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Trends in plasma applications

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Abstract

Plasma processing of materials are an innovative technology which is quickly developing and offers several opportunities in industrial sector like textiles, packaging, energy and biomedical. Plasma technology is a very efficient tool since it is able to produce chemically reactive environment in gas-phase, usually precluded to the usual wet chemistry. We will review results obtained in the recently instituted Center of Excellence PlasmaPrometeo aimed to the research, development and technological transfer in the field of plasmas. Research activity focuses on the development of suitable diagnostics of plasma processing, on modeling of plasmas and their interactions with material surfaces and on the development of new processes of surface modification and functionalization of polymeric materials. Advanced plasma diagnostics tools could be applied to study plasma processing and the interaction of plasma with material surfaces. Here we discuss results obtained in the characterization of atmospheric pressure discharges. In particular we presents results about the streamer regime of a dielectric barrier dicharge in a controlled high pressure gas mixture. Interesting features have been observed in the statistical properties displayed by this kind of intermittent discharges. Plasma modeling includes the development of numerical simulations aimed to the study of the evolution of the chemical kinetics of the plasma gas-phase in discharges at low pressure as well as at atmospheric pressure. We presents results concerning the simulation of streamer regime in dielectric barrier discharges and an analysis of the capability of spark discharges for the use as compact hydrogen reformer devices. The application of plasma processing in several industrial sector gets strongly enhanced whether it is possible to realize treatment of the materials at atmospheric pressure, avoiding the need of vacuum technology. Here we presents results concerning the functionalization of polymeric materials by means of atmospheric pressure plasmas. We discuss grafting processes on textiles and fibers aimed to achive specific surface properties like wettability and hydrorepellence. We presents also results about the deposition of polymeric thin films on material surfaces employing an atmospheric pressure discharge feeded with a suitable monomer vapour.

1. Introduction

Plasma applications are attracting a widening part of the research activity in this field of physics. Technology based on plasma processing spreads over many industrial sectors including flat display panels, lighting and material functionalization. This happens because of the plasma capability at the optical, physical and chemical modification of materials surface [1]. Plasma processing of materials can induce suitable surface modifications through plasma interactions leading to atom or chemical groups insertion (grafting), generation of free radicals (activation), deposition of polymers under shape of thin layers adherent to the surface (film deposition) or the ablation of the material surface (etching). Vacuum plasma processes have reached an advanced level both from the point of view of industrial applications and that of the understanding of the basic mechanism of the plasma-surface interactions.

Now a great interest is developing around atmospheric pressure plasma processes which offer the advantage to avoid the vacuum system and to decrease the time of treatment, simplifying the technological transfer where the processes of production are making in continous mode. A great interest is developing about experiments but also about diagnostics and modeling of the atmospheric pressure plasmas aimed to pursue the optimization of the processes [2-4].

One of the typical discharges employed in applications operating at high pressure is the dielectric barrier discharge (DBD) [5]. The main characteristic of a DBD device is the presence of a dielectric layer within the discharge gap (0.5-5 mm) insulating at least one of the electrodes. To sustain the discharge an AC voltage is applied to the electrodes at a frequency ranging from several hundreds of hertz to a few hundreds of kHz. In general the DBDs are of different types, depending on the experimental conditions; for a high value of the product $p \cdot d$ of gas pressure p and the gas gap width d, the discharge operates in a streamer regime leading to the formation of narrow discharge filament (with an electron density in the range 10^{12}-10^{17} cm^{-3}) of some nanoseconds duration [6]. In particular plane electrode DBDs at atmospheric pressure operates in streamers [6,7] or micro-discharges [8] regime, with current filaments appearing through the gap at seemingly random locations not exactly at the same time during each voltage cycle. However interesting results can be obtained also employing intermittent discharges where the current is not limited by the presence of a dielectric but by the power supply or by the external circuitry. Such discharges, sometimes classified as spark [6,9] lasts for longer times, but particular care should be used in order to prevent transition to arc or substantial heating of the gas and the materials in the discharge region.

Here we presents new results obtained at the PlasmaPrometeo Laboratories in Milan concerning the diagnostics and modeling of DBD and spark discharges as well as the plasmas processes suitable to induce useful surface modifications of materials like polymer films and textile fibers, employed in textile, packaging and energy industrial sectors [10] and in the processing of gas flows aimed to hydrogen reforming for energy production and VOC abatement.

2. Experimental setup and diagnostics

Our DBD reactor was developed to perform experiments in an isolated gas-phase at a fixed pressure under a controlled flow of gases and vapours. A detailed description can be found in an accompanying paper [11]. Here we presents only data needed for the subsequent description. The device is housed in a leak-proof chamber to allow evacuation before a controlled gas mixture is injected and a fixed flow can be maintained. DBD are driven by supplying an oscillating high voltage to two rod electrodes coated with alumina which are located at a small distance a large alumina coated stainless steel cylinder. coated by the same dielectric material (thickness 5 mm). The cylinder is grounded and it can rotate around its axis at a fixed rate. Materials in sheet form can be treated rolling on the cylinder and wrapping outside, otherwise small samples can be treated fixing them on the cylinder surface. Exposure time is determined by the rotating speed of the cylinder and by the number of rotations.

Spark discharges are produced between an hollow pin of tungsten, acting as cathode, and a surrounding coaxial cavity of copper [12,13]. A constant gas flow is feeded through the cavity and helps expanding the discharge region to the whole space. Sparks are produced by means of a high voltage DC generator setting a fixed mean current intensity value. The circuitry includes also an high power resistance which helps in controlling the electrical characteristics of the discharges. Indeed they inhibit the development of a burning DC arc [6] and the discharge assumes an intermittent character.

Both kind of discharges have been viewed through an optical fibre connection. Light emitted from the discharge is analysed in a low resolution spectrometer, to perform Optical Emission Spectroscopy, OES. This allows to gain insight on the composition of the produced gas-phase in the discharges. Electrical characteristics of those discharges have been measured with an high voltage, large bandwidth probe and with a suitable currant probe. For DBD the very short times involved lead us to employ a Rogoski coil current transducer [11,14], while for the spark device, we simply used a shunt resistance in series with the discharge, which was compared with the first probe and shown tom be sufficiently precise.

3. Chemical kinetics modeling

In order to understand the prevailing mechanism involved in the interaction of the plasma state with the surface of a material, it is very important to collect information about the composition and the evolution of the discharge gas-phase in both its charged and neutral components. To this purpose a quantitative understanding of the reactive species composition in the plasma phase can be achieved by studying the fundamental processes occurring during the generation of the plasma in a gas. Besides a more physical modeling needed to investigate the breakdown and the sustainement of the discharges, the composition and evolution of the gas-phase is dictated by chemical kinetics and diffusion processes. Since the time and space scales involved in the latter are quite different from those connected with the discharge formation and propagation it is worthy to implement simulations of the kinetics evolution, treating the formation of the plasma state in a simplified way [13,15]. Indeed, as stated already for the problems with the diagnostics, the basic difficulty in modeling discharges at atmospheric pressure is that

one must solve a strongly coupled set of non-linear differential equations which may be both spatially and temporally dependent. For instance the time scales in DBD spans over many orders of magnitude, from very short involved in streamer formation and propagation (ns) to the slower ones connected with ion recombination, chemical kinetics of neutral species and diffusion (up to ms). Operating conditions impose externally induced scales, like the periodicity of voltage oscillations (10-100 μs), the residence time in the discharge region induced by the hydrodynamical flows and the geometrical features of the discharge region.

Here we presents briefly the guide lines for the modeling of the chemical kinetics in a spark discharge of an argon/methane flow, in order to compare theoretical results from simulation and experimental results [13]. Electrical parameters of the experimental discharges have been used to set model parameters like the mean electron density and energy. In fact, spark electrons, at these high pressures, drift along the electric field with a velocity dictated by their mobility and almost instantaneously reach a mean energy determined by the local amplitude of the field. Neglecting diffusion along the flow, from the chemical kinetics point of view, the process can be approximated as a repetition of isolated discharges each concerning a limited fraction of the gas flow. This means that the spatio-temporal evolution of the gas-phase can be formulated, in the chemical engineering language, as a plug-flow reactor model [16]. Thus the time evolution of the concentration of the different N species in the gas phase is determined by integrating each balance equation for the density n_k of the k^{th} species:

$$\frac{dn_k}{dt} = v \cdot \frac{dn_k}{dz} = \sum_{i<j=1}^{N} K_{(i+j \rightarrow k)}\, n_i n_j - \sum_{i,j=1}^{N} K_{(k+i \rightarrow j)}\, n_k n_i + D_k \nabla^2 n_k + \sum_{h=1}^{N} \Gamma_{(h \rightarrow h(w) \rightarrow k)}\, n_h$$

where K are the reaction rates for the gas phase reactions, D_k are the diffusion coefficients, Γ are the effective rates for the surface processes (modeled as a chain of adsorption, reaction at the surface and desorption) and v is the velocity of the gas flow through the discharge cavity region. The choice of species included in the model was based on existing experimental information based on emission spectroscopy or mass spectroscopy and existing chemical kinetics modeling. The coupled system of differential equations has been integrated to obtain the time evolution by using an adaptive Runge-Kutta routine. Here we discuss only the prediction concerning the production of hydrogen, since they can be compared with results coming from OES diagnostics and mass spectroscopy of the outcoming flow [12]. Data refers to discharges of a 4% CH_4 mixture in argon at different values of the mean supplied current. In Fig. 1 is reported the prediction of the conversion efficiency (the ratio of H_2 produced respect to the total amount of hydrogen initially bonded to carbon in methane). It is in fair agreement with experimental findings concerning both the discharge (the intensity of the H_α emission line of hydrogen, which is connected with the dissociation degree of methane) ands the gas-phase composition (the hydrogen partial pressure measured in the outcoming flow sampled by a mass spectrometer).

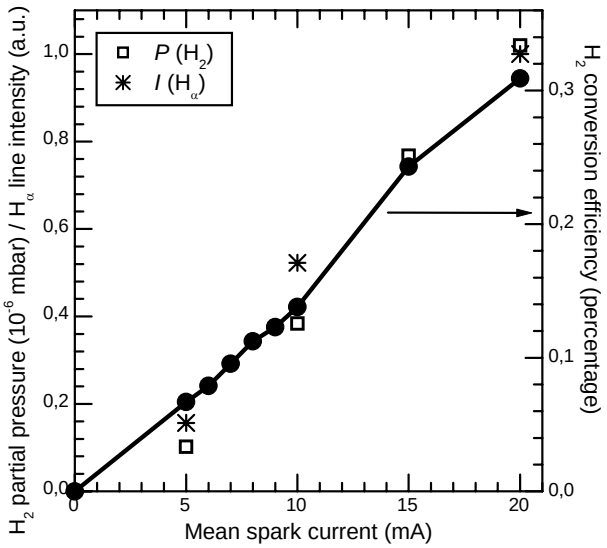

Fig. 1 - Prediction of the numerical simulations concerning the hydrogen efficiency of a spark discharge as a function of the mean current supplied. The trend reproduces the findings regarding OES of atomic hydrogen and mass-spectroscopy of the outcoming flow.

4. Plasma processing of materials

Here we presents a few examples of plasma processing based on atmospheric pressure discharges. The joint effort of suitable diagnostics and modeling of the devices performances and of the physical and chemical characterization of the induced surface modifications was a key point in the optimization of the results, in view of their effective applications.

As a first example we presents results obtained in the plasma treatment of leathers in order to increase their printability. Leathers are a generally a porous and hydrophobic substrate. Thus a dye containing solution does not spread on the surface and the dye is adsorbed in the depth. While this constitutes a disadvantage for leathers dyeing, it is obviously deathly for printing, since there the ink should appear and stay on the surface. This prevent direct printing on leathers and the only solution is to coat the surface with a suitable film which is printed instead of the leather. This however covers the porosity of the leather. Plasma processing is well suited for such an application, since the modification of the hydrophilic/hydrophobic character of a substrate depends mainly by the chemical groups and the morphology present on the surface, both properties that can be easily modified with plasmas.

We have studied treatment of leathers samples in atmospheric pressure plasmas, since this material is poorly compatible with vacuum [17] and the process should be integrated with the printing which is performed in open air. We have employed our DBD reactor and we observed that the wettability of leathers could be improved substantially by air plasma processing. This was observed as a strong reduction in the contact angle for

water droplets deposited on the surfaces and a decrease in the wetting and spreading times of the droplets.

Then we decided to apply this process to printability. Leather samples treated and not treated with plasmas have been printed. Quantitative analysis of the printed surfaces have been performed. All the printed samples have been scannered. The digital images have been printed again on a completely hydrophobic surface (cellulosic triacetate) and then analysed with a spectrophotometer to record the spectrum of the ink deposited on the surface. In Fig. 2 it is displayed the comparison of the recorded adsortion spectra.

An analysis with an optical microscopy of the ink droplets reveals that plasma treatment modify strongly the wettability properties of the surface and the ink is spread in larger spot on the surface. Nevertheless the substrate keeps on being porous, since part of the dye penetrates in the leather.

In the Tab. 1 it is reported the area of spectra in the region 350-700 nm, demonstrating the large increase of the treated samples which are comparable of that of a photographic film.

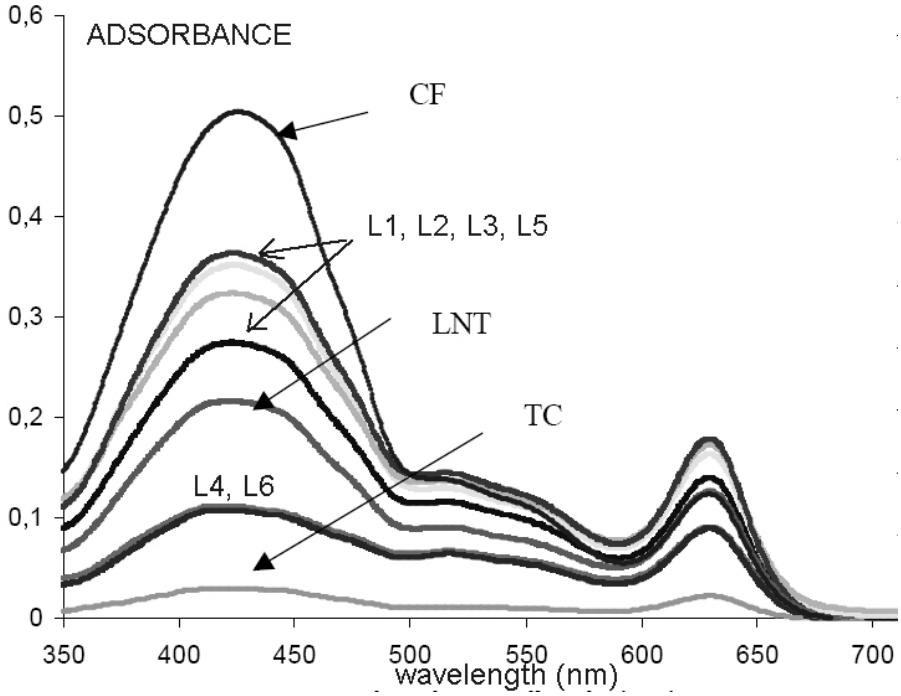

Fig. 2 - Adsorption spectra of the ink deposited on a hydrophobic surface from printout of the digitalized images of leathers treated with plasma and then printed.(CF is a photographic film, LNT the non treated sample, TC the completely hydrophobic triacetate).

Substrate	Photographic film (CF)	Cellulose Triacetate (TC)	Leather Not-treated	L1	L3	L5
Area	68.2	4.8	36.1	45.5	55.9	59.4

Tab. 1 - Relative area of the adsorption spectra of the ink deposited from printout of the digitalized images of leathers treated with plasma and then printed.(CF is a photographic film, LNT the non treated sample, TC the completely hydrophobic triacetate).

The second process that we have studied takes advantage by the capability of performing DBD in a controlled atmosphere. We have deposited hexamethyldisiloxane (HMDSO) films from a mixture of HMDSO vapour (at a fixed mass flow) and a flow of pure nitrogen. In the absence of oxygen, the organic groups of HMDSO does not gets oxidized and are retained partially in the polymer film. In this way very hydrophobic film have been deposited and used to improve properties of cellulosic materials like papers which could be used in packaging. In order to investigate the properties of the HMDSO deposited film, we have measured its infrared adsorption spectra. Measurements were performed on KBr tablets which were exposed to plasma together with PET and paper samples and FT-IRAS spectra of the deposited films were recorded. A typical spectrum of the deposit is shown in Fig. 3 According to literature [17-19] the stronger absorption band in the range 1000-1150 cm^{-1} can be assigned to the Si-O-Si asymmetric stretching mode. Other typical absorption bands can be assigned: the CH_3 symmetric bending in Si-CH_3 at 1260 cm^{-1}, the CH_x symmetric and asymmetric stretching at 2900-2960 cm^{-1}, the CH_3 rocking in Si-$(CH_3)_2$ at 800 cm^{-1} and the CH_3 rocking in Si-$(CH_3)_3$ at 840 cm^{-1} [12]. Bands at 800 cm^{-1}, 840 cm^{-1}, 1260 cm^{-1} and 2900-2960 cm^{-1} indicate retention of methyl group in the plasma deposit, a necessary condition for the creation of hydrophobic surfaces with HMDSO plasma.

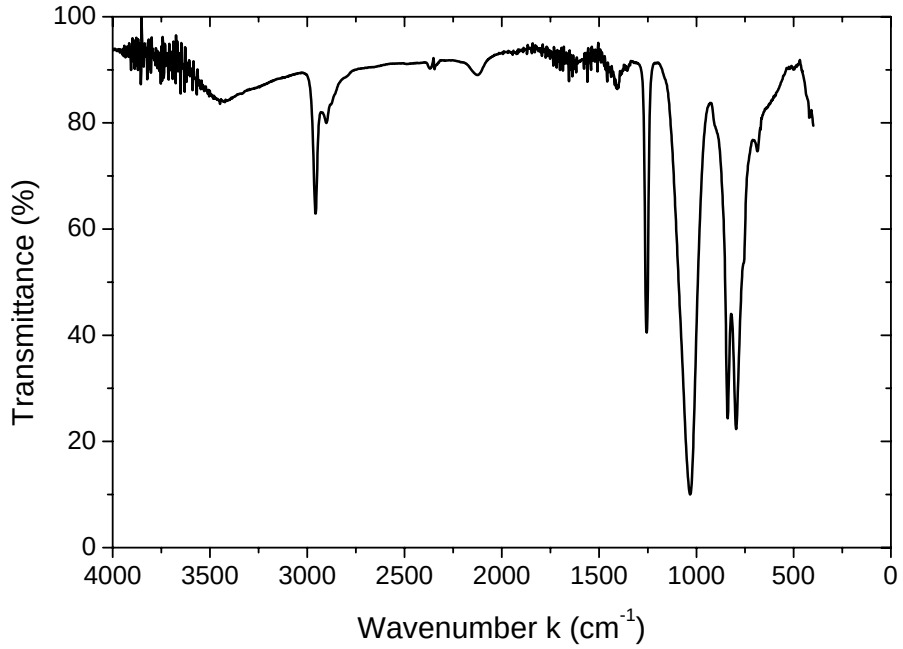

Fig. 3 - FT-IR spectra of the polymer film deposited on a KBr sample from an HMDSO/N2 plasma in a DBD reactor

In order to evaluate the effectiveness of the plasma processing we have studied the modification induced in the wettability of two kind of paper, one used specifically for packaging and the other an an absorbent paper (145.6 g m^{-2}) . We have measured the static contact angle of water droplets of 10 µl deposited on the treated surface. The

droplets have been observed through a calibrated telescope which was able to identify the droplet edge and to estimate the contact angle. Since measurements could be performed repeatedly and automatedly with fixed time step, it was possible also to estimate the adsorption rate (connected with the so called Cobb test [20]). Both are displayed in Fig. 4 and Fig.5 respectively as a function of the flowrate of HMDSO. It can be noted that, while the contact angle gets immediately very high and does not depend on the HMDSO concentration in the discharge, the adsorption rate is continuosly improved by increasing the amount of vapour.

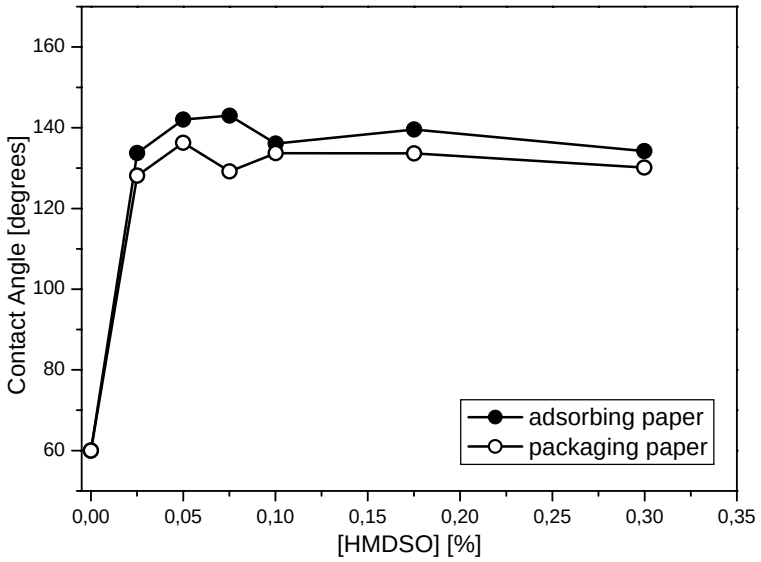

Fig. 4 - Contact angle measured for water droplets deposited on treated paper samples as a function of the HMDSO mass flow in the DBD plasmas

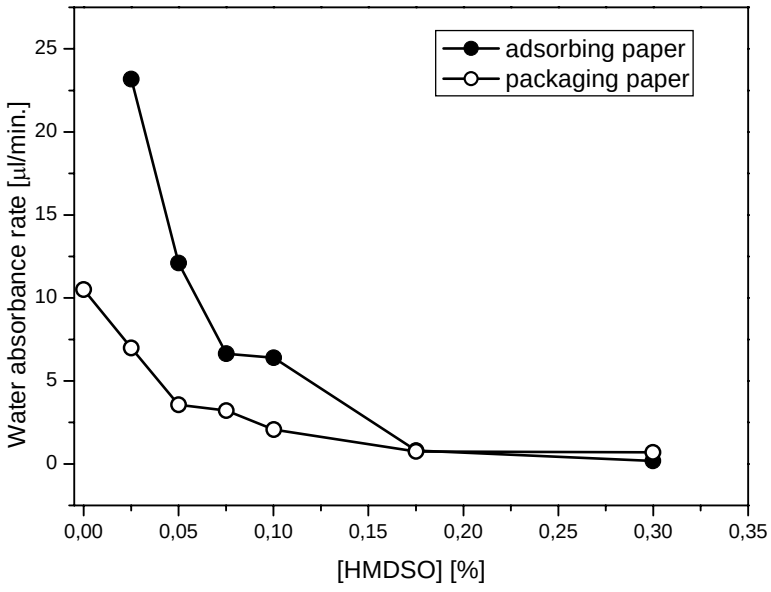

Fig. 5 - Water adsorption rate for water droplets deposited on treated paper samples as a function of the HMDSO mass flow in the DBD plasmas

5. Conclusions

We have presented a few results concerning the capabilities of the atmospheric pressure discharges in realizing plasma processing which could stand comparison with low pressure plasma treatment as well as traditional processes. This enforce the trend toward the tranfer of plasma applications towards atmospheric pressure plasma processes, which have several technological advantage, mainly when the processes of production are making in continous mode. A great interest is developing about experiments but also about diagnostics and modeling of the atmospheric pressure plasmas aimed to pursue the optimization of the processes. We have shown the results that suitable diagnostics could allow to get in order to investigate the mechanism operating during plasma interactions with material surfaces. We have also discussed the modification of a chemical kinetics modeling scheme of low-pressure discharges in order to simulate the evolution of the gas-phase in DBD and in spark discharges at atmospheric pressure. Also theoretical simulations could become an useful tool in order to study the applications of plasmas at atmospheric pressure in streamer regime, as in DBD and also in more peculiar devices like spark discharges which can be used for hydrogen production.

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