DESIGN OF LARGE VOLUME COLD REMOTE PLASMA REACTOR. RELATION BETWEEN THE FUNCTIONALIZATION AND THE ADHESION QUALITY OF POLYPROPYLENE SURFACES TREATED BY A REMOTE NITROGEN PLASMA.

B. Mutel[*], C. Hoyez[†*], O. Dessaux[*], P. Goudmand[*], L. Gengembre[°] and J. Grimblot[°]

[*]Laboratoire de Physicochimie de l'Energétique et des Plasmas EA MRES 1761
[°]Laboratoire de Catalyse Hétérogène et Homogène URA CNRS D04020
Université des Sciences et Technologies de LILLE
59655 Villeneuve d'Ascq cedex France
[†]Reydel S.A. 37, rue J.B. Marquant B.P. 6 - 59147 Gondecourt, France

Abstract :
A large volume cold remote nitrogen plasma reactor is developed for automotive industry. A comparison between the delamination strength and the rate of grafted functions evidenced that a maximum incorporation rate is not necessary to get a maximum adhesion quality. The ageing of treated samples in open air during time ranging from 1 to 360 hours is investigated.

1 - Introduction

The industrial use of polypropylene (PP) is always increasing, especially in automotive industry. Taking into account its low adhesion quality, PP requires surface modifications before most applications (foaming, thermo-covering, glueing, painting...). Processes usually used in the industry are flame, corona discharge, UV irradiation, primer and chemical treatments. Each of these processes corresponds to specific applications of PP, and each shows restristing limits. They all can be replaced by a plasma process which is a more recent technic. Plasma gases usually used are nitrogen, oxygen and air. The short life time of $O(^3P)$ leads to a non homogeneity of oxygen or air plasma. In order to compensate this non homogeneity, complex and expensive installations are required [1]. The long life time of nitrogen atoms [2] allows to obtain nitrogen plasma with possibility of large volume expansion [3, 4]. In previous papers it has been shown that a cold remote nitrogen plasma (denoted by CRNP) treatment can be used to increase the adhesion quality of PP surface, and a CRNP reactor which volume is 160 liters is described [4, 5]. In the first part of this paper, a CRNP reactor developed for the automotive industry is described. The mass production system which planed the treatment of 18 dashboards at a time required a treatment chamber which volume was at least equal to 2 m^3, and the treatment of PP pieces had to be performant and homogeneous in the whole reactor. The relation between the adhesion quality of treated PP surface and the amount of grafted nitrogen and oxygen functions are then studied.

2 - Design of a CRNP treatment apparatus for industrial production

A diagram of the prototype is shown Fig. 1. The nitrogen flow is created by a continuous pumping system provided by Leybold and including a mechanical rotary pump SOGEVAC SV 280 (280 m^3/h) and a mechanical booster pump WAV 501 (500 m^3/h). The nitrogen flow (27 Nl/mn) is measured with a mass flow controller MKS 259B, and the pressure (5 hPa) is controlled by a baratron gauge. The nitrogen flow is excited from a microwave discharge by means of a microwave generator (2450 MHz) SAIREM which delivers an incident power ranging from 0.5 to 3 kW. The electromagnetic field energy is transfered to the gas by means of a microwave resonant coaxial cavity [6]. In order to minimize the investment, there is only one plasma source. The discharge is produced in a quartz tube (60 mm inner diameter) coupled to the aluminium cylindrical treatment chamber which volume can reach 4m^3.

3 - Experimental

Taking into account the industrial application of this work, studies are carried on in industrial conditions : Polypropylene samples (MOPLEN SP 98 F 94 from HIMON) are handly degreazed with SONOCLOR 11 (HCFC from Eulopartmer) and dryed during thirty minutes at ambient temperature before the CRP treatment. Then, they are exposed to the plasma without prior conditioning at low base pressures. After the treatment, they are exposed to the ambient air during 1 hour before any analysis. The adhesion quality is measured from delamination strength which is a test usually used in automotive industry. The amounts of grafted functions are measured by XPS.

3.1. Delamination strength measurements

After the thermo-covering of a PVC coating on PP samples, the delamination strength was measured by a peeling test at a 180° angle, performed on a Hounsfield machine (type H10 KM) equipped with a 1000 N cell. The used scale was ranging from 0 to 50 N. The traction speed was equal to 100 mm/mn. PP samples were rectangular (12 mm x 62 mm). The peeling test was always carried on 24 hours after the termo-covering, and only samples thermo-covered in the same time were compared. The thermo-covering was always performed 1 hour after the plasma treatment. The delamination strength, denoted by F, was given in N/cm. The error on F values, calculated from the average results on 4 samples was lower than 10 %.

3.2. XPS analysis

XPS analysis were performed using a Leybold LHS 10 spectrometer. The Al K α X-Ray source operated at 13 kV and 20 mA current emission. The vacuum during the analysis was about 5.10^{-8} hPa. The nitrogen content relative to the carbon, denoted by x_N, was determined from the intensities of the photopeaks (I) according to

$$x_N = (I_{N1s}/I_{C1s}) . (\sigma_{C1s}/\sigma_{N1s}). (Ek_{C1s}/Ek_{N1s})^{1.77} \times 100.(x_C \text{ being equal to}$$

100 %). σ_{C1s} and σ_{N1s} are the photoionization cross-sections of C1s and N1s levels. Ek is the kinetic energy. x_O was determined in the same manner. XPS studies were performed 1 hour after the plasma treatment.

4 - Performances of the CRNP treatment apparatus

The spatial homogeneity of the reactives species concentration is testified from the yellow luminescence of the CRNP. The spatial homogeneity of the adhesion is controlled from the delamination strength.

4.1. Spatial homogeneity of the reactive species concentration

The yellow luminescence of the CRNP, corresponding to the emission of the first positive system of N_2 is not homogeneous in the whole treatment chamber, implying a non homogeneity of the atomic nitrogen concentration. In order to get a more homogeneous concentration of reactive species of the CRNP a bended device is settled in the entrance of the reactor as it is shown Fig. 1. This device allows to diffuse the plasma homogeneously in the whole reactor. The homogeneity is checked by a titration of the atomic nitrogen concentration by the colorimetric reaction with NO [5] : an equal concentration of atomic nitrogen and NO corresponds to the disparition of the yellow afterglow. This titration is carried on in a pyrex tube ($\emptyset = 15$ mm, l = 400 nm) located successively in position 1, 2 and 3 (Fig. 1). The transmitted microwave power is equal to 500 W. NO is introduced in the entrance of the tube. Table 1 shows the NO flow required to get the extinction in the tube with and without the deflector : the presence of the deflector leads to an equal value of the atomic nitrogen concentration in the three positions. Studies with the reactor empty are always carried on with the deflector.

Table 1 : Influence of the deflector on atomic nitrogen concentration.

Position	Q_{NO} (cm³/mn)	
	without deflector	with deflector
1	0.93	0.68
2	0.68	0.68
3	0.68	0.68

4.2. Spatial homogeneity of the adhesion quality

The determination of the shorter treatment time (denoted by t) required to get the best adhesion quality is first studied. Then, for this t value, the spatial homogeneity of the adhesion quality is investigated. Table 2 shows the evolution of F versus t for samples settled in position "a", and for Pt = 500 W. Taking into account the accuracy on F value (10 %), it seems that F is maximum as soon as t = 6 s. This treatment time is then denoted by tmin. For an industrial application it is interesting to notice that F value is quite stable for t > 6 s : if a treatment time longer than tmin is required, it does not lead to a decrease of the adhesion quality of treated samples. Table 3, which shows the evolution of F values for three positions and for t = 10 s gives evidence for the homogeneity of the adhesion quality.

Table 2 : Evolution of F versus t for PP samples in position "a"

t (s)	2	4	6	10	20	45	60	90
F N/cm	3.1	6.4	15.4	15.7	14.7	15.7	14.9	15.2

Table 3 : Evolution of F versus the position of PP sample in the reactor for t = 10 s.

Position	a	b	c
F N/cm	13.3	14.1	14.4

These two studies were carried on with reactangular (12 m x 62 mm) PP samples treated in the reactor "empty". In industrial conditions (18 dashboards settled in the middle of the reactor) F values between the two extremities of the reactor is homogeneous as soon as t = 30 s, and in these conditions a deflector is no more required to get a good homogeneity of the atomic nitrogen concentration.

5 - Comparison between the adhesion quality and the grafted functions

The evolution of F, x_O and x_N versus t for two transmitted microwave powers are respectively shown Fig. 2 and Fig. 3. Fig. 2a and b correspond to results obtained with samples thermo-covered in the same time, so these plots can be compared. Fig. 2c corresponds to results obtained with samples thermo-covered in the same time but during another experiment : absolute values of this plot cannot be compared with absolute values of Fig. 2a and b.

Whatever Pt value, F, x_O and x_N increase simultaneously when t increases from 0 to 20 s. For increasing t values higher than 20 s, F remains stable while x_O and x_N increase from 20 to 45 s and reach a stable value from 45 s. x_O is always higher than x_N. The increase of x_O and x_N values obtained for t > 20 s while F values remain constant evidences that a maximum nitrogen or oxygen incorporation rate is not necessary to get a maximum adhesion quality.

6 - Influence of an addition of oxygen in the plasma gas

This study is carried on for Pt = 200 W and t = 45 s (for this time x_O, x_N and F are maxima). The evolutions of F, x_O and x_N with addition of oxygen (10 %) to the plasma gas are shown Table 4. When oxygen (10 %) is added to the plasma gas, the oxygen fixation is promoted, while the nitrogen one decreases and these variations have no effect on F values which average is equal to 13.5 N/cm within 5 %. This surprising result leads us to study the modification of C1s, O1s and N1s spectra when oxygen is added to the plasma gas. The O1s peak shifts from 0.3 to 0.4 eV towards increasing binding energy when oxygen is added impliying a modification of the repartition of oxygen functions grafted on the PP surface. In comparison with the C1s peak of untreated PP located at 285 eV, the C1s spectra of N2 treated samples shows, in addition to the peak at 285 eV a broad band ranging from 286.8 to 288.6 eV. This band gives evidence for the incorporation of nitrogen and/or oxygen functions which can be attributed to C≡N, C - O and O - C = O [7-11]. C1s spectra of sample treated with N_2/O_2 mixture can be superimposed with C1s spectra of samples treated by N_2 and only the shoulder is more pronounced. The N1s spectra of samples treated by N_2 located at 400 eV is approximately symmetrical with a F.W.H.M equal to 3 eV. The N1s spectra of samples treated by N_2/O_2 is not symmetrical with a F.W.H.M equal to 3.4 eV, and is shifted about 2 eV towards high binding energy in comparison with the previous one. N1s spectra are fitted by a procedure based on variations of parameters such as peak position, width, height and Gaussian shape . They can be curve-resolved into two separate components located at 400 and 402 eV and showing a F.W.H.M equal to 2.5 eV. The component located at 400 eV can be attribute to C≡N and NR_3 groups. The component located at 402 eV can be due to R-N = 0 groups [12-13].

Oxygen and nitrogen contents relative to the carbon, x_O and x_N can be expressed in atomic percentage α_O and α_N with $\alpha_C + \alpha_O + \alpha_N = 100$ %. The curve-resolved spectra of N1s allow to express $\alpha_N = \alpha_{N1} + \alpha_{N2}$ where α_{N1} and α_{N2} refer to the components located respectively at 400 and 402 eV. Results are shown Table 4. It is interesting to notice that though α_N decreases when oxygen is added, α_{N1} decreases whereas α_{N2} remains constant : among the two nitrogenated functions grafted on PP surface, only one, appearing at 402 eV, may be responsible for the adhesion quality. So, it appears that a good adhesion quality is not provided by high nitrogen incorporation rate, but is strongly affected by the nature of nitrogenated functions grafted.

Table 4 : Evolution of F and of oxygen and nitrogen rates grafted on PP surface for addition of oxygen in the plasma gas.

O_2 content %	F N/cm	x_O	x_N	α_O	α_N	α_{N_1}	α_{N_2}
0	14.1	13.7	3.0	11.7	2.8	2.2	0.6
10	12.8	18.4	0.9	15.4	0.8	0.2	0.6

7 - Study of the ageing of PP surface treated by CRNP

The ageing of treated PP surface in the open air is investigated from the evolution of F, x_O and x_N versus ageing time denoted by δ. Results are shown Table 5. Taking into account the accuracy on the experimental values, it can be concluded that F, x_O and x_N values remains stable for $1 \leq \delta$ (hours) ≤ 360. The chemical functions grafted by the CRNP on the PP surface are stable in ambient condition for long period of time.

Table 5 : Evolution of F, x_O and x_N versus ageing time (δ) for PP treated by CRNP.

δ (hour)	F	x_O	x_N
1	14.6	13.7	3.0
72	14.1	12.2	2.6
360	13.8	11.7	2.5

8 - Conclusion

An industrial cold remote nitrogen plasma reactor of some cubic meters using only one plasma gas source and an operating pressure about 5 hPa is developed. The treatment quality of polypropylene samples is homogeneous in the whole reactor. In industrial conditions, the maximum adhesion quality is obtained as soon as thirty seconds of treatment are reached. The comparison between delamination strength and incorporation rate of nitrogen and oxygen functions evidenced that the adhesion quality is not provided by high fixation rates but is rather imputed to the nature of these functions. The ageing of treated samples in open air during time ranging from 1 to 30 hours has no influence on the adhesion quality nor on the rate of grafted functions.

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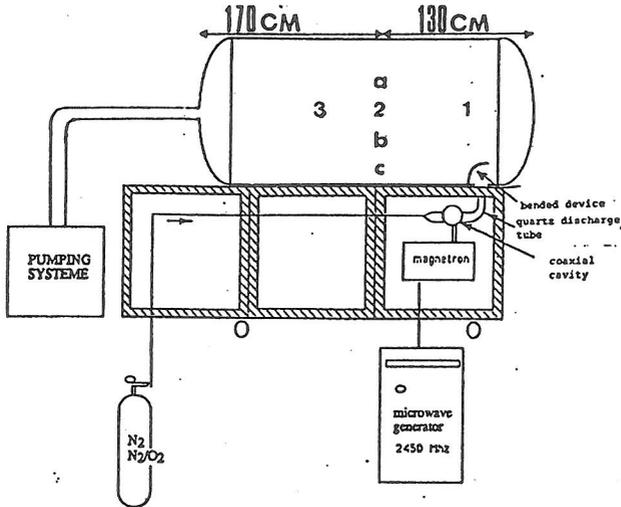[13] Jones C., Surf. Interface Anal. 20, 357, (1993)
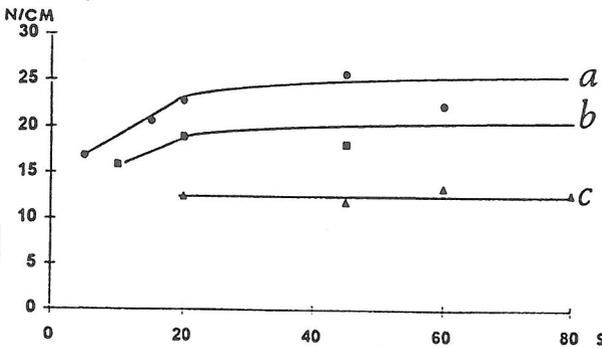
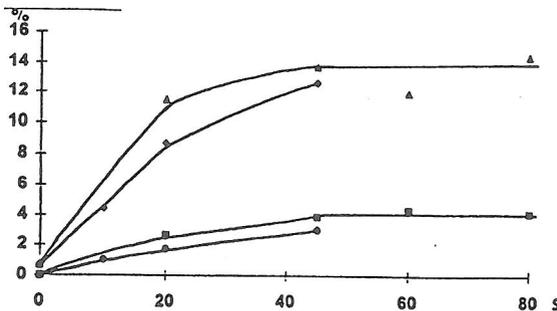Fig. 1 : CRNP treatment apparatus

Fig. 2 : Evolution of F versus t

Fig. 3 : Evolution of x_O and x_N versus t

- x_N, Pt = 100 W
- x_N, Pt = 200 W
- x_O, Pt = 100 W
- x_O, Pt = 200 W