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Comparative XPS Study of Copper, Nickel, and Aluminum Coatings on Polymer Surfaces

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Two nitrogen-containing polymers, polyacrylonitrile and poly(styrene-*co*-acrylonitrile), and three oxygen-containing polymers, poly(vinyl methyl ether), poly(vinyl methyl ketone) and poly(methyl methacrylate), were coated with copper, nickel, and aluminum under ultrahigh vacuum, and their surfaces were analyzed by X-ray photoelectron spectroscopy. It was found that the morphology of the interface is mainly controlled by the properties of the metal, and, to a lesser extent, by the functionalities of the substrate and its physical state. Thus, aluminum condensed quickly on the polymer substrates and formed a uniform metal layer, whereas copper and nickel led to more diffuse interfaces. The mobility of copper inside oxygen-containing polymers was clearly identified, and its diffusion was enhanced by the rubbery substrates, promoting the regeneration of the polymer surface previously degraded by the metal condensation. In contrast to oxygen that did not move during the metallization (except when there was degradation), nitrogen diffused to the metal layer to form nitride species. In all cases (with Cu, Ni, and Al), metal oxide, metal nitride, and amorphous carbon were identified at the interfaces.

Introduction

In the metallization of polymer substrates by thermal evaporation, it is generally recognized that there are two main groups of metals to consider: strongly reactive metals such as Cr, Ni, or Al, and weakly reactive metals such as Cu, Ag, or Au. The strongly reactive metals are tightly fixed to the polymer structure, but the weakly reactive metals are lightly attached to the substrate and can easily move.[1−3] The reactivity of the metal is often found to control the morphology of the coating and the width of the interface; uniform successive layers of metal give a narrow interface whereas mobile metal clusters lead to a diffuse interface. Factors such as the rate of metal deposition and the temperature of the substrate during the metallization process can also slightly modify the morphology.[4,5]

In previous studies, Ni was used to metallize oxygen-containing polymers,[6] nitrogen-containing polymers,[7] and miscible and immiscible polymer blends.[8] Because of the strong reactivity of Ni, changes induced at the polymer surface could be easily identified: (1) the formation of nickel oxide and nickel nitride with, respectively, the oxygen and nitrogen atoms available in the substrate; and (2) the presence of amorphous carbon at the interface as a result of the degradation of the polymer surface which often occurs with the metal condensation.

To elucidate the influence of the metal reactivity on the morphology of the metal coating and on the width of the interface, two metals (Cu and Al), in addition to Ni, well-known for their distinct growth kinetics on substrates,[9] were used in this study to metallize polymer surfaces. Two series of polymers were chosen, one series containing oxygen functionalities, i.e., poly(vinyl methyl ether) (PVME), poly(vinyl methyl ketone) (PVMK), and poly(methyl methacrylate) (PMMA), and a second series containing nitrogen functionalities, i.e., polyacrylonitrile (PAN) and poly(styrene-*co*-acrylonitrile) (SAN). For reference, polystyrene (PS), a unique hydrocarbon polymer, was also metallized with Cu, Ni, and Al. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of the samples, and results were compared to those obtained with Ni deposition. The reactivity of the metal, the morphology of the coating, the physical state of the substrate, and the presence of heteroatoms are all factors which are considered in this study for a better understanding of the formation of a metal−polymer interface.

Experimental Section

PAN, SAN, PVME, and PVMK were purchased from Aldrich Chemicals. PMMA was provided by the Kodak Company, and PS was provided by the Dow Chemical Company. The copoly-

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mer SAN is a random copolymer containing 24.2 wt % of acrylonitrile. The glass transition temperatures of these polymers, determined by differential scanning calorimetry, using Perkin-Elmer DSC-6 or DSC-7 apparati, at a heating rate of 20 °C/min, were found at 98 °C for PS, 99 °C for PAN, 110 °C for SAN, 118 °C for PMMA, 25 °C for PVMK, and at −21 °C for PVME. The polymers were dissolved in an appropriate solvent (chloroform ($CHCl_3$) for PS, PVME, PVMK, and PMMA, dimethylformamide (DMF) for PAN, and tetrahydrofuran (THF) for SAN) at a 3% concentration (w/v). Those solutions were spin coated on glass slides (Fisher Scientific Co., $18 \times 18 \times 0.15$ mm) with a Headway Research EC101 apparatus, at 1500 rpm for 15 s for $CHCl_3$ and THF solutions, and at 1000 rpm for 80 s followed by a 3000 rpm run for 20 s for DMF solutions. Uniform polymer films of about 2−5 μm in thickness were obtained. Samples were kept under an argon atmosphere without any thermal treatment for preventing their surface contamination until they were introduced into the UHV chamber for metallization.

Copper (99.999% purity from Alfa Puratronics), nickel (99.9% purity from Alfa Chemicals), and aluminum (99.998% purity from Alfa Puratronics) were evaporated under a 10^{-9} mbar reduced pressure, using a custom-made evaporator built on the design of Beag et al.[10] The distance between the polymer sample and the metal source was about 25 cm, far enough to prevent sample damage due to the thermal effect of a too-close metal source. Metal vapor was deposited at a rate of 0.1 Å/s, as controlled by a quartz crystal oscillator (STM-100/MF from Sycon Instruments Inc.) that also enables the determination of the thickness of the metal layer effectively deposited on the substrate with an accuracy of ±1 Å. The polymer−metal samples were then transferred to an adjacent analysis chamber without leaving the UHV environment.

XPS spectra were recorded with a VG Scientific Instrument model ESCALAB-MKII photoelectron spectrometer, using a nonmonochromatic Al Kα radiation (1486.6 eV), in a UHV system, at about 10^{-11} mbar. The anode voltage was 15 kV and the emission current was 20 mA. For each sample, a survey scan was first recorded at a low ∼1.8 eV resolution, followed by higher resolution scans for C1s, N1s, O1s, Cu2p, Ni2p, and Al2p orbitals, with a ∼1.1 eV resolution. It was verified that the spectrum accumulation time was too short to induce significant sample degradation, i.e., we observed no change in the shape of the C1s spectra at the beginning and at the end of the recording. Emitted photoelectrons were counted in three directions: 15, 45, and 70° relative to the normal of the sample surface. Atomic proportions were calculated from the area under each signal with the use of the PIXAS software[11] which takes into account the specific element sensitivity. The amount of metal effectively deposited is then determined more precisely (in percentage) from the XPS spectra than with the thickness detector (in Angströms). The detector is particularly useful during the deposition process because a reproducible metal quantity can then be deposited on the substrates.

Band positions were corrected using the Ni 2p3/2 position at 852.7 eV for samples containing more than 10 Å of Ni, while, at lower nickel thicknesses, and for all Cu and Al coatings, the position of a polymer band was used as a reference. The exact position of that contribution was previously established using the corrected bands of samples having high nickel coverages (more than 10 Å). These polymer contributions are the N1s nitrile component at 399.7 eV for PAN and at 399.8 eV for SAN, the O1s ether component at 532.7 eV for PVME, the C1s carbonyl component at 288.9 eV for PMMA and at 287.6 eV for PVMK, and the C1s maximum band at 285.0 eV for PS. The baseline of all experimental bands was systematically modified according to the correction proposed by Shirley.[12]

Results

Figure 1 shows the XPS spectra (C1s, N1s, and O1s bands) of PS, PAN, and PVME covered with 20 Å of Cu, Ni, and Al, as these substrates were used as representative examples of each series of polymers: PVME for the oxygen-containing polymers, PAN for the nitrogen-containing polymers, and PS as a reference polymer because it contains no oxygen and no nitrogen atoms. The XPS bands are given with their respective decomposition peaks obtained by looking for the minimum number of components. For the three metals, and for each element, an additional component is always detected at low binding energy, which was assigned in our previous studies of Ni/polymer interfaces[6,7] to the following: amorphous carbon on the C1s band, nickel nitride on the N1s band, and nickel oxide on the O1s band. Each metal/polymer system gives the same kind of XPS behavior,[13] and the similarity of these systems with the Ni/polymer behavior leads to the conclusion of the presence of the same kind of chemical species at interfaces. In other words, Cu and Al also lead to the generation of amorphous carbon, and to the formation of metal nitride or metal oxide depending on the heteroatom available in the substrate.

Figure 1 shows that the position of the amorphous carbon contribution shifts to lower values by 0.5 eV when going from Cu, to Ni, to Al, as it is located at 283.8 eV for Cu/PS, at 283.7 eV for Ni/PS, and at 283.3 eV for Al/PS. The same observation is made with the nitride position which shifts by 0.8 eV from 398.1 eV for Cu/PAN, to 397.7 eV for Ni/PAN, and to 397.3 eV for Al/PAN. On the other hand, the oxide position remains identical at 531.0 ± 0.1 eV for Cu, Ni, and Al on PVME. Similar shifts to lower binding energy of the amorphous carbon and metal nitride contributions, and a constant binding energy for the metal oxide contribution, were observed for all other polymers investigated.[13] These bands, when they get close to another polymer component, can be under-estimated by the decomposition process.

The shift in position of the different metal nitrides can be attributed to distinct interactions, depending on the metal involved, but this explanation does not hold for the amorphous carbon contribution where a similar shift has been observed. This explanation is too often evoked[6] at the expense, for example, of the spatial distribution of the respective chemical species which could also be incriminated.[8] Nevertheless, the new components most likely represent the same chemical species even if they do not exhibit exactly the same position in the binding energy scale for the three metallic coatings.

The influence of the metallization can be investigated, from the polymer side, by the evolution of N/C and O/C ratios. Figure 2 shows these ratios as a function of the amount of metal deposited, with the full symbols corresponding to Ni and the empty symbols corresponding to Cu. Al is not considered here because of its systematic oxidation during the evaporation process; the strong

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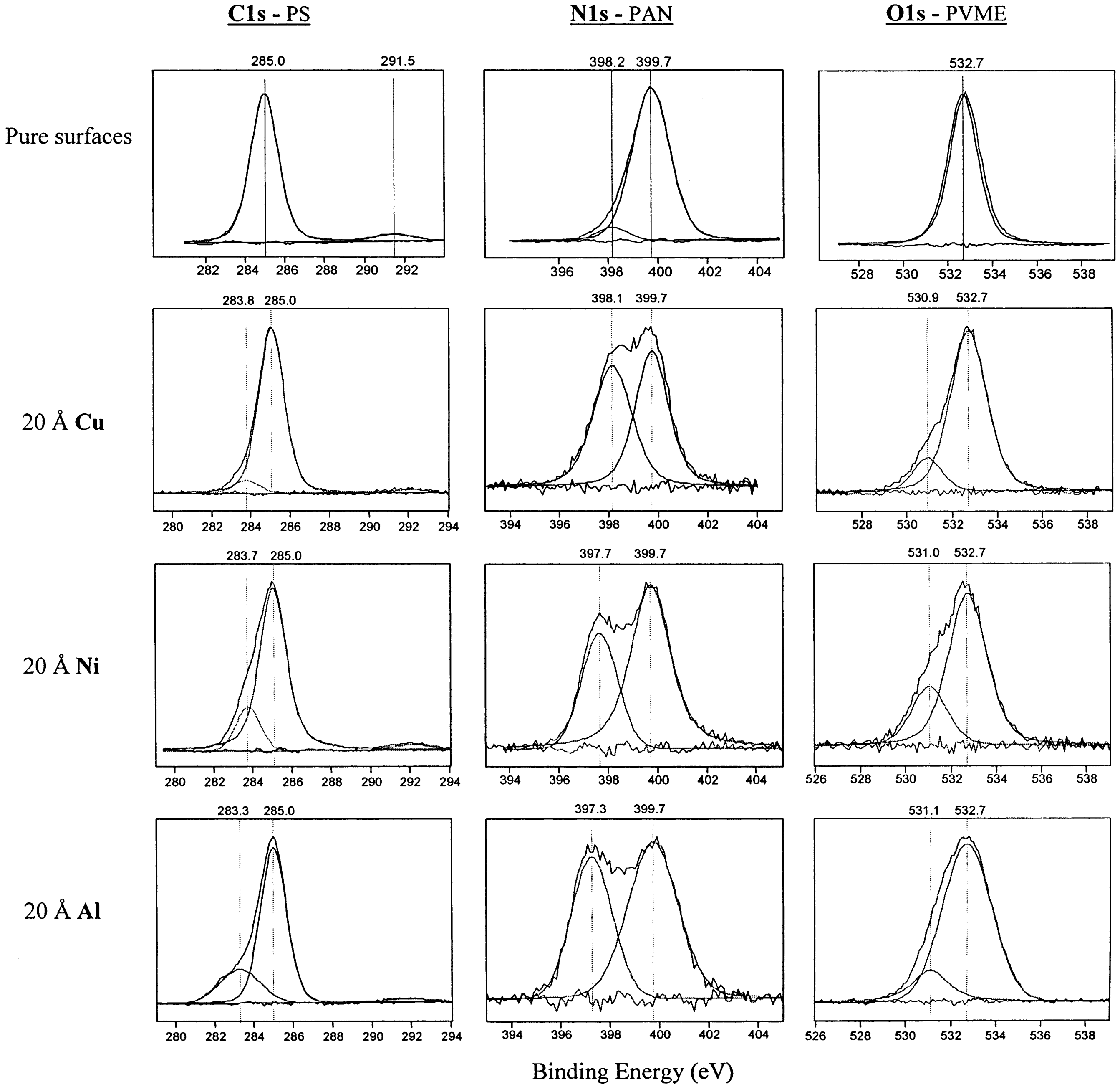

Figure 1. C1s band of PS, N1s band of PAN, and O1s band of PVME for polymers covered with 20 Å of Cu, Ni, and Al.

reactivity of Al with the residual oxygen under 10^{-9} mbar leads to the addition of between 1 and 5% of oxygen on the polymers, modifying the proportion of the other elements in a nonreproducible manner.

In Figure 2, for PAN and SAN (nitrogen-containing polymers), no N/C change can be detected during Cu and Ni metallizations and, therefore, it can be concluded that no nitrogen loss occurs from the substrates during the metallization process. In contrast, for PVME and PVMK (oxygen-containing polymers), the O/C ratio decreases with the addition of Cu and Ni revealing a systematic loss of oxygen from the substrates during metallization. For Ni/PVME and Ni/PVMK, the initial slope is similar, indicating that the kinetic of surface degradation (directly related to the oxygen loss) is likely the same, and it leads to surfaces poorer in oxygen than they were before metallization. A different slope, occurring for a percentage of Ni higher than 20−30%, indicates that the loss of oxygen is even more pronounced in the more superficial zone thus analyzed. Indeed, due to the increasing amount of metal deposited on the surface, the polymer analyzed area becomes gradually richer in interfacial contributions, and poorer in unaffected substrate contributions, located deeper under the metallic layer. This second slope, observed for Ni/PVME and Ni/PVMK, reveals, as already discussed,[6] a highly degraded top polymer surface induced by the Ni condensation.

For Cu/PVMK, the same kind of oxygen loss occurs, as shown by the same initial slope as Ni/PVMK. However, with more than 20% of Cu, the O/C values remain identical, and very distinct from those of Ni/PVMK (different slope). Because the amount of metal deposited is comparable in both cases (similar percentages of Cu and Ni), the analyzed area is also similar (in terms of analyzed depth), and it appears that the highly

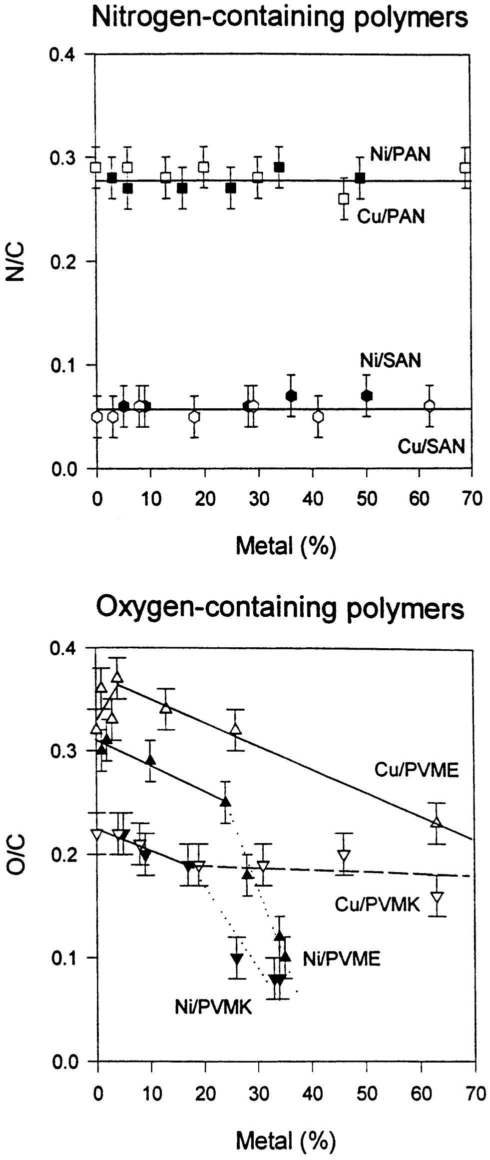

Figure 2. N/C and O/C ratios as a function of the amount of Cu (empty symbols) and Ni (full symbols) deposited on nitrogen-containing polymers (PAN and SAN) and oxygen-containing polymers (PVME and PVMK), respectively.

degraded area, identified in the case of Ni/PVMK, is never reached with Cu/PVMK. In other words, the top polymer surface covered with Cu is less degraded by the metal condensation than the same kind of surface covered with Ni, because the impact strength when metal atoms reach the polymer surface may influence the depth of penetration of the metal into the substrate, i.e., Cu is deposited more softly on the surface than Ni.

For PVME, the same decrease of the O/C ratio is observed with Cu and Ni metallizations, but on a larger range of concentrations for Cu than for Ni (from 5 to 70% with Cu versus a 0−20% range with Ni). Again, the highly degraded area reached at 20% of Ni is never observed with Cu. In contrast, O/C values increase for concentrations of Cu deposited on PVME between 0 and 5% to values higher than the O/C ratio of pure PVME. As the addition of external oxygen is unrealistic under UHV environment, the oxygen increase necessarily originates from the oxygen of PVME, i.e., Cu condensation changes the distribution of oxygen at the PVME surface.

To analyze the polymer located very close to the metal layer (i.e., the very top surface of the substrate) a coating of 20 Å of metal was deposited, and the surface was analyzed by XPS using variable grazing angles relative to the surface normal. In Figure 3, the N/C and O/C ratios of these systems are given as a function of the analyzed depth (which is directly related to the cosine of the angle of analysis), with the top surface (about 20 Å) corresponding to the lowest cosine value (0.34 for 70°), the subsurface (about 90 Å) corresponding to the higher cosine value (0.97 for 15°), and the mid-surface represented by the intermediate point (about 50 Å for a 45° angle).[14−16] For comparison, N/C and O/C ratios of the pure polymer surfaces are also shown in Figure 3 (empty symbols and dotted lines) on top of the metallized polymer values (full symbols and full lines). Even if the analyzed areas are not exactly the same for the pure surfaces and for the metallized surfaces, because in the second case a metal layer is added, a comparison of the distribution of the elements inside the analyzed zone still gives relevant information on the nature of the metal/polymer interfaces.

For PAN, the distribution of nitrogen (seen via the N/C ratio) changes slightly with metallization (Figure 3) because the full lines, for both Ni and Cu coatings, do not have the same shape as they have in pure PAN (dotted lines). With Ni, at the top surface, the N/C ratio is higher than that at the pure PAN surface, indicating a higher concentration of nitrogen close to the nickel layer; with Cu, it is the intermediate point that exhibits the larger deviation. The two distributions (with Ni and Cu) exhibit a very similar concavity in comparison to the pure surface distribution, demonstrating a nitrogen depletion at the mid-surface at the benefit of the top surface area. With these observations, it is suspected that nitrogen (groups) can diffuse locally to the metal layer. For SAN, the nitrogen concentration is too low (the N/C value is too small) to detect such subtle variations, and no significant change can be deduced from the corresponding curves.

For oxygen-containing polymers (PVME, PVMK, and PMMA), the differences between O/C values of pure and metallized substrates are more important than with nitrogen-containing polymers due to the loss of oxygenated products induced by the metal condensation (Figure 2 and ref 6) that leads to significant decreases of O/C ratios. Moreover, for PMMA, the shape of the oxygen distribution at the surface (via the O/C ratio) is similar before (dotted line) and after (full lines) metallization by Cu and Ni. For PVME and PVMK covered by Ni, the oxygen distribution at the surface is very different from that of the pure substrates, with a positive slope for the metallized substrates versus a horizontal line for the pure substrates. The lowest O/C value at the top surface is due to the important degradation of the polymer, more pronounced at its top surface than at its subsurface where more oxygen remains. With Cu, the oxygen distribution is quite different than that with Ni, as already suspected from Figure 2. For Cu/PVMK, O/C values are close to those

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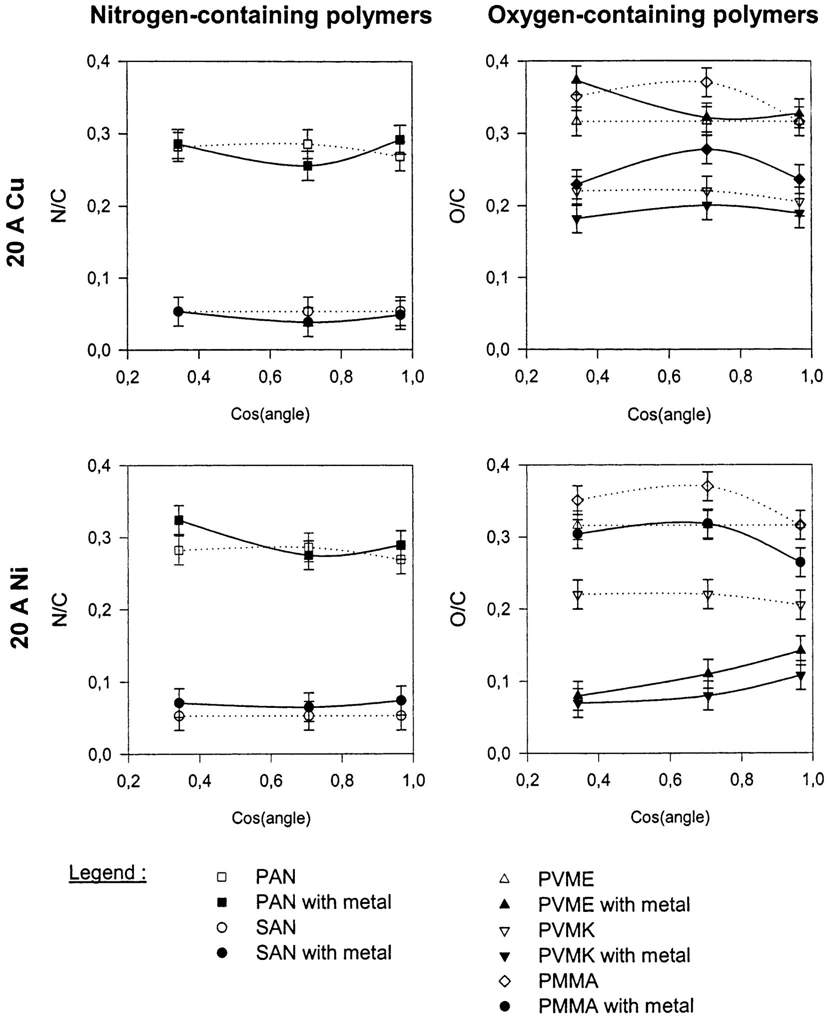

Figure 3. N/C and O/C ratios as a function of the analyzed depth (cos(angle)) for 20 Å of Cu and 20 Å of Ni deposited on, respectively, PAN and SAN, and PVME, PVMK, and PMMA (full line), and for pure polymers (dotted line).

of pure PVMK. However, a small decrease of the oxygen concentration at the top surface can be suspected, in accordance with the surface degradation. For PVME, it is the opposite: a significant increase of the oxygen concentration at the top surface is noted, in agreement with the increase of the O/C value detected in the first steps of the metallization (Figure 2).

From Figure 3, the distribution of heteroatoms at the surface before and after metallization can be summarized as follows: First, there is a nitrogen diffusion to the metal layer; second, the oxygen loss reveals surface degradation; and third, in the case of PVME covered by Cu, there is an increase of the oxygen concentration at the top surface. This last observation has to be elucidated because it is the only case where oxygen seems to diffuse to the metal layer.

To better understand this observation, the distribution of metal inside the surface can be analyzed by changing the angle of analysis for a given metal layer of 20 Å. The corresponding variations are given in Figure 4 for Cu, Ni, and Al coatings on nitrogen-containing polymers (PAN and SAN), PS, and oxygen-containing polymers (PVME, PVMK, and PMMA). In Figure 4, the metal distribution is different from one metal to another, and also from one substrate to another. In the case of Cu, the distribution inside the polymer surface is almost linear for nitrogen-containing substrates and PS, and curved for oxygen-containing substrates. With PVME, the concentration at the top surface is even lower than that at the subsurface, in contradiction with the expectations of having a metal layer covering a substrate. For PVMK and PMMA, the Cu concentration is similar at the top and at the mid-surfaces.

For Ni coatings, the metal distribution decreases from top to bottom, as expected, except with PMMA for which the distribution surprisingly parallels the peculiar oxygen distribution at the PMMA surface (Figure 3). With Al coatings, all surfaces exhibit a progressive enrichment in metal from top to bottom. Even if the distributions of Cu and Al on nitrogen-containing polymer surfaces are almost linear, the metal concentration range involved is different for Cu and Al, with a more pronounced slope with Al (from 30−35% to 50−60%) than with Cu (from 35−40% to 45−55%). The larger the slope with the angle of analysis, the steeper the interface between the metal layer and the polymer surface. Thus, with substrates containing no oxygen, Al leads to a more abrupt interface than Cu. This conclusion is more uncertain for oxygen-containing polymers because a small influence of the substrate can be suspected in the metal distribution. The Ni distribution is similar to

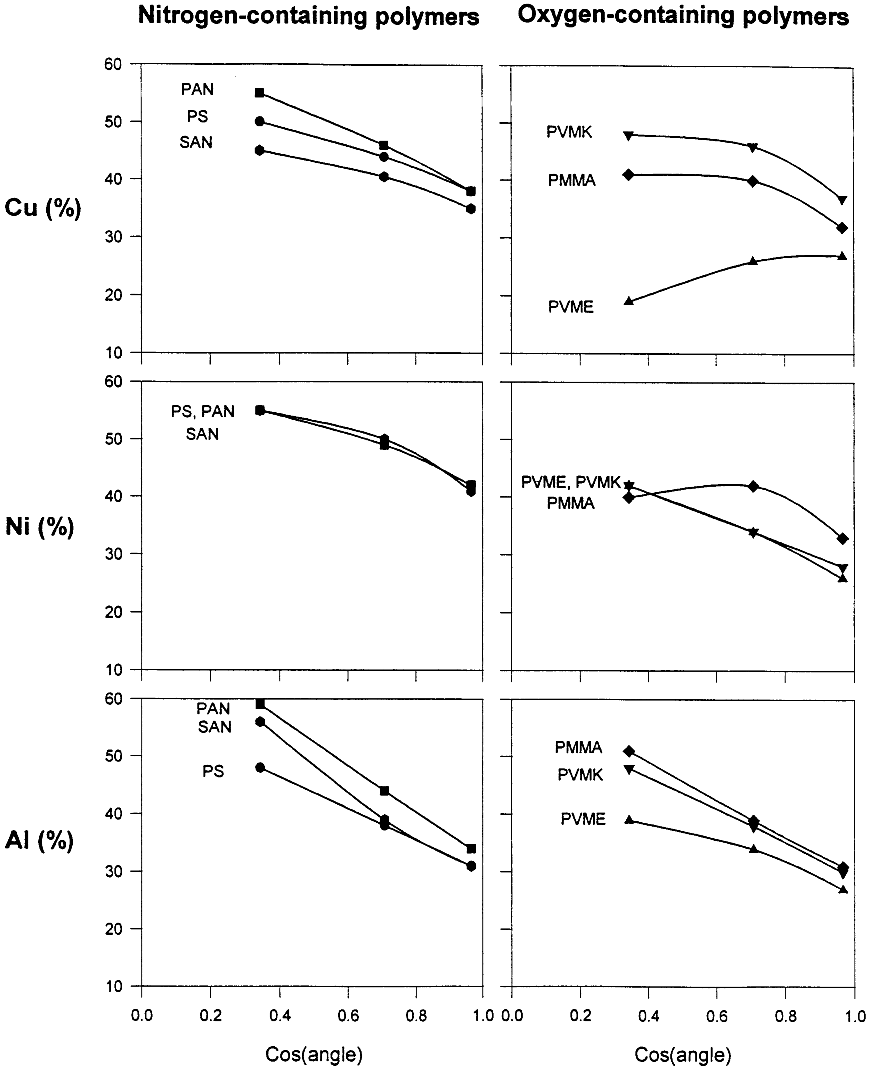

Figure 4. Percentages of Cu, Ni, and Al deposited on the polymer surfaces as a function of the analyzed depth (cos(angle)). Error bars are not given because they are too small, of the order of ±2%.

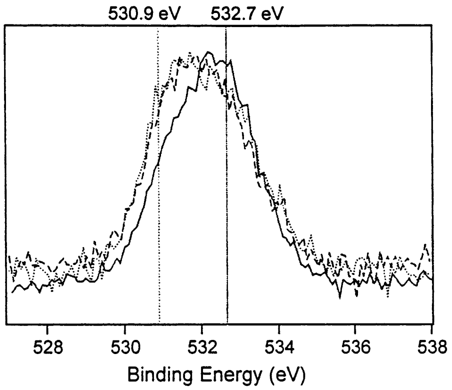

Figure 5. O1s band of PVME covered with 40 Å of Cu, obtained at angles of analysis of 70° (full line), 45° (dotted line), and 15° (broken line) relative to the surface normal.

the Cu distribution in terms of the metal concentration range involved, and the width of the interface must be comparable in those two cases.

In the case of PVME covered with Cu, an oxygen enrichment at the top surface has been detected (Figure 3) while, in the same zone, a Cu default has been noticed. In contrast to nitrogen that diffuses to the metal in order to stabilize the metallic interface by forming nitride species, the oxygen diffusion of PVME does not stabilize Cu. This conclusion is immediately confirmed by analyzing the Cu/PVME O1s band at different emerging angles (Figure 5) since a default of the oxide contribution (530.9 eV) is evident at the top surface (70°), as compared to the 45° and 15° XPS signals. The oxygen surface enrichment then corresponds to the PVME macromolecular structure that moves to the top surface while copper and/or copper oxide diffuse to the core of the PVME substrate. This important surface reorganization is possible because the low glass transition temperature of PVME ($T_g = -21$ °C) keeps the sample in the rubbery state during and after the metallization process.[6]

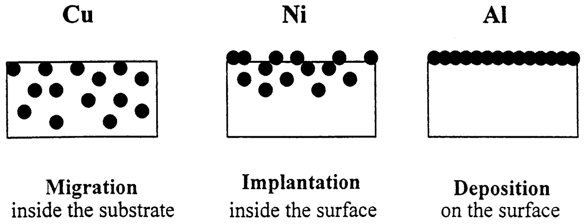

Figure 6. Schematic representation of the polymer surface for the same quantity of Cu, Ni, and Al deposited.

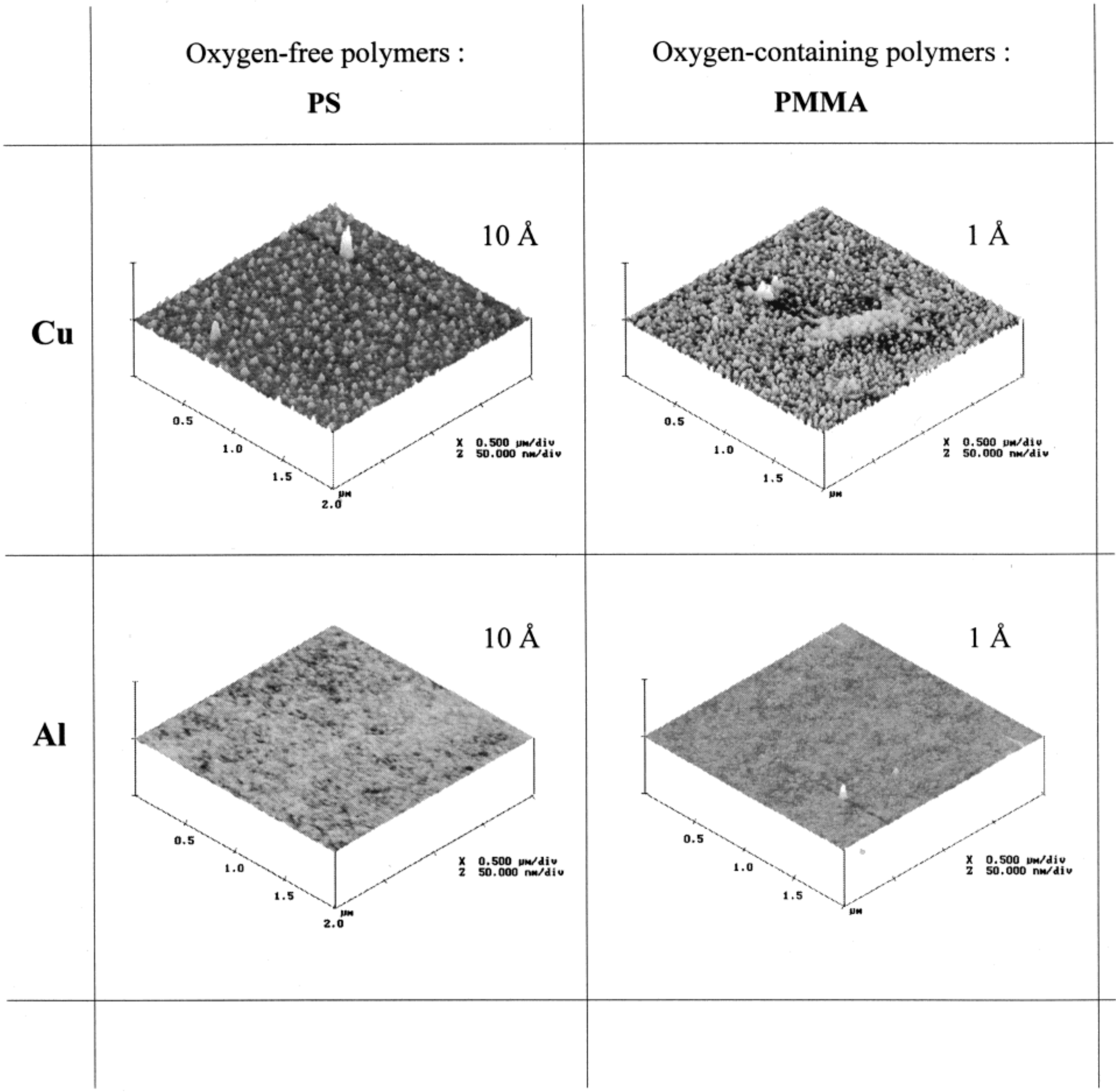

Figure 7. AFM images of PS and PMMA surfaces covered with 1 and 10 Å of Cu and Al.

On the other hand, in PVMK and PMMA substrates which are in the glassy state at room temperature Cu diffusion is very much reduced, and no polymer diffusion is observed at the top surface (Figure 3). However, the rubbery state of the substrate is not the only parameter that leads to the metal diffusion, because for Al/PVME, the Al distribution at the PVME surface stays quite linear, revealing no significant Al diffusion to the bulk of the PVME (Figure 4).

In the case of Ni/PMMA, the peculiar Ni distribution does not need to be interpreted in terms of metal diffusion because the oxygen distribution fits with that of the metal. In this case, Ni seems to be located where the oxygen atoms are. With the condensation energy of Ni ($|\Delta H| = 370$ kJ/mol) being higher than that of Cu and Al ($|\Delta H| = 300$ kJ/mol),[17] Ni reaches the polymer surface with more energy, such that it can presumably penetrate deeper into the substrate than Cu or Al.

Discussion

The results shown in the previous section, and in particular the analysis made at different emerging angles, indicate that Cu diffuses easily into PVME, PVMK, and PMMA, which all contain oxygen, whereas no clear evidence of such a mobility is seen with the other polymers which contain no oxygen. Similar observations were reported in the literature but the phenomenon is not yet clearly understood.[18,19] In our experiments, the Cu diffusion was observed to become dominant in a substrate in the rubbery state. In such a system, the sample surface is not made any more of Cu but predominantly of polymer through the enhanced motion of macromolecular chains in the rubbery state allowing the Cu to diffuse in the bulk.[20]

On the polymer side, it was also noted that oxygen does not diffuse to the metal layer as nitrogen does. The

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distinction between oxygen and nitrogen mobility had never, to our knowledge, been clearly identified before although the fact that some polymer elements could diffuse to the metal interfaces has already been reported in particular cases, mainly for fluoropolymers,[21,22] but also for doped conjugated polymers,[23,24] and in the Al/polyimide system.[25]

Without invoking any diffusion effect, Ni, with its high energy of condensation, is capable of reaching the oxygenated sites of the substrate. This property to reach specific condensation sites (preferentially oxidative sites such as oxygen groups) is actually well accepted.[26,27] The first metallic nuclei in the substrate initiate the growth of the metal layer,[28] and the reactivity of the metal influences the morphology of the growing layer: strongly reactive metals, like Al, react preferentially with the elements of the substrate leading to uniform metal layers,[29,30] whereas weakly reactive metals, like Cu, react preferably with other metal atoms leading to growing clusters.[31,32]

These two distinct behaviors were clearly seen in this study. If the mobility of the metal clusters[33,34] appears to be the main reason for the broadening of the interface,[35] a high energy of condensation of the metal (which is the case of Ni) can also explain the formation of a diffuse interface without any consideration for the metal mobility. Indeed, Cu, which has a high mobility, and Ni, which exhibits a high energy of condensation, lead to more diffuse interfaces than Al, which always exhibits a narrow interface, even with soft substrates such as PVME. A schematic representation of this behavior for the same amount of Cu, Ni, and Al deposited is summarized in Figure 6. The metal dispersion in the substrate with Cu and Ni leads to a broad metal/polymer interface, whereas for Al the polymer substrate below the dense metal layer remains unperturbed, leading to a narrow metal/polymer interface. At a larger scale, the difference between the behavior of Al and Cu leads, in the first case, to a uniform deposition, and, in the second case, to cluster formation, easily seen in atomic force microscopy pictures shown in Figure 7. Neither the polymer substrate (with or without oxygen) nor the thickness of the metal layer (1 or 10 Å) influence the distinct behavior of the two metals which form, in both examples, Cu clusters or a uniform Al layer, whatever the elements available in the substrate. This observation enables one to minimize the influence of the substrate composition on the interface morphology.

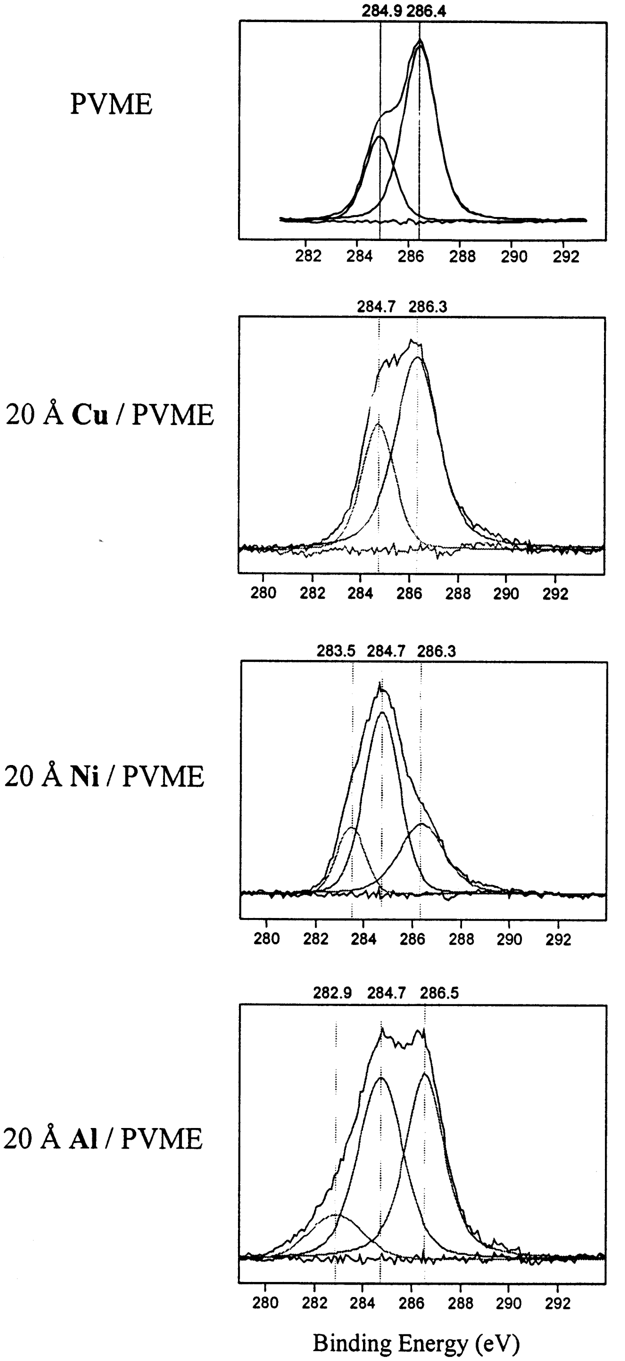

Figure 8. C1s band of PVME covered with 20 Å of Cu, Ni, and Al.

The strong reactivity of Ni is also seen on Figure 8 where the residual C−O contribution (at 286.4 eV) of PVME covered with 20 Å of Ni is significantly lower than the residual C−O component of PVME covered with the same amount of Cu or Al. For Al, which is also a highly reactive metal, the important C−O contribution is mainly due to the fact that Al does not penetrate

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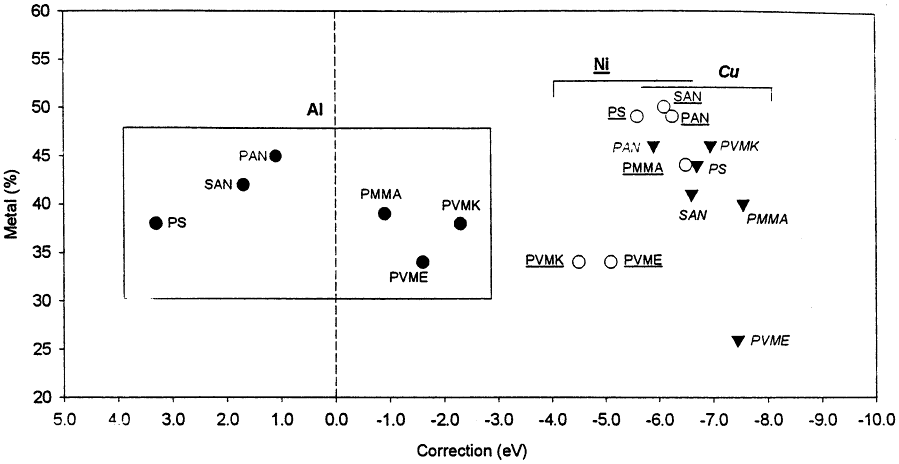

Figure 9. Correction applied to the XPS band position of the metal/polymer systems investigated.

deeply into the substrate but remains at the top surface, forming a uniform metal layer, thus reaching less oxidative sites of the substrate.

The electronic conductivity of the substrate depends on the morphology of the metal coating because a uniform metal layer exhibits a better conductivity than a dispersion of metallic clusters. The charging effect observed in the XPS analysis is, to some extent, representative of the surface conductivity of the sample. The corrections applied to the binding energy scale for all the experimental signals erase this information. The corrections used for coatings of 20 Å of Cu, Ni, and Al on PS, PAN, SAN, PVME, PVMK, and PMMA are given in Figure 9, in which the amount of metal effectively deposited is also considered (Y axis). The polymer acronyms are written in normal, underlined, and italic characters for, respectively, Al (full circles), Ni (empty circles), and Cu (full triangles) coatings. In Figure 9, two groups are distinguishable: the polymers covered with Al on the left side, and the polymers covered with Ni and Cu on the right side. The corrections are larger in the second group (−6 ± 2 eV) than in the first one (0 ± 3 eV). In general terms, conductive substrates require no correction, but insulating substrates exhibit a negative correction. Thus, the surfaces covered with 20 Å of Ni and with 20 Å of Cu appear insulating, but the surfaces presenting a positive correction (Al/PS, Al/PAN, and Al/SAN) can be considered conductive. The Al/PMMA, Al/PVME, and Al/PVMK surfaces require a small correction only (relative to zero) suggesting that the aluminum oxide affects more the conductivity of the metal layer than the very localized aluminum nitride.

Corrections to the XPS band position were applied, similarly, to all polymer bands and to each component of every band. However, under each experimental signals, there are mixed contributions due to the unaffected polymer and to the new species formed at the interface. These two distinct contributions are coming from different areas because the new species are expected to be very close to the condensed metal and the residual polymer signals are expected to be below the new species. It is not realistic to consider that these two contributions, with such different environments (eventually with some conductive phases), require the same correction, or, in other words, exhibit the same electronic charge during the XPS measurements. This difficulty constitutes a known limitation of the composite materials analysis.[36,37]

Conclusion

The metallization of various polymer substrates by copper, nickel, and aluminum leads to similar reactions at the interface:[6,7] metal oxide and metal nitride are formed with, respectively, the oxygen and the nitrogen functionalities of the substrate, and amorphous carbon is always detected as a result of the organic carbon transformation induced by the metal condensation. The surface degradation occurring on oxygen-containing polymers with the loss of oxygenated products is more pronounced with nickel than with copper or aluminum, in agreement with its high energy of condensation. In contrast to oxygen-containing polymers, the surface degradation of nitrogen-containing substrates is detected only by the appearance of an amorphous carbon component (a nitrogen loss is never detected). The analysis of polymer surfaces covered with 20 Å of metal as a function of angle demonstrates the diffusion of nitrogen to the metal layer, and the diffusion of copper into oxygen-containing polymers, which can be enhanced by the rubbery state of the substrate. In the latter case, the macromolecular motions also lead to a renewed pure polymer surface. Narrow aluminum/polymer interfaces and more diffuse copper/polymer and nickel/polymer interfaces have been detected by comparing the metal distribution inside the analyzed surfaces.

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