POLYMERIZATION AND GRAFTING OF 1,1 DIFLUOROETHYLENE BY A NON EQUILIBRIUM PLASMA AT AN ATMOSPHERIC PRESSURE ONTO THE SUBSTRATES PET, PP AND NON IMPREGNATED PAPER.

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ABSTRACT

The polymerization of 1,1 difluoroethylene has been realized by a non equilibrium plasma at an atmospheric pressure on polymeric substrates such as PET and non impregnated paper. The polymer obtained was cross-linked and hydrophobic. The graft copolymerization of the same monomer onto the PP film was carried out when activating the polymeric substrate in the presence of argon. The structure of the polymeric film obtained in this second part depends directly on the oxygen residual in the plasma reactor.

INTRODUCTION

The formation of thin polymer films in a low pressure high frequency glow discharge has been discussed in several recent reviews (2-4). This paper presents an original method of plasma polymerization realized at an atmospheric pressure (1). A non equilibrium plasma was generated in a wire-cylinder type reactor. The details of the experimental set-up is discussed elsewhere (2). The role of the two main parameters of the plasma reactor (current intensity, interelectrode gap), on the polymerization of the gas 1,1 difluoroethylene, were studied.

It was shown that a large amount of very reactive carbon radicals was detected on the surface of PP when activated in a rare gas such as Ar. If oxygen is tempted to be totally excluded in the plasma reactor, each free radical therefore can initiate a copolymerization with the fluorinated polymers obtained in the presence of the monomer.

The physico-chemical properties of the thin polymeric film obtained were investigated by the following methods of analysis: IR (ATR) spectroscopy, ESR, ESCA, contact angle measurements and SEM.

RESULTS AND DISCUSSION

I. PLASMA POLYMERIZATION:

The first part of our experiences concerns the study of the polymerization mechanisms of the monomer C2H2F2 in the aim to decrease the wettability and to improve the dielectric properties (1-3) of polymeric substrates such as PET and non impregnated paper. The improvements in dielectric properties can be noted by the difference appearing between the current voltage curves recorded under negative corona exposure in air with samples pre-exposed to a C2H2F2 discharge and a non pre-exposed one (fig.1).

The superposition of C1s portion of a typical ESCA spectrum of the pretreated substrate on that of the non pretreated one is illustrated in
figures 2 § 3 for PET and nonimpregnated paper respectively. By examining these figures we can identify mainly three new chemical bonds at 288 ± 0.3, 289.6 ± 0.2 and 291.6 eV that can be assigned to C-H, CF and CF2 groups respectively.

The ratios F/C and O/C obtained by ESCA analysis on PET films pretreated at different interelectrode gaps (fig. 3) illustrate a maximum of the F/C ratio at d = 3mm. On the other hand, the surface free energy shows a sharp decrease (Ra ≈ 10 dyne/cm against Ra = 100 dyne/cm for the non-pretreated one) for the same interelectrode gap (d = 3mm).

The growth rate of the polymer formed shows a large increase as a function of the current intensity (fig. 5) with a maximum probably due to the competitive processes between ablation and polymer film formation.

The polymeric film prepared by the plasma polymerization of C2H2F2 was brown, insoluble in usual solvents, with unsaturated structure (IR analysis (3)). The polymer formed on the substrates PET and paper was found by ESR to contain trapped free radicals and consisted of a single symmetrical line approximatively 4-6G wide (3). These radicals are very stable and can be assigned to polyene type radicals trapped in the structure of the polymer. Further investigations by SEM show the morphological modification of the surface of the pretreated PET (photo 1) and the paper (photo 2) obtained by the plasma polymerization of C2H2F2 at an atmospheric pressure.

II. PLASMA GRAFTING (COPOLYMERIZATION):

The second part of our experiences was undertaken to investigate the important role of radicals which interfere in the grafting mechanisms of monomers onto polypropylene films.

In order to create free radical sites on the polypropylene surface, the substrate was exposed to an argon plasma. During the activation period in the presence of the argon discharge, the role of the residual oxygen in the reactor, on the formation and nature of the free radicals created, has been studied. The shape of the ESR spectrum which is attributed to the peroxide radicals is presented in figure 5. This figure illustrates also the variation of the spin concentration in function of the residual oxygen percentage measured just at the moment before the electrical discharge applied. The capacitif current intensity measured in this serie of experiences was in the order of 10-30 mA.

In this way, figure 5 indicates that the concentration of the peroxide radicals increases and becomes 10 times higher than the initial value when decreasing the residual oxygen percentage lower than 10% in the reactor. It is noteworthy to mention that the argon discharge creates reactive carbon radicals which are transformed to peroxide radicals in the presence of oxygen. When the reactor is oxygen free, the carbon radicals can initiate a graft copolymerization in the presence of the plasma polymerized monomers. In this case with the monomer C2H2F2 the ESR spectrum consisted of a single almost symmetrical line approximatively 20G wide which could be attributed to the R-CF2-OO radicals (fig.7.II). The polypropylene films have been pretreated in atmosphere of argon and C2H2F2, (15% C2H2F2, 85% Ar) and the number of fluorine atoms fixed is measured in function of the residual oxygen in the reactor. Thus, by means of ESCA analysis, the F/C ratio is determined showing an enormous increase when oxygen is excluded (fig.7-I). In order to eliminate the short length oligomers and the non fixed homopolymers the pretreated PP films are washed with water (fig. 7-II) and acetone respectively (fig.7-III) The O/C ratio of the PP pretreated in the same conditions was
maximum when the residual oxygen reached 45% and then decreased promptly when the oxygen was further excluded (<10% O2) (fig. 8).

The surface aspect of the pretreated PP films in a mixture of C2H2F2 and Ar examined by SEM shows that when oxygen excluded the polymer grafted consisted of a thin uniform layer (no apparent change in the surface morphology) (photo 3).

CONCLUSION
In the first part of our study it has been demonstrated that the plasma polymerization of the monomer 1,1 difluoroethylene on polymeric substrates at an atmospheric pressure depended on the electrical parameters such as interelectrode distance and current intensity (in the order of a few hundreds of μA). The polymer obtained in this case was crosslinked which gave rise to chemical inertness, interesting dielectric properties and rendered the substrates very hydrophobic. The amount of fluorine measured by ESCA was about F/C ≈ 0.3.

Next, graft copolymerization of the same monomer as above (C2H2F2) has been realized onto the PP films in the presence of the rare gas Ar. It has been proved that the formation and the nature of free radicals obtained on the activated polypropylene depended directly on the residual oxygen in the reactor. In the case of Ar + C2H2F2 plasma, the carbon free radicals formed on the PP surface, due to the excited argon molecules react with those obtained in a C2H2F2 plasma. In this way, it has been shown that if oxygen is excluded the carbon free radical have a sufficient lifetime for initiating the graft copolymerization in the presence of C2H2F2 plasma.

REFERENCES
1. J. AMOUREUX, M. GOLDMAN, F. AREFI, F. ROUZBEHI; French patent n°83125 (1983); USA patent n°634.741 (1984); Japan patent n°158533/84; Europe patent n°84 401 592.5.

Figure 1:
Dielectric behaviour of a negative point-to-plane 5mm air gap modified by the interposition, on the plane, of a paper sheet pretreated by a C2H2F2 discharge.
Fig. 2 - Superposition of the C₁s spectra of a pretreated PET film on a nonpretreated one.

Fig. 3 - ESCA analysis of the carbon peaks for a pretreated sheet of paper and a nonpretreated one.

Fig. 4 - F/C and O/C ratio obtained by ESCA analysis in function of the interelectrode gap.

Fig. 5 - Polymer deposition growth in function of the capacitive current per length of the high tension wire.
Fig. 6 - Variation of free radicals concentration in function of residual air in the reactors operating condition:

- $t = 2.8$ sec
- $\text{Ar flowrate} = 280 \text{ cm}^3/\text{min}$
- $p = 1 \text{ atm}$
- PP thickness $= 18 \mu$

Fig. 7 - $F/C$ ratio obtained by ESCA analysis in function of residual air in the reactor.

- PP pretreated
  - I - after treatment
  - II - washed 1h in $H_2O$
  - III - washed 1h in $H_2O$ and 1h in acetone

Fig. 8 - $O/C$ ratio obtained by ESCA analysis in function of residual air in the reactor.
Photo 1 - Polymeric aspect observed by SEM on paper:
   a) nonpretreated
   b) pretreated (t=30mn, d=3mm, I=200 μA, V=14.3).

Photo 2 - Polymeric aspect observed by SEM on PET film:
   a) nonpretreated
   b) pretreated (t=15mn, d=3mm, I=130 μA).

Photo 3 - Pretreated pp films in a mixture of C₆H₆F₂ + Ar observed by SEM:
   a) nonpretreated
   b) pretreated in presence of 100% air
   c) pretreated in presence of 4.5% air.