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Polysulfone/polyurethane blend degradable hollow fiber membranes preparation and transport–separation properties evaluation

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ABSTRACT

The method of preparation of partly degradable polysulfone/polyurethane (PSf/PU) asymmetric hollow fiber membranes is presented. The membranes built of PSf and polyurethane polymer containing degradable ester groups were obtained by dry/wet-spinning phase-inversion technique then treated with sodium hydroxide solution using the flowing method. The membrane hydraulic permeability (UFC) for pure water and retention coefficients were evaluated for chosen markers before and after applied hydrolysis. An increase in ultrafiltration coefficient was observed while retention coefficient did not change significantly in post-treatment membranes. Hydrolysis caused the partial removal of PU from the membrane structure resulting in the opening of the pore passages and the permeability increase without increasing the pore size. The morphology of the PSf/PU hollow fiber membranes was analyzed using scanning electron microscopy before and after hydrolysis.

Keywords: Hollow fiber membranes; Retention; Degradation; Ultrafiltration coefficient

1. Introduction

Hydrophobicity is a defect of polysulfone (PSf) hollow fiber membranes, which often leads to fouling phenomenon, which is clogging of the membranes' pores. In biotechnological processes, the fouling phenomenon often occurs during conducting of membrane processes resulting in its low productivity [1,2]. Therefore, there is a need to modify the membranes by changing their structure, permeability, and separation properties in a specific way for given application. Membrane structure, chemical constitution, and spinning process parameters have considerable influence on separation properties [3–5]. This is why many authors try to modify the membranes in order to avoid or at least delimit disadvantageous effects. There are a lot of methods applied for modification of the PSf membranes to enhance their permeability for high-molecular compounds and increase in capacity [6]. A low-temperature plasma processing can be used in order to increase the hydrophilicity [7,8], as well as polymerization of monomers on the membrane surface [9,10]. The membrane structure may be modified by adding hydrophilic porophore polymers like polyvinylpyrrolidones (PVP),

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polyethylene glycols (PEG) [11–13], or other hydrophilic compounds [14–17]. Other methods include membranes modification by changing casting solution or process parameters [18–21]. All of these methods often occurred unstable and expensive. Modifications of membrane-forming polymer often lead to worsening membrane properties, especially their biocompatibility and biochemical resistance.

The method of reducing a fouling effect in PSf/PU membranes is presented in our work. We suggest that it is possible to effectively increase the membranes' lifetime during their operation in spite of the fouling process. We used degradable PU as a constituent of our membranes, which has easily removable ester groups in its structure. The polyurethanes, which are generally resistant to hydrolysis and other chemical agents effect, were modified (at Warsaw University of Technology, Department of Chemistry, Chair of Polymer Chemistry and Technology) by adding ester groups to their structure, to make them less resistant to degradation and hydrolysis [22]. During the operation of PSf/PU membranes, the PU component is expected to partially degrade while retaining good mechanical properties. As a result of PU ester group's degradation and the removal of their decomposition products, the membrane porosity increases improving the membrane transport parameters.

The use of degradable polyesters in PSf/PU membranes allows them to act as porophores, although not as classic porophores, which are quickly removed, but ones that are slowly removed over a long period of time, while the membranes can be in operation for specific purposes. While using the membranes in body fluid environment, ester groups slowly degrade because of enzymatic hydrolysis, whereas in an acid or alkaline environment the degradation is caused by acid or alkaline hydrolysis. Hence, factors contributing to ester degradation often occur during membranes' operation. The gradual removal of membrane's material (hydrolysis of ester groups) increases the membrane porosity which should increase its permeability. The incremental clogging of the membrane pores should be simultaneously balanced by the slow removal of the decomposition products of PU ester groups from the membrane, leading to opening the new pores and delimiting the effects of the fouling process. This phenomenon should help to maintain good efficiency of membrane processes over long periods of time despite the fouling process.

2. Experimental

2.1. Materials

Polysulfone (PSf) Udel 1700 NT LCD from Dow Corning M.W. 70 kD, N-methyl-pyrrolidone (NMP) from Sigma–Aldrich, PEG from Fluka, M.W. 4, 15, and 35 kD, chicken egg albumin (CEA) from Fluka, M.W. 45 kD.

The polyurethanes [poly(ester-carbonate-urea-urethane)s] M.W. 26–37 kD, containing 40–65 mol% of carbonate units in amorphous soft segments, structure synthesized at Warsaw University of Technology, Department of Chemistry is presented in Fig. 1.

2.2. Hollow fiber membranes fabrication

Polysulfone and polyurethane were selected as the material for hollow fiber membrane fabrication. The PSf/PU ratio weight was 3/1. 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 being used. The polymers (PSF and PU) concentration in NMP solution was 20% weight. The polymers (PSf and PU) and the solvent were mixed in a flask and stirred at 20°C temperature until the polymers dissolved completely.

The hollow fiber membranes were prepared utilizing the plant constructed for that purpose (Fig. 2). The membranes were obtained by a dry/wet-spinning, phase-inversion technique through extrusion of polymer solution. The polymeric dope solution was extruded by syringe pumps through the spinneret. The bore fluid (pure water) was supplied toward the spinneret via ambient gas pressure. The nascent hol-

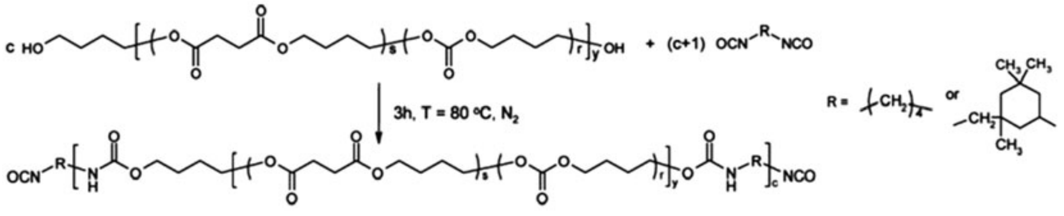

Fig. 1. Synthesis of poly(ester-carbonate-urea-urethane).

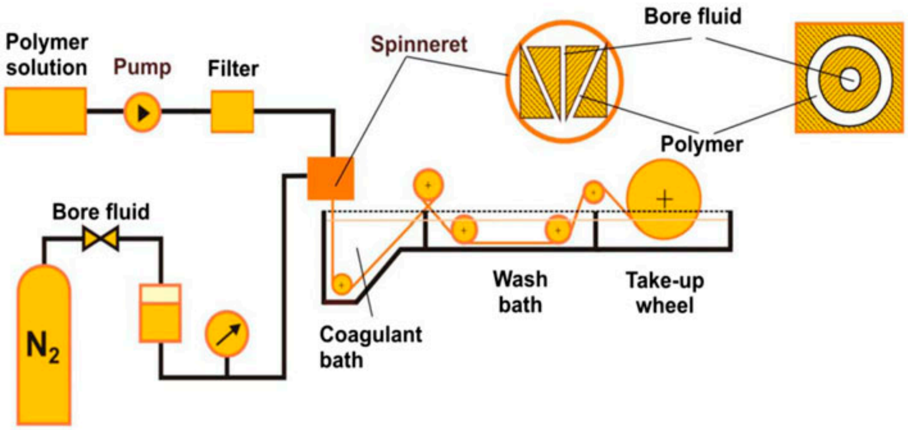

Fig. 2. Schematic diagram of the spinning process for hollow fiber membranes.

low fiber membrane passing through an air gap (the distance between the spinneret and the coagulation bath; distance varying from 5 to 10 cm) was drawn into coagulation baths and then transported over the rollers. The coagulant was pure water in the first bath and tap water in two other ones. A take-up wheel was used to collect the membranes. The membrane formation was controlled using a software program 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 four days for residual solvent extraction. After washing, the membranes were stabilized in a glycerin solution (10% water solution) for one day. The remaining glycerin in the pores increased hydrophilicity of the membranes. Next, the hollow fibers were air-dried at ambient temperature.

The hollow fiber membrane modules were prepared by putting 20 pieces of capillaries of a 6-cm effective length into a polypropylene module (about 25 cm area). Both ends of the modules were sealed with an epoxy resin. Five type of PSf/PU membranes with different R segment in PU membrane (see Fig. 1) were produced. The membranes were marked as PSf/PU-1, PSf/PU-2, PSf/PU-3, PSf/PU-4, and PSf/PU-5. Finally, the membranes were ready for further tests and study.

2.3. Membranes hydrolysis

Membranes were treated with a 2 M NaOH water solution using the flowing method. The 500 cm^3 NaOH solution was passed through the hollow fiber module passing inside the hollow fibers and flowing through the hollow fiber walls to the outside module at 0.2 MPa transmembrane pressure. The flowing time of the etching solution depended on membrane characteristics such as porosity and 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.

The acid hydrolysis (H_2SO_4) application did not allow to achieve the expected results. The loss in PU mass in all membranes after acid hydrolysis was insignificant. The transport–separation parameters did not change. The SEM analysis did not indicate any changes in membrane structure (data not presented).

2.4. Membranes characterization

2.4.1. SEM analysis

The morphology of the obtained membranes was characterized by scanning electron microscopy (SEM), using Hitachi TM-1000 microscope. The samples for SEM were prepared by breaking the membranes in liquid nitrogen in order to avoid deformation during fracture. Afterwards, the 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 hollow fiber membranes was evaluated as a volume of solution passed through the membrane walls during the period of ten minutes under 200 hPa transmembrane pressure. Ultrafiltration coefficient (UFC) was calculated according to the formula:

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

where v—volume of the solution (cm^3), t—time of measure (min), a—nominal hollow fibers 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:

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

where $\boldsymbol{R}$—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) and CEA were successively used for the measurement of retention of each capillary module. The concentrations of markers were measured by a UV-spectrophotometer (HITACHI U-3010) at 190 nm wavelength for polyethylene and 280 nm for CEA.

3. Results and discussion

3.1. Membranes hydraulic permeability (UFC)

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

The viscosities of polymeric dope solutions were different because of the different PU applied in each membrane. Hence the spinning process parameters depending on viscosity differed slightly which led to differences in membrane structure (which is different for each membrane—see SEM photo bellow), the membrane structure has a significant influence on membrane's UFC. Therefore, the UFC values are different for PSf/PU-1–5 membranes.

The coefficients of hydraulic permeability for all produced membranes increased from meanly 22% for PSf/PU-3 membrane to 60% for PSf/PU-2 membrane after hydrolysis. The significant increase in the UFC after hydrolysis was a result of partial removal of the membrane's material which created the dispersed membrane structure making the water flux easier.

3.2. Retention coefficients and molecular weight cut-off

The membrane retention coefficients before and after NaOH hydrolysis for markers: PEG 4, 15, and 35 kD as well as CEA 45 kD were evaluated. The method of measurement is described in Section 2.4.3. Retention coefficient values for different markers of given molecular weights are shown in Figs. 3–7. The values of curves before hydrolysis are marked as triangles and after hydrolysis—as squares.

All retention curves for five types of PSf/PU membranes before hydrolysis were similar, as well as retention curves after hydrolysis. There were no changes observed in retention values for all types of membranes for 4 kD marker evaluation. Also, there were no differences observed in retention values for PSf/PU-1–3 membranes for 15 kD marker after and before hydrolysis. Retention values for PSf/PU-4–5 membranes for 15 kD marker and for all types of membranes for 35 kD marker were higher after hydrolysis in comparison to retention values before hydrolysis. Hydrolysis caused hydrophilic ester groups decomposition and removal from PU polymer which led to an increase in hydrophobicity. It is probable that it caused markers sorption on membrane's surface which led to retention increase. Retention values for all types of membranes for 45 kD marker were similar before and after hydrolysis at amount about 90%. Hence 45 kD value is the molecular weight cut-off (MWCO) for all types of membranes. It was observed that the hydrolysis did not influence the membrane cut-off value. As a consequence, hydrolysis did not change the evaluated membranes separation parameters.

PU polymer removal from the membrane led to two opposite results: (1) increase in membrane porosity, (2) increase in membrane hydrophobicity due to decomposition of hydrophilic ester groups. These two phenomena are connected and therefore there are not evident differences in retention value before and after hydrolysis of the membrane.

Table 1
Coefficient of hydraulic permeability for membranes before and after NaOH hydrolysis

Membrane	PSf/PU-1	PSf/PU-2	PSf/PU-3	PSf/PU-4	PSf/PU-5
UFC before hydrolysis ($cm^3/min \times m^2 \times hPa$)	1.6	4.8	7.4	3.1	1.7
UFC after hydrolysis ($cm^3/min \times m^2 \times hPa$)	2.3	7.7	9.0	4.9	2.7
UFC (%) increase	44	60	22	58	59

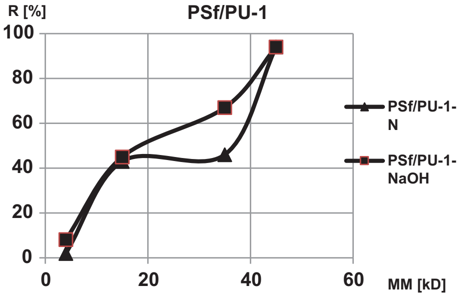

Fig. 3. Retention coefficient values for different markers for PSf/PU-1 membrane before and after hydrolysis.

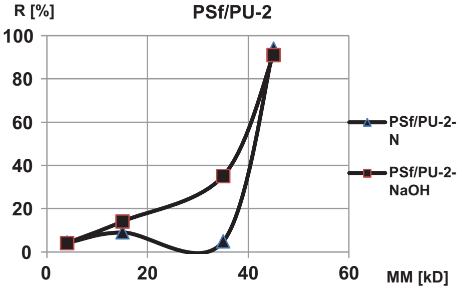

Fig. 4. Retention coefficient values for different markers for PSf/PU-2 membrane before and after hydrolysis.

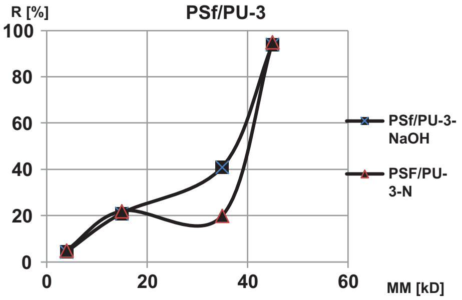

Fig. 5. Retention coefficient values for different markers for PSf/PU-3 membrane before and after hydrolysis.

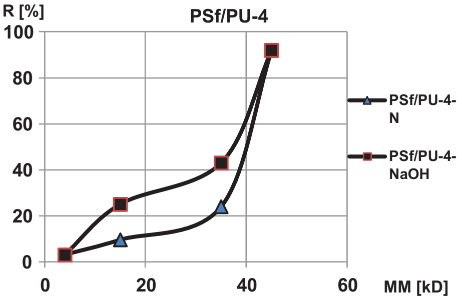

Fig. 6. Retention coefficient values for different markers for PSf/PU-4 membrane before and after hydrolysis.

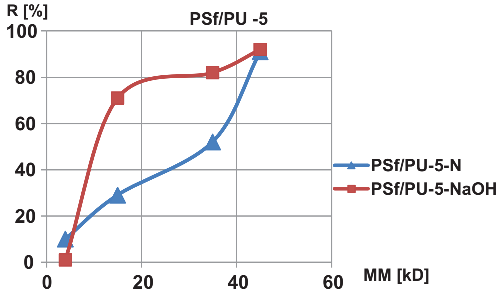

Fig. 7. Retention coefficient values for different markers for PSf/PU-5 membrane before and after hydrolysis.

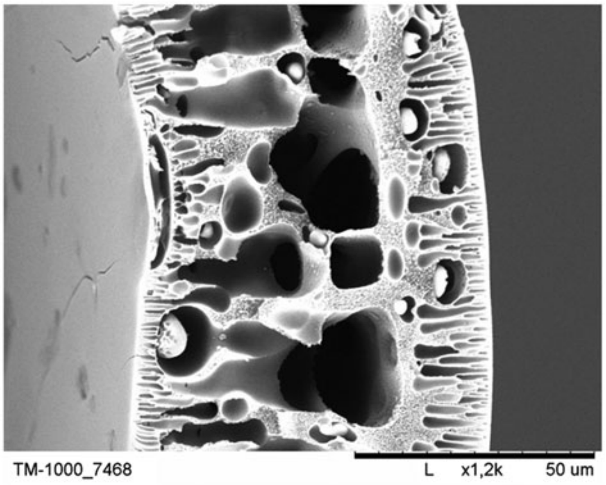

Fig. 8. Cross section PSf/PU-1 membranes before hydrolysis.

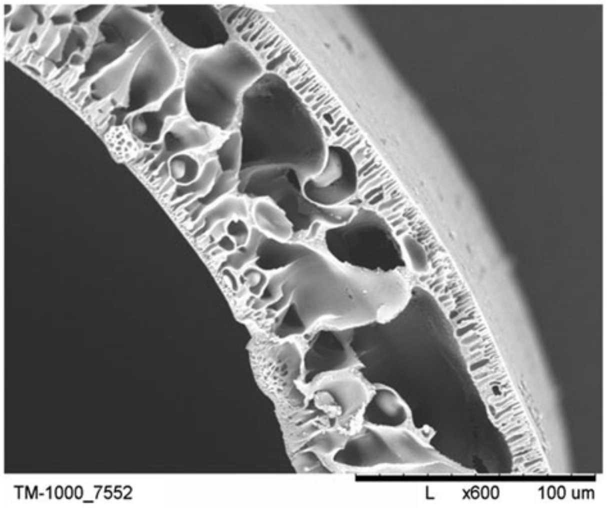

Fig. 9. Cross section PSf/PU-2 membranes before hydrolysis.

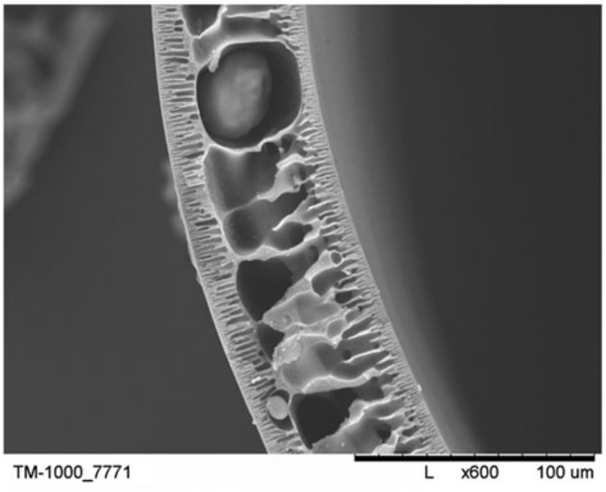

Fig. 10. Cross section PSf/PU-3 membranes before hydrolysis.

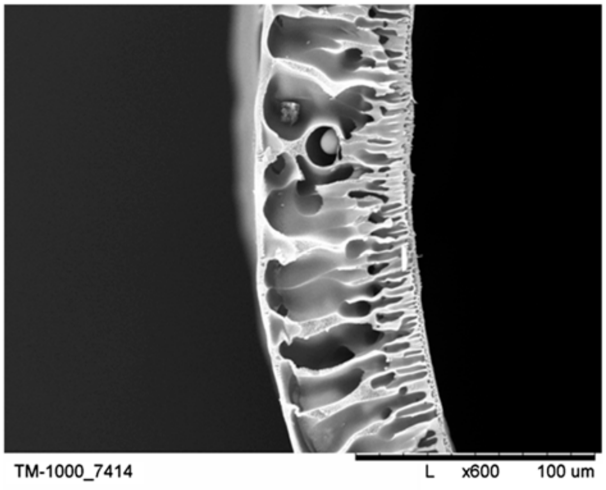

Fig. 11. Cross section PSf/PU-4 membranes before hydrolysis.

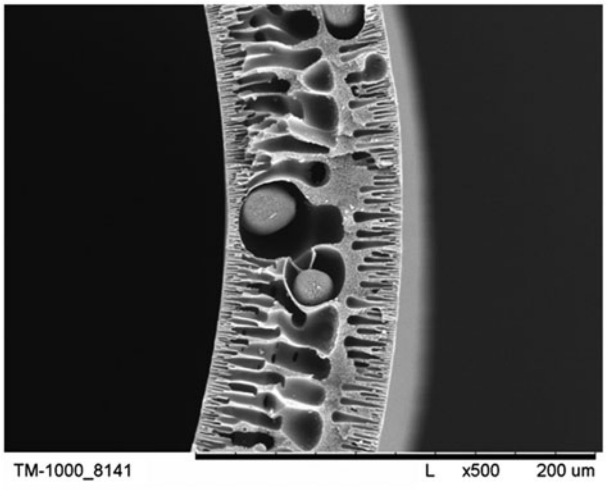

Fig. 12. Cross section PSf/PU-5 membranes before hydrolysis.

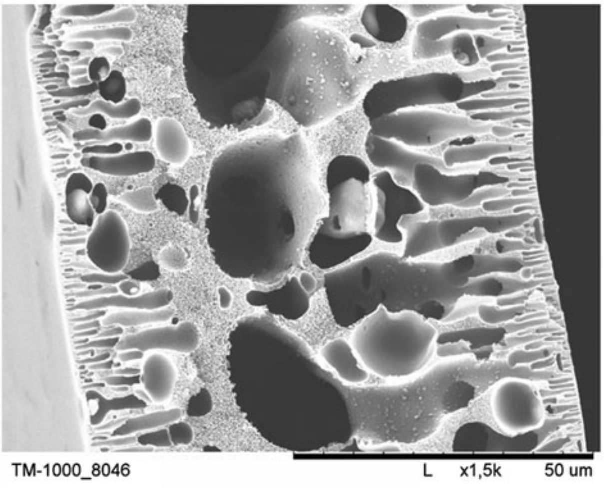

Fig. 13. Cross section PSf/PU-1 membranes after hydrolysis.

3.3. *SEM of membranes*

The PSf/PU membranes cross sections are presented in the figures below. The PSf/PU membranes before hydrolysis are presented in Figs. 8–12. The PSf/PU membranes after hydrolysis are presented in Figs. 13–17.

PU polymer pieces inside PSf structure before hydrolysis (Figs. 8–12) are shown in PSf/PU membranes cross section photographs. PU polymer pieces have globular shape and are fit inside large PSf macrophores. In the cross section photos of PSf/PU membranes after hydrolysis (Figs. 13–17) only minor parts of PU polymer are visible. The major part of PU polymer was removed from membranes as a result of hydrolysis. The removal of PU polymer causes new inner canal openings inside the membrane structure. These changes in structure are the most probable cause of the increased membrane permeability.

3.4. *Membranes mass measurements*

In order to see to what extent and to what amount the NaOH hydrolysis causes part of the membrane material to rinse out from the membrane structure, the membranes' mass was measured before and after

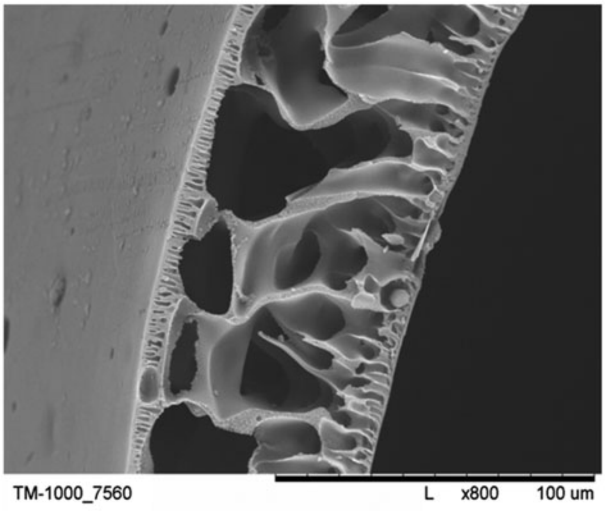

Fig. 14. Cross section PSf/PU-2 membranes after hydrolysis.

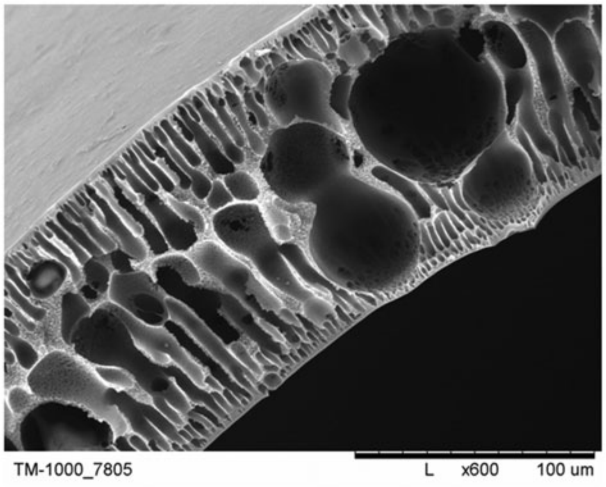

Fig. 15. Cross section PSf/PU-3 membranes after hydrolysis.

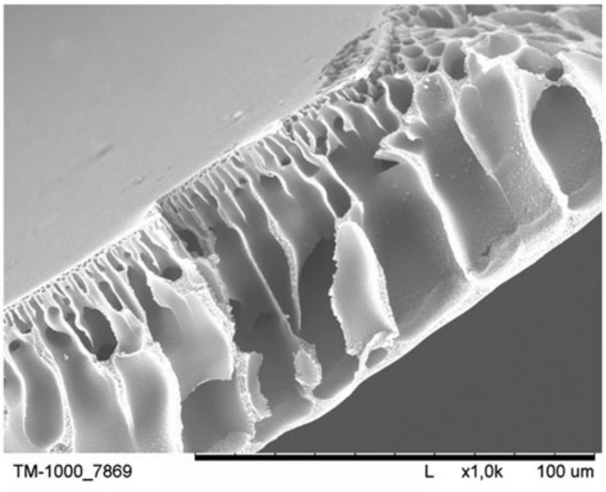

Fig. 16. Cross section PSf/PU-4 membranes after hydrolysis.

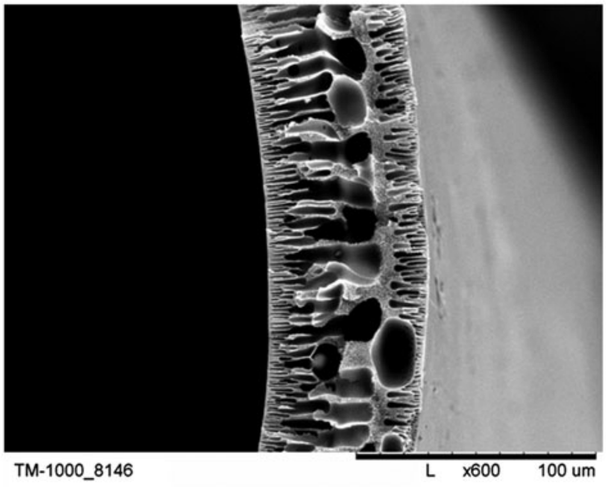

Fig. 17. Cross section PSf/PU-5 membranes after hydrolysis.

Table 2
Measurements of PU membranes mass before and after hydrolysis

Membrane	PU mass before hydrolysis (g)	PU mass after hydrolysis (g)	Difference of PU mass (g)	Difference of PU mass (%)
PSf/PU-1	0.1730	0.1272	0.0458	26.5
PSf/PU-2	0.1730	0.1321	0.0409	23.6
PSf/PU-3	0.1730	0.1296	0.0434	25.1
PSf/PU-4	0.1730	0.1251	0.0479	27.7

hydrolysis process. The PU mass makes up 25% of membranes mass in each module. The measurements were performed in two repeating for each PSf/PU membrane. The results of PU mass change are as shown in Table 2.

For all the types of PSf/PU membranes, the loss in PU mass after hydrolysis is considerable. Loss differences in PU mass for all types of membranes are comparable to each other and range from 23.6 to 27.7% (weight percentage). Such significant loss in PU mass had considerable influence on membrane structure as well as membrane flux.

4. Summary

Presented work described the production of five blended, polysulfone/polyurethane (PSf/PU) partly degradable, asymmetric hollow fiber membranes. The applied polyurethane polymer [poly(ester-carbonate-urea-urethane)s] contained degradable ester groups. All types of PSf/PU membranes were treated with 2 M NaOH water solution using the flowing method.

It was observed that coefficients of hydraulic permeability (UFC) increased significantly for all types of membranes after hydrolysis. Membranes' retention values were similar before and after applied hydrolysis, except for hydrolysis for the 20–35 kD retention range where the values were higher. The membranes cut-off (MWCO) after hydrolysis did not change and remained meanly at 45 kD. Removal of PU decomposition products after hydrolysis did not significantly change the membrane separation properties. For all types of PSf/PU membranes, the loss in PU mass in membranes after hydrolysis ranged from 23.6 to 27.7% (weight percentage). The SEM photos confirmed the majority of the PU polymer removal from membrane after hydrolysis.

The results mentioned above indicated that the decomposition occurred and PU ester groups were removed from the membrane structure as a result of PU ester groups' hydrolysis. The membrane porosity increased as a result of partial removal of membrane material and opening passages and pores inside the membrane, which caused an evident permeability increase in comparison to membranes before hydrolysis process application. The membranes' separation properties did not change after hydrolysis due to retaining unchanged membranes' MWCO. The change in membrane's selectivity was not significant.

The purpose of this work was to obtain the PSf/PU blend membranes of specific properties. The degradable polyesters application in PSf/PU membranes allowed to achieve slow, partial removal of membrane material during membrane's long-term operation time in water environment. The gradual process of porous clogging should balance the slow removal of PU ester groups decomposition products from membrane, reducing the fouling process, which should lead to opening the new porous. These set of membrane properties allows to retain long-term membrane processes efficiency despite the fouling progress.

The fouling phenomenon is an inherent problem concerning the membranes applied in biotechnology. The fouling causes decrease in membrane flux and selectivity. During membrane's working time, the partial degradation of membranes causes the formation of dispersed structure. As the result of that process the flux increases. The duration of the membrane processes is very important, especially in biotechnology, where regeneration or replacement of membranes during its operation is inadvisable or even impossible. The membranes presented in our article can be recommended for biotechnological processes, in which the fouling problem is particularly troublesome.

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