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Modification of Polypropylene Membrane by Ion Implantation and Plasma Treatment

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***Abstract* -**The influence of ion implantation on structure and properties of polymers is a very complex issue. Many physical and chemical processes taking place during modification must be taken into consideration. The complexity of the process may exert both positive and negative influence on the structure of the material. Hence, so important is a correct selection of the process parameters providing for the latter applications of modified materials. The goal of this paper is to investigate the influence of He^{+} implantation and plasma treatment on the properties of polypropylene membranes used in filtration processes and in consequence on fouling phenomena which are very undesirable in biomedical applications.

***Keywords*:** polymer membranes; polymer surface modification; ion implantation; plasma treatment

1. Introduction

The membrane separation methods (Ulbricht M., 2006) have been widely used recently in many branches of industry, e.g. chemical industry, food industry, environmental protection and many others. The main idea of these methods is to use the polymer (or, sometimes, ceramic or metal) membrane as a medium which allows some substances to pass while stops some others. The main advantages of this group of method is a possibility of separate very small compounds of the feed solution, e.g. colloidal particles, bacteria, macromolecules or even single ions. The serious problem concerning with the membrane separation is a phenomenon known as membrane fouling. It consists in adhesion of the feed solution compounds (particles or macromolecules) and thus the blocking of the membrane surface (Chang D.J. et al., 1995). That leads to the reduction of permeate flux and slowing down the filtration. There are many methods of the elimination or reduction of fouling. Last time, the most popular are the modifications of membrane surface i.e. by coating water-soluble polymers or charged surfactants onto the membrane surface (Jonsson A. et al., 1991), coating of hydrophilic polymers on the membrane (Jonsson A.et al., 1991) or grafting monomers to membranes by electron beam irradiation (Kim M. et al., 1991).

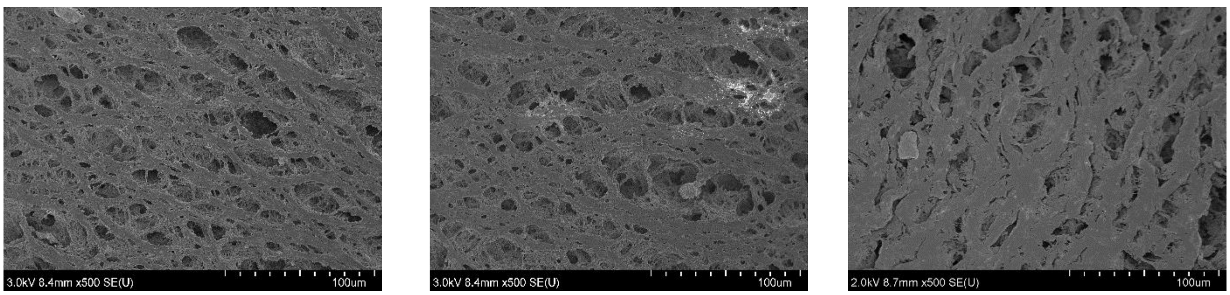
Ion implantation has found widespread application in the field of material engineering, beginning from the metal surface implantation for hardening and mechanical properties improving (Conrad J.R. et al., 1987). The process of high energy ion beam bombardment was carried out by implanter Balzers MPB 202RP. The incident energy of implantation and the ion dose were selected experimentally to achieve the most advantageous properties of membranes. The values of above mentioned parameters were equal, respectively, 30 keV and 1013 ions/cm2.

Plasma treatment of polymer membranes becomes an interesting issue for three reasons: the technique is fast, effective and meets ecological requests for clean technology. Hence, it is understandable why this method has gained an attention for the last decades and why it is still under successful development and evaluation in order to improve membrane properties. When plasma acts on the polymer membrane, two competing processes can take place: ablation and deposition (Bojarska M. et al., 2013). The modification process was conducted in a plasma reactor unit Dionex Series 2000 Plasma Processing Reactor Center. Plasma power 25 W and exposure time 180 s were used. Plasma modification was held in argon environment under pressure 3, 5 Pa.

2. Results and Discussion

2. 1. Morphology of the Modified -Polypropylene Membranes

The membrane morphologies were shown by SEM images as presented in Fig. 1. Membrane modified by plasma treatment (Fig. 1B) does not differ significantly from unmodified membrane (1A). We can observe polymer melting and pore decreasing. Moreover, it can be seen that implantation with helium ions (Fig. 1C) caused bigger polypropylene melting and pore decreasing. Presented results show that ion implantation is more invasive method of modification than plasma treatment.



A B C

Fig. 1. SEM images of top surface of unmodified membrane (A), plasma treatment, (B) and implantation with helium ions (C).

2. 2. Chemical Structures on Membrane Surface

The chemical changes in modified membranes were characterized by FTIR analysis. Fig. 2 presents the FTIR spectrum for unmodified polypropylene (PP) membrane, plasma modified membranes and ion implantation membranes. Comparing unmodified membrane and plasma modified membranes some changes might be observed. Firstly, peak responsible for C – H bond (3000 – 2800 cm^{-1}) decreases in comparison with unmodified membrane. This change may indicate that some new additional groups occurred. Also small “bump” is observed between 3500-3000 cm^{-1}, which is responsible for hydroxyl groups. In plasma modified membranes appeared another additional peak between 1760-1665 cm^{-1}, which is responsible for carbonyl groups. Presence of hydroxyl and carbonyl groups indicates that some carboxyl groups are present on the membrane surface.

In case of implanted membranes we can observe the rise of relatively weak maximum at wave number equal to 3500-3200 cm^{-1} which corresponding to hydroxyl groups. Other peaks which appear in the spectra C correspond to methyl groups (wave number 3000-2800 cm^{-1}) or carbon-carbon bonds (1680-1600 cm^{-1}). The appearance or growth of the number of these groups is the evidence that as an effect of ion bombardment the cross-linking and graphitization of outer layer of the PP membranes takes place.

2. 3. Hydrophilicity of Modified Membranes

The results of contact angle measurement showed that the base membrane had a contact angle of 134,9±5,0. The membrane modified with plasma and He+ ions the contact angles of 107,3±3,4, 114,6±1,2, respectively. Both modifications caused hydrophilicity increasing of the modified membranes. Based on results (Fig. 3), we can see that contact is lower for plasma treatment what can be connected with appearance of carboxyl groups. Moreover, higher hydrophilicity in case of ion implantation can may be caused by structure changes.

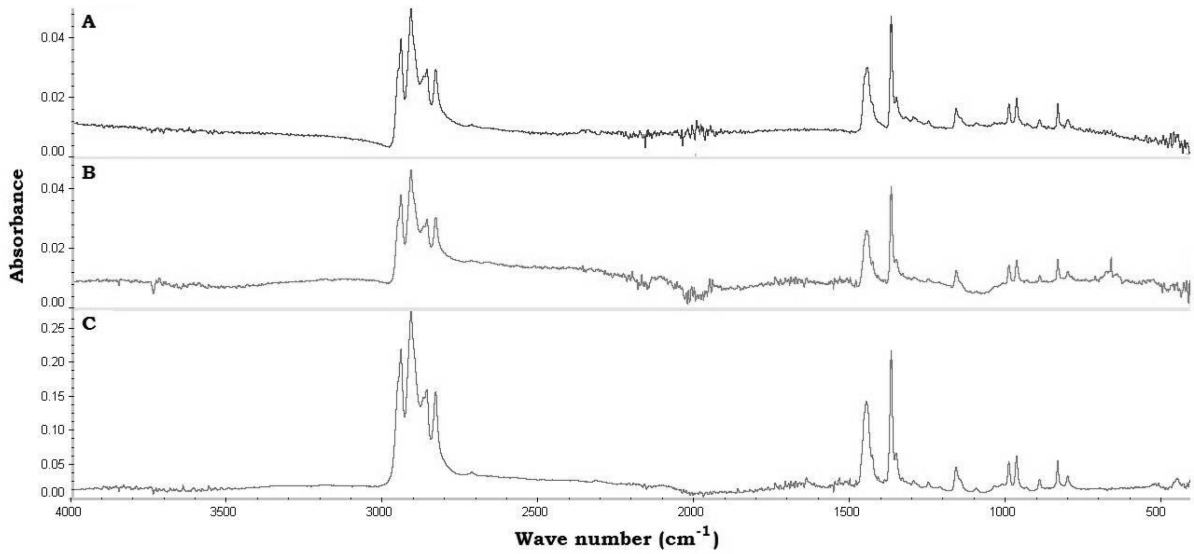


Fig. 2. FT-IR spectra for unmodified membrane (A), plasma treatment (B) and ion implantation (C).

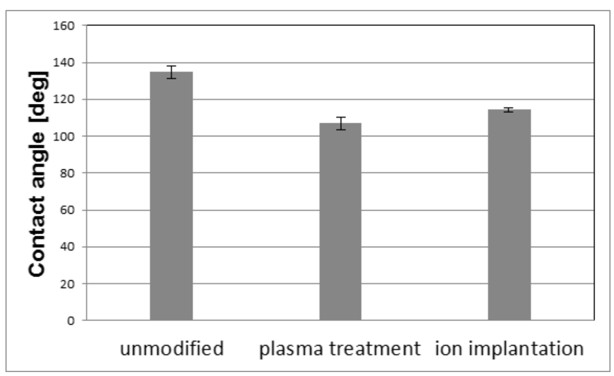


Fig. 3. Contact angle for unmodified membrane, plasma treatment and ion implantation.

2. 4. Protein Adsorption

Fig. 4 shows the results of static BSA adsorption on the membrane surface at pH 7.2. The results show that the base membrane adsorbs 13, 8 mg/cm^2. The membrane modified with plasma treatment and He^+ ions the BSA adsorption is 11, 6 mg/cm^2 and 22,4±3 mg/cm^2, respectively. It is apparent that the unmodified PP membrane has higher amount of BSA adsorption than the plasma modified membranes which is correlated with higher hydrophobicity of the modified membrane.

3. Conclusion

The ion implantation as well as the plasma treatment of the membranes cause melting of the membrane structure. The reason is that the energy of the both is very high. Besides the physical changes of the structure (melting) the modification of the chemical structure of polypropylene membrane has been signalized by the appearance of new peaks in the FTIR spectra. Both the modifications lead to the increase of the hydrophilicity of membranes but plasma treatment gives better results in this field. The protein adsorption after ion implantation is higher, despite the lower contact angle of membrane surface. This is probably the result of changes in the chemical structure of polypropylene and its surface activation. For the better understanding of the process and its influence on the polypropylene membrane structure it is necessary to execute experiments with extended range of the process parameters.

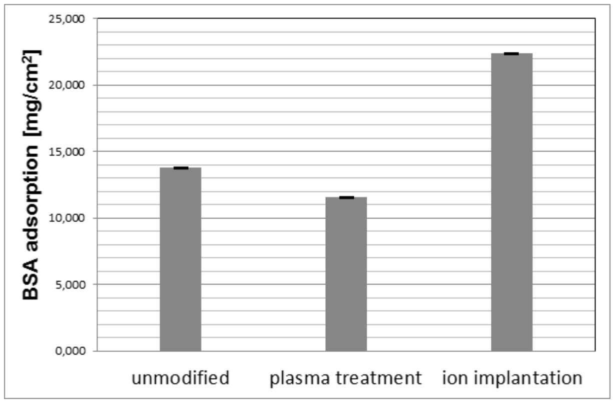


Fig. 4. The amount of BSA adsorbed on unmodified membrane, plasma treatment and ion implantation.

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