STUDY OF POLYPROPYLENE NON-WOVEN FABRICS TREATMENT IN UNDERWATER ELECTRICAL DIAPHRAGM DISCHARGE

GABRIELA NEAGOE[a]*, ANTONÍN BRABLEC[a], JOZEF RÁHEĽ[a,b], PAVEL SLAVÍČEK[a], and MIROSLAV ZAHORAN[b]

[a] *Dep. of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic,* [b] *Dep. of Experimental Physics, Comenius University, Mlynská dolina F2, 84248 Bratislava, Slovak Republic*
gabriela.pirpiliu@yahoo.com

Introduction

Plasma treatment has an explosive increase in interest and use in industrial applications as for example in medical, biomedical, automobile, electronics, semiconductor and textile industry. A lot of intensive basic research has been performed in the last years, also in the field of textiles and technical textiles. This has resulted in an increasing knowledge of the possibilities of this process regarding demands as wettability, dyeability, printability, coating and washability of conventional and technical textile. All day problems of wettability and adhesion, together with the environmental driven forces have increased the interest of industry today. This delivers new materials with new possibilities, which opens perspectives to resolve production or even develop complete new applications.

Production problems are mainly caused by the substitution of the base material to new materials for example polymers, which have not the correct surface behavior for further processing.

Plasma treatment of textiles is becoming more and more popular as a surface modification technique. Plasma treatment changes the outermost layer of a material without interfering with the bulk properties. Textiles are several millimeters thick and need to be treated homogeneously throughout the entire thickness. It is known that hydroxyl radicals generated in low-pressure H_2O plasma may be used to incorporate hydroxyl functionality onto a polymer surface to increase their surface energy and reactivity. Underwater pulse diaphragm discharge is an effective tool in the production of hydrated electrons and hydroxyl radicals, which can be used for material surface modification (bondability, hydrophilicity, surface energy).

Preliminary results on physical characteristics of pulsed underwater diaphragm electrical discharge[1,2] have shown that the discharges burning in tap water, water-chelaton solutions, and some other water based solutions can be used as a potential atmospheric-pressure H_2O – plasma source for surface activation of various materials in the form of fabrics, films, fibers, etc. The discharge burning at atmospheric pressure can substitute low-pressure plasma sources[3–6] when atmospheric pressure on-line surface treatments of polymer products with the low added value in large amounts are required.

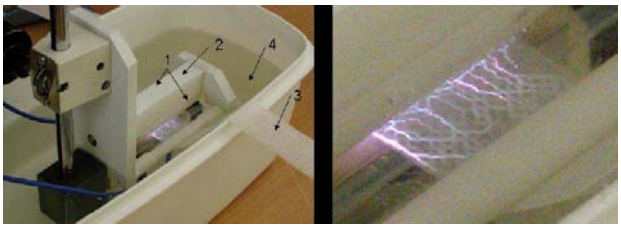

Fig. 1. **Experimental arrangement (left) for underwater diaphragm discharge:** 1 – electrodes; 2 – diaphragm; 3 – polypropylene nonwoven fabric; 4 – water-based solution. **A detail of the discharge treating the textile is also shown (right)**

Underwater pulsed corona discharges generated in liquid water matrix at atmospheric pressure have been demonstrated to be effective in the production of hydrated electrons and hydroxyl radicals[7–11,13,14]. Following the pioneering work of Clements et al.[7] on pulsed streamer corona generated using point-to-plane geometry of electrodes in water, various types of underwater electrical discharges producing hydrated electrons and hydroxyl radicals in liquid water-based media have been tested for the removal of low levels of non biodegradable organic pollutants from ground water and industrial waste water[14]. Very few results, however, have been published on interactions of the active species generated in pulsed electrical discharges in water with polymer materials[1,15,16]. Few applications are helpful for fixing metallic atoms on the polypropylene (PP) surface for metal coating.

In contrast to other types of underwater electrical discharges, in diaphragm electrical discharge the discharged plasma is in a direct contact with the metallic electrodes.

While in ref.[1] and ref.[2] the common features and chemical effects including promising application of this discharge for surface treatment of polymer materials are presented and discussed, the main object of the present paper is to report a more detailed study of the discharge physical properties. Using optical emission spectroscopy the electron number densities have been determined from broadening of hydrogen lines (H_α) *vs.* solution conductivity, frequency of high voltage pulses, speed of fiber movement for fixed applied voltage, length of the slit in dielectric diaphragm, and the diaphragm thickness.

Experiment

The H_2O-plasma treatment was performed using a diaphragm discharge apparatus illustrated by Fig. 1. The discharge was generated in a narrow slit of 0.1×1 mm positioned between two metallic electrodes at 2 cm mutual distance. Both electrodes and the slit (diaphragm) were immersed in water medium. Polypropylene nonwoven fabrics of 50 gsm and 30 mm width was fed trough the slit with an adjustable speed. The electrodes were connected to a pulsed HV power supply based on the double rotating spark gap. The maximum peak voltage was 40 kV DC. The maximum repetitive rate of pulses was 60 Hz. The duration of the electrical pulses was given by the water conductivity. Different water based media were used in this study: deionized water, Cu^{2+} solution with the concentration C = 0.0075 M of $Cu(NO_3)_2$. 3 H_2O; and

CO_2 saturated mineral water. Similar experiment was already realized in ref.[2].

Results and discussion

Initially the plasma starts within the air bubbles trapped inside the porous structure of nonwovens. After the air voids are filled with water a different discharge breakdown mechanism takes place. The high intensity electrical current flowing through the narrow slit is capable of initiating the water vaporization. The discharge starts in the water vapour bubbles created by that vaporization. The discharge manifests itself as thin plasma filaments propagating along the textile surface up to the distance where the metallic electrodes are positioned. The length of propagation is given by the conductivity of water solution and amplitude of the applied voltage.

Typical profiles of H_α are shown in Fig. 2a. To determine electron temperature and density the standard Griem's table (which takes into account the impact broadening by electron and quasi-static broadening by ions) of H_α line profile[17] and the procedure for data processing presented in ref.[1] were used. Note, that all profiles were symmetrical. In our case (rectangular discharge slit) the electron density changes from $1\cdot10^{22}$ m^{-3} to $2\cdot10^{24}$ m^{-3} while the electron temperature was practically constant $\approx 4\cdot10^4$ K in all experimental conditions studied. The same results were obtained as in the previous experiments (for diaphragm discharge). This is an interesting phenomenon and it means that comparable high density of electrons can be reached in the rectangular configuration. The error of the measured electron density was less than 5 %. The error of electron temperature was much higher, which is due to the weak dependence of the line profile on the electron temperature.

In Fig. 2b, the change of electron number density *vs.* conductivity of Cu^{2+} solution is presented. Taking into account the possible dispersion in the electron number density (for example, the corresponding error is always about 5 %), it

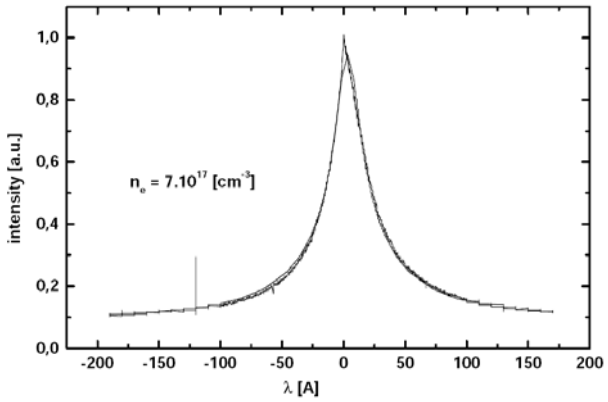

Fig. 2a. **The typical H_α line profile fitted with a model based on Stark broadening**

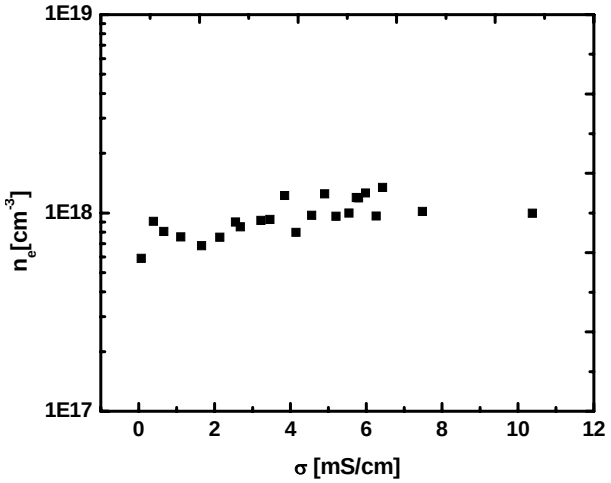

Fig. 2b. **The typical dependence of electron number density *vs.* conductivity for different Cu^{2+} solutions**

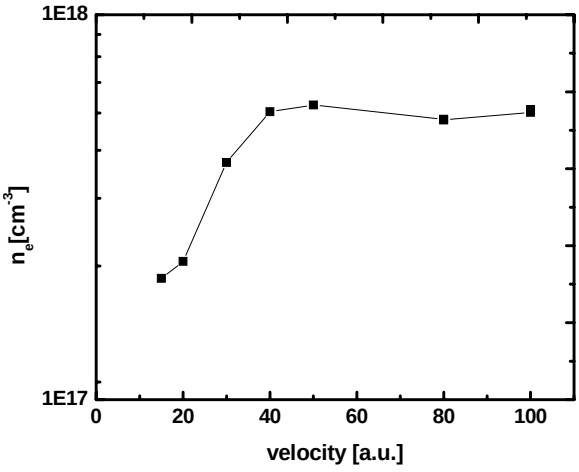

Fig. 3a. **The electron number density (n_e) *vs.* speed of the polypropylene nonwoven fabrics through the discharge for deionized water**

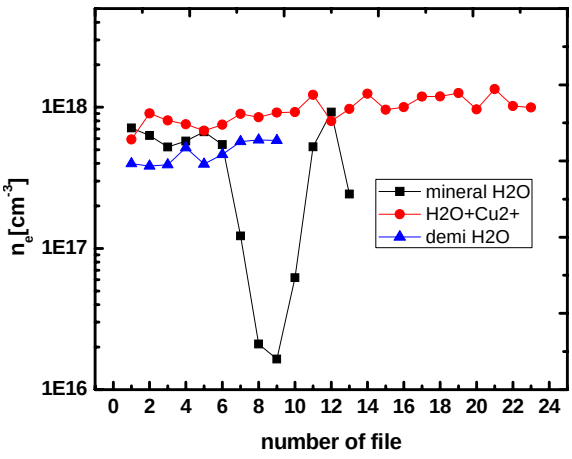

Fig. 3b. **Dispersion of n_e for different solutions during time interval of more than 1 hour is presented**

seems that the conductivity does not influence significantly the electron number density in the specified conductivity range.

In Fig. 3a, there is shown that the electron number density remains constant while the statistics presented in Fig. 3b demonstrate an interesting effect of CO_2 bubbles − the unexpected decrease of n_e in several cases. This phenomenon was also manifested on character of the discharge (suddenly, the intensity was higher, its colour became different). However, in this moment this is only a stochastic effect.

A practical application of diaphragm plasma treatment of PP is shown in Fig. 4a,b.

The textile was treated in water solution of Cu^{2+} in the same conditions as described above. The treatment was repeated after 1 minute on the same sample. Furthermore, we washed the sample in a detergent solution in Ultrasonic Bath for 15 minutes to see how much of copper attached to the textile material. The SEM photographs reveal a presence of copper microcrystals attached to the PP fabrics (Fig. 4a). More than 60 % of these crystals were still attached even after intense washing (Fig. 4b). This implies a strong chemical interaction between the crystals and PP. The chemical (copper) nature of crystal was confirmed by the EDX analysis of the sample. At this moment we are not able to confirm if the crystals are made from Cu only.

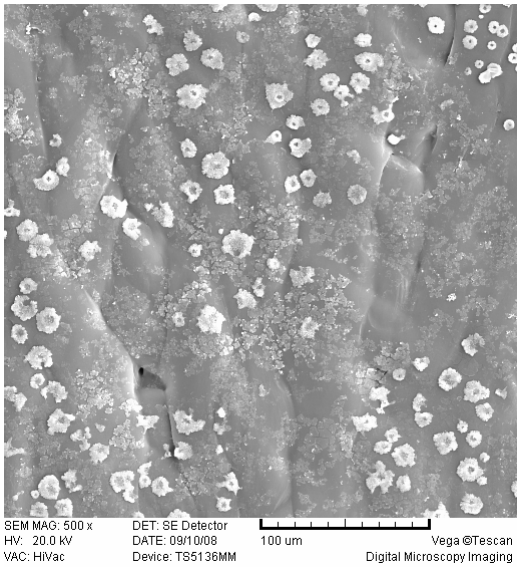

Fig. 4a. **SEM micrographs of textile surface treated twice in water solution of Cu^{2+} without washing**

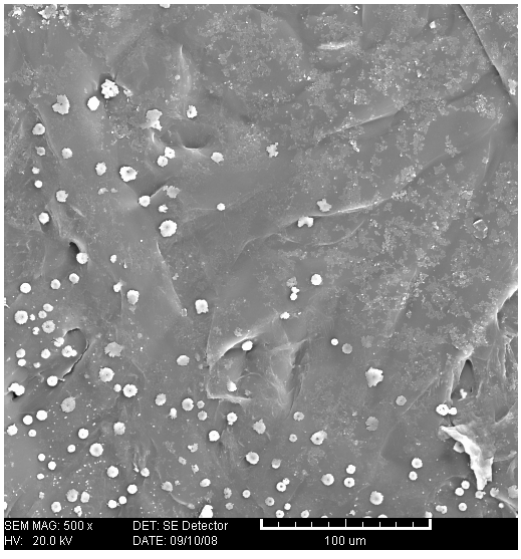

Fig. 4b. **SEM micrographs of textile surface. The textile was washed with detergent in Ultrasonic Bath for 15 minutes after double treatment**

Conclusion

The determination of n_e in case of selected quantities at optimized parameters show that their values do not influence significantly electron density and its fluctuation is almost covered with the confidence interval. It was found that the effect of CO_2 bubbles as well as the role of Cu^{2+} solution (or other metallic atoms) can bring interesting application. Further research is necessary in order to fully understand the influence of the double treatment and washing on the PP fiber and to compare these results with the case of single treatment applied to the PP fiber. By performing diaphragm plasma in the water solution of copper salt we were able to immobilize copper crystals on the PP surface.

This research has been supported by the Czech Science Foundation under the contract numbers KAN101630651 and 202/06/P337 and by the research intent MSM:0021622411 funding by the Ministry of Education of the Czech Republic.

REFERENCES

1. Brablec A., Slavicek P., Stahel P., Cizmar T., Trunec D., Simor M., Cernak M.: Czech. J. Phys. *52* Suppl. D491 (2002).
2. Simor M., Krump H., Hudec I., Rahel J., Brablec A., Cernak M.: Acta Physica Slovaca *54*, 43 (2004).
3. Chan C. M., Ko T. M., Hiraoka H.: Surf. Sci. Reports *24*, 1 (1996).
4. Okazaki S. : E.C. Chemical Co.,Ltd., JP 34425092 (1992).
5. Chou N. J. : US5, 019, 210 (1991).
6. Hayat U.: GB 9124467 (1993).
7. Clements J. S., Sato M., Davis R. H.: IEEE Trans. Ind. Appl. IA-23, 224 (1987).
8. Slobodskoi S. A. : Vopr. Technol. Ulavlivania i Pererab. Prod. Koksovania 71 (1978).
9. Sharma A. K., Locke B. R., Arce P., Finney W. C.: Hazardous Waste & Hazardous Materials *10*, 209 (1993).
10. Grimonpre D. R., Sharma A. K., Finney W. C., Locke B. R.: Chem. Eng. J. *82*, 189 (2001).
11. Lukes P.: *Ph.D. Thesis*, Prague 2001.
12. Sunka P., Clupek M., Lukes P., Simek M., Schmidt J., Cernak M.: Plasma Sources Sci. Technol. *8*, 258 (1999).

13. Sunka P., Babicky V., Clupek M., Kolacek K., Lukes P., Ripa M., Cernak M.: *In Proc. of 18th Symp. Plasma Physics and Technology, Prague, 1977*, 144 (1997).
14. Sunka P.: Phys. Plasmas *8*, 587 (2002).
15. Mikula M., Panak J., Dvonka V.: Plasma Sources Sci. Technol. *6*, 179 (1997).
16. Simor M., Cernak M., Krump H., Hudec J., Stefecka M.: *In Proc. of XXV Int. Conf. on Phenomena in Ionised Gases 4, Nagoya, 2001.* 63 (2001).
17. Griem H. R.: *Spectral line broadening by plasmas*. Academia Press, New York 1974.

G. Neagoe[a]*, A. Brablec[a], J. Ráhel[a,b], P. Slavíček[a], and M. Zahoran[b] *([a] Dep. of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic, [b] Dep. of Experimental Physics, Comenius University, Bratislava, Slovak Republic):* **Study of Polypropylene Nonwoven Fabrics Treatment in Underwater Electrical Diaphragm Discharge**

During the last two decades functionalization of polymer surfaces has been recognized as a valuable tool to improve their adhesion properties. Underwater pulse diaphragm discharge is an effective tool in the production of hydrated electrons and hydroxyl radicals, which can be used for material surface modification (bondability, hydrophilicity, surface energy). For efficient material treatment it is necessary to identify operational key parameters controlling the discharge plasma characteristics and to establish some appropriate diagnostic methods and models for plasma characterization. The plasma parameters – electron number density, temperature of electrons, excitation temperature, have been measured by optical emission spectroscopy completed by the voltage, and current measurement. The sampling optical fiber was installed directly in the slit to minimize the water absorption of light emission. The electron number density will be estimated preferable from spectral line profile of H_α. Our contribution will summarize the results of our experiments.