# SURFACE TREATMENT OF PET FILMS IN A PLASMA REACTOR BY CORONA DISCHARGE

J. Amouroux*, M.F. Revoil**, M. Goldman**

* Laboratoire de Génie Chimique, ENSCP, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.

** Laboratoire de Physique des Décharges, ESE-CNRS, Plateau du Moulon, 91190 Gif/Yvette, France.

## ABSTRACT

The modification of the surface properties of PET treated by corona discharge depends on the functioning of the interelectrode reactor. Our experiments proved the catalytic role of the nature of the electrode, the role of the atmosphere of the treatment, and the influence of the parameters : current intensity, time, distance between the electrodes & duration of treatment.

## INTRODUCTION

The modification of the surface properties of the PET (formula : $H\left[OCH_2 - CH_2O - \overset{O}{\overset{\|}{C}} - C_6H_4 - \overset{O}{\overset{\|}{C}}\right]_n OCH_2 - CH_2OH$) under corona discharge is due to the interaction between excited species and the polymer surface ; the interaction leads to a change in the chemical species at the surface (oxygen, nitrogen), in the physical properties (surface energy & cristallinity). The study of the reactor permits to identify and control the action of the principal parameters on the energy transfer, between electrode, gas & surface.

## 1. PRESENTATION OF THE REACTOR OF TREATMENT

The wire-cylinder reactor of the laboratory (fig. 1) is supplied by a high voltage source (10-15 kV). The nature of the wire, the wire-cylinder distance & the rotation speed of the cylinder are the 3 main technical parameters of the set. The electrical working parameter will be the current intensity, the voltage being connected to it.

The polymer material is a PET film, 50 μm thick, of "Photographic type". The treatment atmosphere may be monitored in pressure, composition & hygrometry.

## 2. CHOICE OF ANALYTICAL TECHNICS

The chemical analysis of the surface is performed by means of ESCA that provides qualitative & quantitative titrations (in fixed O & N).
The analysis of the surface properties has been carried out by means of contact angle measurements (surface tension), electrostatic-lead (surface potential & deposited charges) & by electronic & optical microscopy.

## 3. OPTIMISATION OF THE WORKING CONDITIONS OF THE REACTOR

A systematic study of the parameters : duration of treatment, intensity, wire-cylinder distance & nature of the electrode made us understand the efficiency the reactor. The other parameters have been fixed to the following values : thickness of the film : 50 µm, atmosphere : air, 20 % relative humidity.

a - Influence of the duration (d = 2 mm, I = 200 µA, electrode Mo)

The results (fig. 2,3) show that the fixation of oxygen & nitrogen increases with duration until it reaches a saturation plateau corresponding, after 10 mn, to an equilibrium between oxydation and decarboxylation of the polymer.

Nitrogen is fixed under the form of amines ($NH_2$) (constant amount versus duration) & NO (increasing with duration). Finally, the surface energy follows the same law as the amount of oxygen at the surface of the material.

b - Influence of the current intensity

The wire is fixed at 2 mm of the cylinder. The increase of the amount of fixation of oxygen versus intensity is very large and leads to a saturation level. The fixation of nitrogen reaches a saturation level as well between 140 & 150 µA (fig. 4,5). At 250 µA, we observe a breakdown (formation of an arc) then the phenomenon is complety different.

c - Influence of the wire-cylinder distance (t = 7 mn, electrode I = 200 µA)

The amount of O & N at the surface of the material shows in each case an optimum. The residence time of the reactive species in the reactor plays an important role in the treatment efficiency.

## 4. ROLE OF THE NATURE OF THE ELECTRODES : CATALYTIC ACTION

Mo, Ti, and V are wellknown for their catalytic properties for oxydation. They have been used for the wire.

Table 1

| | O/C | N/C | $\gamma$ dyne/cm |
|---|---|---|---|
| Mo | 0.32 | $22 \times 10^{-3}$ | 49.4 |
| Ti | 0.34 | $23 \times 10^{-3}$ | 49.4 |
| V | 0.225 | $18 \times 10^{-3}$ | 48.6 |

Table 1 shows the important influence of changing the wire on the fixation of oxygen and nitrogen. But it brings few modifications to the surface energy, because it is a global phenomenon.

## 5. STUDY OF THE PHYSICAL PROPERTIES OF THE SURFACE

The study of the polymer by X ray diffraction shows an important decrease of the cristallinity throughout the discharge.

The measurement of the surface potential shows that the material keeps an important residual charge after treatment, the circulation of which is very slow. The study by optical microscopy under polarized light shows a significative variation in the color of the polymer, indicating a variation in the thickness, or the composition of the material.

## 6. INTERPRETATION - CONCLUSION

Figure 9 shows the relative importance of the different pics and that there are 3 different kinds of fixed nitrogen. Figure 10 shows that NH is a reaction intermediate in the fixation of nitrogen, for it reaches very rapidly a steady state when the duration of the treatment increases. After this state, the fixation of nitrogen is realised in the form of oxydes NO, either directly, or by oxydation of the amines already fixed at the surface followed by the fixation of the same amount of amines. And finally the fixation of oxygen follows a mechanism of competition between oxydation and decarboxylation. This is proved by the saturation level reached by the amount O/C versus time or current intensity. The mechanism currently proposed to explain this competition is the following one :

$$RH \xrightarrow{O_2^{*},\ O_2,\ O_2^{+},\ O} R. + OH$$ ;Energy transfer $$R. \xrightarrow{O_2^{*}} ROO.$$ Surface reaction

$$R'OO. + R''H \rightarrow \begin{matrix} R' \\ R'' \end{matrix} > C = O \quad \text{either} \quad \begin{matrix} R \\ R \end{matrix} > C = O \quad \text{or} \quad R - C \begin{matrix} O \\ OH \end{matrix}$$

Reaction between radicals

$$RCOOH \xrightarrow{h\nu\ ,\ e^{-},\ O_2^{*}} R. + CO_2$$ oxygen elimination

The following variables : intensity, time, & distance are macroscopic parameters of the adjustment of an industrial set, but they don't determine the efficiency of the reactor. For the nature of the fixed species does not depend on the operating conditions. But, if we take into account both the reaction step and the saturation level, their concentration depends on the adjustement of these parameters. The surface treatment is not directly related to these variables, but to the physical phenomenon of the energy transfer and to the chemical phenomenon of gaz-electrode & gaz-surface interactions.

## BIBLIOGRAPHY


(1) D.T. CLARK, The investigation of polymer surfaces by means of ESCA,in "Polymer surfaces". Clark & Feast Editors, J. Wiley & Sons 1978.

(2) R.S. SIGMOND, Corona discharges in electrical breakdown of gases, Eds. J.M. Meek & J.D. Craggs (Wiley 1978).

(3) J. AMOUROUX, M. GOLDMAN, M.F. REVOIL, Modification of the wettability of a poly (ethylene terephtalate) film treated by corona discharge in air, Journal of Polymer Science - Part A1 (à paraître).

(4) Brevet France 79.17050 (EDF, Amouroux, Goldman, Revoil), Procédé, dispositif, traitement de feuille de matériau dans l'air.

(5) J. AMOUROUX, M.F. REVOIL, M. GOLDMAN, Application des décharges électriques aux traitements de surface des matériaux polymériques - en particulier le PET - in 10e congrès international (UIE 10) Paris Mai 1981, Comité français d'électrothermie.

(6) M. LECUILLER, R. JULIEN, J. PUCHEAULT, Etude par voie chimique des ions produits par décharge couronne, Journal de Chimie Physique, n° 1 p. 105-111 (1975).

(7) A. & M. GOLDMAN, Chap. IV in Electrical discharges, Merle N. Hirsh Editor, J. Wiley & sons.

(8) M.F. REVOIL, Traitement de surface du poly (éthylène téréphtalate) par décharge couronne, thèse de docteur-ingénieur, Paris 1981.

(9) A. BELL; techniques and application of plasma chemistry, Wiley, Interscience 1974.

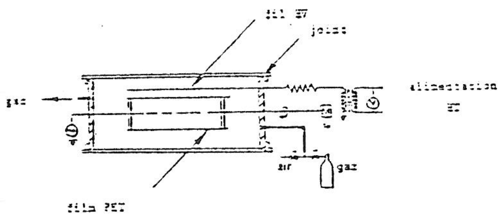


Figure 1 : Laboratory set.

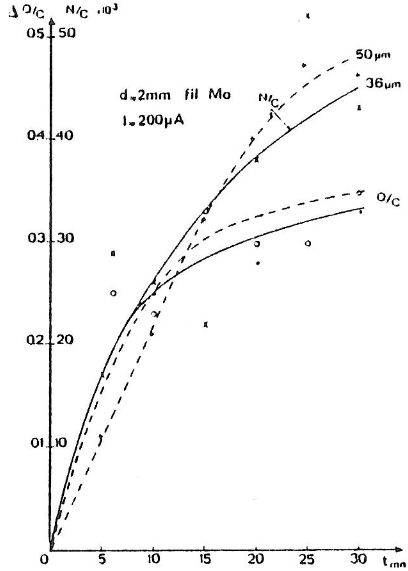



Figure 2 : Variation of the amount of fixed oxygen & nitrogen at the surface of PET versus time.

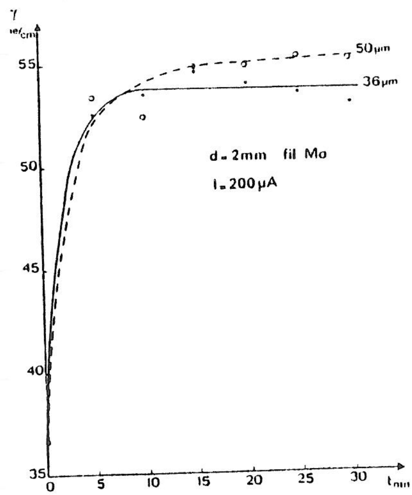



Figure 3 : Variation of the surface tension versustime.

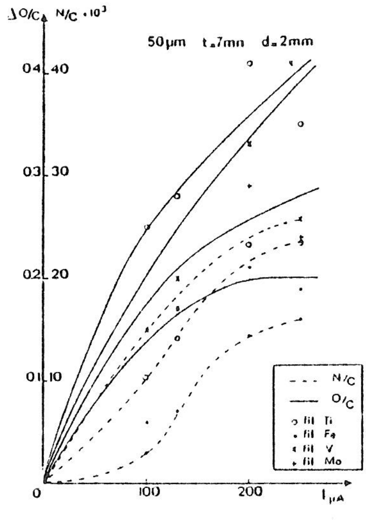



Figure 4 : Variation of O/C & N/C versus current intensity

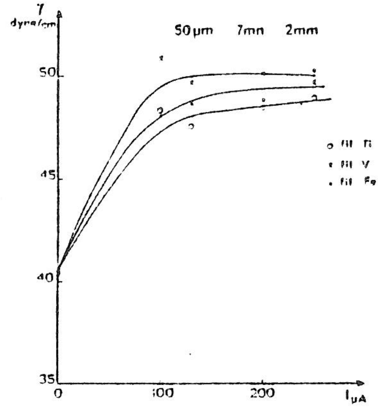



Figure 5 : Variation of the surface tension versus current intensity

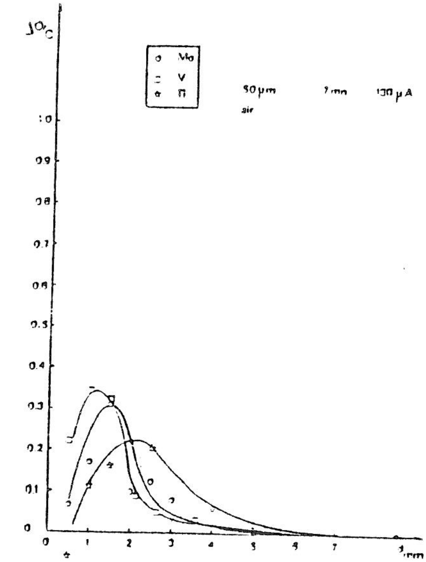



Figure 6 : Variation of the amount of fixed oxygen versus interelectrode distance for different electrodes

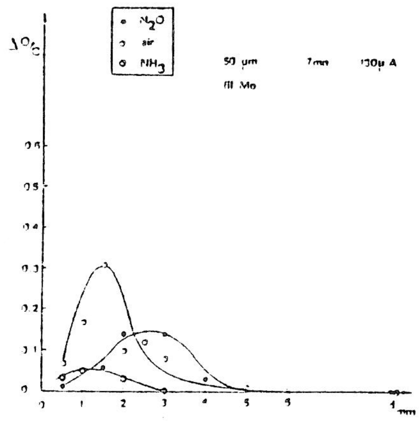



Figure 7 : Variation of the amount of fixed oxygen versus distance for different atmospheres

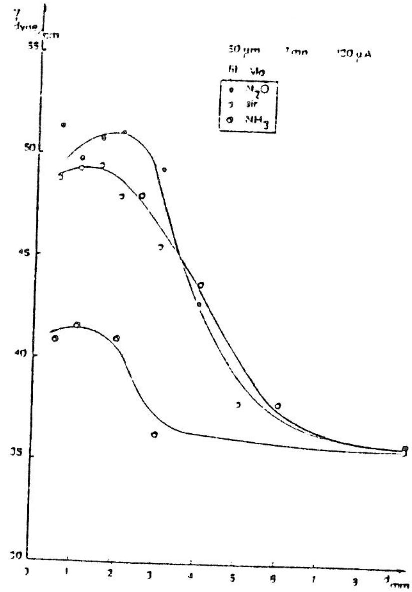
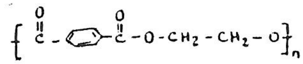



Figure 8 : Variation of the surface tension versus d

PET :


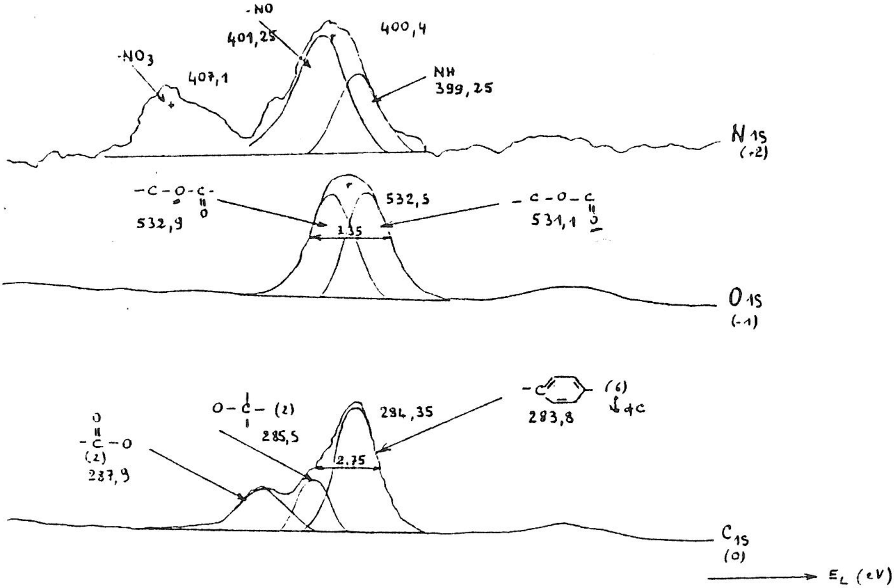



Figure 9 : ESCA spectrum of poly (ethylene terephtalate) treated with a V wire in $N_2O$

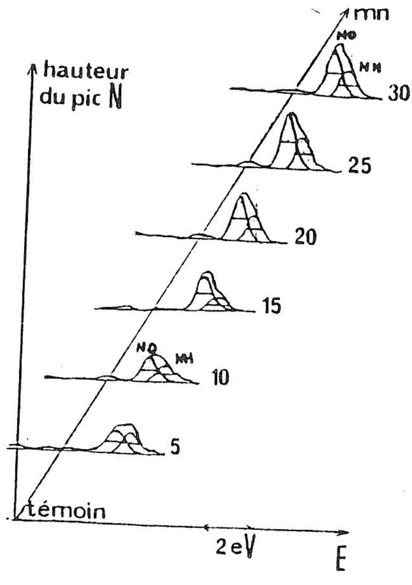



Figure 10 : Evolution of N pic in an ESCA spectrum versus time