

Modification of polysulfone porous hollow fiber membranes by air plasma treatment

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Abstract. Air plasma treatment was used to enhance the surface hydrophilic properties of the polysulfone porous hollow fiber membranes prepared via a dry-wet phase inversion technique in the free spinning mode in air. Membranes prepared had porous asymmetric structure with macroporous support on the shell side and fine-porous selective layer on the lumen side. The wettability of the inner membrane surfaces were checked by contact angle measurements and FTIR was used to compare the surfaces before and after plasma treatment. Membrane morphology was examined with confocal scanning laser microscopy (CSLM). Contact angle measurements confirm that air plasma treatment affords improvement in the wettability of polysulfone membranes and FTIR results show that air plasmas chemically modify the lumen side membrane surface, however, there is no significant change in membranes chemical structure after modification. CSLM data obtained, as well as gas permeability (He and CO₂) measurements show that after plasma treatment pore etching occurs.

1. Introduction

Polysulfone (PSf) is an important material in the field of polymeric membranes because of its mechanical, thermal and chemical stability as well as its excellent film forming properties. It is used in different morphologies, such as flat sheet or hollow fiber membranes, primarily for microfiltration and ultrafiltration separation applications [1].

Modified PSf membranes can be obtained in different ways. One applicable option is adding modifying macromolecules [2] or carbon nanotubes [3], in the polymer dope solution as an additive. By using interfacial polymerization method, polymers could be coated onto PSf membranes [4, 5], and the polymerization occurs at the membrane surface and pore surface.

Low-temperature plasma treatment with non-polymer-forming gases has been used in the last years as a useful tool to modify the surface properties of different materials, including PSf porous membranes [6-14]. This technique is more useful and effective than most chemical and thermal



methods. The active species generated in plasma can activate the upper molecular layers on the surface, thus improving wettability or adhesion without affecting the bulk of the polymer.

Three basic phenomena affecting porous membrane properties can take place in plasma using non-polymer-forming gases [14]: etching and reactions giving volatile products result in increase of pore diameter and porosity; modification of the chemical structure of the surface layer, giving hydrophilization or hydrophobization, depending on plasma conditions; deposition of polymer film made of volatile products that come from the etched surface, which can result in lower porosity. In this study, the air plasma modification of porous asymmetric PSf hollow fiber membrane surfaces has been investigated using confocal scanning laser microscopy (CSLM), IR spectroscopy, contact angle and gas permeability measurements.

2. Experimental

Porous asymmetric PSf hollow fiber membranes were the object of research. Membranes were prepared via a dry-wet phase inversion technique in the free spinning mode in air when bore fluid was brought into liquid polymer solution orifice. Membranes prepared had porous asymmetric structure with macroporous support on the shell side and fine selective layer on the lumen side.

For hollow fiber low-temperature non-equilibrium plasma modification the following experimental setup was used. It includes high frequency generator (HF generator), vacuum chamber, filling gas feed system, high voltage rectifier, high frequency plasma torch (a device for high frequency capacitive discharge generation) and control equipment.

Device for high frequency gas discharge (Fig. 1) is a dielectric gas-filled camera close to dielectric stand-by with two parallel pad electrodes. Pad electrodes are connected with gas-filled camera by loop electrodes with some of them plugged in the HF generator while the rest of them being grounded. Electrodes plugged in the HF generator as well as grounded electrodes are connected in parallel. Electrodes plugged in the HF generator are next but one interspersed with grounded electrodes. All loop electrodes are placed perimeter-wise outside of the dielectric gas-filled camera providing plasma space distribution in the camera. Such electrode configuration when loop electrodes are in-phase plugged in the HF generator and grounded stabilizes electromagnetic component of the field and doesn't produce zero potential points in the bulk of dielectric gas-filled camera which results in plasma burning uniformly and stable in the camera space.

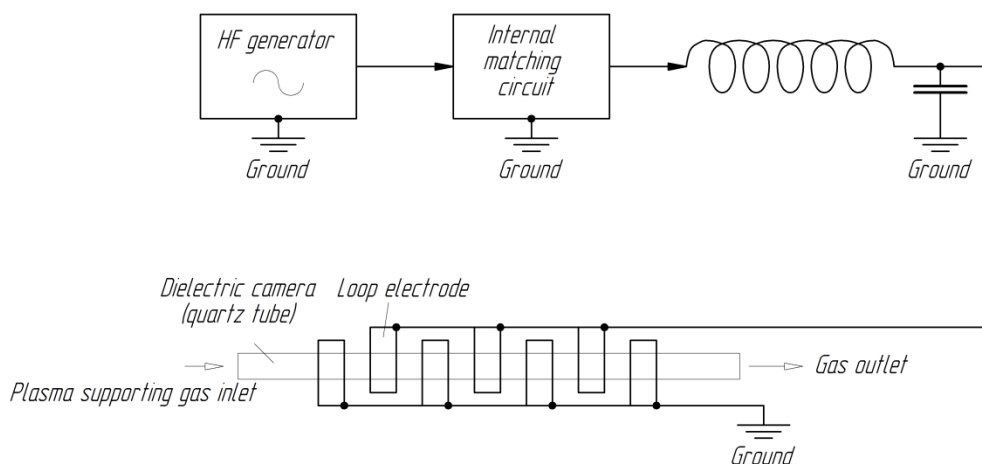


Figure 1. Gas discharge camera electrode connection diagram

Hollow fiber membranes plasma modification was carried out as follows: first, dielectric gas-filled camera was vacuumized; after that, 10 specimens of the membranes were placed into the camera followed by plasma supporting gas transmission at 110 Pa. Air was used as the plasma supporting gas with mass flux 0 to 0.24 g/s.

Turning the HF generator on lets discharging plasma fill the dielectric camera providing spatial uniformity and combustion stability. The duration of plasma treatment was 3 minutes. Dielectric gas-filled camera is made of quartz tube having high optical clarity, mechanical and thermal stability and also small dielectric quartz loss in operating band.

Wetting contact angle measurements of inner surface of the membranes were carried out via a conventional sessile drop method using the LK-1 goniometer. For surface hydrophilicity properties characterization of unmodified and plasma treated membranes and determining their surface energy values water and ethylene glycol were used as testing liquids couple. Such system is widely used for membrane surface energy determination, as surface energy components of both water and ethylene glycol are well-known. For image capture and digital processing of drops images, DropShape software was used providing Laplace-Young contact wetting angle calculation. Measurement error was $\pm 2^\circ$. Experiments were carried out at room temperature ($23 \pm 2^\circ\text{C}$).

Hollow fiber gas permeability was measured via the manometric technique. Carbon dioxide and helium were chosen as operating fluids, as their molecular mass difference provides reliable way to determine Knudsen gas flow on the ideal selectivity value (permeability coefficients of individual gases ratio).

Membrane surface chemical composition analysis was performed via IR spectroscopy technique. IR Fourier spectrometer IRAffinity-1 (Shimadzu, Japan) was used for absorption spectra analysis.

Membrane morphology for both unmodified and plasma treated membranes was examined with confocal scanning laser microscopy (CSLM Olympus Lext OLS-4000, Japan). After scanning, surface images of different points with various magnifications were obtained for each membrane specimen. Based on scanning data, surface micro relief characteristics were calculated. Surface roughness was the key characteristic. When determining the surface roughness main criteria were arithmetic average of the roughness profile (R_a) and roughness height (R_z). Roughness characteristics were evaluated based on all the scan points. For each specimen surface scans were obtained in 10 different points and then R_a and R_z values were averaged.

3. Results and discussion

Active components generated in plasma may activate upper molecular layers of membrane surface, therefore increasing their hydrophilicity without producing changes in the membrane bulk. Under bombardment by plasma ions radicals are produced which may interact with gas molecules. Hollow fiber membranes surface properties analysis shows that under air plasma treatment oxygen-containing functional groups appear on the membrane surface, in particular, carbonyl and carboxyl groups, which formation is connected with terminal groups oxidation under chemical bonds breaking. As can be seen from Table 1, average contact wetting angle value both for water and ethylene glycol decreases after plasma treatment, while surface energy value increases. It indicates that plasma treatment enhances hydrophilic surface properties of both inner and outer surfaces of hollow fiber PSf membranes.

Table 1. Wetting contact angle θ and surface energy γ_s values for unmodified and plasma treated membranes (for lumen hollow fiber surface)

Parameter	Unmodified membrane	Plasma treated membrane
$\theta_{av}(\text{H}_2\text{O}), ^\circ$	81,3	72,5
$\theta_{av}(\text{ethylene glycol}), ^\circ$	69,7	65,3
$\gamma_s^{av}, \text{mJ/m}^2$	24,0	33,2

Table 2 gives gas permeability data for unmodified and plasma treated membranes. Mean pore size (d_{av}) values are derived from calculation based on Dusty Gas Model (DGM), considering both Knudsen and Poiseuille flows contribution.

Table 2. Gas permeability and mean pore size values for unmodified and plasma treated membranes

Parameter	Unmodified membrane	Plasma treated membrane
P/l (CO ₂), (m ³ /m ² *h*bar)	560	880
P/l (He), (m ³ /m ² *h*bar)	1300	1300
Ideal selectivity α (He/CO ₂)	2,3	1,5
d _{av} , nm	24	34

As can be seen from table 2, for plasma treated membranes ideal selectivity value is 1.5, which corresponds to mixed flow mode with Poisselle flow mode prevailing, while for untreated membranes $\alpha = 2,3$ corresponds to Knudsen flow mode prevailing. Membrane selectivity decrease after plasma treatment indicates that average membrane pore size increases because of etching phenomena; such conclusion is in the good agreement with data calculated by DGM.

Fig. 2 depicts photomicrographs for selective layer dimensions evaluation for both unmodified (a) and plasma treated (b) membranes. Thickness variation of the membrane selective layer is observed in the cross-section: for untreated membrane the thickness value was $\sim 28 \mu\text{m}$ while for plasma treated membrane it decreased to $\sim 24 \mu\text{m}$.

As separation selectivity (under constant external conditions) depends exclusively on inner membrane material structure, membrane permeability directly depends on selective layer thickness. Therefore, membrane selective layer thickness decrease increases overall membrane performance as well as the membrane units performance, allowing to reduce overall dimensions of separation plants. Membrane selective layer thickness decrease proves the fact that plasma treatment influences on the inner membrane surface.

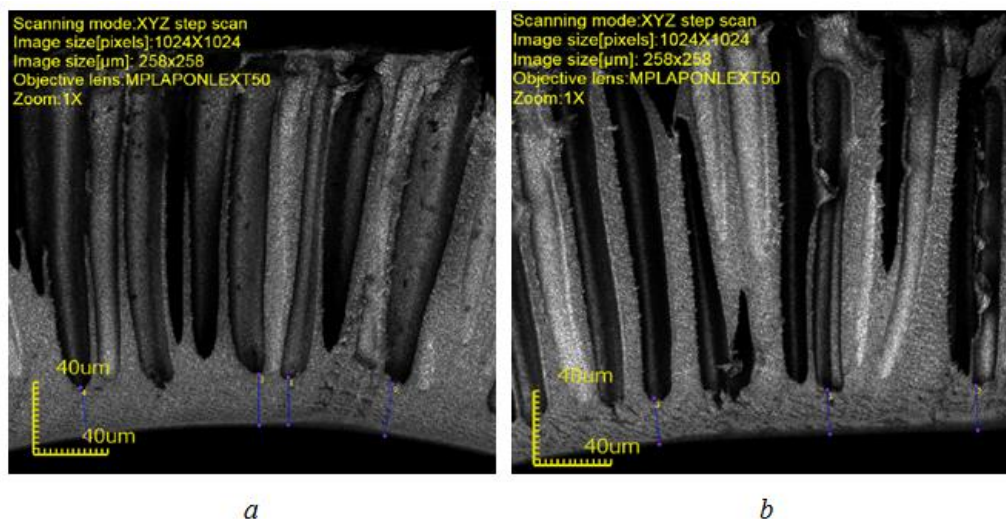


Figure 2. Hollow fiber membrane selective layer dimensions: a – unmodified specimen, b – plasma treated specimen.

The result of low-temperature plasma treatment on the membranes is a change in their surface morphology, which influences on the separation processes characteristics. Data obtained show that after plasma treatment pore etching occurs. Membrane surface topography changes after plasma treatment. For unmodified membrane, arithmetic average of the roughness profile (R_a) is $0.15 \mu\text{m}$ and roughness height (R_z) is $0.68 \mu\text{m}$. Plasma treatment causes minor morphology changes and results in

R_a and R_z values decrease to 0.11 and 0.49 μm , respectively. So, smoothing of surface heterogeneity is observed, and for plasma treated membranes, their surface becomes less rough.

Results obtained by mechanical properties change analysis show that strength properties of membranes don't change significantly after plasma treatment, keeping initial values.

IR spectroscopy data show that there is no significant change in membranes chemical structure after modification. It should be noted that slightly increased absorption is observed near the 1650 and 1685 cm^{-1} absorption bands, which corresponds to carbonyl stretching vibrations, and near the 1041 cm^{-1} , which corresponds to C-O bond stretching vibrations. It proves that oxygen content in the upper membrane layer slightly increases, and hydrophilic surface properties enhance. IR-Fourier chemical structure analysis for plasma treated membranes shows that plasma treatment leads to the surface layer oxidation and oxygen-containing functional groups formation.

4. Conclusion

Hollow fiber porous polysulfone membranes low temperature air plasma treatment was carried out. It is shown that plasma treatment allows membrane surface to get enhanced hydrophilic properties due to the surface layer oxidation. Plasma treatment also reduces membrane selective layer thickness and smoothen its roughness without decline in mechanical properties. Low temperature air plasma treatment can be successfully used to obtain modified polysulfone hollow fiber membranes with enhanced surface hydrophilic properties.

Acknowledgements

This work was performed at the Topchiev Institute of Petrochemical Synthesis and supported by the Russian Science Foundation, project no. 14-49-00101. V.V. Volkov, A.A. Ovcharova and V.A. Bilydukevich acknowledge the financial support of RSF.

References

- [1] Schott K 1997 *Handbook of Industrial Membranes* (Elsevier Science) p 904.
- [2] Korminouri F, Rahbari-Sisakht M, Matsuura M and Ismail A F 2015 *Chem. Eng. J.* **264** 453–61
- [3] Plisko T V, Bilydukevich A V, Volkov V V and Osipov N N 2015 *Petrol. Chem.* **55** 318–32
- [4] Chu L Y, Wang S and Chen W M 2005 *Macromol. Chem. Phys.* **206** 1934–40
- [5] Liubimova E S, Bilydukevich A V, Melnikova G B and Volkov V V 2015 *Petrol. Chem.* **55** 795–802.
- [6] Steen M L, Jordan A C and Fisher E R 2002 *J. Membr. Sci.* **204** 341
- [7] Gancarz I, Pozniak G and Bryjak M 1999 *Europ. Polym. J.* **35** 1419
- [8] Wavhal D S, Fisher E R 2005 *Desalination* **172** 189–205
- [9] Gancarz I, Pozniak G and Bryjak M 2000 *Europ. Polym. J.* **36** 1563
- [10] Castro Vidaurre E F, Achete C A, Gallo F, Garcias D, Simão R and Habert A C 2002 *Mater. Res.* **5** 37
- [11] Kim K S, Lee K H, Cho K and Park C E 2002 *J. Membr. Sci.* **199** 135
- [12] Asfardjani K, Secui Y, Aurelle Y and Abidene N 1991 *J. Appl. Polym. Sci.* **43** 271
- [13] Hopkins J and Badyal J P S 1996 *J. Polym. Sci. A* **34** 1385
- [14] Gancarz I, Pozniak G and Bryjak M 1999 *Europ. Polym. J.* **35** 1419