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# Material processing by atmospheric pressure plasma jets

## *In memory of Riccardo D'Agostino*

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### 1. Introduction

Plasma Enhanced Chemical Vapour Deposition (PECVD) processes have been used for decades for surface processing in a wide range of industrial applications like semiconductor films, low-k films, barrier diffusion. Thin film deposition is especially of high interest for biomedical applications for the production of protective coatings, adhesion layers, hydrophilic or hydrophobic layers. Up to now, beside DBD type treatment of textiles or food-dedicated films, most of used processes are usually realized at low pressure, as so many time beautifully reported by Riccardo D'Agostino and co-workers [1-3]. Actually, there is a great and increasing interest in the development of plasma sources operating at atmospheric pressure. In this talk, we will present results related with plasma polymerization, plasma deposition and plasma surface modification realized with an atmospheric pressure plasma jet (APPJ), the Plasma Gun developed at GREMI [4].

### 2. Polymer thin film deposition

The first part of this work deals with plasma polymerisation of TetraMethylDiSilOxane (TMDSO) (C<sub>4</sub>H<sub>14</sub>Si<sub>2</sub>O, 97%, Sigma Aldrich) with the AP-DBD Plasma Gun. Deposited layers are characterized by Fourier Transformed IR spectroscopy, FTIR, and contact angle measurements. The precursor used was introduced in either liquid or gaseous state. Depending on parameters like voltage, frequency, carrier gas and monomer injection, the deposited polymer appears either as a gel-like coating or a transparent film with fringes. The liquid flow rate was regulated by a peristaltic pump, while the

vapour flow was ensured by bubbling nitrogen or oxygen with a fixed flow rate of 10 sccm. Microscope slides and polished Silicon wafer (100) were used as substrates. The polymerized coatings have been obtained at frequencies between 500Hz and 4 kHz, for applied voltages between 14 and 20 kV and exposure times from 1 to 10 minutes. The deposition were realized with plasma tube edge-to-substrate distances ranging from 3 to 12 mm. Profilometer measurements revealed thicknesses comprised between 500 nm and 1.5 µm at the middle of the deposit. Deposited films analyses clearly show the efficiency of this atmospheric plasma-type TMDSO polymerisation and their similarity with those usually realized under low pressure RPECVD [5]. The most interesting deposited films are obtained when the monomer is introduced under gaseous state, the samples clearly showing a better homogeneity. The influence of the transport gas is not evidenced. It must be stressed that a multi-spot deposition has been obtained from plasma multi-jet delivered by a single Plasma Gun.

### 3. Surface modification

Ultra-high- molecular-weight polyethylene (UHMWPE) has been widely used because of its excellent mechanical properties but is often unsuitable for use due to its poor wettability. Plasma treatment enables the surface modification of polymers without affecting the bulk material characteristics. In the present work, the Plasma Gun (PG) was applied to improve the surface properties of UHMWPE films and HDPE tubes. Surface morphology and chemical compositions were performed by means of ATR-FTIR, AFM, XPS, and contact angle measurements with the

aim of understanding the surface modification effects. The single plasma jet covers only a few square millimeters, which makes it difficult for large-scale treatment of the film surface. To overcome this challenge, we have considered the use of Plasma Gun arrays consisting of many individual jets placed within close proximity of each other, such structure has a potential to greatly enhance the scale of surface treatment as compared to that of a single plasma jet. FTIR and XPS analyses, indicated that helium plasmas introduced mainly oxygen containing functional groups but also unsaturation has also been observed which has been reported to take place at the same time as surface crosslinking of the UHMWPE. The AFM observations show a surface smoothing with PG at different treatment frequencies. Furthermore, the stability of the surface properties of the UHMWPE was studied by the measure of the water contact angle. As shown in Figure 1, the samples treated at higher frequency were less prone to hydrophobic recovery. According to our results, plasma gun has a potential to enhance the surface activation of inner walls of tubes and UHMWPE films. This can be very interesting for biomedical applications such as tissue tolerable polymers, inner walls of vascular grafts and catheters.

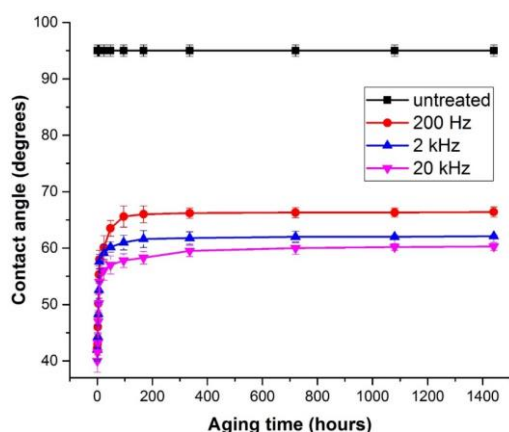


Fig. 1 UHMWPE contact angle: aging of plasma untreated and treated at different frequencies (12 kV, He flow 1 slm)

## 4. Conclusion

From the beginning, Riccardo D'Agostino has been one of the major player and expert in the domain of plasma processing of materials. He contributed to all the main scientific, technological and diagnostic [6] developments that led to the present status. He wrote with his team few of the founder papers including plasma etching [7], plasma deposition [1] and plasma functionalization.

In this talk, after few slides dedicated to Riccardo d'Agostino, and at the light of his inspiring work, we will present results on applications of atmospheric plasma jet material processing essentially dedicated to coating and functionalization. They show the great potential of APPJs in that domain that our recent development of large arrays of such systems clearly reinforce.

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