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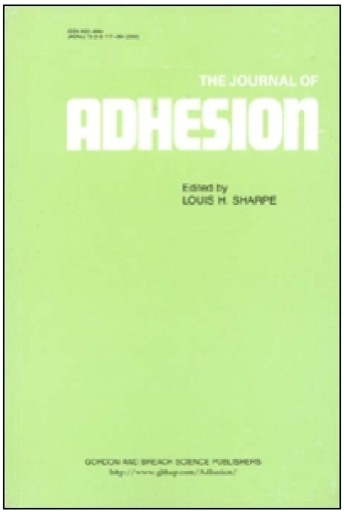

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Adhesive Strength Study and Surface Analysis Using Gas-Phase Chemical Reactions of Atmospheric Pressure Plasma-treated Polypropylene

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Adhesive strength of Atmospheric Pressure Glow (APG) plasma-treated polypropylene was studied for various gas mixtures by a scratching test. An explanation of the high adhesive strength obtained after He/N_2 APG plasma treatment was given. Formation of carbonyl, alcohol, carboxylic and primary amines was investigated by gas-phase chemical reaction. Their evolution during the ageing of the treated samples was followed. Most changes take place during the first few hours of contact with the atmospheric medium. Contact angle measurements on APG plasma-treated PP were done. These results were compared with PP treated by Silent Electric Discharge (SED). The ageing of the wettability properties of the surface after APG plasmas is better than after SED discharge.

Keywords: Atmospheric pressure plasma treatment; silent electrical discharge treatment; adhesion; copper; contact angle measurements; surface functionalization; polypropylene; surface analysis; ageing effects

1. INTRODUCTION

Plasma processes are commonly used in the treatment of solid surfaces, for example, with the view to improve the compatibility of polymers with other materials. The vacuum apparatus needed for most

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of these procedure are expensive and are inadequate for large-scale objects. Different types of atmospheric pressure discharges were applied recently such as, for example, silent electric discharge (barrier discharges) and corona discharge (point-to-plane electrodes) which were developed 120 years ago for ozonizers, but these discharges are not homogeneous and are less effective for surface treatments of polymers.

Since 1988 our group has developed a homogeneous glow discharge at atmospheric pressure. This Atmospheric Pressure Glow (APG) discharge method generates stable glow discharges at atmospheric pressure [1 – 7].

For a stable glow discharge at atmospheric pressure three requirements must be fulfilled: (i) use of helium as dilution gas, (ii) use of a source frequency of over 1 KHz, (iii) insertion of a dielectric plate (or plates) between the two metal electrodes. With these three conditions the creation of an arc discharge can be avoided. Helium gas is used because of its high-energy metastable states (as high as 20 eV). A high energy and non-charged He^* atom will easily diffuse through the discharge. Such a He^* will ionize the mixed neutral gas molecules. These states may help to create glow discharge between the insulated electrodes. We previously reported that the APG plasma method is applicable to most regions of plasma treatments and to most film deposit techniques [8] as well as surface coating of fine powder [9].

The objective of the work presented in this paper is, firstly, to determine the chemical functionalities which are responsible for the adhesive strength of the treated polymer [by following the amounts of the different functionalities at the treated-polymer surfaces with the Gas-Phase Chemical Reactions (GPCM) method and then to compare them with adhesive strength and surface energy] and, secondly, to study the ageing of these functionalities and these properties with ageing. In the case of the polymer surface treatment, the silent discharge is able to produce the same effect as with the industrial corona type apparatus. For this reason, during all this work the silent electric discharges were produced in the same apparatus as the APG ones with pure oxygen, different frequency and a smaller gap. They are created in an "industrial-corona" type apparatus but, because of the presence of an insulating film (the PP film) on the counter electrode, silent electric discharges are created instead of corona.

2. EXPERIMENTAL

2.1. Plasma Treatment of Films

APG plasma conditions: Power: 50 W; 100 W. Frequency: 100 KHz. Flow gas: He = 2000 sccm; N_2 or O_2 = 25 cm^3/min; Gap distance = 5 mm.

Silent electric discharge conditions: Frequency: 3000 Hz. Voltage: 9 KV. Flow gas: APG plasmas and SED discharges were performed in the same reactor.

2.2. Materials

The copper used for the adhesive strength measurements was purchased from NILACO Corporation and the polypropylene from SANPLATEC Corporation.

Poly(acrylic acid) (PAA), Poly(vinyl methyl ketone) (PVMK), 1,12-Diaminododecane (DADD) and di-tert-butylcarbodiimide (Di-tBuC) were purchased from Aldrich Chemicals. Poly(vinyl alcohol) 500 (PVA) and pyridine were purchased from WAKO Pure Chemical Industries, Pentafluorobenzaldehyde (PFB), Trifluoroaceticanhydride (TFAA) and Trifluoroethanol (TFE) from PCR, and Hydrazine from TCI. All chemicals were first-graded chemicals and were used without further purification.

PAA, PVMK, DADD and PVA were dissolved in appropriate solvent and coated onto 1 cm × 1 cm clean silica wafers by heating.

2.3. Adhesive Strength Measurement

The adhesive strength was determined using in-situ copper deposition of constant thickness immediately after treatment (Fig. 1).

After the deposition of copper, a diamond stylus is used to scratch the surface. The minimum value of the load necessary for the stylus to scratch the surface is called the critical load. We assumed this value to be related to the adhesive properties of the polymer.

2.4. Surface Analysis Techniques

A Scanning Electron Microscope (SEM) was used to search for morphological alterations as a function of the treatment gas. The

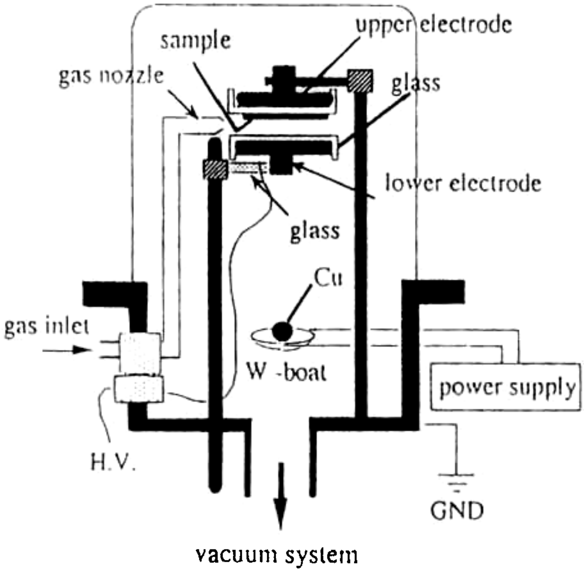


FIGURE 1 Schematic representation of the plasma reactor and copper deposition apparatus.

polymer surface structure was analyzed by XPS (SSI Corporation). The contact angle measurements were performed with distilled water using drops of one microliter volume. The value is obtained by averaging five measurements.

2.5. Gas Phase Chemical Modification

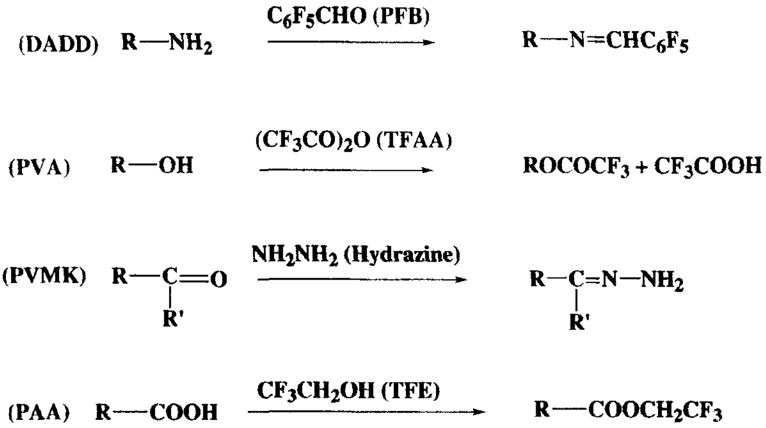
2.5.1. Gas-phase Chemical Modification Procedures

In this part we report the study, by gas-phase chemical modification, of the functional composition of the plasma-treated surfaces and their ageing in ambient atmosphere. After the treatment of a polymer in an APG plasma, numerous different functionalities are created in the surface. A good technique to analyze polymer surfaces is X-ray Photoelectron Spectroscopy (XPS) but in the case of plasma-treated polymers it is very difficult, for example, to distinguish between the different oxygenated functionalities and to determine their quantity.

The spectral decomposition of the C_{1S} peak is very difficult because of the small chemical shift differences. With the chemical modification technique we can label the different functional groups [10-12]. Fluorine-substituted labeling reagents are often used because of the high cross section of the fluorine (and because fluorine is not present on the original polymer).

Typically, the treated polymers (after a given ageing time) were put in a reactor. After creating a primary vacuum, the reactor is isolated, and the reagents introduced. The treated polymers and the model chemicals are then in contact with a saturated gas phase of the reactive reagents. In Scheme 1 we show the chemical reactions which occurred between the reagents and the functionalities created at the surface of the treated polymers.

OH functionalities: The alcohol functionalities were labeled by TFAA. After the introduction of the plasma-treated samples and a model polymer (in the case of alcohol functionalities: PVA) the reactor is sealed. In a second reactor TFAA is frozen in liquid nitrogen and the vacuum is made in the sub-ring containing both reactors. Then the sub-ring is isolated and the TFAA heated for 5 minutes to bring it back to room temperature. We assumed that the sub-ring is filled only with TFAA vapor. The reactor is performed during 2h20 m at room temperature.



$$\text{(DADD)}\quad R{-}NH_2 \xrightarrow{C_6F_5CHO\ \text{(PFB)}} R{-}N{=}CHC_6F_5$$

$$\text{(PVA)}\quad R{-}OH \xrightarrow{(CF_3CO)_2O\ \text{(TFAA)}} ROCOCF_3 + CF_3COOH$$

$$\text{(PVMK)}\quad R{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}O \xrightarrow{NH_2NH_2\ \text{(Hydrazine)}} R{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}N{-}NH_2$$

$$\text{(PAA)}\quad R{-}COOH \xrightarrow{CF_3CH_2OH\ \text{(TFE)}} R{-}COOCH_2CF_3$$

SCHEME 1 Gas-phase chemical reactions.

C=O functionalities: The same procedure as with TFAA was followed but the reaction took place during 4 h at 50°C because of the high T_v, of hydrazine (model polymer: PVMK).

COOH functionalities: In a test tube containing the samples and the model polymer (PAA), TFE (0.9 ml), pyridine (0.4 ml) and Di-*t*-BuC (0.3 ml) were introduced, in this order, every 15 min. The reactor is sealed and the reactions were performed at 35°C during 16 h.

NH_2 functionalities: In a test tube containing the samples and the amine model, 1 ml of PFB is introduced. Then the reactor is sealed. The reaction is performed during 4 h at 35°C.

2.5.2. Estimation of the Chemical Functionality Ratios

For each of the different chemical modifications (involving NH_2, OH, C=O and COOH functionalities) we used a model polymer or a model molecule which possesses the same chemical functionalities (resp. DADD, PVA, PVMK and PAA) to establish the yield.

Figure 2(a) shows the C_{1S} peak of PVA after reaction with TFAA. The yield of the reaction is the ratio between CF_3 component (d) C—O component (b). The usual yield was around 70%.

Then, the atomic ratio of hydroxyl carbon to all the carbon atoms was calculated using the following:

$$R_{COH} = [F_{1S}]/(3[C_{1S}] - 2[F_{1S}])r \qquad (1)$$

where $[F_{1S}]$ and $[C_{1S}]$ are, respectively, the F_{1S} peak area and the C_{1S} peak area with respect to the sensitivity factors and r is the yield of the reaction.

Figure 2(b) shows the C_{1S} peak of PAA after esterification with TFE. The yield of the reaction is given by the ratio between the areas of the CF_3 (d) and COO components (c). The yields were around 80%.

The atomic ratio of carboxylic acid carbon can be calculated by:

$$R_{COOH} = [F_{1S}]/(3[C_{1S}] - 2[F_{1S}])r \qquad (2)$$

where $[F_{1S}]$ and $[C_{1S}]$ are, respectively, the F_{1S} peak area and the C_{1S} peak area with respect to the sensitivity factors and r is the yield of the reaction.

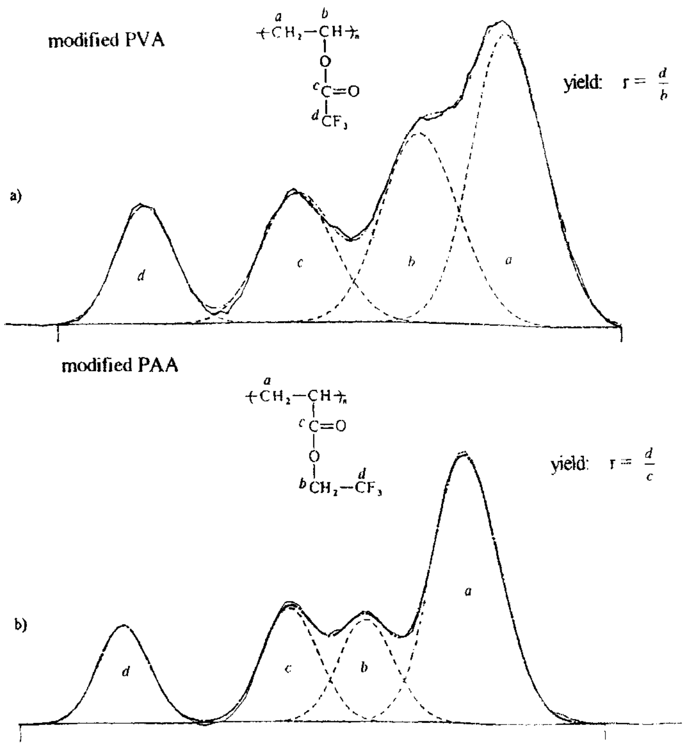


FIGURE 2 (a) C_{1S} peak from XPS spectrum of PVA after esterification with TFAA. (b) C_{1S} peak from XPS spectrum of PAA after esterification with TFE.

The yield of the reaction between primary amine and PFB is estimated, from the XPS spectrum of DADD, by Eq. (3).

$$r = [F_{1S}]/5[N_{1S}] \tag{3}$$

The yields were 100%.

The atomic ratio of primary amine nitrogen to all nitrogen atoms was given by:

$$R_{NH_2} = [F_{1S}]/5[N_{1S}]r \tag{4}$$

where $[F_{1S}]$ and $[N_{1S}]$ are, respectively, the F_{1S} peak area and the N_{1S} peak area with respect to the sensitivity factors and r is the yield of the reaction.

The yield of the reaction between carbonyl and hydrazine is estimated, from the XPS spectrum of PVMK, by:

$$r = ([N_{1S}]/[O_{1S}])/(([N_{1S}]/[O_{1S}]) + 2) \qquad (5)$$

The yields were around 50%.

The atomic ratio of carbonyl carbon to all carbon atoms was given by Eq. (6).

$$R_{C=O} = [N_{1S}]/2[C_{1S}]r \qquad (6)$$

where $[C_{1S}]$ and $[N_{1S}]$ are, respectively, the C_{1S} peak area and the N_{1S} peak area with respect to the sensitivity factors and r is the yield of the reaction.

These reactions, and their specificity, have been frequently studied. In our study, in the case of He/N_2 APG plasma, the presence of nitrogen atoms at the surface after treatment make the calculation of $R_{C=O}$ impossible. Furthermore, TFAA can react, besides reacting with OH functions, with NH and NH_2 functions.

3. RESULTS AND DISCUSSION

3.1. Adhesive Strength

We followed the atomic composition of the treated surfaces determined by XPS with respect to the relative sensitivity factors of the elements. In He/O_2 plasma, O/C ratios increase with treatment times, reaching a value greater than 0.45 for a 10-minutes-treatment time. For the other plasmas the O/C value does not depend on the treatment time. The presence of oxygen on He or He/N_2-treated PP can be explained by post-plasma reactions which occur when the samples are being brought back to the atmosphere. The N/C ratio, in the case of He/N_2 plasma, increases continuously with treatment time.

The best adhesive strength (corresponding to the highest critical load necessary to scratch the surface) is observed for the He/N_2 plasma (Fig. 3). It increases with treatment times up to 3 minutes and then decreases slightly. The adhesive strength after He or He/O_2 plasma

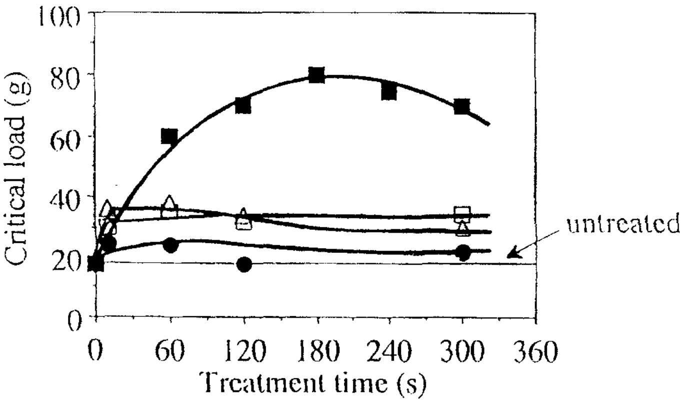


FIGURE 3 Critical load as a function of the treatment time: Δ) He/O_2 APG plasma 100 W; •) He APG plasma 50 W; □) He/O_2 APG plasma 50 W; N/C: ■) He/N_2 APG plasma 100 W.

treatments stays low. Since the O/C ratios with He/N_2 plasma are lower than with the He/O_2 plasma, the oxygen-containing functionalities cannot be considered, as done generally, to be the only species to have an influence on the adhesion.

To explain the strong adhesive strength after He/N_2 plasma we followed the amount of primary amines versus treatment times. These results are shown in Figure 4. The quantities of primary amines were followed by XPS after labeling them with PFB. During the first three minutes of treatment, the N/C and the NH_2/C ratios increase with time in the same way as the adhesive strength. The NH_2 functionalities are the main nitrogen-containing functionalities on the surface. For the longer treatment times, the NH_2/N_{Total} ratio is decreasing, but the total amount of NH_2 is still growing, because of the increasing of N/C ratio.

Copper depositions were performed on a He/N_2 plasma-treated PP, a He/O_2 plasma-treated PP and an untreated PP. We then tried to separate the polymer from the copper. XPS analyses were done on both sides of the failure site the metal side and the polymer side.

In the case of the untreated PP, the Wide-scan Spectrum (WS) of the metal side is the same as the WS of copper and the WS of the polymer side is the same as the WS of PP.

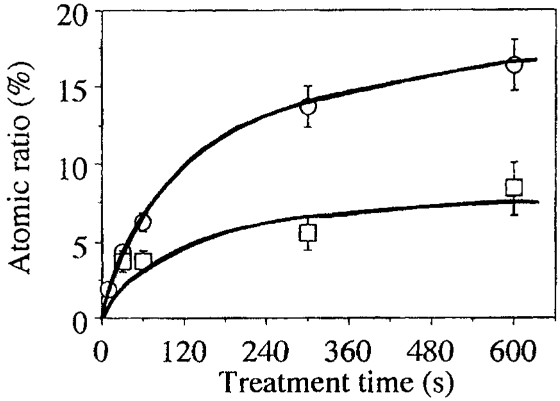


FIGURE 4 N/C ratio and NH_2/C ratios as a function of treatment time (He/N_2 APG plasma); ○) N/C; □) NH_2/C.

Otherwise, for both He/O_2 and He/N_2 plasma-treated PP, the WS on the metal side and on the polymer are identical to the WS of PP (Fig. 5 shows the XPS spectra for He/N_2 plasma treated PP). These results show that the breaking occurs into the polymer and not at the Cu-PP interface. Due to post-plasma reactions (allowing migration of oxygen towards the bulk) and because of its high cross section for XPS detection, as O_{1S} peak is observed.

We observed the changing of the morphology of the surfaces after He, He/O_2 and He/N_2 plasmas with SEM (Photos 1a to d). The surface of the untreated polymer is smooth but, after treatment, morphological changes occur with all of the plasma gases. They are very important in the case of He/N_2 plasma (Photo 1d). The polymer is deeply modified.

The combination of the two following factors can explain the high adhesive strength of the He/N_2-treated PP:

1) The creation of primary amine functions. The formation of chelates between the primary amines and copper can improve the adhesion dramatically (Scheme 2).
2) The great change in the morphological shape. Adhesion by mechanical effects ("anchor effect") can take part in the adhesive processes. The only way to remove the copper trapped between PP is to break the polymer.

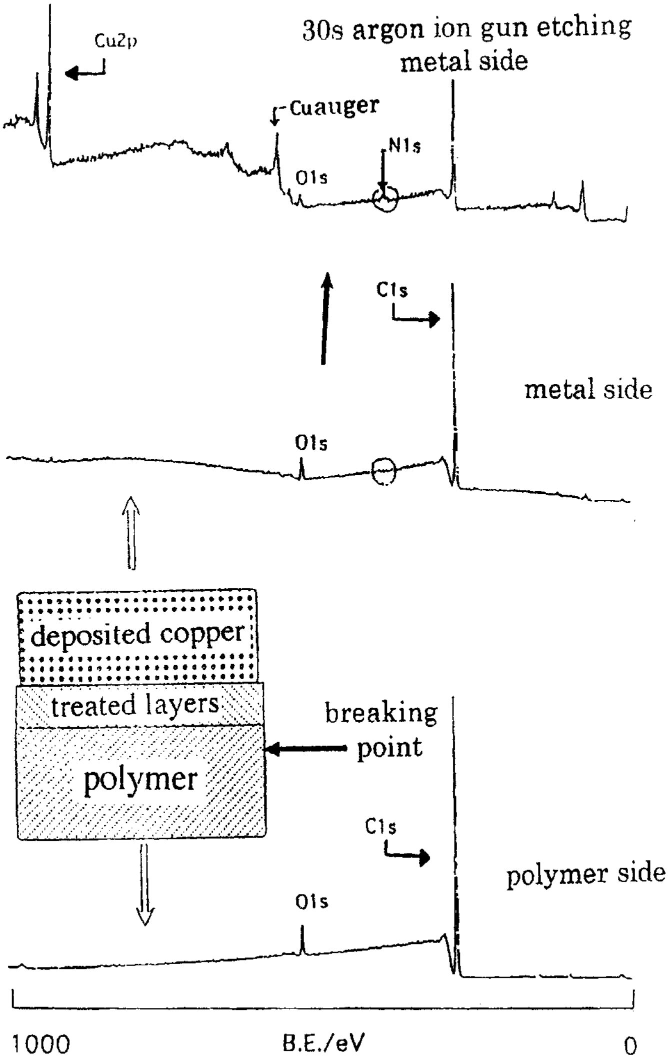
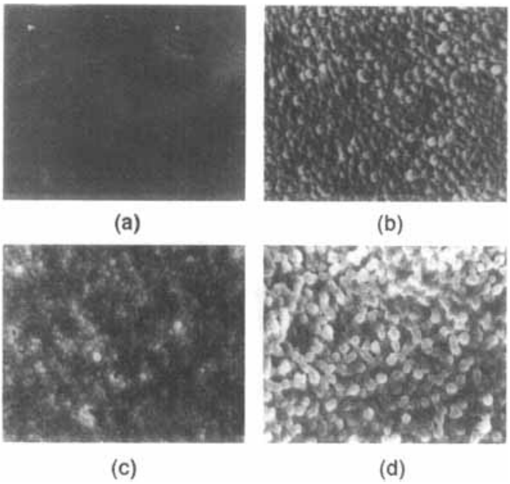
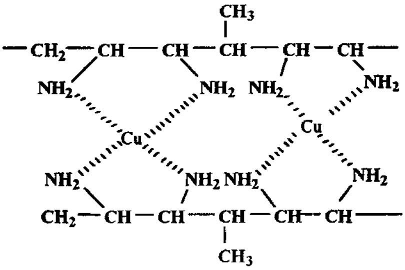


FIGURE 5 XPS wide scans of the surface of He/N_2 APG plasma-treated PP after copper deposition and severing.

The loss of adhesive strength for durations of treatment higher than 3 minutes can be explained by the degradation of the surface and the creation of weak boundary layers.



PHOTOS 1 a) non-treated PP; b) He APG plasma-treated PP; c) He/O_2 APG plasma-treated PP; d) He/N_2 APG plasma-treated PP.



SCHEME 2 Chelates formed between the primary amines and copper.

3.2. Ageing

After plasma treatment, the samples stayed in the atmosphere for ageing until the phase gas chemical reaction and the XPS analysis. To avoid presenting a large number of figures only the most significative ones are shown.

3.2.1. He/N_2 Plasma

After He/N_2 APG plasma treatments the global O/C ratio decreases in the first hours of ageing and then increases slowly but continuously (up to 0.4) (Fig. 6). The evolution of the ageing of O/C is globally the same for all the treatment times.

Concerning the different functionalities at the polymer surface, the $COOH/C_{Total}$ ratio decreases during the first few days then increases slowly but the importance of carboxylic functionalities is minor: less than 5% of total carbons.

The alcohol functionalities are the main O-functionalities at the polymer surface after treatment. Their number decreases dramatically (50%) during the first week, then stay stable followed by an increase after 4 weeks of ageing (as the TFAA reacted with N-functions, constant with ageing, this study can only be qualitative). For both of these oxygen functionalities their evolution with ageing is independent of the treatment time.

The evolution of the O/C ratio and of the oxygenated functionalities can be explained by the removing of superoxidized functionalities from the surface to the gas phase and/or by the migration of oxidized functionalities towards the bulk (partly OH functionalities). After a few days the oxidation of the surface occurs because of its contact with the O_2 and the humidity in the air (mainly OH functionalities).

There is an important diminution of the number of primary amines during the first day. Then there is an increase followed by a long and slow decrease from the third day. After some weeks of ageing the

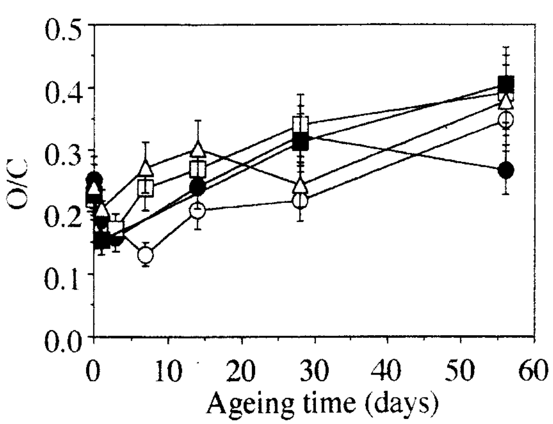


FIGURE 6 O/C as a function of the ageing time in He/N_2 APG plasma: ○) 10 s; •) 30 s; □) 1 mn; ■) 5 mn; △) 10 mn.

primary amine functionality is no longer the main N-containing functionality (Fig. 7). The sharp decrease, in the first hours of ageing, can be related to the loss of primary amines which were on the weak boundary layers. Besides this, NH_2 functionalities are created from the nitrogen atoms which were incorporated in the treated polymer, explaining the increase after one day. Then these functionalities are modified with the oxidation of the surface.

3.2.2. He/O_2 Plasma

With He/O_2 APG plasma treatments the oxidation is very important. Before ageing, the formation of the more oxidized carbons (COOH and C=O functions) are favored with long treatment times, the alcohol functions (less oxidized carbons) are more numerous with small treatment times (Tab. I). We observed such a formation of carboxylic functionalities only in the case of He/O_2 plasma. The global oxygen proportion decreases during the first days, and then stays roughly unchanged (Fig. 8). The O/C values are higher in the cases of the two longest treatment times.

There are only a few changes in the composition of the surface with ageing. After a weak decrease in the first days, there is no ageing effect on the carboxylic functionalities even after 8 weeks. In the same way,

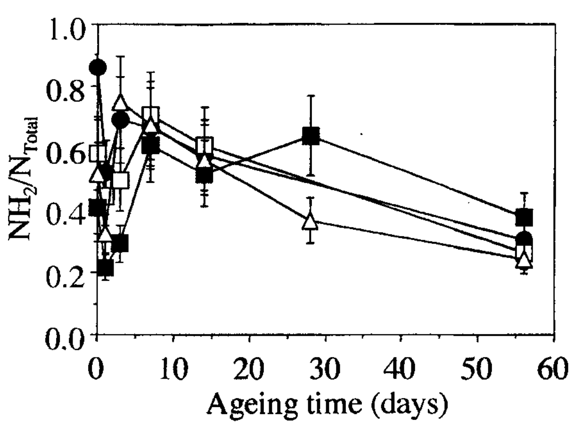


FIGURE 7 NH_2/N_{Total} as a function of the ageing time in He/N_2 APG plasma: ○) 10 s; •) 30 s; □) 1 mn; ■) 5 mn; Δ) 10 mn.

TABLE I Percentage of the carboxylic, alcohol and carbonyl functionalities at He/O_2 APG plasma-treated polypropylene surface (no ageing)

treatment time	*COOH*	*COH*	*C=O*
10 s	7.1	11.2	13.2
30 s	7.4	11.0	12.5
1 mn	8.8	9.1	14.1
5 mn	10.1	9.2	17.6
10 mn	11.3	8.2	19.8

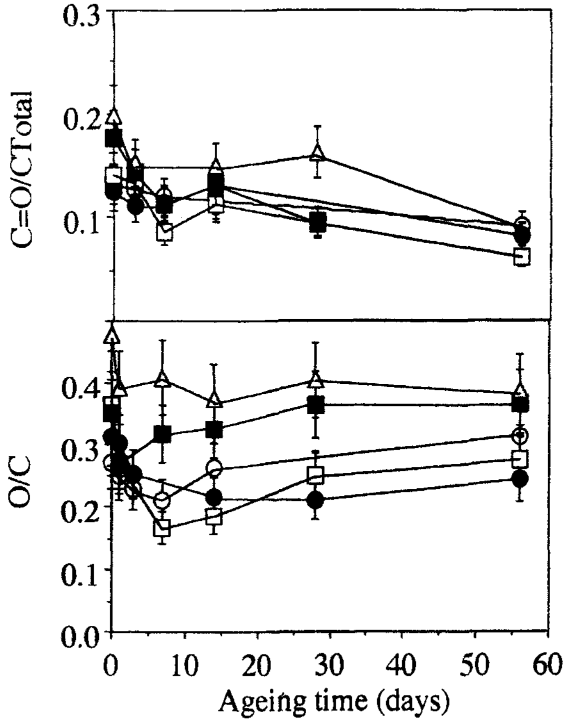


FIGURE 8 Below: O/C as a function of the ageing time in He/O_2 APG plasma: Above: C=O/C_{Total} as a function of the ageing time in He/O_2 APG plasma: ○ 10 s; •) 30 s; □) 1 mn; ■) 5 mn; Δ) 10 mn.

there is no change in the amount of the alcohol functionalities with the ageing whatever the treatment time and the ageing duration. But we observe a decreasing of the percentage of carbonyl functions in the first week, then further decreases but to a lesser extent, finally reaching values around 0.10 (Fig. 8).

The ageing of the surface can be divided in two steps. First a notable loss of oxygen which can be credited to either the migration of oxygenated functionalities to the bulk or the loss of the superoxidized and degraded first layers of the surface, then the level of oxygen incorporation stays the same. From the point of view of the functionalities only the carbonyl ones seem to take part in the ageing process with the exception of the decreasing of COOH during the first days.

3.2.3. He Plasma

The functionality compositions of the He APG plasma-treated PP are summarized in Table II. Only the formation of carbonyl functionalities seems to be dependent of the treatment time. Alcohol functionalities are the main ones at the polymer surface. The evolution of the oxidation is shown in Figure 9. The O/C ratio first increases and then stays constant around 0.25–0.30. The number of carboxylic acid functionalities at the surface is very low after treatment and stays low during all the ageing ($<2\%$). Except for the shorter treatment times (10 seconds and 30 seconds) where the levels of incorporation stay low (0.10) there is a big increase of the carbonyl functionality ratio during the first day and then the ratio seems stable (Fig. 9). The number of alcohol functionalities decreases slowly during all the ageing (the value of COH/C_{Total} stays around 0.10).

In the case of He APG plasma we did not observe a decrease of O/C during the first days of ageing maybe because there are no superoxidized layers at the surface just after treatment (the level of carboxylic functionalities is very low $<2\%$). Furthermore, as helium is chemically inert, free radicals which are created during plasma

TABLE II Percentage of the carboxylic, alcohol and carbonyl functionalities at He APG plasma-treated polypropylene surface (no ageing)

treatment time	*COOH*	*COH*	*C=O*
10 s	1.3	12.1	3.0
30 s	1.7	11.6	4.8
1 mn	1.4	12.4	8.2
5 mn	1.8	12.0	7.3
10 mn	1.7	13.7	11.2

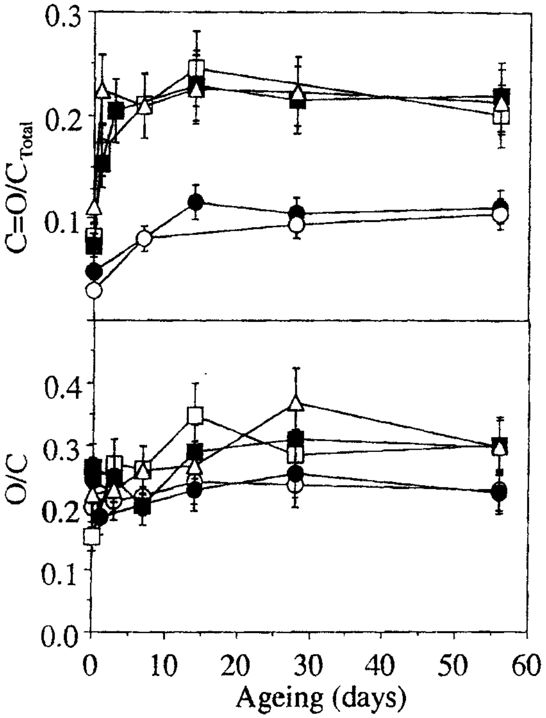


FIGURE 9 Below: O/C as a function of the ageing time in He APG plasma; Above: C=O/C_{Total} as a function of the ageing time in He APG plasma: ○ 10 s; •) 30 s; □)1 mn; ■) 5 mn; Δ) 10 mn.

treatment can only produce crosslinking or react after plasma which can explain the increasing of O/C and of the carbonyl functionalities in the first days of ageing. For the 10-second and 30-second treatments the amounts of free radicals are smaller, and then the increase of carbonyl functionalities and of the oxidation, during the beginning of the ageing process, is smaller.

3.3. Contact Angles

To complete this study we followed the evolution of the water contact angles with treatment times and ageing time with different gas mixtures and compared the results with those obtained with O_2 SED discharge.

The values of the contact angles decrease with treatment time. The decrease is smaller after 1 min, especially for He APG plasma. After 10 minutes of treatment, the contact angles reach the values of 66, 46 and 58 degrees for, respectively, He APG, He/O_2 APG and SED discharges. In the case of the He/N_2 plasma, for 5- and 10-minute treatment times the contact angles evoluate very quickly and reach a value smaller than 10 degrees a few seconds after the placement of the water drop; the measurements were then impossible to make. This behavior can be related to the important changes of the morphological shape.

With the ageing of the sample, the contact angles, after He/O_2 APG plasma treatment, increase during the first day (10%), and then keep on increasing but more slowly. After 8 days the value of the contact angles is still lower than for untreated polymer (Fig. 10).

For the other gas the increase of the contact angle during ageing is slow: after 8 days of ageing the values of the contact angle are still less than 80 degrees (untreated value is 100 degrees).

The important changes observed in the first day of ageing by gas-phase chemical modifications are only observed with contact angles in the case of He/O_2 APG plasma.

In the case of a O_2 SED discharge, the contact angles increase faster with ageing than after APG treatments but the values after one week

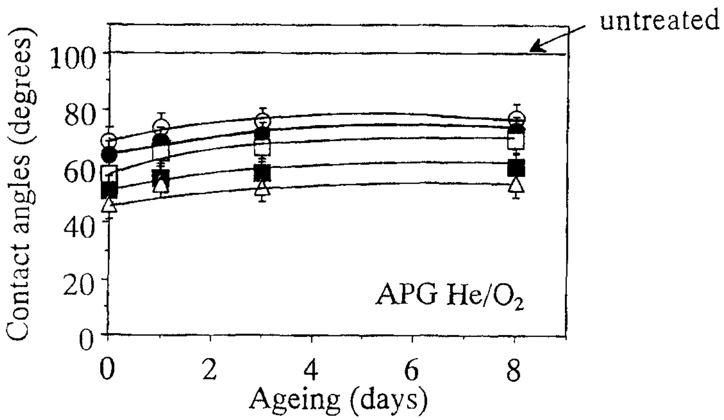


FIGURE 10 Contact angles as a function of the ageing time in He/O_2 APG plasma: ○) 10 s; •) 30 s; □) 1 mn; ■) 5 mn; △) 10 mn.

stay below the contact angles of untreated PP. In comparison with APG plasmas, the surface properties created by SED discharge disappear rather quickly with ageing.

4. CONCLUSION

1) The relatively large adhesive strength of the He/N_2 APG plasma-treated PP can be explained by the formation of chelates between copper and primary amines and by the "anchor effect" due to the big change in the morphological shape of PP produced by the treatment.
2) Gas-phase chemical reactions allowed us to follow the evolution of the main functionalities produced on the surface of the plasma-treated PP. We saw that the biggest part of the chemical evolution with ageing took place in the very first days. These changes resulted partly from the reorganization of the polymer and partly from chemical reactions in contact with air. For the most part, the created functionalities seemed stable. The treatment times have an influence on the level of incorporation of the different functionalities but not on the ageing trend.
3) The contact angle ageing study showed that the effects of APG plasmas on contact angles is more lasting than after SED discharge.

To complete these results, a study of the evolution of the adhesive strength with ageing, for both SED and APG discharges, is in progress.

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