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Polysulfone/cellulose acetate blend semi degradable capillary membranes preparation and characterization

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ABSTRACT

The method of preparation of partially degradable polysulfone/cellulose acetate (PSf/CA) asymmetric, capillary, ultrafiltration membranes is presented. Membranes were obtained by dry/wet-spinning phase-inversion technique, then treated with sodium hydroxide solution using the flowing method. Membranes mass measurements before and after the hydrolysis process confirmed almost complete CA removal from them. The membrane hydraulic permeability (UFC) for pure water was measured and retention coefficients were evaluated for chosen markers before and after applied hydrolysis. Hydrolysis caused the removal of the CA from the membrane structure resulting in the opening of the pores and the permeability increased due to the increased pore size. The morphology of the PSf/CA capillary membranes was analyzed using scanning electron microscopy (SEM) before and after hydrolysis.

Keywords: Capillary membranes; Pore former; Retention; Degradation; Ultrafiltration coefficient

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1. Introduction

The hydrophilic additives, such as polyethylenes glycol (PEG), polyvinylpyrrolidones (PVP), Pluronic F127 and polyethylenes oxide (PEO) are added to polymeric membranes as pores former to change their structure and performance [1–8]. Another method of change membranes parameters is a modification of membrane surfaces [9–11]. Pores formers are added to dope solution and after the membrane is produced, the pores former is removed from their structure. The extent to which the pore former is removed from the membrane depends on membrane washing time and pores former molecular weight, but the process is never complete. Some parts of the pores former remain in membrane structure after the washing process. During membrane working time in water solution, a pores former loss is still present, so the exact marking of its quantity remaining in a membrane is impossible. Such situation makes physico-chemical measurements of membrane processes difficult. During membrane operation some compounds may react with pores former and disturb the separation process. One way of complete removal of pores former is the treatment with sodium hypochlorite (NaOCl) [12–14]. The membrane treatment with NaOCl effectively removes PVP from its structure. Hypochlorite causes PVP to be removed from the membrane structure as a result of opening the pyrrolidone ring or cutting PVP chain, what reduces its molecular mass and makes elution easier [15]. Nonetheless, a search for new, easily and completely removable pores former is intensively conducted.

Cellulose acetate (CA) and polysulfone (PSf) have been used to prepare blend, semi degradable PSf/CA ultrafiltration capillary membranes. PSf polymer has been used as a stable membrane material due to its high chemical, thermal,

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mechanical resistance and hydraulic stability [16,17]. Thus, PSf membranes have a wide range of applications. CA polymer has been used as a classic pores former completely removable from membrane structure after its preparation. In fact, CA is suitable membrane material, due to its advantages such as a moderate flux, high retention properties, cost effectiveness, relatively easy manufacture, renewable source of raw material and non-toxicity. Both polymeric materials, PSf and CA, due to easy fabrication and modification, high separation efficiency and low cost, have attracted considerable attentions [18]. Blending PSf with CA as a highly hydrophilic polymer can be an alternative for improvement of the performance of PSf membranes. Both polymers (PSf and CA) mix together completely in any ratio with organic solvents and form a homogenous mixture.

Widely used pores former (PVP, PEG) are soluble in water and washed out from the membrane after the membrane spinning process, whereas CA is insoluble in water and forms stable PSf/CA membrane structure. After forming the PSf/CA membrane, CA polymer can be easily and completely removed by using the basic hydrolysis method. At the end, pure PSf membrane without residue pores former in its structure is obtained. Membrane porosity is adjusted by quantity of the added/removed CA –the more CA removed, the more pores a membrane has. The limitation of this method is the mechanical stability of PSf membrane after CA removal.

2. Experimental

2.1. Materials

PSf Udel 1700 NT LCD from Dow Corning M.W. 70 kD; CA from Sigma-Aldrich M.W. 37 kD; N-methyl-2-pyrrolidone (NMP) from Sigma-Aldrich; polyethylene glycols (PEG) from Fluka, M.W. 4, 15, and 35 kD; chicken egg albumin (CEA) from Fluka, M.W. 45 kD; and bovine serum albumin (BSA) from Fluka, M.W. 67 kD were used in the discussed study.

2.2. Capillary membranes fabrication

PSf and CA were selected as materials for blend capillary membrane fabrication. Polymers were dried overnight under vacuum at 100°C before dope preparation. NMP was used as the solvent for polymeric materials. NMP was dried with a molecular sieve before use. Polymers (PSf and CA) and the solvent were mixed in a flask and stirred at 20°C until polymers completely dissolved. The PSf/CA weight ratio was 2/1, 1/1, 1/2, and 1/3. Polymers (PSf and CA together) concentration in NMP solution was 20% of its total weight. PSf and CA polymers did not connect with each other by means of chemical bonds formation in polymeric solution. Therefore, it was possible to selectively remove CA from the membrane structure without damaging the membrane's shape; the PSf/CA membrane had been created.

Capillary membranes were prepared utilizing the plant constructed for that purpose (Fig. 1). Membranes were obtained by a dry/wet-spinning, phase-inversion technique through extrusion of polymer solution. The membrane formation was controlled using a software enabling quick changes of the process parameters. The spinning process was conducted at room temperature. Membranes were cut into small pieces and placed in the clean water bath for 4 d for residual solvent extraction. After washing, membranes were stabilized in a glycerine solution (10% water solution) for 1 d. The glycerine remaining in pores increased hydrophilicity of the membranes. Next, capillaries were air-dried at ambient temperature.

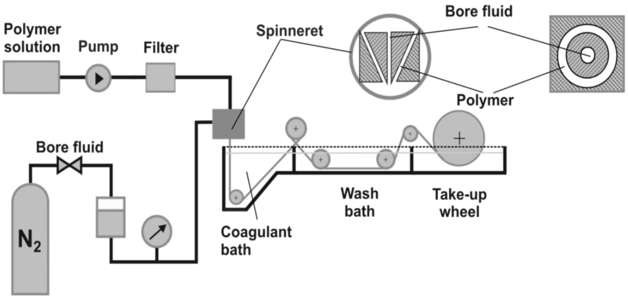

Fig. 1. Schematic diagram of the spinning process for capillary membranes preparation.

Capillary membrane modules were prepared by putting twenty, 6-cm length pieces of capillaries into a polypropylene module (about 25 cm^2 area). Both ends of the module were sealed with an epoxy resin. Four types of PSf/CA membranes with different PSf/CA weight ratio were produced. Moreover, the virgin (non-modified) PSf membrane was produced as a reference to properties of modified PSF/CA membranes. Membranes were marked as PSf (PSf virgin), PSf/CA 2/1, PSf/CA 1/1, PSf/CA 1/2, and PSf/CA 1/3. Finally, membranes were ready for further tests and study.

2.3. Membranes hydrolysis

PSf/CA membranes were treated with a 2 M NaOH water solution using the flowing method. 400–800 cm^3 NaOH solution was passed through the capillary module inletting to the capillaries and flowing through their walls to the outside of the module at 0.2 MPa transmembrane pressure. NaOH solution quantity depended on the CA content in the membrane. 400 cm^3 passed for PSf/CA 2/1 and PSf/CA 1/1 weight ratio, 600 cm^3 for PSf/CA 1/2 weight ratio, and 800 cm^3 for PSf/CA 1/3 weight ratio.

The flowing time of the etching solution depended on membrane characteristics such as porosity and Ultrafiltration coefficient (UFC) and ranged from 4 to 6 h. The hydrolysis process was held at the temperature of 20°C. After membrane hydrolysis, pure water was flushed in both directions through the membrane walls in order to remove residual sodium hydroxide and products of hydrolysis decomposition. Finally, pure PSf membrane was obtained.

2.4. Membranes characterization

2.4.1. SEM analysis

The morphology of obtained membranes was characterized by scanning electron microscopy (SEM), using Hitachi TM-1000 microscope. Samples for SEM were prepared by breaking membranes in liquid nitrogen in order to avoid deformation during fracture. Afterwards, samples were coated with a 10-nm gold layer, using a sputtering device (EMITECH K 550X).

2.4.2. Permeability measurements

The hydraulic permeability of capillary membranes was evaluated as a volume of solution passed through the membrane walls after 10 min by 200 hPa transmembrane pressure. UFC was calculated according to Eq. (1):

$$UFC = \frac{v}{t \times a \times p} \tag{1}$$

where v – volume of the solution (cm^3), t – time of measure (min.), a – nominal capillary area in module (m^2), and p – transmembrane pressure (hPa)

2.4.3. Retention measurements

The retention coefficient characterizes membrane separation features. The membrane retention R (%) is defined as Eq. (2):

$$R = \{1 - (C_P / C_R)\} \cdot 100\% \tag{2}$$

where R – retention coefficient, C_P – concentration of marker in permeate (g dm^{-3}), and C_R – concentration of marker in retentate (g dm^{-3}).

PEG (4, 15 and, 35 kD), CEA, and BSA were successively used to the measurement of retention of each capillary module. Concentrations of markers were measured by UV-spectrophotometer (HITACHI U-3010) at 190 nm wavelength for polyethylenes and 280 nm for CEA.

3. Results and discussion

3.1. Membranes hydraulic permeability (UFC)

The hydraulic permeability of membranes was measured (according to Eq. 1) before and after NaOH hydrolysis. The observed values are shown in Table 1.

Table 1
Hydraulic permeability coefficient (UFC) for membranes before and after NaOH hydrolysis

Membrane	PSf/CA 2/1	PSf/CA 1/1	PSf/CA 1/2	PSf/CA 1/3
UFC before hydrolysis (cm × min^{-1} × m^2 × hPa)	4.0	4.4	4.6	5.6
UFC after hydrolysis (cm × min^{-1} × m^2 × hPa)	5.2	5.5	5.7	7.3
UFC (%) increase	30	25	24	30

Hydraulic permeability coefficient of PSf/CA membranes increased from 4.0 (cm^3 × min^{-1} × m^{-2} × hPa^{-1}) for PSf/CA 2/1 membrane to 5.6 (cm^3 × min^{-1} × m^{-2} × hPa^{-1}) for PSf/CA 1/3 membrane. PSf (virgin) membrane hydraulic permeability coefficient was 3.5 (cm^3 × min^{-1} × m^{-2} × hPa^{-1}). CA membrane material is more hydrophilic than PSf and has a higher flux, hence the increase of CA polymer in PSf/CA membrane caused the permeability increase (from 4.0 for PSf/CA 2/1 to 5.6 for PSf/CA 1/3). The noticeable increase in the UFC after hydrolysis (from 24% to 30%) was a result of CA removal from the membrane, which created the higher pores void volume (see SEM photo in Figs. 8–12) making the water flux easier.

3.2. Membranes weight measurements

In order to see to what extent the NaOH hydrolysis caused the membrane material to be rinsed out from the membrane structure, membranes' weight was measured before and after hydrolysis process. CA weight corresponded from 33% to 75% of membranes mass in module. Measurements were repeated twice for each PSf/CA membrane. The results of CA weight change are as shown in Table 2.

Of all the types of PSf/CA membranes, the loss in CA weight after hydrolysis was almost complete. Loss differences in CA weight in all types of membranes were comparable and ranged from 93.8% to 98.1% (weight percentage). Such significant loss in CA weight had considerable influence on membrane structure as well as membrane flux. CA was effectively removed from the membrane structure and acted as a typical pores former.

3.3. Membranes retention coefficients

Retention coefficients were evaluated before and after NaOH hydrolysis for membranes PSf/CA and PSf virgin using markers such as: PEG 4, 15, 35 kD, CEA 45 kD, and BSA 67 kD. The procedure is described in section 2.4.3. Retention coefficients for different markers of particular molecular weights are shown in Figs. 2–5. The curves corresponding to particular membranes are marked as follows: for virgin PSf as triangles, for PSf/CA before hydrolysis and after hydrolysis – as diamonds and as squares, respectively.

The virgin PSf membrane had higher retention values than all PSf/CA membranes. The virgin PSf membrane was more hydrophobic than membranes with CA component (CA is more hydrophilic than PSf). All retention values after hydrolysis were lower than the retention values before hydrolysis for all four types of PSf/CA membranes. In the first case, PSf/CA membranes after hydrolysis lost CA

Table 2
Measurements of membranes weight before and after hydrolysis

Membrane	Membrane weight before hydrolysis (*g*)	CA weight before hydrolysis (*g*)	CA weight loss after hydrolysis (*g*)	CA weight loss after hydrolysis (%)
PSf/CA 2/1	0.0845	0.0281	0.0268	95.4
PSf/CA 1/1	0.0769	0.0385	0.0361	93.8
PSf/CA 1/2	0.0853	0.0569	0.0557	97.9
PSf/CA 1/3	0.0778	0.0583	0.0572	98.1

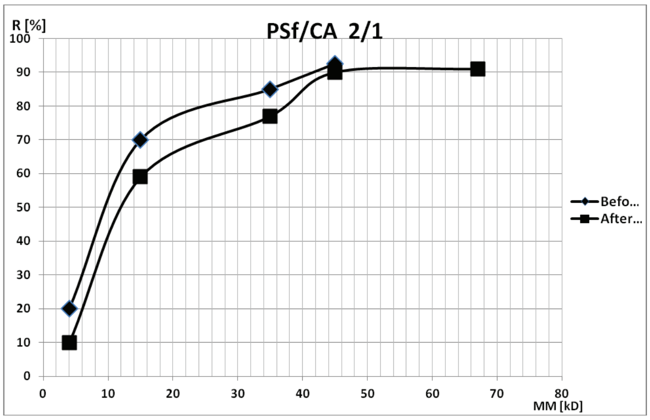

Fig. 2. Retention coefficients of different markers for PSf, PSf/CA-2/1 membranes before and after hydrolysis.

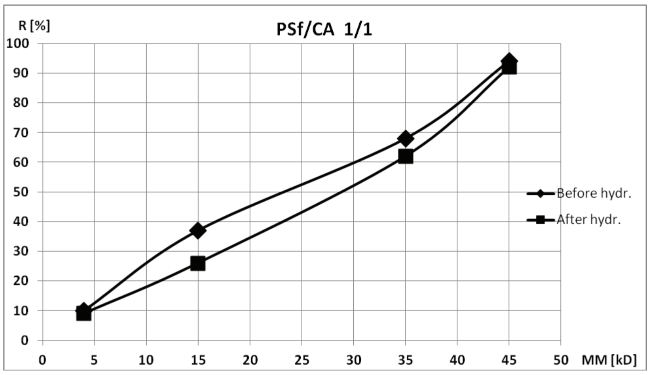

Fig. 3. Retention coefficients of different markers for PSf, PSf/CA-1/1 membranes before and after hydrolysis.

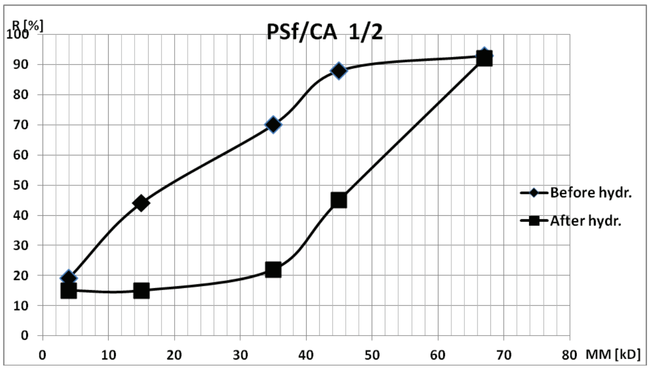

Fig. 4. Retention coefficients of different markers for PSf, PSf/CA-1/2 membranes before and after hydrolysis.

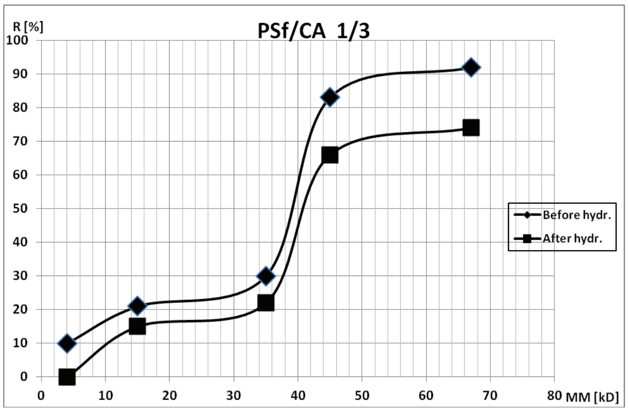

Fig. 5. Retention coefficients for different markers for PSf, PSf/CA-1/3 membranes before and after hydrolysis.

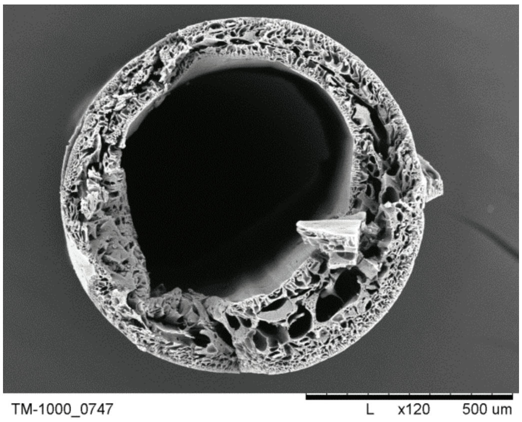

Fig. 6. Cross section of PSf/CA-2/1 membranes before hydrolysis.

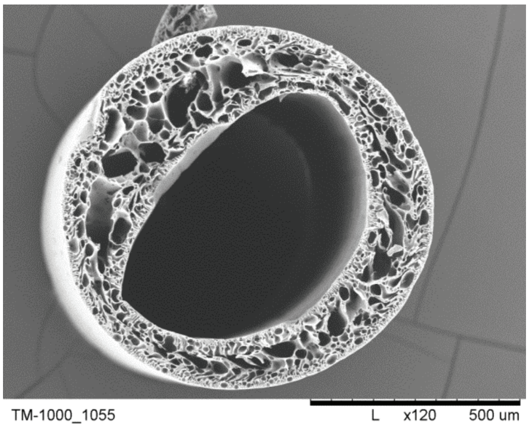

Fig. 7. Cross section of PSf/CA-2/1 membranes after hydrolysis.

component and a significant weight loss was observed. CA polymer removal from the membrane led to the increase in membrane porosity and enhanced membrane flux. Therefore, there were evident differences in retention values before and after membrane's hydrolysis. The retention values of PSf/CA (1/2 and 1/3) membranes, i.e., ones with the largest content of CA before hydrolysis, clearly decreased after hydrolysis (see Figs. 4 and 5). The significant loss of membrane weigth after removal CA polymer caused the formation of large macropores in membrane structure, hence retention values differences were most noticeable for PSf/CA (1/2 and 1/3) membranes. In conclusion, CA removal from membranes reduced retention parameters and allowed to pass molecules of the larger molecular weight.

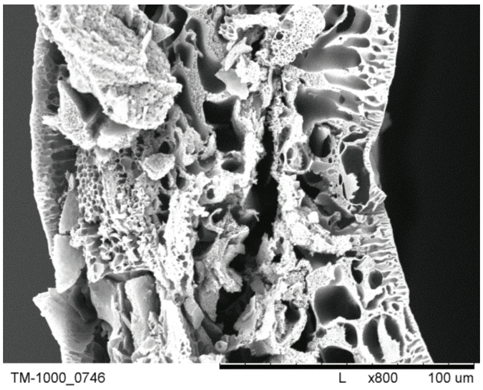

Fig. 8. Part of cross section of PSf/CA-2/1 membranes before hydrolysis.

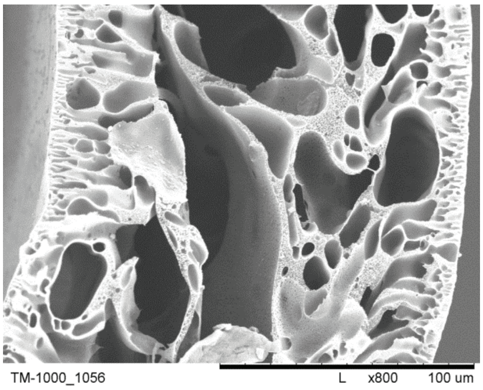

Fig. 9. Part of cross section of PSf/CA-2/1 membranes after hydrolysis.

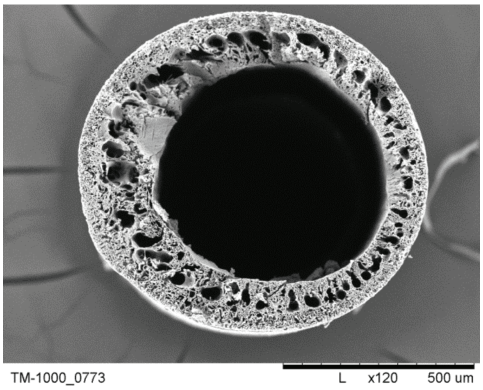

Fig. 10. Cross section of PSf/CA-1/1 membranes before hydrolysis.

3.4. Scanning electron microscopy (SEM) of membranes

PSf/CA membranes cross-sections micrograph are presented in the Figs. 6–21. The method of micrographs taking is described in section 2.4.1. PSf/CA membranes before hydrolysis are presented in Figs. 6, 8, 10, 12, 14, 16, 18 and 20. PSf/CA membranes after hydrolysis are presented in Figs. 7, 9, 11, 13, 15, 17, 19 and 21.

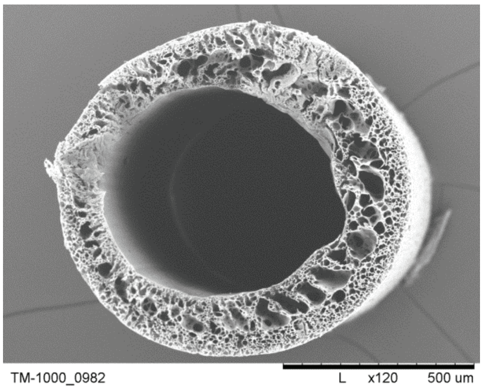

Fig. 11. Cross section of PSf/CA-1/1 membranes after hydrolysis.

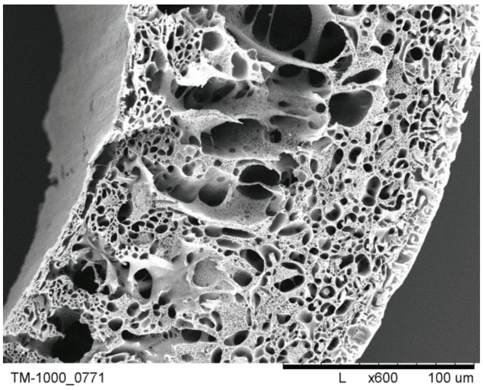

Fig. 12. Part of cross section of PSf/CA-1/1 membranes before hydrolysis.

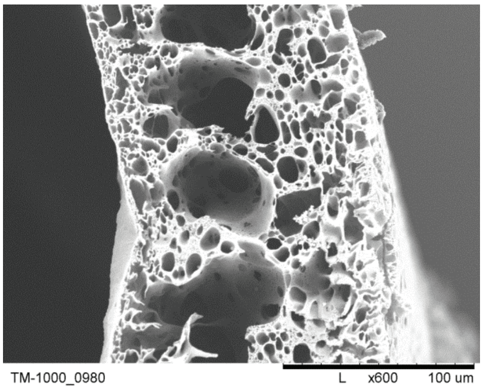

Fig. 13. Part of cross section of PSf/CA-1/1 membranes after hydrolysis.

As a result of hydrolysis, CA polymer was removed from PSf/CA membranes. PSf/CA-2/1 membrane had 33% of CA before hydrolysis. After the removal of CA, the created structure was more dispersed and porous (Figs. 8 and 9). PSf/CA-1/1 membrane (50% CA content), as a result of hydrolysis and CA removal, gained a porous structure with thinner walls (Figs. 12 and 13). PSf/CA-1/2 membrane's diameter (67% CA contents), after CA removal, became smaller (Figs. 14 and 15) and its walls became thinner (Figs. 16 and 17). It was the result of significant weight loss. PSf/CA-1/3 membrane (75% CA contents) after hydrolysis had two times smaller diameter

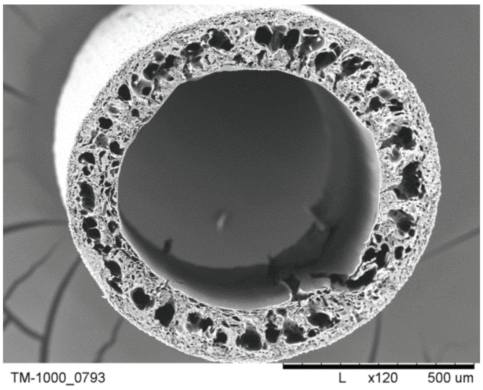

Fig. 14. Cross section of PSf/CA-1/2 membranes before hydrolysis.

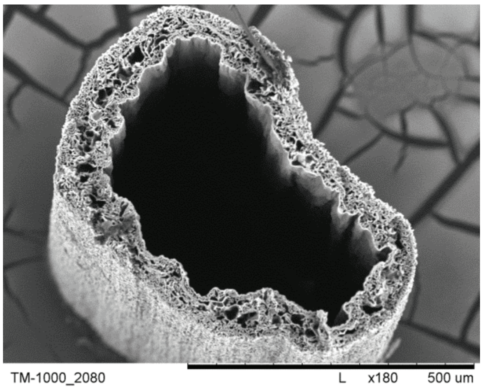

Fig. 15. Cross section of PSf/CA-1/2 membranes after hydrolysis.

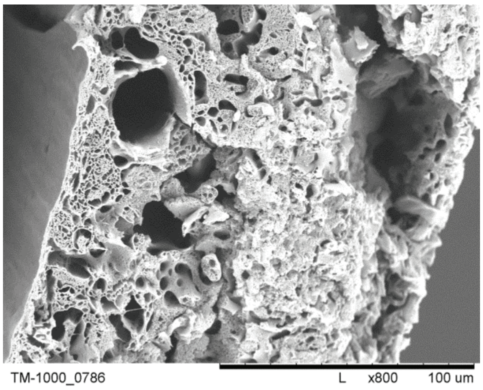

Fig. 16. Part of cross section of PSf/CA-1/2 membranes before hydrolysis.

and three times thinner walls (Figs. 18–21). Due to this fact, even with the reduction of diameter and wall thickness, PSf membrane after CA polymer removal retained its shape and did not degrade.

4. Summary

In the presented work, the production of blended, partially degradable, asymmetric PSf/CA capillary membranes is decribed. CA polymer was applied as a classic, degradable pores former to improve membrane porosity and permeability.

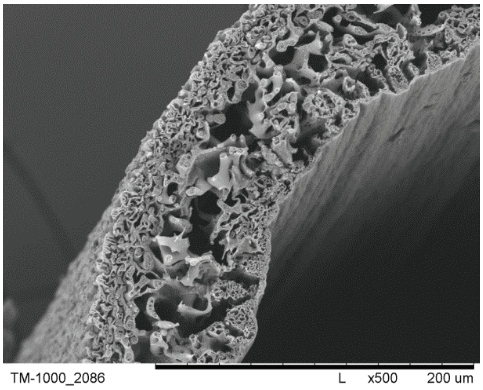

Fig. 17. Part of cross section of PSf/CA-1/2 membranes after hydrolysis.

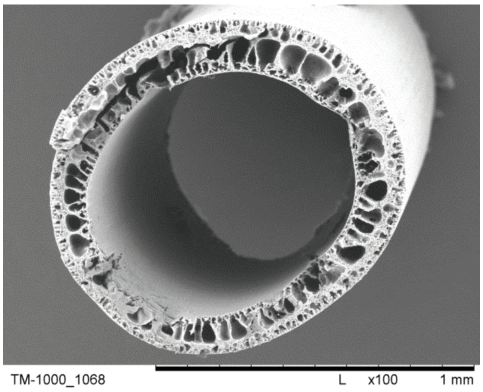

Fig. 18. Cross section of PSf/CA-1/3 membranes before hydrolysis.

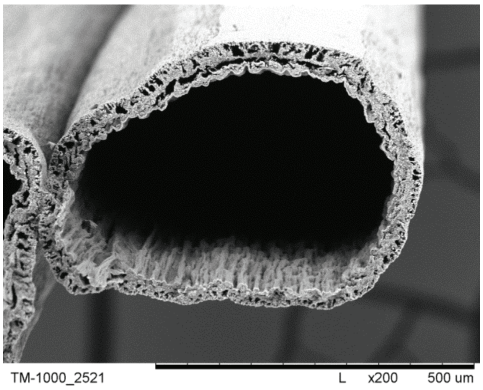

Fig. 19. Cross section of PSf/CA-1/3 membranes after hydrolysis.

Four types of PSf/CA membranes with different PSf/CA weight ratio were obtained. CA polymer content in PSf/CA membrane were 33%, 50%, 67%, and 75%, respectively. All types of PSf/CA membranes were treated with 2 M NaOH water solution using the flowing method. CA polymer was removed from membranes structure as a result of hydrolysis. As a redult, pure PSf membranes were obtained. Membranes weight measurements before and after the hydrolysis confirmed almost total CA removal from membranes (from 93.8% to 98.1% of weight). SEM photos confirmed CA polymer removal from membranes and formation of more porous

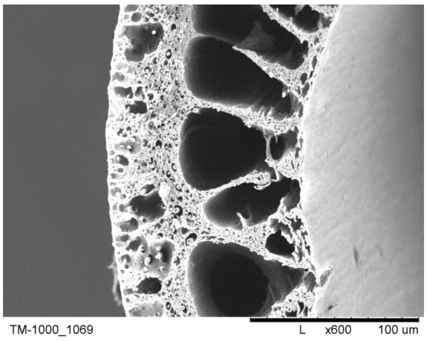

Fig. 20. Part of cross section of PSf/CA-1/3 membranes before hydrolysis.

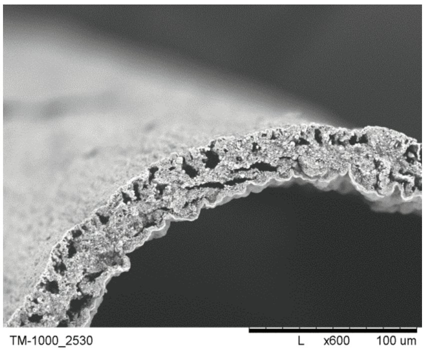

Fig. 21. Part of cross section of PSf/CA-1/3 membranes after hydrolysis.

membranes' structure after hydrolysis. As a result of the significant membrane weight loss, an interesting phenomenon was observed, i.e., reduction in diameters and wall thickness of membranes after hydrolysis, especially for the PSf/CA-1/2 and PSf/CA-1/3 membranes. An increase in hydraulic permeability coefficients (UFC) from 24% to 30% for all types of membranes after hydrolysis was observed. Membranes' retention values were lower after hydrolysis, especially for the PSf/CA-1/2 and PSf/CA-1/3 membranes, which had the largest content of CA before hydrolysis.

The application of the CA polymer as pores former for PSf membrane allowed the membrane characteristics to change. The removal of CA polymer caused new inner canal openings inside the membrane structure. These changes in structure caused the increase in membrane permeability. PSf membranes after CA removal had higher porosity, lower retention and higher membrane flux efficiency than initial PSf/CA membranes. CA polymer acted very well as a classic pores former. The most important advantage of using CA as a pore former was the production of pure, PSf membrane, without any residue of pores former in the membrane structure.

PSf membrane after CA removal had significant different transport-separation parameters than a virgin PSf membrane. CA polymer was applied as pores former, hence structure of PSf membrane after CA removal was more porous than of a virgin PSf membrane. Therefore, PSf membrane (after CA removal) had higher permeability and lower retention values than a virgin PSf membrane. Production of the virgin PSf membrane with such parameters would be more complicated. Therefore, pores former application is often necessary in order to obtain efficient membrane flux.

References

[1] Y. Liu, G.H. Koops, H. Strathmann, Characterization of morphology controlled polyethersulfone hollow fiber membrane by the addition of polyethylene glycol to the dope and bore liquid solution, J. Membr. Sci., 223 (2003) 187–199.

[2] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, J. Membr. Sci., 309 (2008) 209–221.

[3] J.H. Kim, K.H. Lee, Effect of PEG additive on membrane formation by phase inversion, J. Membr. Sci., 138 (1998) 153–163.

[4] J.F. Li, Z.L. Xu, H. Yang, Microporous polyethersulfone membranes prepared under the combined precipitation conditions with non-solvent additives, Polym. Adv. Technol., 19 (2008) 251–257.

[5] S.J. Shin, J.P. Kim, H.J. Kim, J.H. Jeon, B.R. Min, Preparation and characterization of polyethersulfone microfiltration membranes by a 2-methoxyethanol additive, Desalination, 186 (2005) 1–10.

[6] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci., 327 (2009) 125–135.

[7] W. Zhao, Y.L. Su, C. Li, Q. Shi, X. Ning, Z.Y. Jiang, Fabrication of anti-fouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent, J. Membr. Sci., 318 (2008) 405–412.

[8] Y.Q. Wang, T. Wang, Y.L. Su, F. Peng, H. Wu, Z.Y. Jiang, Remarkable reduction of irreversible fouling and improvement of the permeation properties of poly(ethersulfone) ultrafiltration membranes by blending with Pluronic F127, Langmuir, 21 (2005) 11856–11862.

[9] G. Khang, H.B. Lee, J.B. Park, Biocompatibility of polysulfone I surface modifications and characterizations, Bio Med. Mater. Eng., 5 (1995) 245–158.

[10] J.Y. Ho, T. Matsuura, J.P. Santerre, The effect of fluorinated surface modifying macromolecules on the surface morphology of polyethersulfone membranes, J. Biomater. Sci. Polym. Ed., 11 (2000) 1085–1104.

[11] K.S. Kim, K.H. Lee, K. Cho, C.E. Park, Surface modification of polysulfone ultrafiltration membrane by oxygen plasma treatment, J. Membr. Sci., 199 (2002) 135–145.

[12] J.-J. Qin, F.S. Wong, Y. Li, Y.T. Liu, A high flux ultrafiltration membrane spun from PSU/PVP(K90)/DMF/1,2-propanediol, J. Membr. Sci., 211 (2003) 139–147.

[13] I.M. Wienk, R.M. Boom, M.A.M. Beerlage, A.M.W. Bulte, C.A. Smolders, H. Strathmann, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, J. Membr. Sci., 113 (1996) 361–371.

[14] J.-J. Qin, M.-H. Oo, Y. Li, Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, J. Membr. Sci., 247 (2005) 137–142.

[15] I.M. Wienk, E.E.B. Meuleman, Z. Borneman, Th. Van den Boomgaard, C.A. Smolders, Chemical treatment of membranes of a polymer blend: mechanism of the reaction of hypochlorite with poly(vinyl pyrrolidone), J. Polym. Sci. Part A: Polym. Chem., 33 (1995) 49–54.

[16] H. Ohya, S. Shiki, H. Kawakami, Fabrication study of polysulfone hollow-fiber microfiltration membranes: optimal dope viscosity for nucleation and growth, J. Membr. Sci., 326 (2009) 293–302.

[17] M. Mansourizadeh, A.F. Ismail, Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO_2 absorption, J. Membr. Sci., 348 (2010) 260–267.

[18] R. Mahendran, R. Malaisamy, D.R. Mohan, Cellulose acetate and polyethersulfone blend ultrafiltration membranes. Part I: preparation and characterizations, Polym. Adv. Technol., 15 (2004) 149–157.