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CHEMICAL ACTIVATION OF POLYMER MICROFILTRATION MEMBRANES BY SURFACE ENGINEERING

Key words

Polymer membranes, plasma treatment, activation, functionalization.

Abstract

This paper presents the results of a chemical activation of polymer membranes obtained by plasma treatment. Plasma activation may be considered a final functionalization or as an intermediate step for chemical modification. Materials treated with argon plasma under different process conditions become less hydrophobic as a result of oxygen introduction into the activated chemical structure of polypropylene. The surface of activated polymer containing chemically bound oxygen is more reactive and susceptible for further functionalization, increasing the variety of potential applications.

Introduction

Research on surface functionalization technology (not only of membranes) is currently the leading problem in the field of utility materials. There are plenty of application possibilities for these types of materials, such as dressings and bacteriostatic clothes, polymer membranes for haemodialysis, and blood oxygenation, artificial blood vessels of anti-inflammatory properties,

photocatalytic membrane bioreactors, and many others [1, 2]. Properties of these polymers are acquired in the process of the physical implementation of additional functionalizing material. However, the study is focused on physical and chemical modification of the materials' surfaces altering their functionality [3, 6]. The main sources in the production of filtration membranes are polymers such as polyethylene and polypropylene, polyamide, as well as polysulfone [4]. Nowadays, the membrane should not only be a good selective barrier, but it is also expected to act as functional part of the system. It may be done by flame exposure, radiation, plasma, chemicals, photons, electrons, and ions [7]. One of the most significant methods in polymer functionalization is plasma treatment, which is highly reactive including its components such as ions and free radicals [3]. They are able to break energetic barriers of the reaction, which is essential to the activation of synthetic polymers.

During the process of surface activation, the material is bombarded with electrons, ions, and atoms as well as multi-atom molecules. As a result, the kinetic energy is transferred to the surface due to the interaction between ions and the surface. Ions play a major role in the process of plasma activation causing many phenomena (Fig.1).

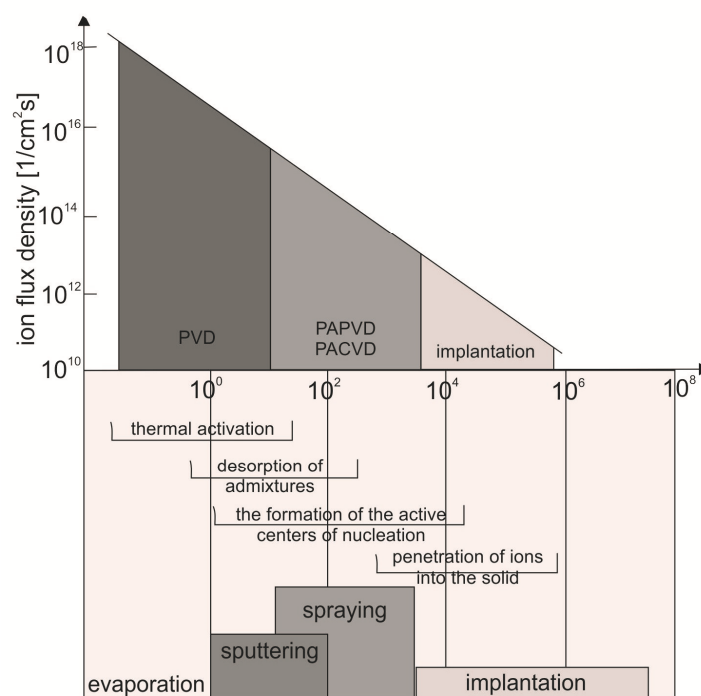


Fig. 1. The effect of ions energy on the processes occurring in the outer layer of activated material [8].

Ions with energy $W_j < 10$ eV are the part of plasma processes in which an activation is carried out on the isolated material immersed in the plasma (non-conductive material). In the case of ions with the energy of few electron volts, collision energy is transferred to the localized states of the electron and photon in the solid. Ions with energy of less than ten electron volts may cause a local increase in the temperature and an acceleration in the processes of chemisorption and desorption of the gas adsorbed on the surface that intensify the surface diffusion into the substrate [8]. The influence of these phenomena on the quality of material surface is time dependent. In order to assess the influence of variable process parameters, low temperature argon plasma was used for the functionalization of polypropylene membranes.

1. Materials and methods

During the study, capillary polypropylene microfiltration membranes with the outer diameter of 2.6 mm and average pores size of 0.2 μm were used. Experimental sets were based on argon plasma processing in variable conditions of power discharge and exposure time. The fundamental assumption of using argon plasma was to modify hydrocarbon chains onto material surface (especially external methyl and ethyl groups) in such a way that multiple bonds were enhanced. Moreover, due to the exposition of the activated surface to the ambient air, the increase in organic oxygen compound was expected. The scheme of the potential effects is depicted in Fig. 2.

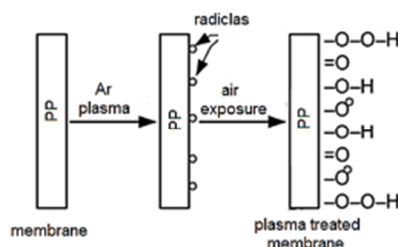


Fig. 2. Chemical changes on the polymer surface subjected to plasma argon activation and exposure to atmospheric air [6]

The plasma activation process was carried out in the commercial apparatus WU-2M. The table in the reactor chamber was polarized with negative voltage from an RF generator (radio frequency) in order to enhance the kinetic energy of ions. The temperature did not exceed 100°C to avoid thermal degradation of polypropylene. The first set of experiments was performed in order to assess the influence of the exposure time to the properties of PP with a constant discharge power. In the second set of experiments, the time of the process was set to 3.5 min, where the highest intensity of changes was observed. The range of process parameters are shown below in Tables 1 and 2.

Table 1. Technological parameters of argon plasma activation (various process time)

No.	Voltage U_{bias} [V]	Pressure in the vacuum chamberp [mbar]	Process atmosphere	Time t [min]	Discharge power [W]
1	-100	5.0×10^{-3}	100% Ar	3.5	50
2	-100	5.0×10^{-3}	100% Ar	5	50
3	-100	5.0×10^{-3}	100% Ar	10	50
4	-100	5.0×10^{-3}	100% Ar	15	50
5	-100	5.0×10^{-3}	100% Ar	20	50

Table 2. Technological parameters of argon plasma activation (various reactor power)

No.	Voltage U_{bias} [V]	Pressure in the vacuum chamberp [mbar]	Process atmosphere	Time t [min]	Discharge power [W]
1	-100	5.0×10^{-3}	100% Ar	3.5	50
2	-100	5.0×10^{-3}	100% Ar	3.5	100
3	-100	5.0×10^{-3}	100% Ar	3.5	200

Changes in material properties at the chemical level were analysed by the FTIR technique using Jasco FT/IR – 6200 with a single beam adapter by PIKE. Membrane samples (5 mm in length) were pressed to a crystal using a built-in handle. Each time the crystal was wiped with acetone. Once it dried, the spectral background was determined. The spectral background was generated in the range of wave numbers between 4000 and 600 cm^{-1} , 30 scans, data acquisition % T, resolution 4 cm^{-1} with a TGS detector.

Alterations of chemical properties of the surface may have a great impact on the change in surface energy. In order to demonstrate this fact, the contact angle was measured. For this purpose, a Kruss K121 apparatus was used. Surface tension of the samples (about 10 mm in length) towards water was determined using the Wilhelmy method. Ten measurements were performed for each type of material, and then the arithmetic mean was calculated. Furthermore, the microscopic images of samples were captured using a Hitachi TM3000. Taking into account the fact that PP is nonconductive (dielectric), the samples were

coated with gold and attached to the microscope table using conductive copper tape.

2. Results and discussion

The first step of the research involved the assessment of plasma processing time on the properties of PP membrane surface. Membranes subjected to plasma treatment did not visually differ from non-modified samples. Microscopic images revealed only slight changes in the appearance of outer polymer layers. The longer the time of process, the greater were the changes in the image.

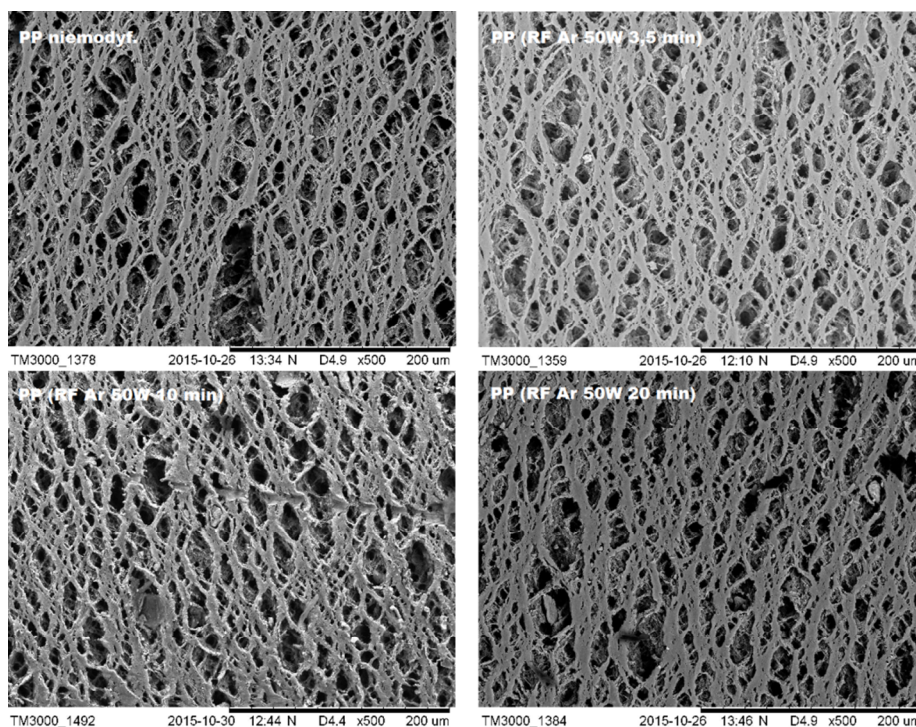


Fig. 3. SEM Scans of the of membrane samples after non-metallic plasma processing at different exposure times

The amount of thin structures in the material decreased and the wider ones emerged. Probably it was a result of crosslinking on the surface caused by reactive plasma components or a local increase in the temperature above 120–155°C (softening temperature of PP).

Thorough analysis of FTIR spectra of the samples after plasma activation and exposure to atmospheric oxygen revealed a lower intensity of typical signals for tested material (1376–1457 cm^{-1} , 2033–2161 cm^{-1} and 2918–2950 cm^{-1})

proportional to the length of plasma processing. Simultaneously, the signals at the wave number of 1646 cm^{-1} (Fig. 4) as well as small changes in the range of $3200\text{--}3400\text{ cm}^{-1}$ were noticed, which means an increase in carbon-carbon double bonds and possible hydrogen-oxygen bonds.

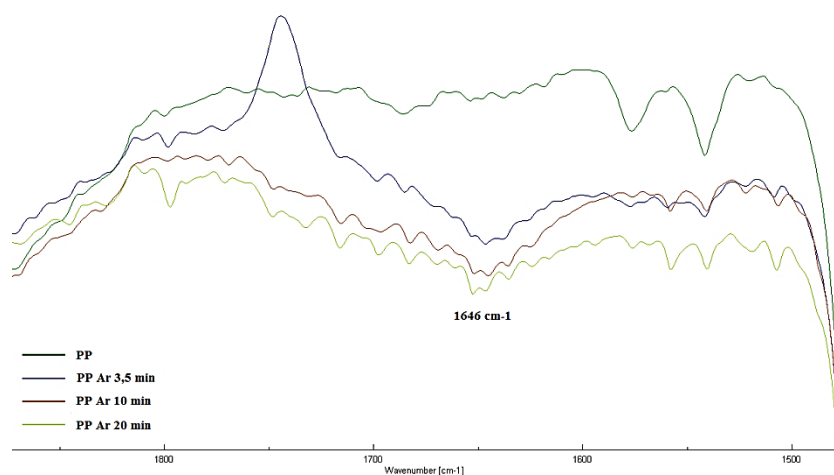


Fig. 4. FTIR spectrum of the region corresponding to C-C bonds

Double bonds are formed as a result of the sharing electron pairs of adjacent carbon atoms lacking some substitutes in the plasma process. Signals derived from carbon-oxygen-hydrogen might display a free radical characteristic of the reaction with oxygen that is carried out during aeration of the reactor chamber. Hydrophobic polymer chemical groups containing oxygen might improve the wetting of the surface. This fact finds the confirmation in wetting measurements in Table 3.

Table 3. Measurements of the contact angle for samples modified by non-metallic plasma within different exposure times

Sample	Contact angle
PP (unmodified)	$\sim 127^\circ$
PP-Ar ⁺ 3.5 min.	$\sim 81.5^\circ$
PP-Ar ⁺ 10 min.	$\sim 81.6^\circ$
PP-Ar ⁺ 20 min.	$\sim 81.9^\circ$

It was observed that argon plasma contributes to increased wetting. The strongest effect was detected after the shortest process. Further lengthening the time of process does not reveal any significant changes (results on measurement error border). These observations might bear out the assumption that the longer

processes cause a gain in the intensity of surface cross-linking and a greater share of nonpolar chemical groups. Therefore, the time process of 3.5 min was considered as optimal and accepted as a constant parameter in a further study described below.

The next set of experiments involved analyses of the impact of process power on PP membrane properties occurring within 3.5 min. The microscopic images below (Fig. 5) reveal great alterations in the structure of polymer outer layers of membranes that intensify with increasing discharges powers. It was observed that the amount of subtle material structures decreases according to the power level. This is considered the effect of a local increase in the temperature of the sample and cross-linking phenomenon.

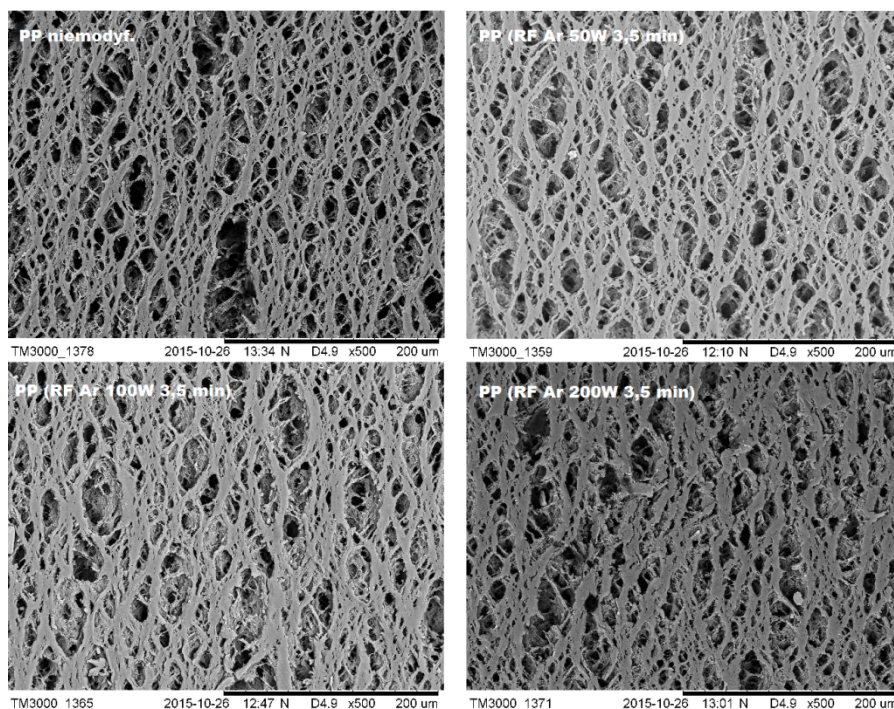


Fig. 5. SEM images of membrane samples after processing in non-metallic plasma with different powers supplied to the reactor

Analysis of FTIR spectra showed a reduction in the intensity of typical signals for polymers with the following range of wave numbers $1376\text{--}1457\text{ cm}^{-1}$, $2033\text{--}2161\text{ cm}^{-1}$ and $2918\text{--}2950\text{ cm}^{-1}$, which were proportional to the power of plasma treatment. In this case, it was observed that signals around a wave number of 1646 cm^{-1} (Fig. 6) and slight changes in the range of $3200\text{--}3400\text{ cm}^{-1}$ meant a greater contribution of double carbon-carbon bonds as well as the formation of hydrogen-oxygen bonds.

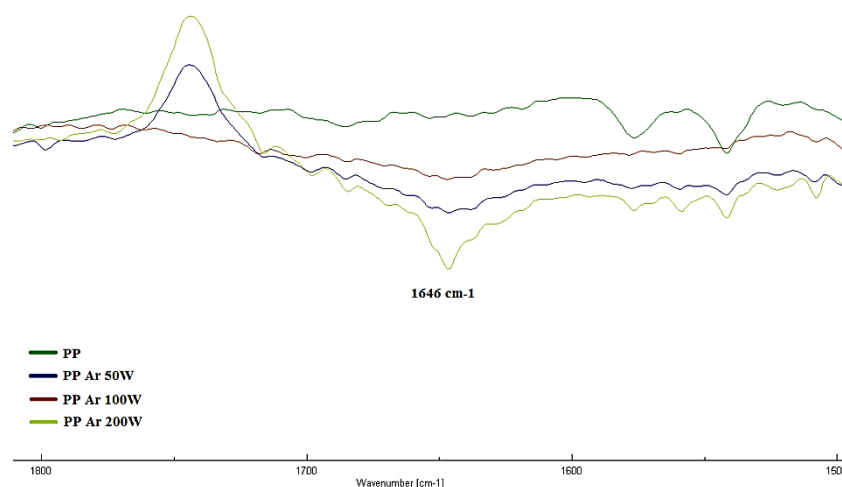


Fig. 6. FTIR spectra in the range of signal characteristics for double carbon-carbon bonds

It is noteworthy that the greatest increase of signals for those chemical bonds occurred in the power range of 50 W. The wetting of polymer samples was also examined concerning changes in contact angle (Table 4).

Table 4. Measurements of the contact angle for samples modified by non-metallic plasma within different process powers

Sample	Contact angle
PP (unmodified)	~127.2°
PP-Ar ⁺ 50 W/3.5 min.	~81.5°
PP-Ar ⁺ 100 W/3.5 min.	~84.9°
PP-Ar ⁺ 200 W/3.5 min.	~85.8°

The most desirable changes of wettability occurred within the lowest power level ($P = 50 \text{ W}$). The higher the value of discharge power, the weaker is the influence on the wettability (higher contact angles).

3. Summary

Results of the experiments indicate significant changes in the properties of polypropylene membranes treated with argon plasma. As a result of the process, the membranes with a higher contribution of double carbon-carbon bonds and chemically enriched with oxygen were obtained. It was observed that the most beneficial changes occur mainly in mild process conditions (low power discharge and short exposure time). Surface alterations affected the chemical reactivity of polypropylene via opening new possibilities for the functionalization in either the material itself or filtration membranes made of

such materials. Commercially available, low-cost products were used for processing, which makes the process highly value-added. When taking into account that the membranes maintain prime process parameters, it is possible to apply them in the same applications without any considerable alteration in technological set-ups.

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Aktywacja polimerowych membran mikrofiltracyjnych plazmowymi metodami inżynierii powierzchni

Słowa kluczowe

Membrany polimerowe, aktywacja plazmowa, PVD, funkcjonalizacja.

Streszczenie

W artykule przedstawiono rezultaty prac eksperymentalnych nad plazmową obróbką polipropylenu ukierunkowaną na jego właściwą modyfikację lub wstępną aktywację w procesach funkcjonalizacji membran polimerowych. Zastosowanie plazmy pozwala kształtować cechy materiałów w sposób szybki, ekonomiczny i przyjazny środowisku, a wprowadzone zmiany mają wysoki potencjał aplikacyjny. W rezultacie obróbki polipropylenu plazmą argonową wywołano wzrost hydrofilowości powierzchni pierwotnie apolarnego polimeru, będący efektem wzrostu udziału powierzchniowych grup tlenoorganicznych. Dzięki temu zwiększa się ogólna reaktywność chemiczna materiału i tym samym zakres możliwości dalszych modyfikacji. Prowadzone procesy obróbki nie spowodowały radykalnych zmian w obrazach mikroskopowych badanych obiektów, co pozwala przypuszczać, że nie uległy pogorszeniu ich pierwotne cechy aplikacyjne.