

# Plasma polymerization and surface treatment of polymers

F. AREFI, V. ANDRE, P. MONTAZER-RAHMATI, J. AMOUROUX

Plasma Chemical Reactor Laboratory - P. & M. Curie University  
ENSCP - 11 rue Pierre et Marie Curie 75231 PARIS CEDEX 05

**Abstract** : In this article surface treatment of polymers by both surface modification and plasma polymerization has been discussed. A low pressure 70 kHz discharge with corona configuration of electrodes (H.V. hollow blade - grounded cylinder) has been employed in order to simulate the industrial surface treatment of polymers. In the case of non polymerizing plasmas such as N<sub>2</sub> the modifications created on the surface of a polymer such as polypropylene (PP) have shown to be the cleaning effect, crosslinking polymer fragmentation, oxidation and nitrogen incorporation for very short treatment times (100 ms - 7 s). These effects lead to an increase of the wettability, the surface conductivity and the adhesive properties of the PP films. Indeed the latter has been detected by a study of the PP-Al interface by AES and the measure of the peel-strength. In the case of the polymerizing system such as CF<sub>4</sub> + H<sub>2</sub> mixtures, the role of the gas composition and the polymer substrate structure have been pointed out on the growth mechanisms and the structure of the deposited polymer. By varying the hydrogen percentage in this mixture a wide range of surface energies (from non wettable to wettable surfaces) has been obtained.

## INTRODUCTION

Plasma polymerization is a unique technique to fabricate thin polymer films (100 Å - 1 μm) from a variety of organic and organometallic starting materials. Plasma polymerized films are pinhole-free and highly crosslinked and therefore are insoluble, thermally stable, chemically inert and mechanically tough. Furthermore such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces. Due to these excellent properties they have been undertaken very actively in the last few years for a variety of applications such as permselective membranes (ref. 1 & 2), protective coatings (ref. 3) biomedical materials (ref. 4, 5, 10) electronic (ref. 6 - 8), optical devices (ref. 7 - 9) and adhesion promoters (ref. 11 & 12). After a brief review of the plasma polymerization mechanisms, the surface modification of polymers will be discussed both by non polymer forming plasmas and by deposition of plasma polymerized thin films on their surface. By appropriate plasma surface treatments, new properties such as optical reflection, adhesion, friction coefficient, surface energy (wettability and water repellancy), permeability, surface conductivity and biocompatibility of conventional polymers can be obtained (ref. 11 - 15, ref. 1 - 3). An attempt has been made to understand by means of simultaneous OES and surface diagnostic techniques the role of the polymeric structure on the plasma polymer interactions and the growth mechanisms in the case of a polymerizing system. By using different but complementary surface diagnostic techniques, the modifications created by very short treatment times on polymers have been explained to our knowledge for the first time. Finally one of the most important surface properties obtained i.e. adhesion improvement has been investigated by a simultaneous AES spectroscopic approach of the interface and peel test measurements in a Al - pretreated PP film.

## 1. PLASMA POLYMERIZATION

### Mechanisms; important parameters; deposition techniques

A cursory survey of the literature concerning plasma polymerization reveals that due to the complexity of plasma the bulk of the research has been concentrated on establishing the dependence of the macroscopic and spectroscopic properties of the product on the major process variables e.g. power, monomer type, gas flow rate, pressure etc.

However different models have been proposed for the plasma polymerization based on ions, electrons and neutrals which are extensively reviewed recently (ref. 10, 16). Amongst these different models Poll et al (ref. 50) discussed the role of ion bombardment and pointed to a competition between etching and deposition processes in plasma polymerization and in the same domain Yasuda proposed the CAP (Competition - Ablation - Polymerization) mechanism for glow discharge polymerization (ref. 1). Bell et al (ref. 18) by combining a certain number of kinetic modeling studies reported a model for the plasma polymerization of hydrocarbons. A more general description was given by Yasuda et al (ref. 1) who identified two regimes of plasma polymerization in which the mechanisms differ dramatically i.e. the monomer - deficient and the energy deficient plasma. Indeed the composite plasma process parameter W/FM (where W is the discharge power and FM is the mass flow rate of monomer) has shown to be very efficient to control the chemical structure of the polymer. In fact at a relatively low input energy level (energy deficient region) a plasma polymer is obtained characterized by a chemical structure and properties similar to those of conventional polymers. By increasing W/FM (monomer deficient region) due to the relatively high energy of the impinging particles, the deposited material is characterized by a short range order combined with a high crosslinking density. Due to this irregular structure of the deposited films Yasuda

has proposed the rapid step growth polymerization  $[M_m^* + M_p^* \rightarrow M_{m+n}] \times N$  where the (\*) in the equations represents any activated species and  $\times N$  represents the number of repetitions of similar reactions. In order to account for the geometrical factor of the reactor system in the deposition of plasma polymers, Yeh *et al.* (ref. 17) by investigating the fundamental mass balance in the plasma polymerization reactor defined the average local deposition rate  $DR_m = Y_p (X'/S_e) FM$ . In the latter,  $Y_p$  is the yield of the plasma polymer deposition (i.e. the fraction of feed-in monomer that takes part in the formation of plasma polymer),  $X'$  is the fraction of feed-in monomer that flows in the glow discharge zone,  $S_e$  is the effective area of any surface in physical contact with the plasma (i.e. the reactor design factor) and  $FM$  is the total mass flow rate of monomer. Furthermore the polymer deposition yield ( $Y_p = DR_m S_e / (X' FM)$ ) obtained from the polymer deposition data in different reactors varies little with the W/FM parameter when a certain W/FM value is reached. Therefore polymer deposition in different reactor systems seems to be best compared based on the polymer deposition yield  $Y_p$ .

D'Agostino *et al.* studied extensively the competitive etching and polymerization processes in the deposition of fluorocarbons (ref. 38). In particular it has been shown that the polymerization rate increases by increasing the  $[CF_x] / [F]$  ratio and the degree of charged particle bombardment (either fast electrons or ions) since they have proposed an Activated Growth Model (AGM) for the polymer growth. Indeed, it has generally been observed that the deposition rate on the substrate increases as the bias voltage becomes more negative up to a certain point. E. Kay (ref. 19) reported that in the case of tetrafluoroethylene a solid deposit is obtained up to a negative bias of 600 V. He also mentioned that a mild (10 eV) positive bombardment generally increases the plasma polymerization rate via production of surface free radicals.

Amongst the different power supplies, and flow configuration that can be used for plasma polymerization, the use of the dc cascade arc as a plasma source in low pressure processes is a fairly recent development. The earliest studies were performed by Kroesen and Beulens (ref. 20). The high exit velocity of the carrier gas from the cascade arc into the deposition chamber prevents monomer diffusion into the cascade arc column, so that plasma formation and monomer excitation occur separately. The deposition rates reported are somewhat greater than those for the rf glow discharges even though the input power per unit mass is one or two orders of magnitude less for the cascade arc. In deposition of carbon based hard materials on silicon substrates, rates of 100 nm/s have been reached with this system by injecting methane through the nozzle of the cascaded arc.

## 2. SURFACE MODIFICATION OF POLYMERS BY PLASMA TREATMENT

Surface treatment of polymers by non-polymer forming plasmas (Ar, He, N<sub>2</sub>, O<sub>2</sub>, etc) are extensively used to modify surface properties of polymers. The treatment gives rise to the formation of free radicals at the surface and further down in the polymer which react with the excited species in the plasmas. Therefore treatments in O<sub>2</sub>, N<sub>2</sub> or inert gases give rise to in particular oxygen functionalities (hydroxyls, carbonyls, and in some cases carboxylic groups). This has been interpreted as being partly due to the reaction of long-lived free radicals which can react with oxygen upon exposure to air after plasma treatments. Recently Occhiello *et al.* (ref. 21), by using the <sup>18</sup>O<sub>2</sub> have contributed to the long debate issue pertaining whether the introduction of oxygen to the surface is only due to their O<sub>2</sub> plasma or partially to the interaction of the sample when taken to air with atmospheric oxygen. Indeed by comparing the SSIMS spectra of samples treated in <sup>18</sup>O<sub>2</sub> plasmas and aged in <sup>16</sup>O<sub>2</sub> with those treated in <sup>16</sup>O<sub>2</sub> plasma and aged in <sup>18</sup>O<sub>2</sub> they have concluded that the introduction of oxygen due to reaction of active sites with atmospheric oxygen seems negligible. The surface treatment also leads to a crosslinked skin produced by recombination of polymer radicals. Chain scission occurs simultaneously with cross-linking and oxidation. Small molecule degradation products are constantly removed by evaporation and sputtering, while polymeric scission products remain intermeshed with undegraded polymers and cross-linked networks.

The modified depth has been determined to be typically 50 - 500 Å (ref. 22). For example in the case of the fluorination of polyethylene by tetrafluoroethylene the diffusion depth of fluorine has been estimated by RBS to be about 400 Å for a treatment time of 2.7 min (ref. 23). Furthermore the depth of polymer fluorination has been measured by various techniques for a variety of polymers (ref. 49). Yasuda *et al.* studied the effect of four nonpolymerizing gases i.e. He, Air, N<sub>2</sub> and CF<sub>4</sub> on different fibers and fabrics (ref. 24). They had found that in some cases the etching of the fiber was accompanied by the implantation of specific atoms into its surface. The model studies performed with nylon have shown that plasma treatment, similar to plasma polymerization, may be carried out in the power - deficient range as well as in the gas deficient range. Therefore these two regions should stimulate different changes in the polymer surface introduced by plasma treatment. Furthermore they have concluded the applicability of the CAP model to plasma treatment due to the fact that ablation supplies the gas phase with various chemical species, some of which may be able to form deposits especially in mixtures with such non reactive gases as hydrogen or ammonia.

At present the most serious problem which prevents wide application of plasma treatments is the durability of the treatment i.e. upon aging the wettability is reversed. The most probable reason for this has been considered to be the "overturn" or migration of the created polar groups into the polymer (ref. 25). The lack of durability has been attributed largely to the surface rearrangement of macromolecular segments which is truly physical but not due to the loss of chemical moieties introduced by the surface treatment. Furthermore the aging seems to depend on the chemical nature of the substrate. Indeed Briggs (ref. 26) has reported that the increased wettability of air corona treated PET (polyethylene terephthalate) films disappears upon aging. In fact the low molecular weight species on the PET surface readily migrate into the polymer and rapidly disappear from XPS sampling depth, whereas in the case of the air corona treated PE (polyethylene) films the good wettability remains and the aging phenomena have not been observed (ref. 28). The difference observed in these two studies has been interpreted in terms of the substrate polarity that is: PET films with polar functionalities (COO) allow an overturn of the plasma created moieties and their stabilization by internal hydrogen

bondings. The non polar character of the PE films opposes to an overturn of the polar groups and so they remain at the surface. We have observed the same phenomena in the case of the wettability of PE and PET films when treated by a corona discharge in a mixture of Ar + CF<sub>4</sub> + O<sub>2</sub> at atmospheric pressure (ref. 27). Recently Occhiello et al (ref. 21) have shown in the case of an oxygen-plasma-treated polypropylene, that when contacted with air the surface layer (less than 5 nm thick) rearranged by macromolecular motions within itself since interdiffusion with the bulk polymer seemed forbidden in the case of polypropylene. They have reported that these motions are thermally activated and it was possible to obtain an apparent activation energy (58.1 kJ/mol) close to those reported for other vinyl polymers. Yasuda et al (ref. 29) have proposed that by applying an extremely thin layer of a relatively tight plasma polymer of methane prior to the subsequent plasma treatment of the surface, the durability of the effect of surface treatments can be greatly enhanced.

The other possibility to modify surface properties of polymers is by deposition of a thin plasma polymer on the surface of the polymeric material. As an example we can mention the adhesion improvement measured by scotch tape and lap shear of PE by plasma polymerization films obtained from methane, acetylene and ethylene (ref. 30). Tetramethyl silane (TMS) as well as (TMS + O<sub>2</sub>) have been used to increase the adhesion and the surface hardness of PE, PTFE and PC (ref. 31). A 1000 Å thick metallic film (C/Sn < 0.3) has been deposited on PP from tetramethyltin as a water vapor barrier. The permeability of such film was as low as that of a thin copper layer. Due to their considerable wettability, thin films prepared from TMT + O<sub>2</sub> were used as intermediate adhesive layers on PP (ref. 32). We have also prepared organometallic films from TMT + O<sub>2</sub> on the surface of PP films with  $R \approx 10^9$  in order to prevent the electrostatic charging of the polypropylene films (ref. 33).

Furthermore it has been possible to obtain a wide range of wettabilities (17 mJ/m<sup>2</sup> - 42 mJ/m<sup>2</sup>) on PE films by plasma polymerization of CF<sub>4</sub> + x % H<sub>2</sub> mixtures (cf section 6). These films have shown to be very crosslinked, with wettabilities which are durable upon ageing (ref. 45). However with respect to the surface treatment with non-polymerizing gases, in the case of plasma polymers, it is important not only to control the deposition rate and the film quality (especially, surface properties), but also to enhance the adhesion strength of plasma polymerized films on polymer films.

The grafting, polymerization and etching phenomena involved in the plasma polymerization and surface treatment of polymers will be presented through different surface treatment examples carried out at low pressure. Optical emission spectroscopy (OES, AOES) has been employed in a systematic manner as a diagnostic tool in order to characterize the excited species and their energetic aspects in the plasma phase. The results obtained with this technique are then correlated to the surface diagnostic investigations i.e. AES, XPS, RBS, SSIMS, image processing contact angle (ref. 35) and potential decay measurements to identify the heterogeneous reactions taking place at the polymer surface.

### 3. EXPERIMENTAL SET-UP

For the surface treatment of polymer films a bell jar type reactor with a corona discharge configuration of electrodes (hollow electrode-grounded cylinder) was used (Fig.1). This special configuration provides the ability to simulate the continuous industrial surface treatments of polymer films (ref.34). In the reactor with the help of the pumping unit composed of a primary pump and a turbo-molecular one, a background pressure of about  $4 \times 10^{-4}$  Pa was established. The working pressure varied between 80 to 1000 Pa, the discharge was established by means of an industrial 800 watts excitation source with a frequency of 70 kHz. Furthermore a strict control of the atmosphere was possible with the help of a Balzers quadrupole mass spectrometer. Commercially available UHP gases were used without further purification (purity of CF<sub>4</sub>: 99,7 %; O<sub>2</sub>:  $\geq 99,35$  %; H<sub>2</sub>: 99,995 %; N<sub>2</sub>: 99,9 % and Ar: > 99,995 %) which were introduced through MKS mass flow controllers and the pressure was monitored with an MKS capacitive gauge. Thus the final composition of the atmosphere and in particularly the residual composition of N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> & H<sub>2</sub>O was controlled in this way in situ.

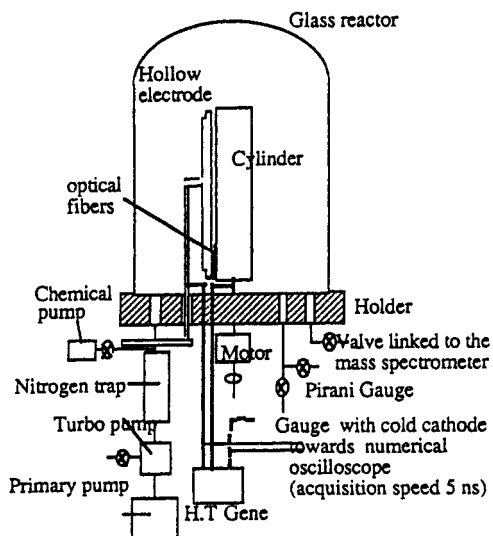


Fig. 1 : Apparatus used for the surface treatment

The electrical characteristics of the discharge were measured by a 9400 Lecroy digital oscilloscope with a sampling frequency of 100 MHz. The axial radiation from the discharge was sampled by an optical fiber, placed in the interelectrode gap, of 200  $\mu\text{m}$  core diameter and focused by means of a quartz lens on the plane slit of a Jobin Yvon HRS monochromator equipped with a 1200 grooves/mm grating to analyze the spectral range varying from 300 nm - 850 nm. We have also used a 1 m Jobin Yvon HR monochromator equipped with a 3600 grooves/mm holographic grating for the 225 nm - 450 nm spectral domain and finally a Jobin Yvon HR 320 monochromator equipped with a 1200 grooves/mm grating for the analysis of the 190 - 500 nm spectral region. An Hamamatsu photomultiplier is used for each monochromator.

#### 4. CHARACTERIZATION OF THE LOW PRESSURE PLASMA WITH CORONA CONFIGURATION OF ELECTRODES BY EMISSION SPECTROSCOPY

OES has been used to study firstly the excited species and the energetic characteristics of our low frequency discharge and secondly to compare our discharge with a capacitively coupled RF (13.56 MHz) glow discharge which is most commonly used for the surface treatment of different substrates. This has been carried out in a  $\text{CF}_4$  discharge and in  $\text{CF}_4 + \text{H}_2$  mixtures.

##### 4.1 $\text{CF}_4$ discharge

The emission spectra of  $\text{CF}_4$  at 150 Pa observed in the 190 - 850 nm range are given elsewhere (ref. 36). Two different continua were detected with maxima centered around 300 nm and 580 nm which were assigned to  $\text{CF}_2^+(4b_2 - 6a_1)$  and excited  $\text{CF}_3$  radical respectively. The latter undergoes a transition to a repulsive state to yield  $\text{CF}_2 + \text{F}$ . Furthermore the lines of fluorine atom emission at 685.6 nm, 703.7 nm, 730.9 nm and 739.8 nm were observed. No  $\text{CF}_2$  ( $A^1B_1 - X^1A_1$ ) bands were detected in this particular type of discharge. Nitrogen being present as traces, the ratio of  $\text{N}_2^+(\text{B})$  at 391.4 nm over  $\text{N}_2(\text{C})$  at 394.3 nm was used to estimate the mean electronic temperature in our discharge (ref. 36). In this way the mean electronic temperature being  $T_e > 6$  eV, the  $\text{CF}_2$  radical ( $A^1B_1 - X^1A_1$ ) bands which have a threshold energy of 4.6 eV were not detected in our particular discharge whereas in the case of a capacitively coupled 13.56 MHz glow discharge  $\text{CF}_2$  as well as  $\text{CF}$  bands ( $B^2\Delta - X^2\Pi$ ) were present due to the lower estimated mean electronic temperature ( $T_e \approx 3$  eV). Furthermore the voltage-current characteristics of the discharge point out that we are in an abnormal glow discharge (ref.45).

##### 4.2 Polymerizing $\text{CF}_4 + \text{H}_2$ discharges

The main difference that exists between the emission spectra of  $\text{CF}_4 + \text{H}_2$  mixtures with respect to that of  $\text{CF}_4$  is the presence of two additional lines at 656.2 and 486 nm corresponding to  $\text{H}_\alpha$  and  $\text{H}_\beta$  lines respectively (ref. 37). By means of actinometry using argon as the actinometer; the concentration trends of atomic fluorine and excited  $\text{CF}_2^+$  ions were determined as a function of the additive percentage of hydrogen in the feed (Fig. 2). The fluorine atom concentration passed through a minimum at 2 % hydrogen owing to the formation of the stable compound HF, and then increased substantially from this point on. Moreover by following the variations of the intensity of the argon line, which is an image of the excitation efficiency by the electrons, a mechanism has been proposed for the decomposition of  $\text{CF}_4$ , in which vibrationally excited hydrogen plays an important role (ref. 27). D'Agostino, et al have studied the effect of addition of hydrogen, a scavenger of fluorine atoms to  $\text{C}_n\text{F}_{2n+2}$  discharges (ref. 38) in a 13.56 MHz glow discharge. They reported that in all cases the fluorine atom concentration fell to a minimum at a hydrogen percentage varying between 10 % and 18 % but in the case of  $\text{CF}_4$  discharge the fluorine atom increased only slightly after this point (ref. 38). One of the main reasons for the difference which exists in the nature of the excited species and their relative concentrations in our discharge with respect to a RF capacitively coupled one, is the excitation frequency. Indeed in low frequency excitation systems (20 kHz - 400 kHz) the transition time of the ions in the sheath is less than the half-period of the applied field. Therefore the ions show a tendency to disappear during every period on one electrode or the other. It has been shown that the emission of secondary electrons from the electrodes by ionic impact, is the predominant mechanism to sustain the discharge. Indeed the plasma electronic cloud is carried from one electrode towards the other

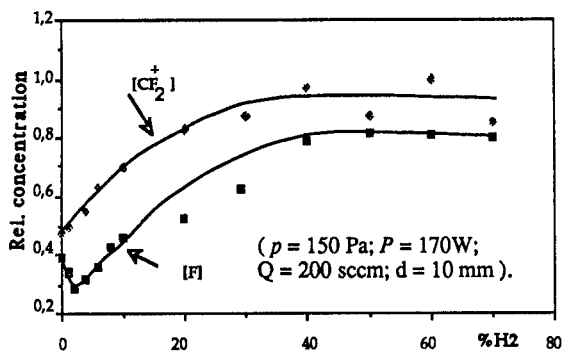


Fig. 2 : Relative concentration of fluorine (685.6 nm) and  $\text{CF}_2^+$  ions (310 nm) obtained by actinometry vs %  $\text{H}_2$  in the  $\text{CF}_4 + \text{H}_2 + 2\%$  Ar mixture

every half period where it loses a great number of particles. These losses are compensated by secondary electronic emission and corresponding ionization of the gas (ref. 39) That is the reason why in our low frequency discharge (70 kHz) with a relatively small interelectrode gap ( $d = 1$  cm), a considerable concentration of  $CF_2^+$  ions has been detected. These ions should play an important role in the deposition process by causing bond dissociation at the surface, leading to a substantial concentration of reactive species at the surface and therefore to high deposition rates.

## 5. ROLE OF PLASMA ON SURFACE MODIFICATIONS OF POLYMERIC FILMS

XPS and SSIMS have been used to assess the surface composition of untreated and plasma-treated surfaces. SSIMS allows us to obtain compositional information relative to a layer about 1 nm thick, therefore is complementary to XPS. SSIMS being more sensitive than XPS has been in particularly very useful to point out modifications created for treatment times as short as fraction of seconds.

### 5.1 Modifications created by a $N_2$ low pressure plasma on the surface of polypropylene (PP)

Isotactic, 8  $\mu m$  PP films were treated in a  $N_2$  discharge ( $p = 150$  Pa,  $d = 7$  mm,  $V = 1$  kV;  $I = 100$  mA for very short treatment times (100 ms - 7 s). The static SIMS spectra were obtained with Xe - 4 k eV ions and a total ion dose lower than  $2 \cdot 10^{13}$  ions/cm<sup>2</sup>.

First of all it has been shown by static SIMS (ref.40) that the surface composition of the non treated samples present a greater inhomogeneity with respect to the treated samples. This inhomogeneity has been attributed to low molecular weight contaminants which give rise to peaks with random intensities for masses  $\leq 41$  a.m.u. The  $N_2$  plasma brings about some homogenization of the polypropylene surface composition. Therefore the contamination layer is partially removed by evaporation, sputtering and scouring during the treatment pointing out in this way the cleaning effect of the  $N_2$  plasma. By comparing the static SIMS spectra obtained on the reference polypropylene (Fig. 3a) with that of the treated one (Fig. 3b), it is clearly seen that the relative intensity of the molecular fragments with masses greater than 100

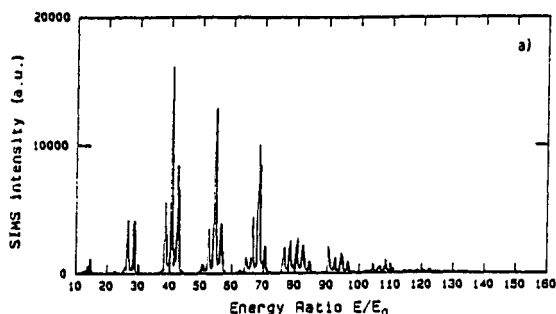


Fig. 3a : SSIMS on a virgin polypropylene

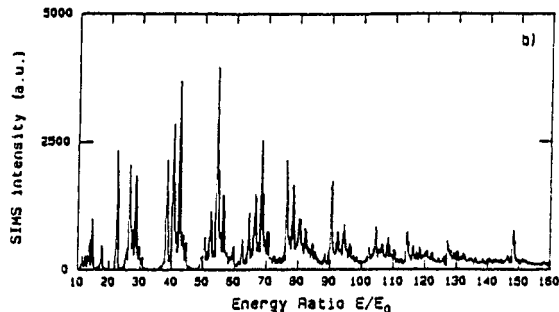


Fig. 3b : SSIMS on  $N_2$  treated polypropylene (7 s)

amu, increase with the  $N_2$  plasma treatment. Fig. 4 shows the increase of these fragments with treatment time. These fragments ( $> 100$  amu) are essentially aromatic ones occurring at masses 105, 115, 128. This may be interpreted as a result of unsaturation (typical aromatic fragments at 77 and 91 are also observed for masses  $< 100$  amu). Therefore these results point out that the plasma treatment may give rise to fragmentation of the polymer backbone for treatment times in the order of a few seconds. In addition to these observations, the overall ion yield decreases with increasing plasma treatment times as seen on Fig. 3 : this may be caused by crosslinking induced by the  $N_2$  plasma treatment.

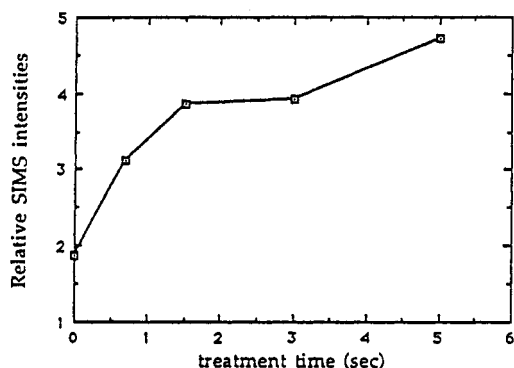


Fig. 4 : High mass clusters observed by SSIMS ( $> 100$  a.m.u.)

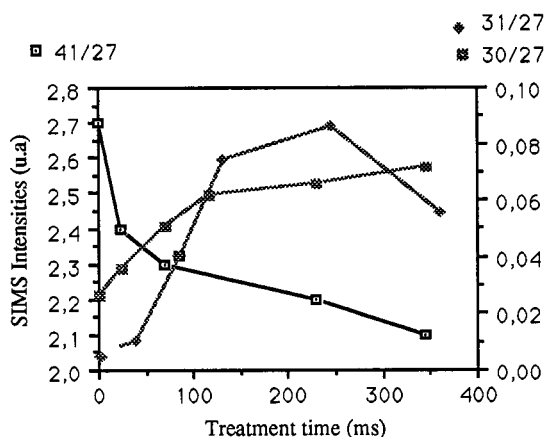


Fig. 5 : Variation of the 41/27, 31/27 and 30/27 mass ratio obtained by SSIMS measurements with treatment time [ $N_2$  plasma treated PP,  $d = 280$  sccm,  $d = 7$  mm,  $V = 1$  kV,  $I = 60$  mA,  $p = 200$ Pa]

As for very short treatment times (23 ms - 400 ms), the decrease of the low molecular weight hydrocarbons assessed by the decrease of the 41/27 fragments intensity ratios (Fig. 5; 41 :  $C_3H_5$ , 27 :  $C_2H_3$  cluster intensity is used as a reference for the  $C_X$  cluster intensities (ref. 42)) with time can point out the cleaning effect of the plasma treatment which was proposed in an earlier work for treatment times in the order of a few seconds (ref. 40) The slight oxidation of the polymeric surface is assessed by the increase of the 31/27 (Fig. 4; 31:  $COH_3$ ) fragments which shows a maximum before decreasing beyond 250 ms. On the contrary the occurrence of nitrogen containing fragments which take place at even atomic mass units (ref. 43) seen from the 30/27 fragments intensity ratios (Fig. 5; 30 :  $CNH_4$ ) increases with the treatment time. The variation of other oxygen (45 :  $COOH$  or  $C_2 OH_5$ ) or nitrogen (28 :  $CNH_2$ ) containing fragments show similar trends to those presented in Fig. 5 (ref. 47). The intensity of the masses > 100 amu does not seem to vary for treatment times in the order of fractions of second (23 ms - 500 ms) showing that for such treatment times the plasma does not show a degradation effect (ref. 47).

## 6. ROLE OF THE CHEMICAL NATURE OF THE SUBSTRATES ON THE REACTIONS TAKING PLACE AT THE PLASMA-POLYMER INTERFACE

For this study, the plasma polymerization of ( $CF_4 + H_2$ ) mixtures has been carried out on two different substrates polyethylene (PE) and a fluorine-containing polymeric substrate i.e. polyvinylidene fluoride (PVDF). The AOES results performed in different  $CF_4 + H_2$  compositions showed that the reactive fluorine atom concentration passed through a minimum at 2 % hydrogen (Fig. 2). Therefore, knowing that fluorine atom is an important etching agent, a maximum of polymerization rate should be expected at 2 % hydrogen in the  $CF_4$  discharge. Indeed the deposition rate recorded on PE by gravimetric measurements was maximum for this particular feed composition (Fig. 6). From this point on the etching by means of fluorine atoms and hydrogen species in the discharge becomes predominant with respect to the polymerization. In this way the deposited polymer is etched leading to a decrease of the polymerization rate on the PE surface (Fig. 6). XPS was employed to determine the surface composition of the deposited fluorocarbon films at different relative concentrations of  $CF_4$  and  $H_2$  in the feed (ref. 37 & 45). These results confirm what was observed by emission spectroscopy (Fig. 2) i.e. the fluorine content of the deposited polymer on PE surface was greatest for 2 % hydrogen in the feed. Thus with this feed composition as soon as the discharge was put on, a hydrofluorinated polymer was formed on the PE surface whereas with longer treatment times ( $t > 30$  s) when the fluorine content of the deposited polymer increased ( $F/C = 1$ ), the polymerization decreased ; etching became competitive with polymer deposition. Furthermore the plateau obtained for the polymerization rate after 1.5 min (Fig. 7) was due to the equilibrium established between the polymerization and etching processes. The deposition rate estimated in the polymerization region was around 35 nm/s.

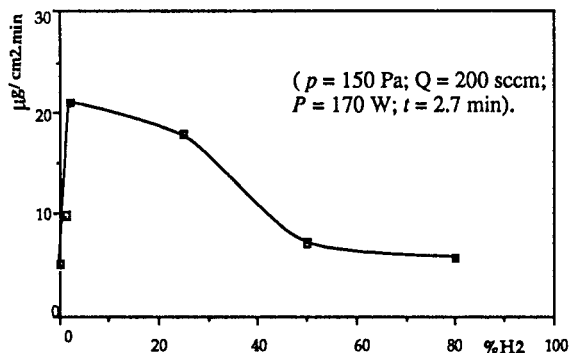


Fig. 6 : Polymerization rate of  $CF_4 + H_2 + 2\%$  Ar mixture vs  $\% H_2$  in the feed on a PE substrate

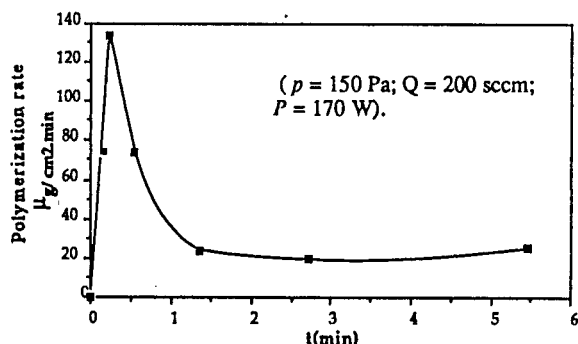


Fig. 7 : Polymerization rate of  $CF_4 + 2\% H_2 + 2\%$  Ar mixture vs treatment time on a PE substrate

The PVDF substrate was itself hydrofluorinated from the start with an F/C ratio equal to unity, and therefore with this particular feed composition, for short treatment times (less < 75 s), there was no polymer deposition but only etching of the PVDF substrate (Fig. 8). This is consistent with the phenomena observed with the PE substrate at longer treatment times ( $t > 30$  s). Consequently since the fluorine containing in the substrate contributes to the growth mechanisms, the optimum hydrogen percentage in the feed (corresponding to the maximum polymer growth rate) will not be the same in the case of the two substrates PE and PVDF. Indeed for the PVDF substrate with respect to PE a higher percentage of hydrogen is necessary ( $\approx 4\%$ ) to neutralize the fluorine coming from the surface of the substrate. As seen in Fig.9 on PVDF, the polymerization rate was the greatest for a hydrogen percentage around 4% : whereas for PE the optimum value was 2% hydrogen (Fig. 6).

Furthermore XPS has shown that with this particular feed composition ( $\text{CF}_4 + 4\% \text{H}_2$ ) the hydrofluorinated polymer deposited on PVDF presents the highest F/C ratio (ref. 45). This study has shown that the nature of the substrate interferes in the growth mechanisms of the  $\text{CF}_4 + \text{H}_2$  mixtures, but as soon as the polymer begins to build up on the surface of the fluorine containing substrate i.e. for treatment times  $t > 75$  s under our experimental conditions, the chemical composition and the surface energy of the deposited fluorocarbon film analyzed by XPS and contact angle respectively, became the same on both of the substrates (ref. 45). Contact angles measured on films prepared with different hydrogen percentages in the  $\text{CF}_4$  discharge, on PE pointed out a large domain of surface energies (from non-wettable  $17 \text{ mJ/m}^2$  to wettable surfaces  $42 \text{ mJ/m}^2$ ). Moreover it has been shown by XPS and FTIR-ATR that by increasing the hydrogen percentage in the feed, the fluorine content of the films decreased leading to very crosslinked films with very stable wettability properties.

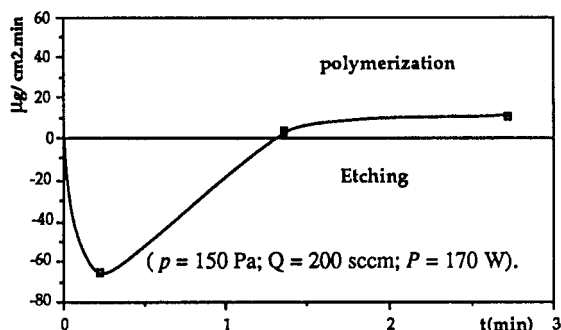


Fig. 8 : Polymerization rate of  $\text{CF}_4 + 2\% \text{H}_2 + 2\% \text{Ar}$  mixture vs treatment time on a PVDF substrate

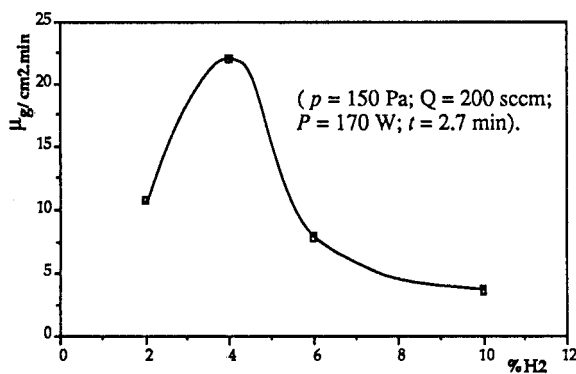


Fig. 9 : Polymerization rate of  $\text{CF}_4 + \text{H}_2 + 2\% \text{Ar}$  mixture vs  $\% \text{H}_2$  in the feed on a PVDF substrate

## 7. ADHESION IMPROVEMENT OF THE PLASMA PRETREATED POLYMER WITH ALUMINIUM. AES ANALYSIS OF THE POLYMER-METAL INTERFACE

In this section as an application of plasma processes, thin polypropylene (PP) films ( $8 \mu\text{m}$ ) were pretreated in a  $\text{N}_2$  low pressure plasma prior to metallization in order to improve the polymer-metal adhesion. The results displaying the influence of the  $\text{N}_2$  plasma pretreatment were presented in section 5 of this article. Thin aluminium coatings ( $\approx 20 \text{ nm}$ ) were deposited in situ by evaporation at  $10^{-3} \text{ Pa}$  on the PP films.

### 7.1 AES analysis of the polymer-metal interface

AES depth profiling of metallized polypropylene films was achieved in order to approach the chemical composition of the Al deposit and to identify species which may be involved in the adhesion mechanisms at the Al-PP interface.

The role of the experimental conditions of the AES analysis on the obtained profiles, the recommended procedure for the AES intensity measurements and the main parameters for a quantitative approach were previously published (ref. 46).

Typical depth profiles (ref. 46) performed on a thin Al film deposited on a pretreated PP substrate shows at the top, a contaminating carbon layer which covers a thin alumina film. Below this natural layer built during the air transfer, a rather clean aluminium coating appeared showing only some C and O traces related to the level of the residual pressure in the metallization process. At the vicinity of the interface, Al (met) transition quickly falls down, while Al (ox) reappears with simultaneously a sharp increase of the carbon profile produced by C atoms of the polymer. A first determination of the interface location can be achieved by extrapolating Al (met) profile of the deposit or C profile of the polymer substrate to the zero intensity scale.

It has been pointed out that independently of the pretreatment carried out on the polypropylene, the interface consists of an oxidized film estimated to be  $4 \text{ nm}$  thick (ref. 46). Moreover nitrogen due to the  $\text{N}_2$  plasma treatment was never detected at the interface by AES.

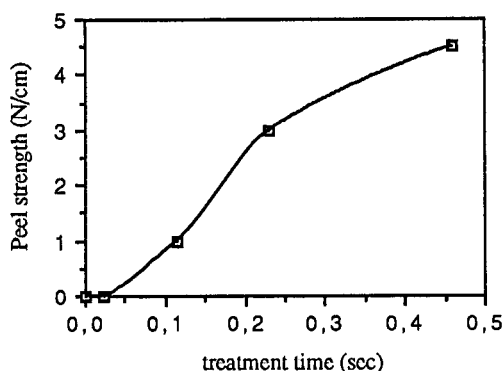


Fig. 10 : Variation of the peel strength in function of the treatment time

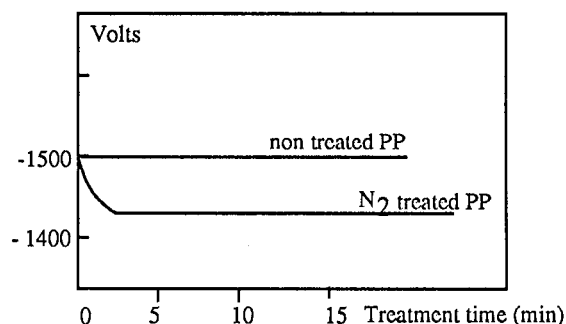


Fig. 11 : Potential decay measurements on treated and non treated PP. (d = 7 mm, V = 1 kV, I = 60 mA, p = 200Pa)

When reaching the interface, due to the fact that the polymeric substrate is exposed successively to ion and electron bombardments, charge effects usually occur and disturb AES spectra acquisition. Such artifact was turned to good account to appreciate the pretreatment efficiency in relation with the polymer metal adhesion (ref. 44). The charge effect gives rise to an energy shift observed on all of the signals (Al-ox, Al-met, O, C) up to 700 eV in the case of an Al-nonpretreated PP interface. Thus the charge effect appeared at the vicinity of the interface, reached a maximum at this point and then decreased sharply, whereas in the case of the Al-pretreated PP interface the charge effect was nonexistent or hardly observed (50 eV), showing therefore a more conducting interface in this case.

These results are in agreement with the potential decay measurements carried out on the non metallized pretreated PP films. Indeed the surface conductivity of the N<sub>2</sub> treated PP films was examined by exposing the samples to an injection of negative charges produced by a corona discharge (ref. 48). The potential decay was then recorded by an electrostatic probe in function of time. Without a plasma pretreatment, the surface potential remains constant. The increase of the surface conductivity in the case of the plasma treated film might be due to the cleaning effect of plasma, observed by SSIMS giving rise to a homogenization of the surface by a partial elimination of the contamination layer composed of low molecular weight fragments. In the case of the non treated polymer, the surface defects act as charge traps and in this way prevent the surface potential to decay.

## 7.2 Measure of the polymer-metal adhesive force

The polymer-metal adhesion was quantified by a U form peel test adapted to very thin coatings on flexible substrates (ref. 47). It has been shown that in function of treatment time the measured peel strength increases (Fig 11). Furthermore a saturation level is obtained at approximately 1 second of treatment time (ref. 47). The comparison of the variation of the peel strength with Fig. 5 shows that the adhesive strength at the interface is closely correlated to the nitrogen moieties (30/27 fragments).

The different results obtained by SSIMS, AES analysis, surface conductivity measurements and the measure of the peel strength point out that the increase of the adhesion of the Al-pretreated PP films for treatment times as short as fractions of seconds (100-500ms) could be due to the cleaning effect of plasma, the increase of the surface conductivity as well as incorporation of nitrogen moieties. As for oxygen, negative SSIMS performed on N<sub>2</sub> pretreated films should help us to obtain a better understanding of its role in the adhesion phenomena. However some interesting results have been obtained by AES concerning the oxygen observed at the interface (ref. 44).

## CONCLUSION

The research work in this area points out the problems due to the durability of the surface properties in the case of the plasma modified surfaces by non polymerizing gases. The possibility to obtain a variety of applications by the deposition of a highly crosslinked plasma thin films on polymeric substrates from plasma polymerization of organic and organometallic molecules seems to be a promising route for a wide application of plasma treatments. As an example the CF<sub>4</sub> + H<sub>2</sub> mixtures offers the possibility to obtain thin films with a wide range of wettabilities (from wettable to nonwettable) and which are highly adherent to polymeric substrates.

Furthermore SSIMS, being complementary to XPS and contact angle measurements has revealed to be extremely useful to assess the mild modifications created in particular for very short treatment times. However for a judicious selection of the plasma polymer combination, best suited to a specific application, a better understanding of the effect of the plasma reactor configuration and the processing parameters on the surface modifications created is indispensable. That is why OES has been employed to correlate the nature of the reactive species to the final properties and their reproducibility. In order to better understand the deposition mechanisms, we are developing a model which simulates in the case of a low pressure diode reactor the flow velocities, the surface temperature and the concentration of the different species in the plasma which arrive at the surface (ref. 51). This has been possible by solving two dimensional Navier-Stokes conservation equations, and the coupling with the kinetic model of decomposition of an organic starting material such as C<sub>2</sub>F<sub>4</sub>.

## Acknowledgements

Collaboration with, Y. De Puydt and P. Bertrand, PCPM Université Catholique de Louvain, G. Lorang and J.P. Langeron, CECM - CNRS and M.Goldman, LPD-ESE/CNRS, has been a pleasure and is acknowledged here. The authors are grateful to EDF for the financial support.



## REFERENCES

1. H. Yasuda, Plasma Polymerization (1985), Academic Press, New York, London
2. P.V. Hinman, A.T. Bell and M. Shen, J. Appl. Polym. Sci., **23**, 3651 (1979)
3. D.L. Cho and H. Yamada in Proceedings of the ACS Division of Polymeric Materials, **57**, 599 (1987)
4. H. Yasuda and M. Gazicki, Biomaterials, **3** 68 (1982)
5. R. Hollahan and A.T. Bell, Techniques and Applications of Plasma Chemistry, John Wiley and Sons (1984)
6. S. Hattori, J. Tamano, M. Yasuda, M. Ieda, S. Morita, K. Yoneda and S. Ishibashi Thin Solid Films **83**, 189 - 194 (1981)
7. S. Morita and S. Hattori, Appl. of plasma Polym., Plasma Deposition, Treatment and Etching of Polym. Edited by R. D'Agostino (1990), Academic Press, Boston
8. Y. Osada, A. Mizumoto and H. Tsuruta, J. Macromol. Sci. Chem. A **24** (3 & 4), 403 - 413 (1987)
9. P.K. Tien, G. Smolinski and R.J. Martin, Appl. Optics, **11** (3) 637 (1972)
10. H. Biederman and H. Osada, Plasma Chemistry of Polymers, **57** - 109 (1989) Editor : G. and S. Olive
11. A. Moshonov, Y. Avni, (1980) J. Appl. Polym. Sci. **25**, 771
12. N. Inagaki and H. Yasuda, J. Appl. Polym. Sci. **26**, 3333
13. P. Spartacus, M. Goldman, and J. Amouroux, Proc. ISPC - 8, K. Akaski and A. Kinbara Eds., Tokyo, (1987), 1799 - 1804
14. T. Wydeuen (1977) Appl. Opt. **16**, 717
15. E. Sacker, J.E. Klemberg - Sapiena, H. P. Shreiber and M.R. Wertheimer ( 1984) Polym. Sci. Appl. Polym. Symp. **38**, 163 - 172
16. N. Morosoff, in an Introduction to Polymerization, Plasma Deposition treatment and etching of Polymers, Edited by R. d'Agostino, Academic Press, Inc Boston (1990)
17. Y. S. Yeh, I.N. Shyy and H. Yasuda, J. Appl. Polym. Sci. - Appl. Polym. Symp. **42.1** (1988)
18. R.J. Jensen, A.T. Bell and D.S. Soung (1983) Plasma Chem. Plasma Process. **3**, 163
19. E. Kay (1986) Z. Phys. D - Atoms, Molecules and Clusters **3** : 251
20. J.J. Beulens, G.M. W. Kroesen, D.C. Schram and C.J. Timmermans, J. of Appl. Polym. Sci. : Appl. Polym. Symp. **46**, 527 - 540 (1990)
21. E. Occhiello, M. Morra, G. Morini, F. Garbassi and P. Humphry, J. of Appl. Polym. Sci. **42**, 551 - 559 (1991)
22. S. Wu, Polymer Interface and Adhesion, Marcel Dekker, New York, (1982)
23. P. Montazer-Rahmati, F. Arefi, J. Amouroux, in Proc. of ISPC 10, Bochum, Germany (1991)
24. T. Yasuda, M. Gazicki and H. Yasuda, J. of Appl. Polym. Sci. : Appl. Polym. Symp. **38**, 201 - 214 (1984)
25. H. Yasuda, A.K. Sharma, T. Yasuda (1981) J. Polym. Sci. Polym. Phys. Ed. **19** : 1285
26. D. Briggs, D.G. Rance, C.R. Kendall, A.R. Blythe Polym., **21**, 895, (1980)
27. F. Arefi, P. Montazer-Rahmati, V. Andre and J. Amouroux, J. of Appl. Polym. Sci. : Appl. Polym. Symp. **46**, 33 - 60 (1990).
28. A.R. Blythe, D. Briggs, C.R. Kendall, D.G. Rance and V. J.I. Zichy, Polym., **19**, 1273 - 78 (1978)
29. T. Yasuda, T. Okuno, K. Yoshida and H. Yasuda, Proc. of the ACS Division of Polym. Mat. : Sci. and Engin., Vol. 56 Denver Colorado pp. 240 - 243 (1987).
30. N. Inagaki and H. Yasuda, J. Appl. Polym. Sci. **26**, 3333. (1981)
31. K.S. Chen, N. Inagaki and K. Katsuura, J. Appl. Polym. Sci. **27**, 4655 (1982)
32. R.K. Sathir, W. J. James and R.A. Auerbach, Thin Solid Films, **97** (1982) 17
33. F. Tchoubineh, F. Arefi, J. Amouroux and M. Goldman, Proceeding of ISPC 8 Tokyo (1987) 1263
34. F. Arefi, F. Tchoubineh, J. Amouroux and M. Goldman EDF French Patent No. 8803821 (1988)
35. P. Montazer-Rahmati, F. Arefi, R. Borrin, A. Delacroix and J. Amouroux Bull. de la Soc. Chim. de France, **5**, 811-816 (1988)
36. P. Montazer-Rahmati, F. Arefi, J. Amouroux and A. Ricard, Proc. of ISPC 9 (IUPAC), **2** 1195-1200 (1989) Pugnociuso, Italy
37. P. Montazer-Rahmati, F. Arefi, and J. Amouroux, Surface and Coating Technology , **45** (1991) 369-378
38. R. d'Agostino, F. Cramarossa, F. Fracassi, Plasma Polymerization of Fluorocarbons in Plasma Deposition, Treatment, and Etching of polymers, Edited by R. D'Agostino Academic Press, Boston (1990)
39. G. Turban, Interactions Plasma froids-materiaux, 79-112 Journée d'Etudes "OLERON 87" (1987) - Scientific Editor GRECO 57 du CNRS (SPI)
40. V. André, F. Arefi, J. Amouroux, Y. de Puydt, P. Bertrand, G. Lorang and M. Delamar, Thin solid Films, **181** (1989) 451-460
41. V. André, Y. de Puydt, F. Arefi, J. Amouroux P. Bertrand and J.F. Silvain ACS Books Metallization of Polymers Chap. 31, 423-432 (1990)
42. W.J. Von Ooij R. H. G. Brinkhuis, Surface and Interface Analysis, Vol. 11, 430-440 (1988)
43. M. Budzikiewicz, C. DJerassi and D.H. Williams, in Mass Spectrometry of Organic Compounds, Ed., Holden Day : San Francisco, (1967)
44. G. Lorang, V. André, F. Arefi, J. Amouroux and J.P. Langeron, to be presented at ECASIA 91 oct. (1991) Budapest (Hungary)
45. P. Montazer-Rahmati, P. & M. Curie University Doc. Thesis Janv. (1991)
46. V. André, F. Arefi, J. Amouroux and G. Lorang, Surface and Interface analysis, **16**, 241-245 (1990)
47. V. André, F. Arefi J. Amouroux, G. Lorang, Y de Puydt and P. Bertrand in Proc. of International Conference on Polymer-Solid Interface 2-6 Sept (1991) Namurs, Belgium to be published.
48. R. Cohelo, J. Levy, and D. Serrail, Phys. Stat. Sol. **94** (1986) 595
49. F.D. Egitto, Pure & Appl. Chem. Vol. 62, N° 9, pp 1699 - 1708 (1990)
50. H.U. Poll, M. Arzt, and K.H. Wickleder (1976) Eur. Polym. J. **12**, 505.
51. K. Hassouni, S. Cavadias, A. Gicquel, E. Utku and J. Amouroux, in Proc. ISPC 10, Bochum, Germany (1991)