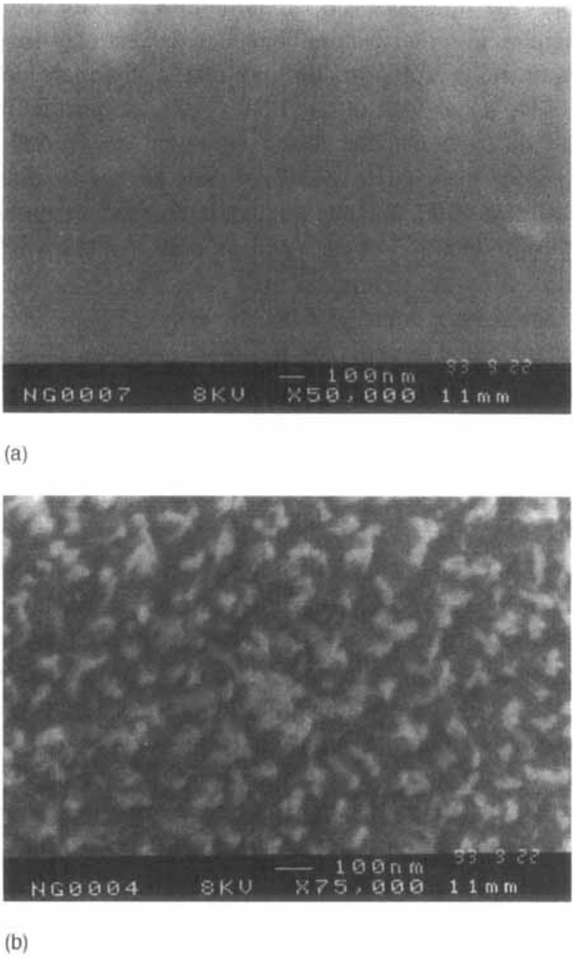


FIGURE 7 XPS profiles of carbon (●), oxygen (▲) and copper (■) in the interfacial layers of: a) untreated PPV-Cu sample (empty symbols); b) 15 minutes argon-oxygen plasma-treated PPV-Cu sample (filled symbols).

samples. It can be seen that the thickness of the treated sample interface is much larger than that of the untreated one (approximately threefold). This deep penetration of oxygen into the polymer surface seems to facilitate the diffusion of copper in the interface of the treated sample while its concentration profile appears sharper in the untreated one.

Comparing XPS results obtained in both cases, we can see that the interface has been strongly modified by the plasma treatment. The formation of new species is similar to the case of the PPV-Al interface, especially the metal-oxygen-carbon complex. The presence of larger amounts of oxygen could have favored the chemical reaction of copper with oxygen. The new compound is apparently not homogeneous since both oxygen and copper peaks shift continuously within the thickness of the layer. Its actual composition cannot be determined but, from the XPS spectra analysis, we may state that increased oxygen concentration would be produced in the middle part of the interface. The complex, at first sight, may be related to the enhancement in adherence strength of the copper to the PPV substrate, since correlation between adhesion properties and chemical reaction at the polymer-metal interface has been established for several cases [16–18].

In the case of PPV, previous study of the adhesion of an Al layer to an Ar—O_2 plasma-treated sample has shown that the presence of a complex in a large thickness of the interface would cause the observed enhancement of adherence. This, moreover, involves the change of the morphology of the surface of the film induced by plasma. As a matter of fact, observation by SEM of the treated film surface (Fig. 8) reveals that it is granular while the pristine film is uniformly smooth.



(a)

(b)

FIGURE 8 Micrographs of: a) a pristine PPV film, × 50000; b) an Ar—O_2 plasma treated PPV film (15 minutes), × 75000.

The roughening of the surface would greatly favor the anchorage of the metallic atoms to the polymer, allowing also a greater area of contact between layers. Thus, from the present analysis results, it seems that two factors can be considered for the adhesion improvement in the case of plasma-treated PPV films: morphology change and chemical reaction with formation of a compound in the interface. It is difficult to conclude about the efficiency of each of them. However, qualitative comparison of the critical loads reported in Table I indicates that the adherence is better for copper than for aluminum in treated samples, all other factors being equal. This may suggest that the nature of the complex species may play a dominant role in the adhesion of the metal layer on the PPV substrates. Further investigations using different metallic layers deposited on treated samples would be needed to elucidate the role of these factors. In addition, the plasma treatment of the polymer film could also induce surface cross-linking by recombination of the polymer radicals [19] which would not be detected by the techniques used here. The formation of these bondings could also contribute to the enhancement in adhesion strength of the metal layer to the polymer substrates as observed in some systems [20, 21].

4. CONCLUSION

In summary, this study has clearly pointed out that the argon-oxygen plasma treatment of the PPV substrate prior to copper layer deposition has significantly improved the adhesion strength of the metal layer. Two processes could be accounting for the observed enhancement. Firstly, the plasma treatment of the polymer film has modified the morphology of the film surface, creating cavities and offering a larger area for contact to metallic atoms which should favor their mechanical anchorage to the substrate. Secondly, the treatment has also produced polar groups on the surface of the film which, in turn, favored the reaction of copper with the polymer backbone to form copper oxide and a copper-oxygen-carbon complex in the interface region. These phases could reinforce the bonding of the copper atoms to the PPV substrates and, consequently, increase its adhesion to the polymer film. Qualitative comparison between treated Cu-PPV and

Al-PPV systems suggests that the chemical process plays a dominant role in the adhesion properties of metal on the investigated polymer films.

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