Topic number: 5.

DIAGNOSTICS AND APPLICATIONS OF HIGH FREQUENCY DISCHARGES IN BIOMEDICAL TREATMENTS AND TREATMENT OF TEXTILES

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One of the leading techniques for material engineering is plasma treatment, irreplaceable in fabrication of semiconductor devices, integrated circuits, optical devices and solar cells. Possibilities of plasma treatment surely do not end here. The choice of the plasma system used for treatment is usually guided by the kind of samples that are treated and effect these plasmas are intended to have on the samples. Interest in plasma treatment of biological and sensitive systems has grown recently.

Partly, the motivation is to develop new medical techniques as plasma offers some possibilities for inducing desired processes with minimum damage to the living tissue [1, 2, 3, 4]. The other related issue is the treatment of organic materials, such as textile fibers, which has become a technology in production in the last decade [5, 6]. Here we will present results obtained with several different plasma systems working in a wide range of pressures (from low pressure to atmospheric pressures).

In case of plasma treatment of textiles low pressure plasmas can be used and with appropriate choice of plasma system and regulation of optimum operating conditions (gas type, gas rate, pressure, power, exposure time) different plasma-chemical reactions and hence, desirable effects can be obtained. Research so far was focused on imparting the enhanced wettability, dyeability and printability as well as shrink-resistance and antipilling properties to wool fibers [6, 7].

Latest studies opened up some new perspectives to plasma that could be utilized for engineering of durable nanocomposite textile materials [8]. The modification of textile materials with TiO_2 NPs seems to be a viable alternative to conventional finishing processes since these nanoparticles in small quantities simultaneously provide good antibacterial, UV protective and self-cleaning properties. However, the lack of chemical bonding between hydrophobic polyester (PES) fibers and TiO_2 NPs makes the deposition of TiO_2 NPs onto PES fabrics highly challenging.

A capacitively coupled plasma (CCP) reactor designed to operate at a frequency of 13.56 MHz in a highly asymmetric mode was used for treatment of PES fabrics in order to facilitate the anchoring of metal and metal oxide nanoparticles (NPs). The aim of this study was to compare the potentials of extremely reactive oxygen and inert argon RF plasmas at low-pressure to activate the PES fiber surface and thus, enhance binding efficiency of the colloidal TiO_2 NPs. The UV blocking ability was evaluated and chemical changes on the surface of PES fibers induced by plasma treatment and deposition of TiO_2 NPs were analyzed by XPS.

Antibacterial activity of PES fabrics was tested against Gram-negative E. coli bacteria (see Figure 5.). We can see that both plasma treatments (in O_2 and Ar) improve significantly bactericidal properties of the PES fabrics. Even after washing, the treated PES fabrics with O_2 plasma are still highly efficient in killing bacteria. On the other hand, PES samples activated in Ar plasma lose significantly their bactericidal properties after washing.

Table 5. Antibacterial efficiency of PES fabrics loaded with TiO_2 NPs [Radetic submitted]

Sample	Initial number of bacterial colonies (CFU)	Number of bacterial colonies (CFU)	R, %
UPES		1.5×10^5	
UPES+TiO_2	3.7×10^5	1.3×10^4	91.3
UPES		9.0×10^4	
O_2PES+TiO_2	4.2×10^5	<10	99.9
UPES		1.2×10^4	
ArPES+TiO_2	3.6×10^5	<10	99.9
After washing			
UPES		9.0×10^4	
O_2PES+TiO_2	4.2×10^5	<10	99.9
UPES		1.9×10^4	
ArPES+TiO_2	6.5×10^5	3.6×10^2	98.1

Unlike textile samples which can undergo low pressures biological samples like mammal or plant cells have to be treated by plasmas that operate at atmospheric pressure. Desire to use plasma for in-vivo treatments have made several requirements for plasma sources to be met. On a plus side no expensive vacuum systems are needed, while on the other hand it is much more difficult to achieve non-equilibrium (non-thermal) mode of operation that is equally essential. Heat sensitivity of biomedical samples narrows the choice to non-thermal plasmas. There are many types of plasmas that can be generated under ambient pressure and temperature conditions suitable for treatment of sensitive samples [1, 2, 3].

Some of the plasma devices designed for in-vivo treatments are μ-APPJ and plasma needle which operate at 13.56 MHz at atmospheric pressure. Micro atmospheric plasma jet was developed by Schultz van der Gathen and coworkers [9] and this plasma source is interesting both for applications as well as for the study of fundamental processes. Diagnostics of this plasma system was made by using derivative probes in order to determine power transmitted to the plasma and the operation mode of the discharge [10]. Besides derivative probes we have used mass spectrometry in order to analyze plasma products formed by μ-APPJ [11].

Another plasma source that meets all the necessary conditions for treatment of organic materials and living tissues is plasma needle. Like in the case of μ-APPJ we have used derivative probes and mass/energy analyzer Hiden HPR60 in order to determine real applied power and the composition of the discharge, respectively.

Analysis of the composition of ions has several motivations, to check which species are formed in the discharge and thereby use that as a test of possible plasma chemical models, to identify which dissociation channels may contribute to production of some radicals, to check which ions may be used after acceleration to induce damage to the tissue and finally to have a basis to test the performance of the mass analyzer this time without the uncertainty induced by contribution of the ionizer to possible dissociation. It was found that predominant ions created by the plasma are O_2^+, O^+, H_3O^+, N_2^+, N^+, NO^+ [12].

When it comes to plasma treatment of samples of biological origin ions that are of interest are O^+, N^+ and NO^+ [see Fig. 1]. We can see that the most abundant ions created in the plasma are NO^+ ions which are believed to be the key factor in treatment of cells or tissues. This molecular ion is definitely the result of chemical reactions rather than ionization of NO, while both N^+ and O^+ may be created directly from the more abundant molecules in dissociative ionization.

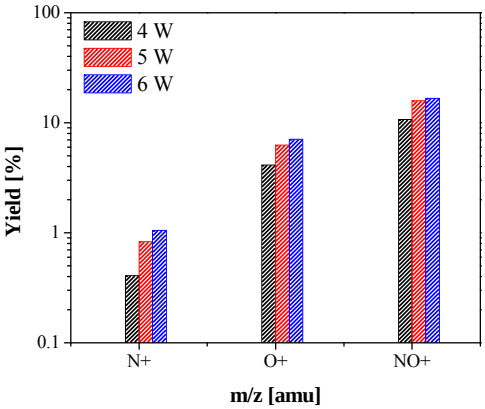

Fig. 1. Yields of N^+, O^+ and NO^+ ions created in the discharge for 3 different powers. Distance between the tip of the needle and the orifice of mass spectrometer was 1.5 mm while the flow of the buffer gas was 1 slm [12].

Plasma needle has been used to induce killing of *Streptococcus mutans* and *Escherichia coli* bacteria. Also, we have analyzed plasma interaction with normal, living cells and for these experiments we have used human peripheral blood mesenchymal stem cells (hPB-MSC), as a model system to predict the degree of possible damage to the cell responses [13].

Many factors are responsible for bacterial inactivation. Direct exposure of the bacterial samples to the plasma is always more effective than remote exposure. Although even in the cases of remote exposure significant killing can be obtained as well [14]. Another factor that determines the efficiency of the specific treatment is bacteria sample type [15]. All our samples were prepared as planktonic samples. These are liquid samples with inoculated bacteria, with varying concentrations of bacterial colony-forming units per ml (CFU/ml).

In Fig. 2 and 3 concentration of bacteria after treatment for two different treatment times (60 s and 120 s) are shown for several initial densities. From these figures one can conclude that the plasma created when the flow of buffer gas was 0.5 slm was more effective than in the case of He flow of 1 slm. It is important to note that for both flows of the buffer gas plasma did not make any effect on the bacteria count in the case of the highest initial concentration.

As far as plasma goes some further optimization may be made for localized accurate treatment of cells or sterilization. With good knowledge of the power deposited into the plasma, and control of radicals that are produced together with spatial emission profiles indicating changing of the regime of operation sufficient control of reproducibility of plasma needle operation is achieved. Other sources may be sought for more refined interaction with living cells.

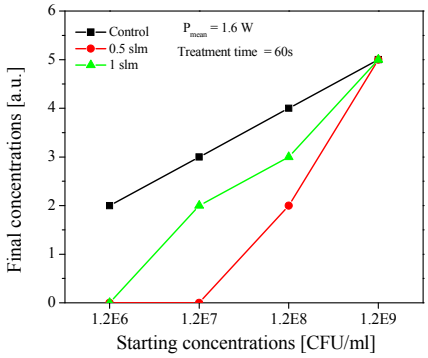

Fig. 2. Bacterial colonies *Staphylococcus aureus* after plasma treatment for two different gas flows. Treatment time was 60 s and applied power was 1.6 W [13].

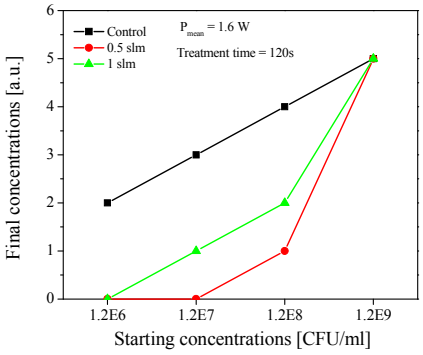

Fig. 3. Bacterial colonies Staphylococcus aureus after plasma treatment for two different gas flows. Treatment time was 120 s and applied power was 1.6 W [13].

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