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Modification of polysulfone membranes
3. Effect of nitrogen plasma

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Abstract

The paper considers properties of porous membranes modified by action of nitrogen plasma. The membrane material was polysulfone — the polymer most frequently used in production of ultrafiltration membranes. It is shown that 2.45 GHz nitrogen plasma generates various kinds of surface functionalities both of acidic and basic character. The surface changes during the first week after plasma treatment, some groups disappear some others are shifted towards surface. In consequence, surface hydrophilicity gained during plasma treatment decreases but does not disappears completely. It is shown that modified ultrafiltration membranes are less prone to protein fouling than their untreated analogues. This protection is extended on a wide range of retentate pH-values. Plasma action alters also morphology of membranes. During first 2 min of action, polymer ablation seems to dominate. Pore diameter becomes larger and pores size distribution wider. Longer exposition to plasma does not affect pores any more — the rates of ablation and deposition seem to be balanced. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Protein filtration; Surface character; Pore size; Transport properties

1. Introduction

In many areas of polymer application the character of the surface, including the nature of chemical groups, their spatial distribution and surface roughness or texture, has a great effect on its performance. Low-temperature plasma treatment gives possibility to tailor surface properties to satisfy a particular request. It can smooth the surface or make it more rough. Usually, it alters dramatically the surface tension. In case of porous membranes, pore size and pore size distribution can be also changed to the large extent.

In our previous papers [1,2] we have shown that introducing acidic groups on the surface of ultrafiltration polysulfone membrane significantly improved their filtration properties. Here we investigate influence of nitrogen plasma on wettability, morphology and transport properties of the same membranes. Nitrogen is the reactive plasma medium that induces an incorporation of various chemical functionalities onto the polymer surface. On exposure to nitrogen plasma, such groups as amine, imine, amide, nitrile and others could be created [3–10]. Air-exposure of the treated sample results in considerable uptake of oxygen that makes the surfaces highly hydrophilic [3,9,11,12]. In some cases, polymer degradation and etching processes are

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also observed [3,5–7,12,13]. Nitrogen is often used in a mixture with other gases like He [9,14], O_2 [11,15] and H_2 [8,16]. The main application of nitrogen plasma modification is enhancement of adhesion between two materials [4,14,16–19].

The aim of this paper is to show how nitrogen plasma treatment alters properties of ultrafiltration polysulfone membranes.

2. Experimental

2.1. Materials

Polysulfone (PSU) Udel P-1700 was purchased from Amoco Co., USA. Polyvinylpyrrolidone (PVP) with average molecular weight of 10 000 g/mole was supplied by Aldrich Chem. Co. Ltd, England. Analytical grade *N*,*N*-dimethylformamide (DMF) and chloroform ($CHCl_3$) were received from POCh, Gliwice, Poland. Diiodomethane was supplied by Sigma Chemical Co. and nitrogen gas by Linde Gas, Poland.

2.2. Membranes

Polysulfone membranes were prepared as described previously [1]. Gel membranes were casted from 20 wt% DMF solution onto glass plates and dried 10 h in 120°C. Porous ultrafiltration membranes were prepared by the phase inversion method. PSU concentration was set at 15 wt% in DMF. PVP — 10 wt.% referring to PSU — was added to polysulfone solution. Water was used as coagulant. To calculate total porosity of these membranes swelling experiments was performed. Membrane was immersed in water, equilibrated and weighted (W_1). Then it was dried to the constant weight (W_0) at 120°C. Porosity was calculated as $\frac{W_1-W_0}{W_1}100\%$ and was on an average 78%.

2.3. Plasma treatment

A microwave plasma generator of 2.45 GHz frequency (Plazmatronika, Poland) was used throughout this study. Plasma was generated in a quartz tube at the top of a reaction chamber. Membrane sample was attached to a Teflon table and placed 60 mm from the edge of plasma. Pulsed plasma with pulse frequency of 125 Hz and 25% of duty time was applied. Plasma power (counted on continuous plasma) was adjusted to 60 W. Initially, the reaction chamber was evacuated to 5×10^{-3} mbar. Gas flow rate was set at 20 cm^3/min what gave the final pressure in the reactor chamber of 0.4 mbar. Time of treatment was changed in the range of 0–20 min.

2.4. Surface characterization

2.4.1. Contact angle measurements

Advancing contact angles of liquid droplets (*ca* 3 μL) were measured using TM 50 System (Technicome SA, France) equipped with Panasonic GL 350 camera. Each reading was repeated at least 20 times. Gel PSU membranes, modified in exactly the same conditions as porous specimens, served as a test sample. Two liquids were applied for evaluation of surface free energy: water (double distilled) and diiodomethane (stabilized with Ag). Surface tension and its polar and dispersive component were calculated according to harmonic averaging [20]. Polar and dispersive components of surface tension for selected liquids were taken after Kuznietsov [21].

Surface stability was evaluated by keeping the samples in double distilled water for a respective long time. Then they were dried in air for 1 h at 60°C. Their surface tension was calculated according to protocol of contact angle measurement.

2.4.2. Fourier Transform Infrared Spectroscopy

For spectroscopic study gel membranes were casted from chloroform. All FTIR spectra were obtained by the attenuated total reflection (ATR) technique using Perkin–Elmer System 2000 spectrometer with horizontal ATR device (Ge, 45°). 64 scans were taken with 4 cm^{-1} resolution. Sampling depth was calculated according to [22] assuming the refractive index of PSU to be equal $n = 1.633$.

2.5. Ultrafiltration properties and pore size determination

Details of UF apparatus and procedure were described elsewhere [1]. The performances of ultrafiltration membranes were determined with deionized water, 0.1 M barbital buffers of pH = 3 or 9 and buffered solutions (pH = 3 and 9) of bovine serum albumin (BSA, 1 g/L). The volume flux was determined through consecutive collection of permeate fraction. Fouled membranes were cleaned with a conventional procedure — alternative washing with 0.1 M NaOH and HCl. Values of fouling index ($\mathrm{FI} = 1 - J_b^f/J_b^o$), flux recovery after membrane cleaning ($\mathrm{FR} = J_b^c/J_b^o$), reduction of the flux in filtration ($\mathrm{RF} = 1 - J_p/J_b^o$) and solute rejection ($\mathrm{SR} = 1 - c_p/c_o$) were calculated as described earlier [1,2].

The pore size distribution (PDD) was calculated from dextrane ultrafiltration results, according to the procedure described in [23]. Glucose and nine dextran standards (Polfa, Poland and Pharmacia, Sweden) of molecular weight ranging from 1500 to 2 000 000 were used. The analysis of dextran concentration in reten-

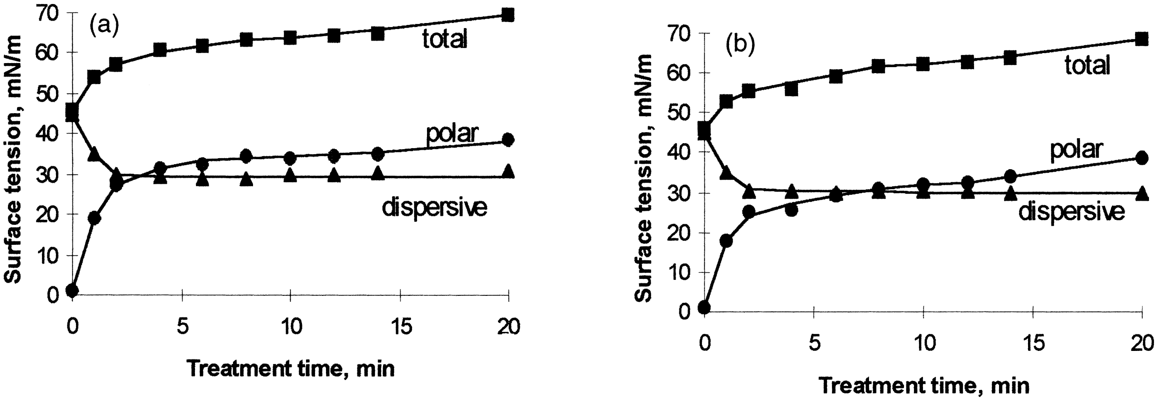

Fig. 1. Surface tension, its polar and dispersive component as a function of nitrogen plasma treatment time: (a) 1 h after treatment; (b) after 24 h in the air atmosphere.

tates and permeates was performed by means of liquid chromatography.

3. Results and discussion

3.1. Surface characteristics

3.1.1. Surface tension

Contact angle measurement is one of the simplest methods to determine changes that take place in the very outer layer of materials during their surface treatment. We used this method to evaluate surface tension of polysulfone specimens (gel membranes) modified in nitrogen plasma. Correlation of surface tension and its both components with time of plasma action are shown in Fig. 1.

Data collected for modified polymer films indicate a significant increase of hydrophilicity (Fig. 1a). The sharp decrease of water contact angle (from 87.3 for virgin PSU to 43.6 degree for plasma treated polymer) takes place during first 2 min of plasma action. After that time, hydrophilicity of samples increases slowly but steadily. Twenty minutes of plasma action leaves the polysulfone surface with total surface tension of 69.5 mN/m and with polar component a little higher than dispersive contribution.

It is commonly known that hydrophilicity gained by plasma modification is not stable; the effect can get lower and even disappear completely. One day of storage in the air results in a decrease of the surface tension of about 3.5%. In the same time, the polar component decreases more dramatically — of about 8%. The observed effect may have two reasons: mobility of surface functionalities or sorption of hydrophobic moieties appearing in laboratory air. To verify the extent of both processes plasma treated membranes were kept in double distilled water. This procedure protects, or at least limits, surface against deposition of organic molecules.

The direction of changes of surface character seems to point at surface rebuilding as the dominant process. Up to 7–8 days of storage, the character of surface clearly changes. Polar component decreases while dispersive contribution becomes higher. After first week both components reach plateau and stay unchanged for next three weeks of storage (Fig. 2). It should be pointed out however, that polar component though lower than just after treatment, is still much higher (12.4 mN/m) than that determined for the virgin sample (0.9 mN/m). This relationship agrees with our preliminary assumption: some polar functionalities move towards bulk polymer. The rest of them modify the surface properties to make them different than virgin samples have.

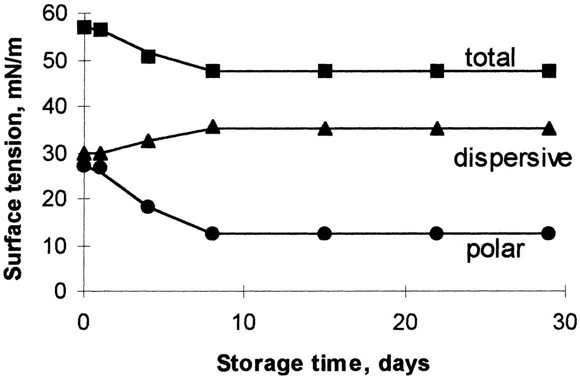

Fig. 2. Surface tension of nitrogen plasma treated polysulfone (time of treatment — 2 min) as a function of storage time in water.

3.1.2. Spectroscopic study

Sampling depth of FTIR ATR is dependent on wavelength and for PSU is in the range of 800 (for 850 cm^{-1}) to 170 nm (for 4000 cm^{-1}). This is two orders of magnitude bigger than thickness of plasma modified layer. It is commonly accepted, that plasma treatment introduces functionalities in the outer few nanometers layer of material. That difference implies that in the IR spectra one would see mainly bands coming from the polysulfone; the new bands being the result of modification if appear at all, are expected to be of very low intensity.

Spectra taken after various times of treatment appear to be identical. All of them are very complicated with many new absorbance regions. According to the literature, nitrogen plasma grafts various nitrogen functionalities on the surface [3–10]. It creates also significant amount of radicals that after treatment react with air giving oxygen-containing groups.

Fig. 3 shows the most significant absorbance regions of PSU surface after N_2 plasma modification and their changes within storage in the air. Most of them are found in the range of 1800–1650 cm^{-1}. They indicate a rather large number of different structural features of carbon–oxygen double bonds present as aldehyde, ketone, amide, acid and ester groups. The presence of C=N, C=C bonds and harmonic and combinatorial bands for benzene derivatives is also possible. This part of spectrum is very similar to spectrum of PSU membrane modified with CO_2 plasma [1]. The most prominent bands are those at 1636, 1647, 1653 and 1742 cm^{-1}, and their possible assignment is given in our previous paper [1]. In the case of nitrogen plasma, most of them disappear or get smaller during the first day of storage in the air. Absorbance at 1539 is also common for N_2 and CO_2 plasma [1]. It can come from stretching C—O vibration of carboxylic acids, N–H vibration in *N*-monosubstituted amides or C—N=O in alkilesters of nitrous acid. Appearance of band at 2853 cm^{-1} and observed movement of some bands in that region (shift from 2968 cm^{-1} to 2963 cm^{-1} or from 2933 cm^{-1} to 2924 cm^{-1} for virgin and treated PSU) can be assigned to CH_2 or CH_3 groups which appear in quite different environment after treatment. Their intensities grow with storage. Aromatic CH absorbances seem to be unchanged what suggest that plasma attacks mainly aliphatic groups in polysulfone. One more adsorption band, wide, small but distinctive with the maximum around 3275 cm^{-1} is observed in the IR spectrum. This one may be assigned to the presence of amine groups but contribution of OH and CO—NH can not be eliminated.

3.2. Pore size determination

After plasma treatment, structure of porous membrane may change essentially. Depending on plasma gas and process parameters, increase or decrease of pore size is observed. The former is a result of plasma etching, the latter-deposition of plasma polymer or redeposition of etched material inside the pores.

Pore size distribution of virgin PSU membrane as well as membranes after 2 and 10 min of nitrogen plasma treatment are shown in Fig. 4. Plasma etching effect can be seen just after 2 min of treatment. Average pore size becomes slightly larger and distribution wider. Prolonged excitation time however practically did not change that situation, some equilibrium between etching and deposition processes must be achieved.

3.3. Transport properties

3.3.1. Water permeability

Changes of surface tension as well as membrane pore size distribution should have a significant effect on membrane transport properties. Determined pore size distribution would suggest that water flux of the N_2-plasma modified membrane should increase. The

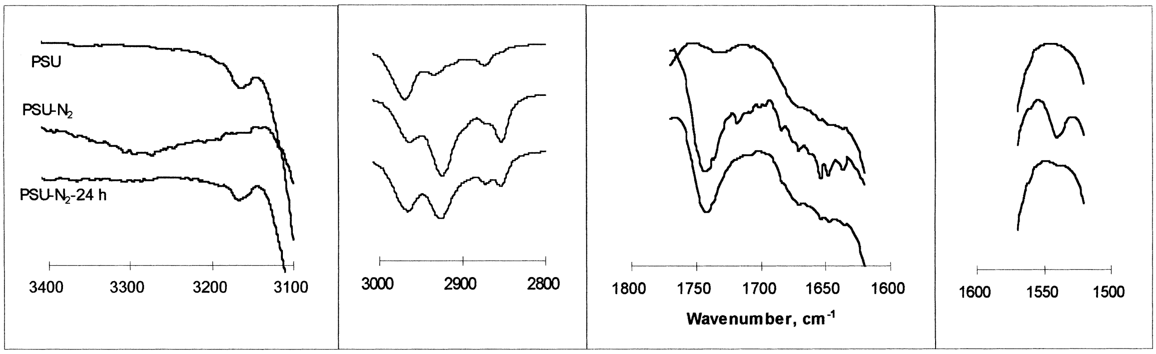

Fig. 3. FTIR spectra of virgin PSU and nitrogen-plasma modified samples immediately after and 24 h after treatment.

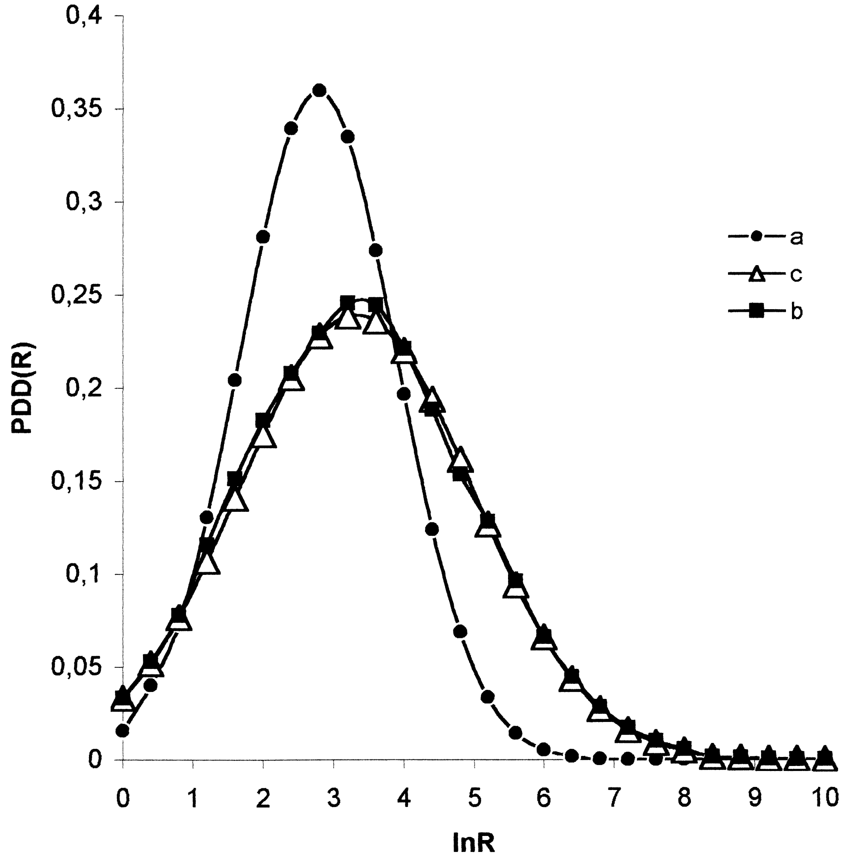

Fig. 4. Pore size distribution function: (a) untreated membrane; (b) membrane treated with N_2 plasma for 2 min; (c) membrane treated with N_2 plasma for 10 min.

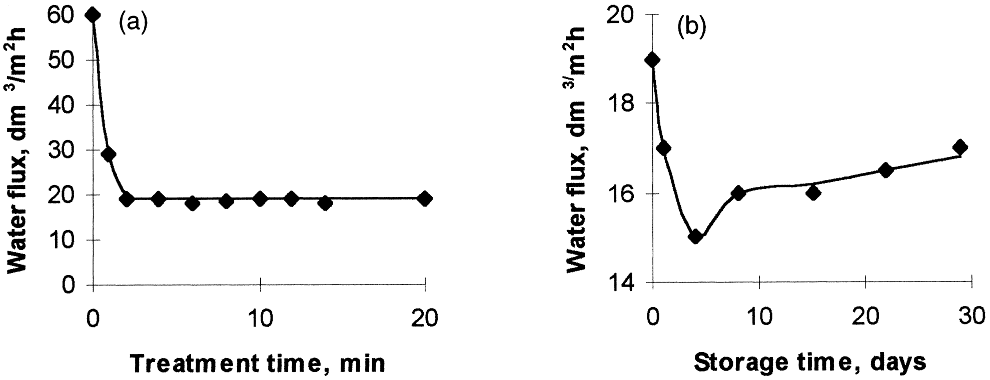

Fig. 5. Water flux through the polysulfone membrane: (a) effect of treatment time; (b) membrane modified with nitrogen plasma (2 min) and stored in water.

Table 1
Fluxes of buffers and BSA solution through untreated membrane (PSU) and membrane after plasma treatment (N_2-PSU) for two values of pH

Filtered medium	Volume flow (dm^3/m^2 h) pH = 3 PSU	N_2-PSU	pH = 9 PSU	N_2-PSU
Buffer (J_b^o)	58.8	19.9	55.7	17.3
Buffered BSA solution (J_p)	10.3	7.5	15.1	6.9
Buffer after filtration of BSA (J_b^f)	23.6	10.4	25.9	9.4
Buffer after membrane cleaning (J_b^c)	45.9	17.3	38.1	15.5

Fig. 5 shows entirely opposite effect — up to 2 min of plasma treatment water flux decreases dramatically. Prolonged excitation time does not alter membrane permeability at all. This phenomenon is not fully clear for us. One hypothesis we can consider is that structure and character of pores wall considerable changed after plasma treatment. Redeposited material might create more rough layer on the inner walls of pores or plug numerous small pores.

Storage in water also affects membrane permeability. The character of flux changes follows surface tension relationship (see Fig. 2). Preliminary decrease of flux followed by its stabilization perfectly show that post plasma phenomena may have an important effect on transport performances. When surface becomes less hydrophilic the flux is decreasing. Spectroscopic studies also confirm that conclusion. Storage causes disappearance of some absorption band assigned to polar functionalities (see Section 3.1.2).

3.3.2. Filtration of protein

For ultrafiltration experiment, membrane modified by 2 min with nitrogen plasma was selected. In Table 1 one can find numerical values of fluxes of buffers and BSA solution through the virgin and plasma treated membranes. For comparative task of various membranes performance some filtration indices were calculated and their numerical values are juxtaposed in Table 2.

Table 2
Fouling index FI, flux recovery after cleaning FR, reduction of the flux RF and solute rejection SR in protein filtration. Virgin and N_2 plasma (2 min) modified PSU membranes were compared at two pH values

	Filtration indices (%) pH = 3 PSU	N_2-PSU	pH = 9 PSU	N_2-PSU
FI	59.9	47.5	53.5	45.5
FR	53.2	87.0	68.4	89.5
RF	82.5	62.5	72.9	59.8
SR	95.0	95.5	98.6	97.8

Comparison of collected data allows us to state that N_2-plasma modification makes membranes less prone to fouling than their virgin analogues. Hence, fouling is not so destructive and flux reduction not so high. Additionally, the modified membranes behave much better in conventional regeneration. It means that protein molecules absorption is weaker. That observation covers both forms of protein: positively and negatively charged. Hence, N_2-plasma modified membranes are protected against fouling in the wide range of solution pH. Previously synthesized membranes [24], bearing only one type of functionalities, expressed its antifouling activity only in limited pH-range. This behaviour suggests that surface of the nitrogen plasma modified polysulfone exhibit an amphoteric character. The postulate that N_2-plasma modified surface has various basic and acidic functionalities is in good agreement with the surface titration results presented elsewhere [25]. One can note that nitrogen plasma modification did not affect separation properties in chosen by us conditions. Tested protein was rejected to the same extent as at virgin PSU membranes despite of changes in membrane pores size.

4. Conclusions

It is clearly seen that the modified membrane behaves in filtration process better than its virgin analogue — fouling is lower and flux recovery after cleaning higher than for PSU. It is confirmed that surface hydrophilization improves membrane performance and makes fouling less troublesome. Regeneration of modified membranes is more efficient. The amphoteric character of surface makes membranes more universal. They are not so sensitive to pH controlled protein deposition as the membrane bearing only one kind of functionalities. ATR-FTIR studies confirm presence of many functionalities that are formed on the PSU surface after N_2-plasma treatment. The surface is under reconstruction through the first week after treatment and then its properties do not alter significantly. Fortunately, surface does not return to the beginning hydrophobic state and the polar component of surface tension stays higher than for virgin polysulfone.

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