

## PLASMA DEPOSITION AND PLASMA TREATMENTS OF POLYMERS FOR VARIOUS APPLICATIONS

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### ABSTRACT

Low pressure plasma technology for polymer processing for some relevant applications will be examined. In particular, the processes for producing hydrophobic coatings, transparent barrier films, activated surfaces for adhesion, bio-compatible surfaces will be considered. Emphasis will be given to the use of plasma and material diagnostics for gaining an insight on the mechanisms and for producing control process tools of industrial relevance.

### 1. INTRODUCTION

Low Pressure Plasmas (LPP) are largely utilized for plasma processing of polymers, *i.e.* deposition, treatment and etching of thin polymer films, for many important applications since almost a couple of decades. The versatility of LPPs relies in the fact that the precursors, the active species, and the positive ions in the gas phase can be varied in a large range of compositions or of accelerating potentials (for the ions). This has allowed to design an entirely novel class of materials with variable stoichiometry and *ad hoc* properties, which have contributed to solve some of the most important problems of materials, mostly without affecting their bulk properties.

In this note the immense contribution of LPP technology to microelectronics is ignored on purpose, while emphasis is given to some other applications relevant to the field of polymer processing, such as hydrophobic coatings, transparent barrier films, surface activation for metal adhesion, metal containing coatings. These are, in fact, some research lines of our laboratory with a very large fall-out in polymer applications.

### 2. The approach to plasma processing of polymers

Our approach to the study of plasma processing of polymers is based on the combined use of *in situ* and continuous plasma diagnostics, *e.g.* emission spectroscopy (actinometry), IR absorption spectroscopy (IRAS), mass spectrometry, and of film diagnostics, *e.g.* ESCA and FTIR, as well as on the comparison with the *ad hoc* analysis of the performances of materials, *e.g.* adhesion strength, wettability, gas transmission rates of O<sub>2</sub> and H<sub>2</sub>O, resistance to bacterial colonization, cell adhesion, etc, depending on the particular application. This approach has allowed us to find the linkage between *species in the gas phase* (A), the *surface composition* (B), the *material performances* (C). While understanding the connections be-

tween A and B is essential to give an insight to the mechanism of the various processes, the A vs. C connections provides very unique and direct tools for controlling the performances of processes. This latter issue is of great industrial importance in

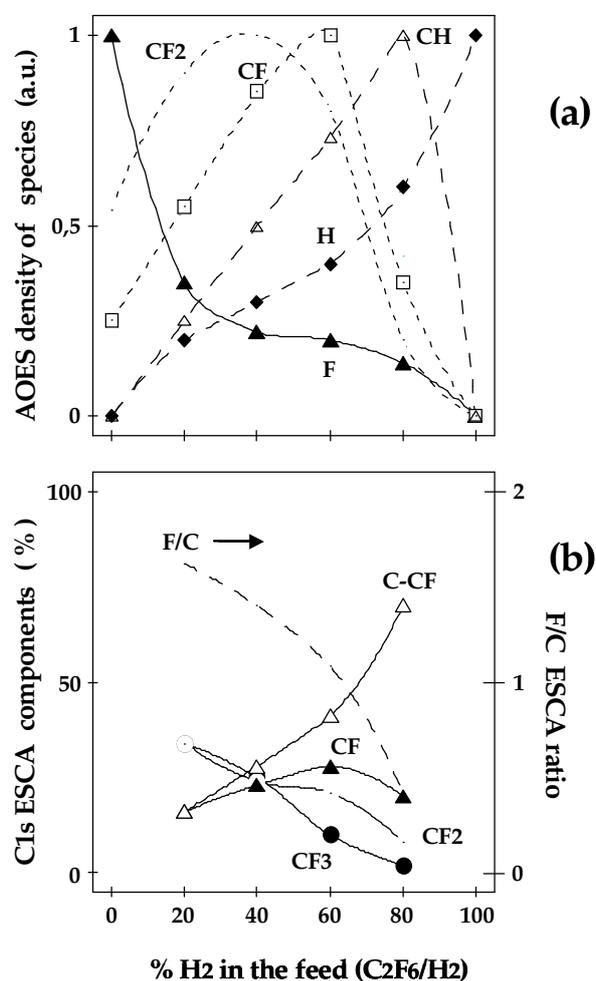


Figure 1 - a) Distribution of radicals and atoms detected by Actinometric Optical Emission Spectroscopy (AOES) in the gas phase for H<sub>2</sub>-C<sub>2</sub>F<sub>6</sub> glow discharges, as a function of the feed composition; b) relative abundancy of chemical groups, as well as the F/C ratio, in the coatings deposited from H<sub>2</sub>-C<sub>2</sub>F<sub>6</sub> glow discharges.

that can solve some of the most frequent constrains in the industrial use of LPP technology.

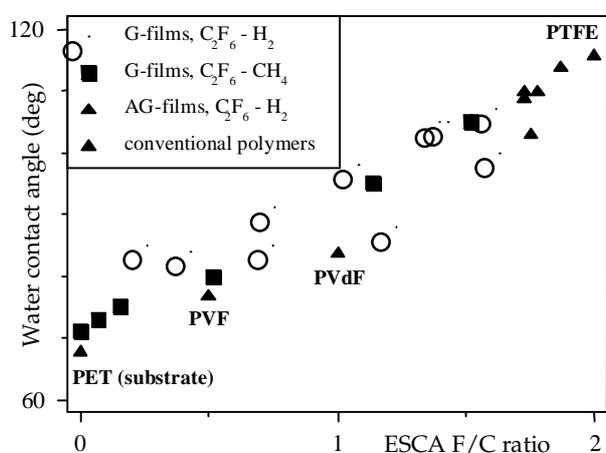


Figure 2 – Advancing water contact angle of G- and AG-teflon-like films as a function of their F/C ratio. Values for conventional fluoropolymers are also reported: PET = polyethyleneterephthalate, PVF = polyvinilfluoride,  $(\text{CH}_2\text{-CHF})_n$ ; PVdF = polyvinil idenefluoride,  $(\text{CH}_2\text{CF}_2)_n$  PTFE = polytetrafluoroethylene,  $(\text{CF}_2\text{CF}_2)_n$ . [3]

### 3. HYDROPHOBIC COATINGS

We have produced a great deal of work in the field of fluoropolymers, known also with a different jargon as the Teflon-like coatings, since the early 80s, and the reader can refer to ref. [1] and [2] for an extended review.

The most relevant feature of our study is the comparison of the distribution of gas phase species with the chemical groups abundance in the film, as a function of a plasma parameter. An example is given in Figure 1 where the gas phase and material pictures are compared as a function of the feed composition ( $\text{H}_2\text{-C}_2\text{F}_6$ ).

From this analysis the role of  $\text{CF}_x$  radicals in “building” the chemical structure of the polymer comes out straightforward: e.g. at 20%  $\text{H}_2$  in  $\text{C}_2\text{F}_6$ ,  $\text{CF}_2$  radicals are the main building blocks and the polymer has a higher Teflon character (high F/C ratio), while at 60%  $\text{H}_2$ , CH radicals are the predominant precursors, along with carbon atoms, and the film is highly cross-linked and has a low F/C ratio. What can be concluded here is that by controlling the gas phase composition (even with a simple actinometric technique) one can control the F/C ratio of the polymer. This consideration, along with the fact that Favia et al. [3] have shown that the wettability (and other properties, such as the interaction with proteins) solely depend on the F/C ratio, suggests that hydrophobic/hydrophilic - as well as biological - performances of the material can be conveniently controlled this way. (Figure 2) from the gas phase.

At this point is worthy to report that with a proper modulation of RF  $\text{C}_2\text{F}_4$  discharges super-hydrophobic (water contact angles  $>160^\circ$ ) coatings have been obtained [4] In order to get super-hydrophobicity it is necessary to have a combined contribution of the surface chemistry (high values of F/C ratios)

and morphology (nanostructured surfaces), as it is shown in figure 3.

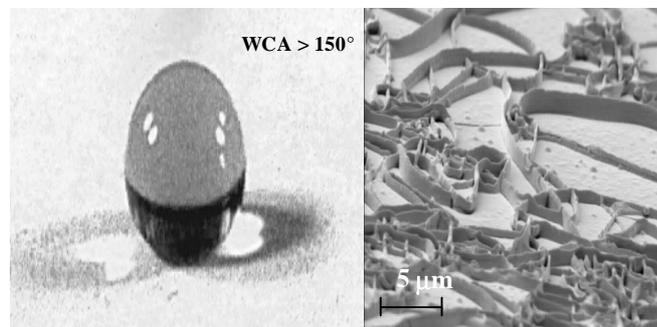


Figure 3 – Left side: enlarged micro-drop of water onto a surface of PE coated with super-hydrophobic fluoropolymer obtained by modulating a  $\text{C}_2\text{F}_4$  discharge. Right side: morphology of the coating (SEM picture) showing an evident nano-structuring of the material.[4]

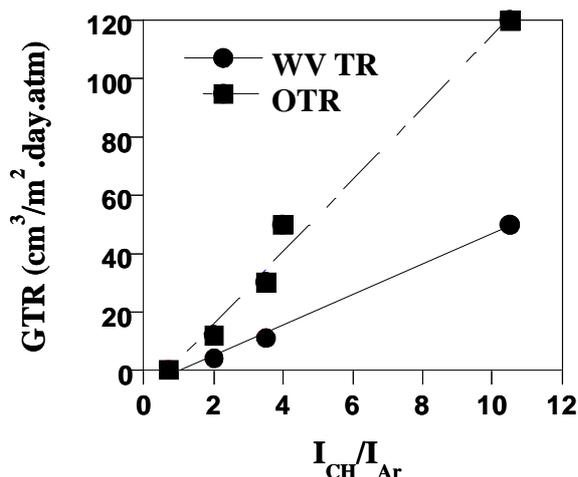


Figure 4 – GTR<sub>O2</sub> and GTR<sub>H2O</sub> of 12  $\mu\text{m}$  PET coated with 500  $\text{\AA}$   $\text{SiO}_x$  as a function of the gas phase actinometric density of CH radicals. CH actinometric emission monitor the performances of the coatings.[5]

### 4. TRANSPARENT BARRIER FILMS

LPP technology is now commercially available for producing very thin – 200-500  $\text{\AA}$  - transparent  $\text{SiO}_x$  coatings onto PET and other plastics which increase their barrier performances to  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and aromas of more than two orders of magnitude. Mostly the glow discharges are fed with oxygen diluted organosilicon compounds, as for instance hexamethyldisiloxane (HMDSO).

One of the main concern is the *in situ* control of barrier properties in the commercial roll-to-roll coaters, in fact Gas Transmission rates (GTR) measurements are not suitable to be performed *in situ* and requires measuring times of the orders of hours, while the winding speed of the webs to be coated is

of the orders of a few 100 meters per min. For this reason can be very important to identify the gaseous species from which the GTR of the coating is (well or badly) affected. If such species are available they become the “key” for realizing an effective process control, once they can be conveniently detected in a continuous way.

We have found three such key species: CH radicals[5], detected by actinometric optical spectroscopy, and SiOH and SiO<sub>x</sub> species, or even better their ratio SiOH/SiO<sub>x</sub>[6] monitored by IRAS. CH radical, or better its actinometric emission, behaves as a controlling parameter up to medium-high barrier performances, which are considered good for most commercial applications and corresponds to GTRO2 in the range of 1-3 cm<sup>3</sup>m<sup>-2</sup>day<sup>-1</sup>atm<sup>-1</sup>. Then, SiOH/SiO<sub>x</sub> ratio can be used as a (negative) test for high quality barrier performances (up to GTRO2 of the order of 0.3 cm<sup>3</sup>m<sup>-2</sup>day<sup>-1</sup>atm<sup>-1</sup>). For this latter case, what is particularly important to consider at this point is that both the ratio of IR spectral features of the film, i.e. (SiOH/SiO<sub>x</sub>)<sub>film</sub>, and of the gas phase, i.e. (SiOH/SiO<sub>x</sub>)<sub>plasma</sub>, can be well utilized as good check parameters of GTRs. In other words, a continuous infrared inspection at two frequencies of either the gas phase or of the deposited material (which can easily be accomplished within a roll-to-roll equipment) can produce a signal for adjusting the experimental condition up to optimisation of the performances. Figure 4 shows the linkage between CH gas phase and GTRs for oxygen and water. Figures 5, on the other hand, shows that the trends of GTR, of (SiOH/SiO<sub>x</sub>)<sub>film</sub>, of the gas phase (SiOH/SiO<sub>x</sub>)<sub>plasma</sub>, are all very similar, so that the spectroscopic parameters (both of plasma or film) can be used as marker of high quality materials

## 5. PET ACTIVATION FOR ENHANCING AL ADHESION

Metal-polymer adhesion is an important issue for food and pharmaceutical packaging, and a great deal of work has been produced for activating polymers as PET for enhancing Al adhesion. Mostly, oxygen or air discharge are utilized for activation, while very few researches have been performed with NH<sub>3</sub> with this purpose. Probably the lack of works with ammonia reflects the fact that usually it has been utilized under experimental conditions similar to those of oxygen, i.e. high energy doses (high power and/or long treatment times).

We have shown, however, that very short NH<sub>3</sub> treatment times (TT), of the order of 0.1 sec, with moderate power inputs, allow to improve by a factor of three the best results obtained with oxygen at TT 50-100 times longer.[7] Only very short TTs with ammonia are, in fact, effective to promote adhesion because this is affected by the relative basic strength of N-containing groups and only a few such groups are needed for anchoring Al.

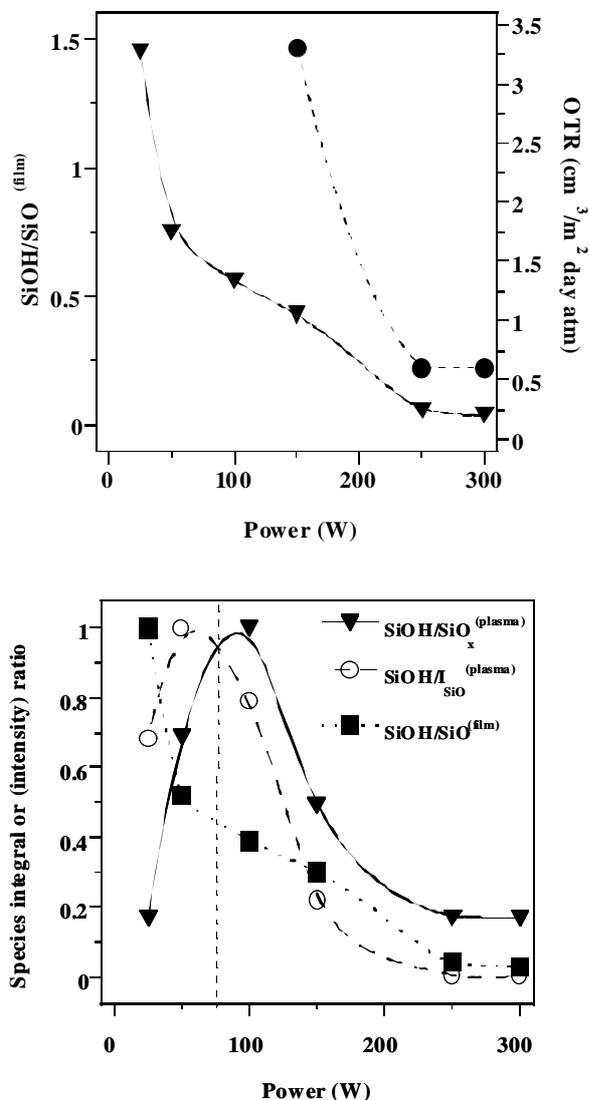


Figure 5 – Up: SiOH-to-SiO surface ratio (FTIR) of SiO<sub>x</sub> film and Oxygen Transmission Rate (OTR) of 12 μm PET coated with 500 Å SiO<sub>x</sub> as a function of RF power input. Down: Trends of (SiOH/SiO<sub>x</sub>)<sub>film</sub>, (SiOH/SiO<sub>x</sub>)<sub>plasma</sub>, and of the mixed IR visible parameter SiOH/SiO plasma, determined using IRAS for silanols and actinometry for SiO. All have a similar trend and all trends resembles those of high quality barrier films. All the trends can be used as in situ markers of high quality barrier films.[6]

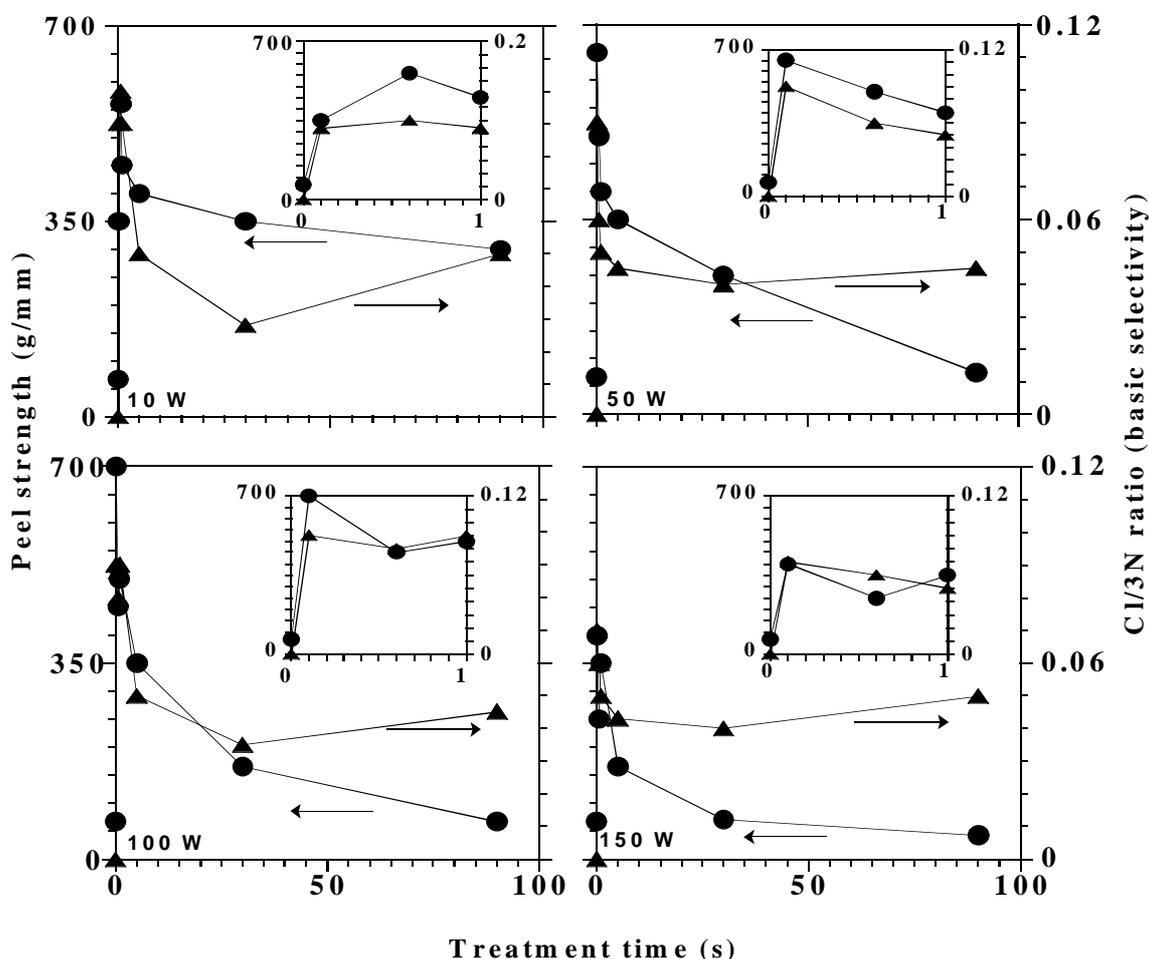


Figure 6 Comparison of Al-adhesion (peel strength of Al) to PET ammonia-treated in different power conditions, with the basic selectivity of N-grafted groups. Here the Lewis basic selectivity, shown as Cl/3N (see text) [7], has been measured by ESCA with a derivatization method sensitive to basic groups.. In this figure the treatment time range of 0.1-1 sec is enlarged in the insert in order to see what happens at very short times.

What it has been found, in fact, is that the lower is the number of grafted N-functionalities the higher will be their Lewis-basic character, which is the only important parameter to tightly bind Al atoms and/or clusters. This effect, which has been described as the “non hindered growth model of Al coating”, is clearly evidenced in figure 6, where the trends of Al-peel strengths and of the relative basic selectivity are plotted both as a function of the treatment times at various power inputs. It should be noticed that the basic selectivity of figure 6 is shown as the ESCA parameter Cl/3N. The chlorine revealed by XPS analyses arises after exposing the treated PET films to vapors of chloroform, CCl<sub>3</sub>-H, which has a Lewis acid character and acts as a differential marker of the basic strengths of the various N-groups. The parameter plotted is then rationed as Cl-to-3N to account for the fact that one basic

N-functionality eventually anchoring chloroform will be revealed by 3 Cl atoms.

From an inspection of figure 7 it appears that the trends of basic selectivity and peel strength are impressively equal up to about 30 sec TT. For longer TT a weak boundary layer is likely formed which reduces adhesion because Al is now attached to polymer fragments. The reader can refer to [7], where this point is explained in detail.

## 6. METAL CONTAINING COATINGS

Plasma deposited (Ag/PEO-like) Ag-containing Polyethyleneoxide-like films[8] are very interesting materials for their biological performances: they merge in fact the non fouling character of PEO films with the properties of silver.

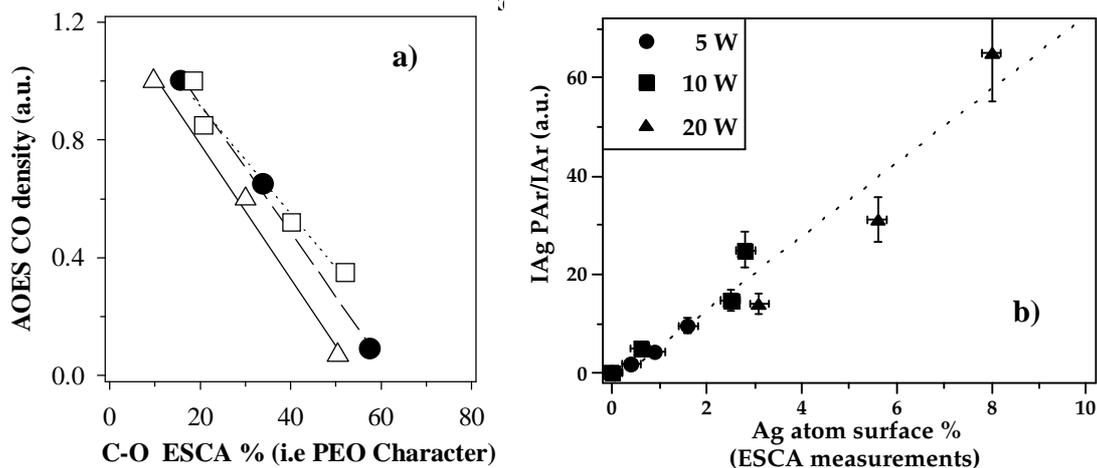


Figure 7 – (a) Actinometric trend of CO produced in the gas phase vs. the retention percentage of (CH<sub>2</sub>-CH<sub>2</sub>O) unit in Diglyme (black circles and white squares) and Triglyme (white triangles) fed glow discharges, with (white squares) and without (black circles and white triangles) Ag sputtering, during the deposition of PEO or Ag/PEO-like films. (b) Actinometric trend of Ag as a function of its incorporation in Ag/PEO-like coatings.

Such coatings can be deposited in RF glow discharges fed with vapor of diethyleneglycol-dimethyl-ether (or other glyme vapors) and argon, provided the cathode is covered with silver, in order to provide sputtered Ag.

If PEO-like films have high structure retention of the -CH<sub>2</sub>-CH<sub>2</sub>O- ethylene oxide unit, they can show non-fouling properties. We have shown that actinometric spectroscopy of CO and Ag allows an excellent and simple control knob for the composition of the composite material. Figure 7a shows that the actinometric trend of CO is inversely proportional to the structure retention of the (CH<sub>2</sub>-CH<sub>2</sub>O) unit. The higher is gas phase concentration of CO, in fact, the higher will be the monomer fragmentation and the lower will be the structure retention of the deposited material. Figure 7b, then, shows that actinometry of silver perfectly controls Ag-incorporation in the material, under all experimental conditions.

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