

Plasma Modification of Polymers

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Abstract

Plasma processes developed in our laboratory, of interest for biomaterials, barrier coatings for food packaging and corrosion protection, are briefly reviewed in this contribution. Particular attention is devoted to diagnostics aimed to rationalize plasma-surface interactions and to identify parameters and correlations to be utilized for process control.

Low pressure plasma techniques

Low-pressure plasma deposition, treatment and etching processes, when properly supported by plasma and surface diagnostic techniques, can be rationalized for fundamental studies and controlled at a molecular level, thus becoming powerful surface modification tools in a relevant number of applications. Among the features of plasma processes, most attractive for surface-modifying polymers, it is worth to mention: a) their ability of modifying *in continuo*, in a controlled and unique way, surface chemistry and properties of materials, with no change of the bulk; b) their intrinsic sterility; c) the possibility of scale-up processes to industrial sizes and throughputs, with a variety of substrates (webs, inside of tubes, fabrics, non woven materials and foams, lenses ...) of different shapes and nature; d) the environment friendly approach. Medicine and biology, for example exploit the capability of plasma processes of modifying the surface of biomedical polymers and tuning their surface properties in vascular prostheses, membranes and filters, intra-ocular and contact lenses, plastic wares, catheters, sensors, and other devices, as well as for sterilization.

Superhydrophobic and nanostructured coatings

Radiofrequency (RF, 13.56 MHz) glow discharges fed with tetrafluoroethylene (TFE, C₂F₄) modulated with duty cycles < 10%, and a total period of 100 ms, form thin highly fluorinated (F/C > 1.7) amorphous films, with crystalline ribbon-shaped structures superimposed. These Teflon-like ribbons are many microns long and tens of nanometers thick and exhibit spectacular hydrophobicity (water contact angles 160-175°). The gas phase diagnostics has been performed by IR absorption spectroscopy and time resolved emission spectroscopy during the time ON period, in order to evaluate the effect of CF₂ precursors in the plasma. The material characterization has been made by XPS, SEM, AFM and X-ray diffractometry [1, 2]. Figure 1 shows a typical SEM morphology of the nanosized m-long ribbons of crystalline Teflon-like.

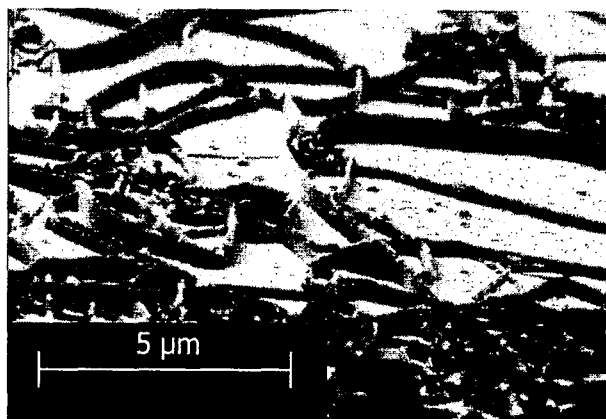


Figure 1 – Tens of nanometers thick, m long ribbons of highly fluorinated Teflon-like coatings obtained in modulated discharges fed with C_2F_4 with duty cycles <10%

Non fouling and bacterial resistant coatings, -COOH functional coatings

Polyethyleneoxide (PEO)-like coatings with non fouling properties for proteins, cells, bacteria, and biological systems in general can be deposited from continuous [3, 4] and modulated [5] PE-CVD processes fed with glycols (e.g. DEGDM or TEGDME, Di (tri) EthylGlycolDiMethyl Ether, $CH_3O(CH_2CH_2O)_nCH_3$, $n = 2/3$) or crown ethers, characterized by $-CH_2CH_2O-$ (EO) units in their structure. Mild fragmentation conditions allow to the fraction of intact EO moieties (PEO character) keep as high as possible in the coating, a feature which is correlated to non fouling properties. PEO character and non fouling properties are associated with the relative content of the ether groups (C1 component, ~ 286.5 eV of Binding Energy) in the C1s XPS signal, and can be quantified easily.

In a properly configured parallel plate reactor (asymmetric with a silver plate cathode), under certain conditions, it is possible [6] to couple the deposition of PEO-like coatings with the sputtering of Ag atoms. This way Ag/PEO-like coatings results, *i.e.* PEO-like coatings with embedded Ag clusters, which show marked bacterial resistant properties. This is an important feature for catheters and other devices, and is due to the leach of Ag^+ ions in wet conditions. PEO character and Ag content of PEO-like and Ag/PEO-like coatings are correlated with the actinometric densities of CO (which marks the fragmentation degree of the monomer) and of Ag atoms present in the plasma [6, 7]. This is a simple way to predict and control the composition of the coating by means of *in situ* spectroscopic control.

Glow discharges fed with vapors of acrylic acid (AA), or of other carboxylic compounds, deposit thin organic films (pdAA coatings) characterized by $-COOH$ and other oxygen-containing groups. Such functional coatings can be utilized in engineering biomedical surfaces to improve the spreading and growth of cells [8], and to immobilize biomolecules (enzymes, peptides, non thrombogenic, etc.) by means of “spacer arm” species [9] of a certain length, that keep them tethered at the surface with their biological activity unaltered.

The fragmentation of the monomer, as usual for organic species, is reflected in the composition of the coating, and has to be kept low when the retention of the monomer structure is requested (*e.g.* a high density of $-COOH$ groups in the coating). The surface density of $-COOH$ groups can be adjusted easily by tuning the experimental parameters under spectroscopic control of the plasma. As for PEO-like coatings, in fact, it has been found that surface density of $-COOH$ groups is well correlated with the actinometric plasma density of CO [7, 10], which can be considered a “marker” of AA fragmentation. When more CO is revealed in the plasma, a more intense fragmentation is experienced by AA, and the density of $-COOH$ groups in the coating is decreased.

Micro-patterning biomedical surfaces

Random and geometrical patterns (morphological, chemical domains) at micrometric and nanometric scales can be transferred onto biomedical polymers, since it is known their ability, in certain contexts, to drive the behaviour of cells in a number of interesting ways for fundamental and practical studies (biosensors, diagnostic kits, tissue engineering). Plasma processes have been recently utilized for this purpose, with the aim of driving the behaviour of cells (contact guidance) in tissue engineering. We have utilized different processes on substrates covered with “physical masks” [11] in order to transfer different geometrical chemical domains (*e.g.* tracks of cell-adhesive pdAA spaced with cell-repulsive PEO-like zones) in micro-patterns. This allows to alternate, at the micron scale, non fouling and cell adhesive zones, as shown in Fig. 2. Physical masks are micron-thick polymer or metal foils where holes of the proper size/shape are precisely drilled (*e.g.* by laser); when properly fixed onto the polymer under modification, and utilized with selected plasma treatment, etching or deposition processes, such masks allow to transfer thin films or grafted groups onto selected zones of flat polymer samples with a space resolution of a few microns. These features allows to design substrates with proper anisotropic tracks of living cells.

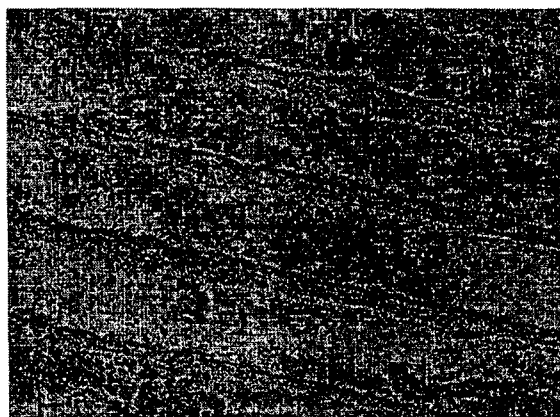


Figure 2. Alignment of 3T3 fibroblasts on micro-structured PS samples (cell-adhesive pdAA tracks about 30 μm wide, cell-repulsive PEO-like spaces).

Transparent Barrier Coatings: Food Packaging and Corrosion Protection

Thin (20 –50 nm) transparent SiO_x coatings are currently produced by packaging industries for increasing the gas-barrier performance of plastics (PET and polyolephins) towards O_2 , H_2O , and aromas. However, one of the main issues is that in commercial coaters, Gas Transmission Rates (GTR) measurements are not suitable to be performed *in situ* and requires measuring times of the orders of hours. The spectroscopic diagnostics of the plasma in this field can be used for an *in situ* control of the barrier properties, with clear advantages for the factory.

Our experiments onto HMDSO/ O_2 fed plasmas has been carried out coupling the investigation of the chemical-physical properties of the surface with that of the plasma phase, by means of actinometric OES and IR absorption spectroscopy (IRAS). It has been found that the plasma density of CH radicals and the ratio SiOH/SiO_x of the IR absorption bands integrals can act as process control parameters.

As shown in Fig. 3, up to medium-low permeability ($1-3 \text{ cm}^3\text{m}^{-2}\text{day}^{-1}\text{atm}^{-1}$) the CH actinometric density, which well correlates with the carbon content in the coating, can be used to monitor O_2 and Water Vapor transmission rates.

For a better control of the barrier properties of the coating, down to $0.3 \text{ cm}^3\text{m}^{-2}\text{day}^{-1}\text{atm}^{-1}$, when the carbon content is negligible (low Monomer/ O_2 ratio in the feed gas and/or high power), the CH actinometric density is not sensitive enough. In fact, in this case a main role is played by the silanol groups (SiOH) content in the coating, because this functional groups induce breaks in the silica network. In fig. 4 it can be observed that the OTR reduction is correlated to the SiOH/SiO_x IR absorption ratio in the plasma phase as well as to the same ratio determined in the coating.

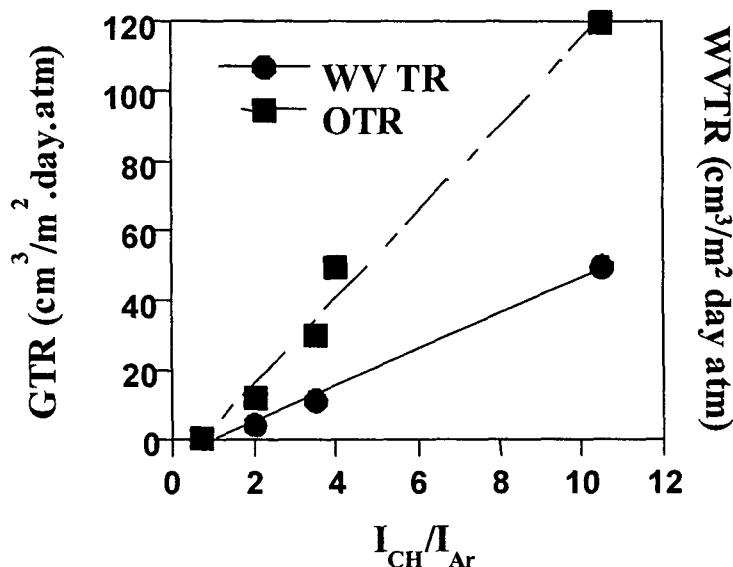


Figure 3 – GTR_{O_2} and WVTR of $12 \mu\text{m}$ PET coated with 500 \AA SiO_x as a function of the gas phase actinometric density of CH radicals [12].

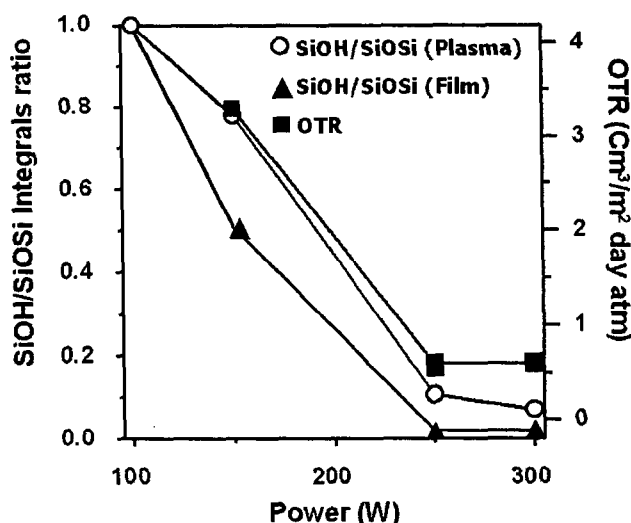


Figure 4 – Left axis: SiOH-to-SiOSi surface ratio (FTIR) of SiO_x film and of plasma phase; Right axis: Oxygen Transmission Rate (OTR) of $12 \mu\text{m}$ PET coated with 500 \AA SiO_x as a function of RF power input. All have a similar trend and all trends resembles those of high quality barrier films. [13]

The protection of metals from corrosion is a very important problem from the economical point of view and serious environmental concerns are involved. We have studied the plasma

deposition onto various metals and alloys from different organosilicon monomers in mixture with O₂ and Ar. In particular we have studied the corrosion protection of steel and magnesium, and the inhibition of tarnish phenomenon on silver (darkening of the surface exposed to sulfur containing compounds)[14]. In the case of Steel and Mg it has been found that pre-treating the surface with suitable plasma can improve the corrosion protection of several order of magnitude as shown in Table 1. In particular an O₂ plasma is effective as a pretreatment of steel surface, because of the removal of organic contaminants and of the oxidation of the iron. On the other hand, for magnesium protection, the H₂ plasma is the right one, because of the reduction of the porous oxidized native layer. Using similar SiO_x coatings and a H₂ plasma pretreatment has been found beneficial also in preventing the tarnishing of Silver alloys.

Table 1. Comparison between the best charge transfer resistance obtained with EIS on steel and Mg alloy as a function of the pretreatment. EIS measurements have been performed in 0.1 M Na₂SO₄ for steel and 0,1 M NaCl for Mg (1 h immersion).

	Untreated	SiO _x Coated	Pretreated and coated
Steel	250 Ω	1275 Ω (1300 nm)	2.2 MΩ
Magnesium	60 Ω	1150 Ω (2500 nm)	2.5 MΩ

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