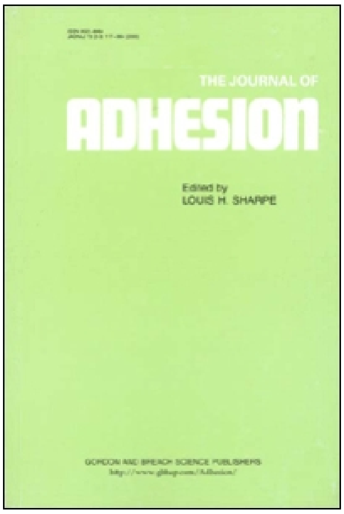

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Plasma Treatment of Polyacetal-Copolymer, Polycarbonate, Polybutylene terephthalate and Nylon 6, 6 Surfaces to Improve the Adhesion of Ink

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To cite this Article Coen, M. Collaud , Nowak, S. , Schlapbach, L. , Pisinger, M. and Stucki, F.(1995) 'Plasma Treatment of Polyacetal-Copolymer, Polycarbonate, Polybutylene terephthalate and Nylon 6, 6 Surfaces to Improve the Adhesion of Ink', The Journal of Adhesion, 53: 3, 201 — 216

To link to this Article: DOI: 10.1080/00218469508009939

URL: http://dx.doi.org/10.1080/00218469508009939

J. Adhesion, 1995, Vol. 53, pp. 201–216
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Plasma Treatment of Polyacetal-Copolymer, Polycarbonate, Polybutylene terephthalate and Nylon 6, 6 Surfaces to Improve the Adhesion of Ink

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(Received November 21, 1994; in final form April 5, 1995)

Polyacetal-copolymer (POMB), polycarbonate (PC), polybutylene terephthalate (PBT), and nylon 6, 6 (PA6, 6) have been treated in an electron cyclotron resonance (ECR) plasma chamber to improve their adhesion properties towards ink. The chemical composition, the surface free energy, and the macroscopic adhesion have been studied by X-ray photoelectron spectroscopy (XPS), contact angle measurements, cross-cut tests, and the Scotch Tape test. Their dependence on the neutral gas, the treatment time, the pressure, and the ageing in air have been investigated. The XPS results reveal that the plasma treatment allows one to clean the surface and, if reactive gases are used, to incorporate new chemical species. The static and dynamic contact angles decrease with the plasma treatment and continue to decrease after contact with air. Very slow hydrophobic recovery is visible in the advancing contact angle, whereas the receding contact angle remains non-measurable even after more than a week of air exposure. Lower pressures and longer treatment times (120 s) lead to better macroscopic adhesion and reproducibility. For optimal treatment conditions (0.5 Pa, 120 s N_2 plasma treatment time), the improvement of the adhesion remains excellent after seven days exposure of the sample in air.

KEY WORDS polymers; plasma treatment; effect of air exposure; adhesion; ageing; XPS; contact angle measurements

1 INTRODUCTION

In the last few decades, the industrial application of polymeric materials has grown because of their interesting mechanical, chemical, and physical properties of polymers, and of their low cost. They are extensively used in automobile and aeronautical industries, in electronic devices, and in packaging. Their technical application often requires coating, printing, metallization, sticking, or gluing. However, most of the polymers, and particularly the cheapest ones (polyolefins, PET), have bad intrinsic adhesion properties. Therefore, some pretreatment is necessary to obtain good adhesion. These surface treatments can be achieved by wet chemical cleaning or by dry processes such as flame treatments, corona discharge or plasma treatments. These last methods are more and more used because of their ecologically-favorable balance.[1]

The industrially mostly used pretreatment is certainly the corona discharge. The advantage of this technology is the avoidance of a vacuum system. Low pressure plasma reactors involve high vacuum technology, but allow one to have well-defined plasma conditions, low energy consumption and a very small amount of gas.[2] The main advantage of ECR-rf plasma is that the ECR process[3] allows one to have high ion density, namely, a great amount of active species. In this case, the plasma treatment is well-defined, and we are able to study the effects of the plasma parameters on the polymer surface, and to optimize the tratment.

A non-equilibrium or cold plasma consists of a broad range of neutral, excited and ionized species, of high energetic electrons, and of a large spectrum of UV and VUV radiation. The plasma parameters, namely, the degree of dissociation and of ionization, the ion and electron energy, flux, and density, and the intensity of the electromagnetic radiation, can be varied by the external parameters (neutral gas, pressure, energy density in the plasma, treatment time, geometry of the reactor, etc.). However, the plasma parameters usually can not be adjusted separately, and the plasma efficiency has to be understood as a synergy between the effects of all its components.[4, 5]

Plasma treatment of polymers induces several surface modifications depending on the material and on the treatment conditions:[2] cleaning of organic contaminations, ablation of material (micro-etching), crosslinking and branching, and surface chemical modifications. Crosslinking and etching are constantly in competition in every plasma. All these plasma effects take place to some extent and can lead to an improvement of the adhesion.

When two surfaces are brought together to be adhered, intrinsic forces have to be generated at the interface to ensure a strong adhesion. Depending on the type of interaction, different *mechanisms of adhesion* are referred to:[5] mechanical interlocking, diffusion, electronic and adsorption. Each mechanism of adhesion can contribute to some degree to create a strong interface, and all pretreatments that induce changes in the mechanical, electronic interaction or chemical properties of the substrate surface can favour the adhesion. However, the term "adhesion" does not only relate to a strong interface between two components, but takes into account the total system response between the bulk of the substrate and the bulk of the coating. This set of successive layers is commonly called the interphase. The bond will break in the weakest layer of the interphase, which is not always the interface.

Numerous studies have evidenced the ability of plasma treatment to improve the adhesion of polymers.[6–11] In this study, we have treated technical polymers, namely POMB, PC, PBT, and PA6, 6 in an ECR-rf plasma. The chemical composition of the surface, the surface free energy and the adhesion strength have been investigated as a function of the neutral gas, the treatment time, the pressure, and the ageing in air. This allows one to correlate the surface modification with the ion kinetic energy and dose, and to determine the effects of several gas species. XPS, contact angle measurements and cross-cut tests are the experimental methods that have been applied to test the effects of the plasma on the substrate surface and the adhesion improvement induced by this pretreatment. Therefore, we try to link the macroscopic adhesion (sometimes called practical adhesion) with the microscopic adhesion, namely with the state of the surface after the pretreatment. Moreover, the treatments were optimized for one polymer (POMB), and we attempt to transfer the results to other polymers.

2 EXPERIMENTAL

The substrates involved in this study are commercial high-crystalline polyacetal-copolymer (POMB) [/-CH_2-O-/$_n$-/CH_2-CH_2-/$_m$] from Hoechst (Hostaform C 9021) with no additional agents, amorphous polycarbonate (PC) [/-O-(C_6H_4)-C(CH_3)$_2$-(C_6H_4)-O-CO-/$_n$] from Bayer (Makrolon 6557), that is stabilized against UV-radiation, semicrystalline polybutylenterephtalate (PBT) [-CO-(C_6H_4)-CO-O-(CH_2)$_4$-O-/$_n$] from Bast (Ultradur B 4500) with no additive agents, and thermally stabilized semicrystalline polyhexamethylenadipidiamide (PA6,6) [/-NH-(CH_2)$_6$-NH-CO-(CH_2)$_4$-CO-/$_n$] from DuPont (Zytel E 103 HSL-C). The samples were not cleaned before the plasma treatment.

The treatments were performed in an ECR plasma chamber, whose base pressure was 5×10^{-6} Pa. The plasma was ignited by an electron cyclotron resonance (ECR) process, with rate-earth permanent magnets, at 2.45 GHz microwave frequency. The input micro-wave power was 400 W; however, a part of the microwave was reflected before it reached the plasma. The plasma chamber was not optimized for this parameter. The samples were treated in the plasma, 3 to 5 cm under the plasma ignition area. The treatments were made in the pressure range between 3×10^{-2} Pa and 5 Pa with argon, oxygen, nitrogen and air.

The plasma chamber, described in more detail elsewhere,[12] was directly connected by vacuum line to the XPS spectrometer, so that no atmospheric contact occurs between the treatment and the XPS analysis. The spectrometer was a VG ESCALAB 5 operating at a base pressure lower than 10^{-7} Pa. A non-monochromatized Mg Kα radiation (1253.6 eV) source operated at 200 W (10 kV, 20 mA) was used. Survey spectra were taken with 50 eV pass energy and detailed spectra with 20 eV. To increase the surface sensitivity, some samples were measured with a photoelectron emission angle of 30°, instead of an emission normal to the surface. The charging of the polymer samples under the X-rays was corrected for, by setting the hydrocarbon peaks at 285 eV.[13, 14]

The chamber for the contact angle measurements was directly connected to the plasma chamber by vacuum lines at a base pressure of 0.1 Pa. A goniometer allows one to measure both static and dynamic contact angles. The sample and the needle for dispensing liquid drops are static and the goniometer can be moved in the three directions. Therefore, dynamic contact angle measurements (advancing and receding angles) can be performed without change in the lateral position of the needle towards the liquid drop. This allows more accurate measurements. The liquid used was glycerol, whose surface free energy in the vapor phase is $\gamma_{lv} = 64.0\,\mathrm{mJ/m^2}$ (dispersive surface free energy $\gamma_{lv}^D = 34.0\,\mathrm{mJ/m^2}$ and polar surface free energy $\gamma_{lv}^P = 30.0\,\mathrm{mJ/m^2}$).[5] Before the introduction of the syringe through a fast-entry lock, the chamber was filled with argon. Therefore, the major part of the oxygen contamination due to atmospheric contact can be avoided. For each sample, static (with the syringe needle located outside the drop) and, afterwards, advancing and receding contact angles[5, 15, 16] were measured on both sides of the drop. All reported values are the mean of both these measurements. The reproducibility for non- zero angles is 1–2°; the uncertainty in the angle reproducibility is 4–5° for proper and smooth surfaces. For contact angles smaller than 3°, the measurement becomes difficult to perform and the error increases greatly. Therefore, what is reported on the graphs is a hypothetical value of 2° and a reproducibility error of ± 2°.

For macroscopic adhesion tests, the plasma-treated samples of polymers were coated by tampon-print with air-drying varnish. After a drying period of 24 hours, the adhesion of the varnish-layer to the respective polymer was investigated according to the standard ISO 2409 "Paints and varnishes cross-cut test". The results are classified into 5 cross-cut values (CC); zero corresponds to very good adhesion and five to very poor adhesion.

A previous study and other references[6, 19] show that the best adhesion improvement is found after nitrogen plasma treatments. Therefore, this study has been mainly done with this plasma. All polymer samples suffer degradation under the X-rays during the XPS measurements. The pressure in the analysis chamber of the spectrometer rises up to 1×10^{-5} Pa, because the X-ray exposure induces an etching of hydrogen and hydroxide components. This degradation becomes visible to the eye through a yellow coloration and a matte surface on the sample. It is worth noting that the sample also sometimes only becomes matte with the plasma treatment, but never changes color. The samples present some roughness due to the fabrication process. On one side of the sample, the roughness structure is clearly visible to the eye. All the measurement were performed on the smoother side of the sample. However, the roughness induces some inhomogeneities for the contact angle measurements. These differences in the contact angles, depending on the orientation of the substrate, are negligible for as-received and plasma-treated samples, but become important for polymer surfaces exposed to X-rays. Therefore, different samples were used for the ESCA analysis and the contact angle measurements. For the ageing time dependence, a new sample was used for each measurements.

3 RESULTS

3.1 About the Plasma Treatments on POMB Surfaces

3.1.1 Effects of the plasma treatment analyzed by in-situ methods

We shall first describe the effects of the plasma treatment on the polymer surface before exposure to the atmosphere. Figure 1 shows detailed XPS Cls, Ols and Nls spectra of a) untreated, b) Ar plasma, c) N_2 plasma, and d) O_2 plasma-treated POMB at 0.2 Pa for 30 s. The Cls spectra have been fitted with 2 eV wide peaks. The untreated surface contains a small amount of Si and Na contaminations that disappears after some seconds of plasma treatment. The deconvoluted Cls spectrum shows the C-H functionalities at 285 eV (57%) and the O-C-O bonds at ~ 288 eV (43%), binding energies that correspond to the literature.[14] The surface composition corresponds well to the chemical structure of the copolymer.

We can see in Figure 1 that Ar and N_2 plasma treatments lead to a decrease of the oxygen content of the POMB, and to a diversification of the bonds. This etching induced by the plasma treatment is particularly efficient in the Ar plasma (28% of oxygen), and generally in all noble gas plasmas.[2, 17] The loss of oxygen species is also clearly visible in the Cls peak, where the carbon-oxygen functionalities have been

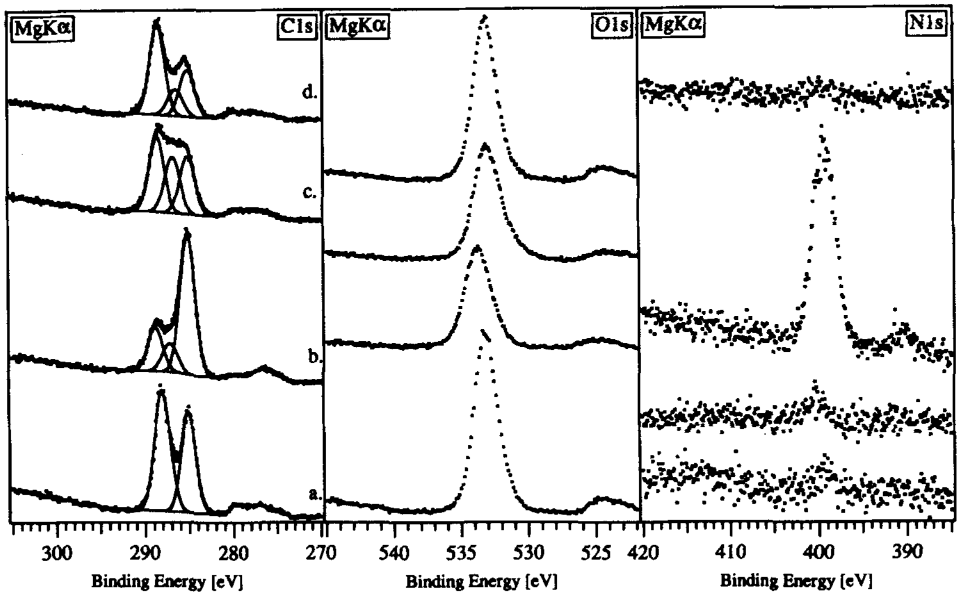

FIGURE 1 Cls, Ols, and Nls detailed XPS spectra of: a) untreated, b) Ar plasma treated, c) N_2 plasma treated, and d) O_2 plasma treated POMB. The treatments were done at 0.2 Pa for 30 s.

drastically reduced. Moreover, the Cls peak deconvolution involves three peaks. The central peak corresponds to oxygen-carbon groups that are not contained initially in the POMB [$\Delta E(\mathrm{C{-}OH}) = 1.55\,\mathrm{eV}$, $\Delta E(\mathrm{C{-}O{-}C}) = 1.45\,\mathrm{eV}$, $\Delta E(\overset{\mathrm{O}}{\mathrm{C{-}C}}) = 2\,\mathrm{eV}$].[14] The N_2 plasma treatment leads to an oxygen reduction and to a nitrogen incorporation (10%). The nitrogen-carbon bonds are mostly visible in the central peak of the Cls deconvoluted spectra [$\Delta E(\mathrm{N{-}C{-}O}) = 2.8\,\mathrm{eV}$, $\Delta E(\mathrm{C=N}) = 1.7\,\mathrm{eV}$, $\Delta E(\mathrm{C^+ - C=N}) = 1.4\,\mathrm{eV}$].[14] The O_2 plasma treatment leads to no great changes in the oxygen content. However, the impossibility of fitting the Cls peak with two components proves that O_2 plasma treatments also induce a destruction of the POMB chains. In both of the reactive gas plasmas, the etching process and the incorporation of new chemical species are in competition during the treatment. The dominating phenomenon depends on the treatment conditions, namely, on the ions energy and flux.[17] Figure 2 shows the contact angles of glycerol on untreated, Ar plasma, N_2 plasma, and O_2 plasma-treated POMB at 0.2 Pa for 30 s. These measurements were done under Ar atmospheric pressure prior to air exposure. The three plasma treatments lead to a decrease of all contact angles, which represents an increase of the surface free energy. However, the hysteresis between the static, advancing and receding angles remains unchanged. It is a sign of the roughness of the surface and of inhomogeneities between hydrophobic and hydrophilic surface compounds.[5] The hysteresis is also believed to be due to reorientation of the hydrophobic moiety of the polymeric molecules with liquid contact.[18] The receding angles become unmeasurable with any plasma treatment, whereas the untreated sample has a 20° receding angle. The N_2 plasma treatment induces the most wettable

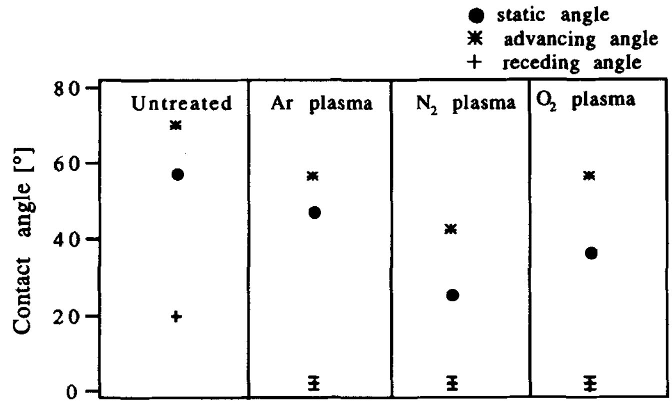

FIGURE 2 Static and dynamic contact angles of glycerol on untreated, Ar, N_2, and O_2 plasma treated POMB. The treatments were performed at 0.2 Pa during 30 s and no contact with the atmosphere occurred before the measurement.

surface, whereas the Ar plasma treatment leads to the smallest change in contact angle. Actually, the Ar plasma treatment reduces the oxygen content and, therefore, the number of highly-polar bonds. The treated surface becomes free of contamination, but contains more hydrocarbon species than the untreated or the reactive gas plasma treated POMB samples. Therefore, it is more wettable than the untreated surface, but less hydrophilic than the N_2 or O_2 plasma treated POMB surfaces.

3.1.2 *Effect of the treatment time*

Figure 3 presents the carbon, oxygen, and nitrogen concentrations as evaluated from XPS core level intensities as a function of the treatment time for nitrogen plasma treatment at 0.2 Pa. The nitrogen uptake shows a rapid slope during the first 60 s (0–15%), and on saturates at 20% after 5 min treatment. It was shown in previous study that the nitrogen saturation level and the dynamics of incorporation depend on the pressure and on the rf-bias, namely, on the ion energy.[20]

The cross-cut tests as a function of the nitrogen plasma treatment time are presented in Figure 4. For each treatment, three samples were tested. The size of the points on the graph depends on the number of samples (small point = 1 sample, big point = 3 samples) that gave the same cross-cut (CC) value for the same pretreatment. The untreated POMB gives completely unsatisfactory results (CC = 5) and is not suitable for any printing or coating application. The adhesion on 15 s nitrogen plasma treated samples is improved, but the scatter of the results denotes a poorly- reproducible treatment. Longer treatment times induce cross-cut values of 0 and a good reproducibility, showing good adhesion of the ink to the POMB surface. Scotch Tape tests lead to similar results. Some additional experiments were done with 30 s treatments. The last samples were exposed to 120 s of plasma. They have better adhesion and reproducibility in all of the analyses.

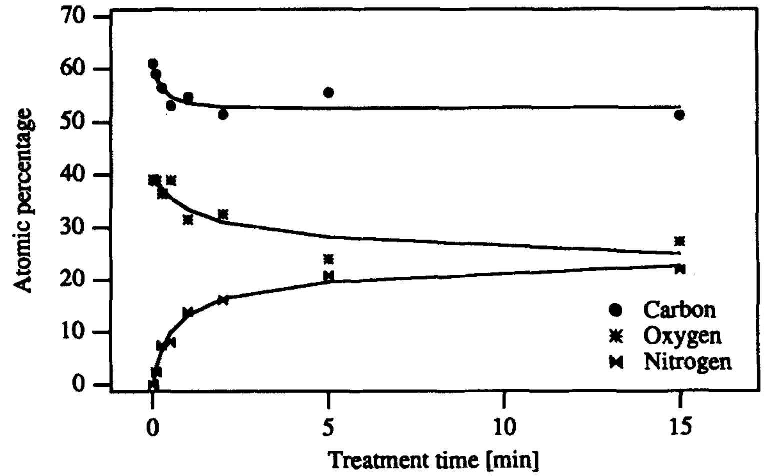

FIGURE 3 Composition of N_2 plasma treated POMB surfaces at 0.2 Pa as a function of the treatment time. This composition was determined by *in-situ* XPS analysis.

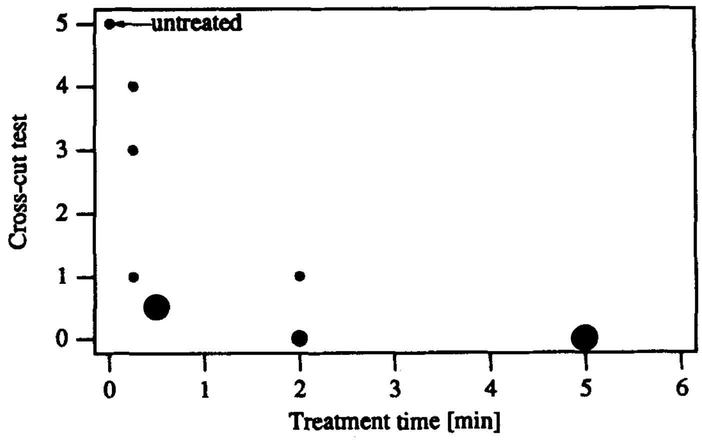

FIGURE 4 Cross-cut tests as a function of treatment time for N^2 plasma treated POMB surfaces at 0.2 Pa. The size of the points is a measure of the number of similarly treated samples inducing the same macroscopic adherence result.

3.1.3 *Effect of the neutral gas pressure*

Table I displays the carbon, the oxygen and the nitrogen concentration on POMB surfaces after 30 s plasma treatment at various pressures and with several gases. As we have seen in Figure 1, Ar plasma treatment leads to a reduction of the oxygen species. Lower pressure induces higher ion energy and flux (a plasma treatment at 0.03 Pa corresponds to an ion energy of 18 eV and a dose of $2\,10^{15}$ ions/cm^{2}s and a plasma treatment at 5 Pa leads to an ion energy of 8 eV and a dose smaller than

TABLE I
Composition of Ar, N_2, and O_2 30 s plasma treated POMB as a function of the pressure in Pa, without atmospheric exposure

	Ar plasma			N_2 plasma			O_2 plasma		
Pressure	carbon	oxygen	nitrogen	carbon	oxygen	nitrogen	carbon	oxygen	nitrogen
0.03	76	22	2	54	37.5	8	63	36.5	0.5
0.2	70.5	28	1	57	31.5	11	56	43	0.5
5	72	27.5	0.5	55	41	4	56	43	0.5

0.3×10^{15} ions/cm^{2}s)[12, 21] and, therefore, a faster etching process and lower oxygen content (21%). The nitrogen content is due either to contamination of the POMB or to a small percentage of residual N_2 in the plasma atmosphere.

N_2 plasma treatments lead to an incorporation of ~ 10% nitrogen at low pressures and only few percent at a higher pressure (4% at 5 Pa). This is in agreement with a previous study of N_2 plasma treatments on polypropylene (PP),[20] where higher pressures induce higher maximal nitrogen content, but a very slow incorporation rate (saturation level for treatment times greater than 15 min).

For O_2 plasma treatments the etching and incorporation process seem to be equivalent at low pressure (0.03 Pa). Therefore, the oxygen content is similar to the content in the untreated POMB, even if the chemical structure of the POMB is greatly modified (Cls peak has to be fitted in 3 peaks). For higher pressures, where the etching process is smaller due to a lower ion kinetic energy, a small increase in oxygen content takes place. Figure 5 shows the cross-cut tests as a function of the pressure for 30 s O_2, N_2, and air plasma treatments. The size of the symbols in the graph is related to the number of samples (maximum 3 samples) exposed to the same treatment and leading to

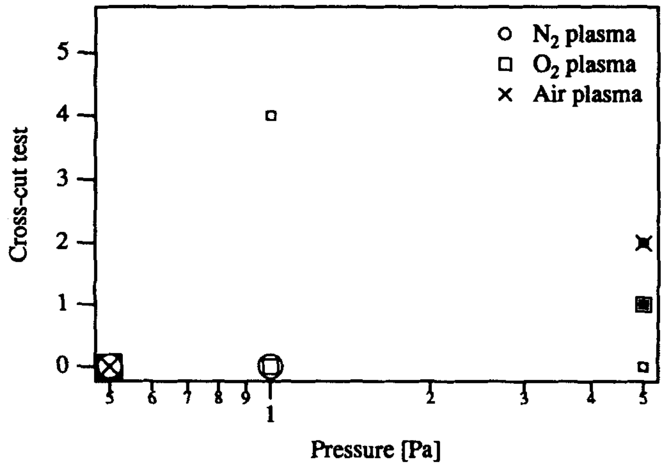

FIGURE 5 Cross-cut tests as a function of pressure for N_2, O_2, and air plasma treated POMB surfaces at 30 s. The size of the symbols is a measure of the number of similarly treated samples inducing the same macroscopic adherence result.

the same cross-cut value. First, it is clear that the behaviour as a function of the pressure does not depend on the nature of the plasma gas. Secondly, better adhesion occurs at lower pressures. As was described before, lower pressures induce stronger treatments (ion energy and flux). An adhesion improvement at the interface is, therefore, not surprising. Moreover, plasma treatments at 0.5 Pa seem not be able to create a weak boundary layer under the interface which would weaken the interphase.

3.2 About the Air Exposure of Plasma-Treated POMB, PC, PBT, and PA6, 6 Surfaces

3.2.1 *Effect of the Exposure to air*

Figure 6 presents the PC, PBT, and PA6, 6 Cls XPS spectra of a) as-received sample, b) 120 s N_2 plasma-treated sample, and c) N_2 plasma-treated sample after a 2h air exposure. The composition (at. %) of these polymers before and after N_2 plasma treatment and after 2 h air exposure are reported in Table II. The spectra and the chemical composition of untreated PC and PBT correspond well to the theoretical composition of the polymers. On the contrary, the untreated PA6, 6 contains not enough nitrogen (2% instead of 12%). A hydrocarbon or oxygen-carbon contaminated first layer can induce such an effect, so that the as-received surface does not correspond to a bulk PA6, 6. Moreover, some potassium also is detected (K2p at 293 eV and 296 eV). PA6, 6 contains 0.013 atomic percent of potassium in an additive that acts as a thermal stabilizator. Therefore, a surface segregation of this component occurs.

For all polymers, this N_2 plasma treatment incorporates ~ 20% of nitrogen species that are visible on the Cls peak by an increase in intensity of the shoulder in the

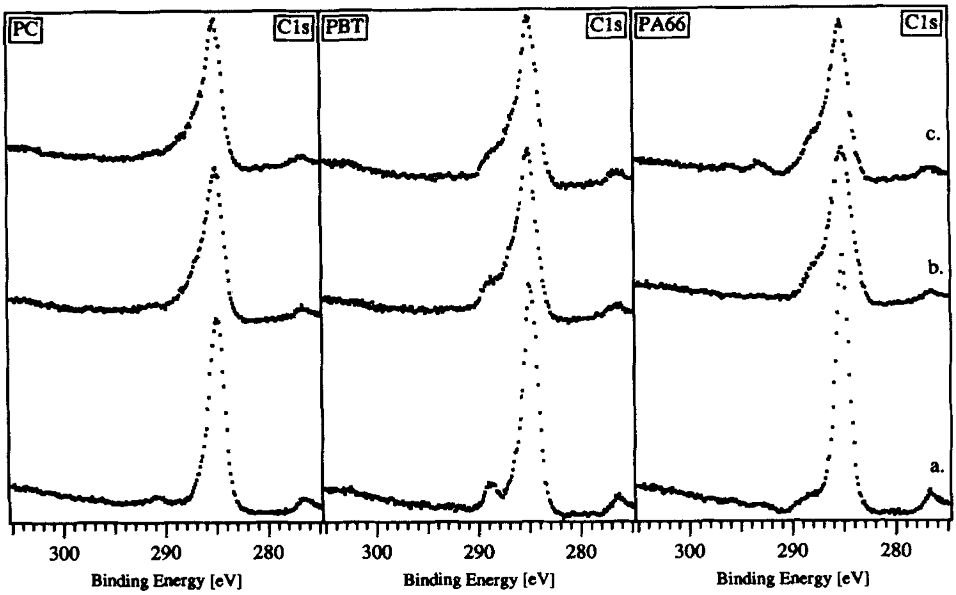

FIGURE 6 Cls XPS, spectra of untreated, and N_2 plasma treated PC, PBT, and PA66, *in situ* and after 2 hours atmospheric exposure. The treatments were performed at 0.5 Pa during 120 s.

TABLE II
Composition of untreated, and N_2 plasma treated POMB, *in situ* and after 2 hours atmospheric exposure. The treatments were performed at 0.5 Pa during 120 s

	PC			PBT			PA66		
	carbon	oxygen	nitrogen	carbon	oxygen	nitrogen	carbon	oxygen	nitrogen
Untreated	81	18	1	78	20	0.5	87	11	2
in-situ	69	11.5	19	66.5	16	17.5	71	7	22
2 h. in air	68	15	17	68.5	14.5	17	69	11	19

high-binding-energy side of the hydrocarbon peak. As was reported before, the measured nitrogen content of as-received PA6, 6 samples does not match the chemical formula of this polymer. Therefore, the increase in nitrogen species after N_2 plasma treatment can be attributed to two phenomena. First, a nitrogen incor-poration should occur and, secondly, a removal of the first contaminated layers would allow one to measure bulk nitrogen. Therefore, it is difficult to evaluate the amount of new incorporated chemical species, as well as the chemical state of these new atoms or molecules (carbon-nitrogen or oxygen-nitrogen bonds). This phenomenon is certainly also present for the other polymers, but to a lesser extent.

In the industrial applications, the polymers are often exposed or stocked in the atmosphere between the pretreatment and the coating, printing or metallization. As the plasma treatments are believed to create unsaturated radicals at the surface, a reaction of the activated polymer surface with the air constituents can be expected. A previous study has shown that N_2 molecules can not be chemisorbed at the plasma-treated polymeric surface.[22] Therefore, all the measured nitrogen is either a natural polymeric constituent or is incorporated during the plasma treatment.

PC and PA6, 6 treated surfaces do incorporate a small amount of oxygen during atmospheric contact (3.5% and 4%, respectively). After the air contact, the potassium content of the PA6, 6 surface increases. The PBT surface remains similar to the plasma-treated one without air exposure. Therefore, the atmospheric contact induces almost no XPS measurable changes in the chemical composition of the PC, PBT and PA6, 6 samples after a N_2 plasma treatment.

The contact angles of glycerol on POMB, PC, PBT, and PA6, 6 surface for, a) as-received sample, b) 120 s N_2 plasma-treated sample, and c) N_2 plasma-treated sample after a 2h atmospheric exposition are reported in Figure 7. For all polymers, the plasma treatment induces a decrease of all the contact angles. Actually, the receding angle becomes non-measurable after the pretreatment, and does not change with atmospheric contact. The static angles after the pretreatment are similar for all polymers, namely, 30°–40°. The exposure to the air generally induces a 10° decrease of the advancing angle, and a small lowering of the static angle. This can be explained by the chemisorption of new hydrophilic species (H_2O, HO, O_2, etc.) or a reorientation of these species, during the air exposure, that allows a better wettability by the glycerol.

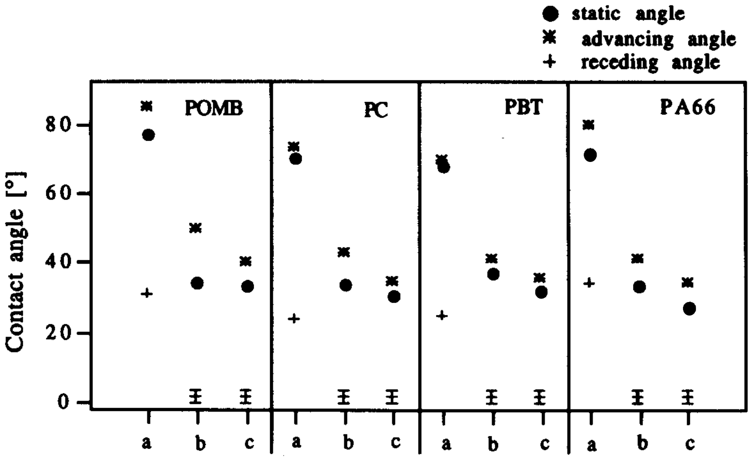

FIGURE 7 Static and dynamic contact angles of glycerol on samples: a) untreated, b) N_2 plasma treated, and c) N_2 plasma treated and stored two hours in air. The treatments were performed at 0.5 Pa during 120 s for POMB, PC, PBT, and PA66 samples.

3.2.2 *Effect of the ageing into the air*

Figure 8 shows the carbon, oxygen, and nitrogen concentration of N_2 plasma-treated POMB samples as a function of the ageing time in air. These XPS measurements were done with a 30° photoelectron emission angle, namely, with a four-time-smaller probing depth than the usual XPS spectra. The first point (0 ageing time) was measured immediately after the vacuum transfer of the plasma-treated surface. We can see once again that the exposure to the air induces a small oxygen incorporation. However, longer ageing time does not change the chemical composition of the top

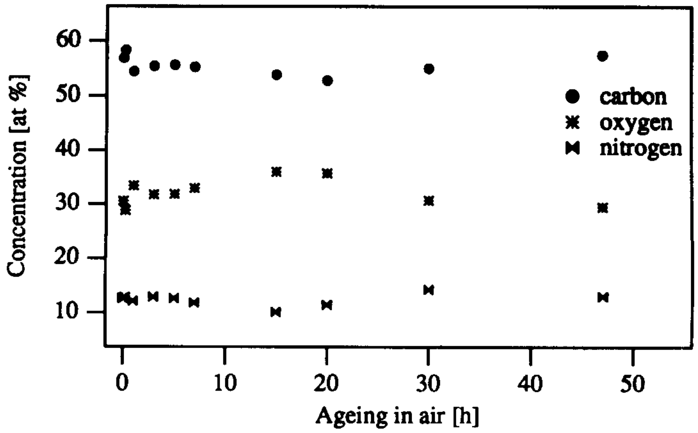

FIGURE 8 Composition of 30 s N_2 plasma treated POMB at 0.5 Pa as a function of the ageing time under atmospheric conditions. The XPS analysis were done with 30° photoelectron emission angle.

monolayers. The same measurements on PA6, 6 samples at 90° photoelectron emission angle over a period of 7.5 days lead to similar results. Figure 9 shows the PA6, 6 Cls spectra for various ageing times in air. The first spectrum, a), presents an untreated surface. The characteristic shoulder due to C = O functionality is clearly visible. The incorporated nitrogen species during the plasma treatment and oxygen species by the air exposure induce a broadening and an increase in intensity of the shoulder on the high-binding-energy side of the hydrocarbon peak (Fig. 9b). Even if the oxygen content does not increase with ageing time, the shoulder due to carbon-oxygen and carbon-nitrogen functionalities becomes more distinguishable with the time of air exposure. The potassium surface content also clearly increases with ageing time. Therefore, a restructuring of the polar functionalities and a segregation of the additive content in the surface occurs.

Figure 10 presents contact angle measurements on nitrogen-plasma-treated PA6, 6 as a function of the ageing time. The receding angles still remain unmeasurable after more than 7 days in the air. The static and advancing contact angles increase some degrees during the first hours and remain stable for longer air exposure. The behaviour of contact angles as a function of ageing time on nitrogen-plasma-treated POMB is

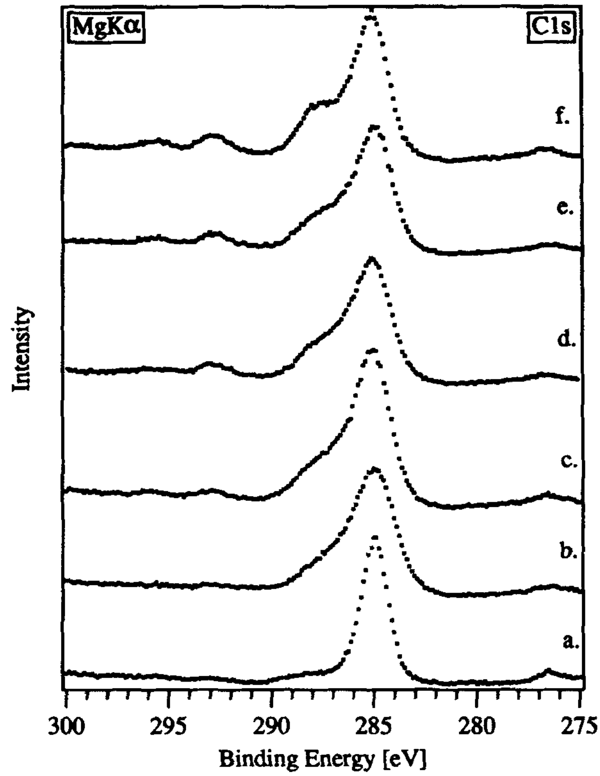

FIGURE 9 Cls XPS spectra of 120 s N_2 plasma treated PA66 at 0.5 Pa as a function of ageing time: a) untreated, b) 5 min, c) 8 hours, d) 1 day, e) 4 days, f) 7.5 days.

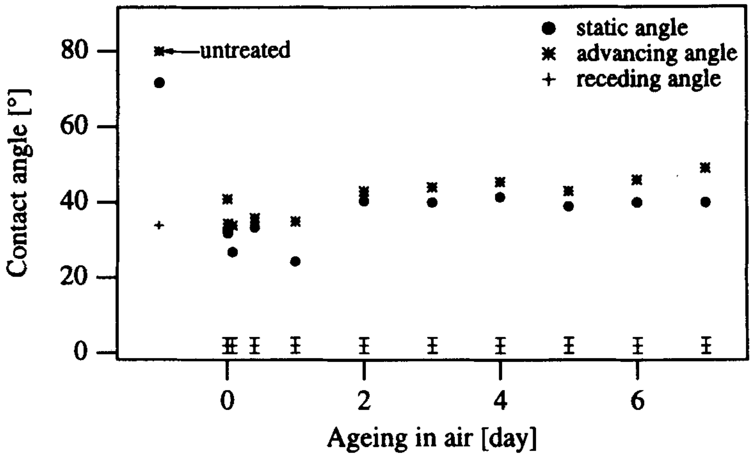

FIGURE 10 Static and dynamic contact angles on 120 s N_2 plasma treated PA66 samples as a function of the ageing time in air.

completely similar. Therefore, the low surface free energy induced by the plasma treatment is only slowly influenced by the ageing in the atmosphere.

Cross-cut tests on 120 s N_2 plasma-treated POMB, PC, PBT, and PA6, 6 samples were performed during 7–8 days after the pretreatment. The results for POMB and PA6, 6 samples are excellent (CC = 0) during all this ageing time. For the PC and particularly the PBT samples, the mean cross-cut values are also very good, but some scatter in the results occurs. Therefore, the adhesion improvement due to the pretreatment is stable during more than a week. The plasma treatment optimized for the POMB surface was found also to be good for the other polymers. However, the plasma treatment needs to be adjusted for every polymer in order to obtain excellent results in every case.

4 DISCUSSION

As can be seen from the XPS spectra of the untreated polymers (Figs. 3 and 8), the POMB, PC and PBT surface compositions are in good agreement with their chemical structure, but the PA6, 6 surface composition differs greatly from the reference for the bulk polymer. In this case, the sample surface is certainly covered by some hydrocarbon or oxygen-carbon contamination. This pronounced effect on the PA6, 6 surface can also occur to a small extent on the other polymer surfaces. Moreover, the manufacturing process induces a rough surface. The effects of the plasma treatment are first to remove the contamination, then to break polymeric chains, leading to an etching of low molecular weight species (hydrogen, C—O groups, ester groups, etc.) from the surface and, with reactive gas plasmas, to incorporate new chemical species (Figs. 1, 6). Secondly, radicals and polar groups are created and incorporated by the pretreatment; they induce a surface which is reactive and has a high surface free energy. This is clearly evidenced by the decrease of contact angles with the plasma treatment and the air exposure. The important role played by the ions of the plasma in modifying polymeric surfaces has been described in previous studies.[17, 20]

The behaviour as a function of the ageing in air, namely, undetectable changes in the oxygen concentration measured by XPS and a slow increase of the contact angles, can easily be correlated with the results of other studies. For example, Griesser *et al.*[23] studied the stability of plasma-treated fluorinated ethylene propylene (FEP) with storage time in air. They found a rapid increase of the contact angle during the first twenty days and an almost constant angle for longer exposure time (up to 240 days). Even after such a long exposure to air, the contact angles still remain lower than on the untreated FEP. This stable level is lower for treatment times of some minutes than for shorter treatments. The XPS-measured oxygen contents of the FEP denote only small changes with the storage time, that can not be related to the large modifications of the contact angles. Morra *et al.*[10] also found no modification of the XPS-measured oxygen content with ageing, but good correlations between CH^- to $^{18}O^-$ SSIMS intensity ratio and contact angles have been found, namely, a decrease of the surface oxygen functionalities with ageing time. This observation was attributed to rearrangements of the polar bonds at the surface. Therefore, changes in the surface chemical composition seem not to be detectable by XPS, even at a small take-off angle.

The slow recovery of the contact angle connected with small changes in the polar group content is usually attributed to reorientation of macromolecules at the top surface (first monolayers).[10, 18, 23] The reorientation of the hydrophilic moiety of the polymer molecules towards the bulk can explain the hydrophobic recovery of the plasma-treated samples with storage in air. This chain rearrangement towards lower surface free energy is impeded by the crystalline or highly-crosslinked region of the polymer, where the polymer chains have less mobility than in amorphous parts. The ageing environment relative humidity of air, storage in water or other liquid, temperature, etc. can influence the dynamics and the kind of reorientation. However, crosslinked and crystalline regions forbid a complete recovery.

The macroscopic adhesion tests show that a great improvement of the adhesion of ink on POMB, PC, PBT, PA6, 6 happens with plasma treatments, according to other studies on several polymers.[6, 9, 10] Usually, treatments between some seconds and some minutes allow a maximal adhesion increase, and the plasma-induced polymer modifications remain stable upon air exposure for at least some ten days. As the effects of the plasma treatment depend on the treatment parameters, a further improvement and optimization by a specially-developed plasma reactor for industrial applications seems possible.

In every case, plasma treatments allow one to clean the surface and to increase the surface free energy. This constitutes one explanation for the adhesion improvement. Due to the plasma treatment and/or to the air exposure, polar groups are always present at the surface, and they determine the interface composition. However, the oxygen functionalities are not better suited than nitrogen functionalities to improve the adhesion. Therefore, even if the presence of polar bonds at the surface should play an important role in adhesion, there is no correlation between the oxygen content at the surface and the adhesion. Moreover, it was proved, in a previous study,[24] that Ar and N_2 plasma treatment induce similar maximal sticking coefficients towards Mg. Ionic or covalent bonds are not the only forces that contribute to the adhesion improvement. In general, greater ion energy and dose induce a better adhesion. No overtreatment phenomenon was evidenced during this study, but the ion energy does not go over 20 eV and the ions can, therefore, not induce great damage.

5 CONCLUSION

Plasma treatments are able to modify polymeric surfaces in a way that allows excellent adhesion for industrial applications. Lower pressures plasma treatments, namely, treatments with a greater ion kinetic energy ($\sim 15\,\mathrm{eV}$), induce better wettability and greater macroscopic adhesion. For ion kinetic energy greater than 10 eV the adhesion is good. The neutral gas seems not to be a determinant parameter. Good adhesion was found for 30 s treatments, but 120 s treatments are necessary to have good reproducibility in the plasma treatments. These treatment conditions depend on the plasma reactor and can certainly be improved for industrial processes. The plasma treatment induces a cleaning of the polymer surface and an incorporation of new chemical species if reactive gases are used. This leads to an activated surface and to an increase of the surface free energy both before and after air exposure. Due to the incorporation of hydrophilic species through atmospheric contact, the contact angles decrease after air contact. The samples can be aged during more than a week in atmospheric conditions before printing without altering the effect of the plasma treatment towards adhesion. However, a reorientation of the polar bonds towards the surface occurs, as well as a surface segregation of additives in some cases. All four of the polymers react similarly to the plasma treatments and to the storage in the air.

Acknowledgements

We thank E. Schaller, R. Sanchez, and M. Amman for their assistance in this study. This work was supported by the Kommission zur Forderung wissenschafticher Forschung, contract KWF 2447.1.

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