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Evaluation of separation characteristic of polysulfone membranes modified by polymer solvents etching

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ABSTRACT

In our work we have found a method of increasing the pore size of ready PSF membranes. We suppose that it is possible to effectively increase the membrane pore size without its degradation by acting on the membrane with a solvent of the polymer. We have found several solvents of the membranes and tested their effective action on ready membranes. Methyl acetate, ethyl acetate and methyl-ethyl ketone were checked as solvents. Ethanol was used as the non-solvent. For each membrane the etching conditions (solvent's content in ethanol, time of etching) were selected. When permeating the solvent/non-solvent solutions through the membrane walls, slight dissolution of the membrane structure which caused an evident increase in porosity was observed. The retention value of etched membranes from human blood serum macromolecules like: albumin, immunoglobulin IgG and IgM, cholesterol HDL and LDL was evaluated. There is a possibility to obtain membranes of different retention values, allowing to completely retain or pass all blood serum compounds. The retention features depending on etching conditions. Therefore there is a possibility to separate some of the selected compounds with the blood serum. Scanning electron microscopy was performed in order to determine membranes structure changes before and after the modification with etching solvent.

Keywords: Polysulfone capillary membranes; Retention; Treatment; Markers; Ultrafiltration coefficient

1. Introduction

Hydrophobility is a defect of polysulfone capillary membranes [PSF], which often leads to fouling, that is clogging of the membranes' pores. This results in a low productivity of the membrane process. This is why many authors try to modify the membranes in order to avoid or at least limit these disadvantageous effects. Many methods modifying the PSF membranes are known which are used to enhance their permeability for high-molecular compounds and increase of capacity. A low-temperature plasma processing was used in order to increase the hydrophilicity, as well as polymerization of monomers on the membranes surface. [1–4]. The membranes' structure was modified by adding porophores, or other hydrophilic compounds [5–9]. Other methods include modifying membranes by changing the casting solution or changing the process's parameters [10,11]. These methods are often unstable and expensive. Modifications of membrane-forming polymer often lead to worsening membrane properties, especially their biocompatibility and biochemical resistance.

While looking through the literature on the topic, we haven't found a satisfactory and efficient method

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which would modify the PSF membranes' structure and increase their cut-off point to 150–200 kDa. Therefore we started looking for a new method.

2. Experimental

2.1. Materials

Polysulfone [PSF] Udel 1700 NT LCD (Dow Corning) m.w.70000, N,N-dimethylfornamide [DMF] (POCH), N-methyl-2-pyrrolidone [NMP] (MERCK-Schuchardt), dimethylacetamide [DMA] (Sigma), polyvinylpyrrolidones [PVP] (Sigma), m.w. 10 and 55 kDa, polyethylene glycol [PEG] (Sigma), m.w. 15 and 35 kDa, ethyl acetate [EA], (Chempur), methyl acetate [MA], (Aldrich), ethyl methyl ketone [EMK], (Chempur), ethanol 96%, inulin, m.w. 5 kDa, (POCH), bovine serum albumin [BSA] (Fluka), m.w. 67 kDa, human blood serum.

2.2. Fabrication and modificated membranes

PSF capillary membranes we obtain have molecular weight cut-off (MWCO) ranging 10–60 kDa. In order to use them in separation of molecules having larger size than 60 kDa, their MWCO must be increased above that value.

In our work we undertook an attempt to increase the cut-off point of ready PSF membranes (made by us on our own capillary spinning installation) by increasing their pore size. To achieve this, we had to find a way to increase their pore size or cause some degradation of the membranes' structure, which would enable the molecules the size of proteins to pass easily. An original hypothesis was made, that it is possible to effectively increase the membrane's pore size without its degradation, by acting on the membrane with polymer solvent, which would minutely dissolute the polymer on the edges of the pores.

We found several polymer solvents of the membranes and tested their effective action on ready membranes. Methyl acetate [MA], ethyl acetate [EA] and methyl-ethyl ketone [EMK] were used as solvents of the polymer. We tried to dilute solvent by non-solvent, neutral to membranes, because their effect on the membranes was too strong. The most convenient would be the water, but unfortunately it creates two-phase system. Therefore 96% ethanol, being a polymer non-solvent itself, was used as the non-solvent, easily combining with the above mentioned solvents

We tried to use strong solvents of polymer, such as: DMF, NMP or DMA. They have the advantage of combining with water in every rate. They were used diluted with water, the concentration in the 2–10% range. Such strong solvents didn't have any visible effect on the membranes, whereas the concentration of 10% and higher resulted in instantaneous degradation of the membrane causing large holes on its surface. We haven't found the optimal concentration of the strong solvent of polymer, which would evenly dilute the polymer on the membranes' edges on their whole surface.

We modified the membranes after placing them on glass filtration modules with the capillaries' surface area in the range 30–32 cm^2 (including from 8 to 10 capillaries in module), which are resistant to solvents we used.

Treatment of membranes by solvents leads to weakening their mechanical properties. The membranes with thin walls (less than 80 μm) sometimes break after the treatment when the pressure is above 50 mmHg, because of the weakening of the capillary walls in the treatment process. That is why we chose three PSF membranes with the thickest walls, which parameters are seen in Table 1. Ultrafiltration coefficients (UFC) and retention values for: inulin (5 kDa), PEG (15 and 35 kDa) and bovine serum albumin (BSA) were measured for all above mentioned membranes before the treatment process.

Ultrafiltration coefficient was evaluated by measuring the volume of the solution passed through the membrane walls during ten min with stable transmembrane pressure.

[UFC = $V / P_{TM} \times S \times T$], where: V- volume of the solution, P_{TM}- transmembrane pressure, S- nominal capillary area, T- time of measure.

All the membranes have low UFC and complete retention for BSA. Their cut-off points are nearly the same and range 43–44 kDa. Curves of the characterizations of the markers molecular weight from retention values of chosen membranes are shown on Fig. 1.

Table 1
Parameters of membrane PSF 1–3

Membrane	Wall thickness [μm]	Inner diameter [μm]	UFC [cm^3/min cm^2 mmHg]	Retention BSA [%]	MWCO [kDa]
PSF -1	85	900	1.1	100	44
PSF -2	135	1075	2,0	100	43
PSF -3	185	1100	3,0	100	44

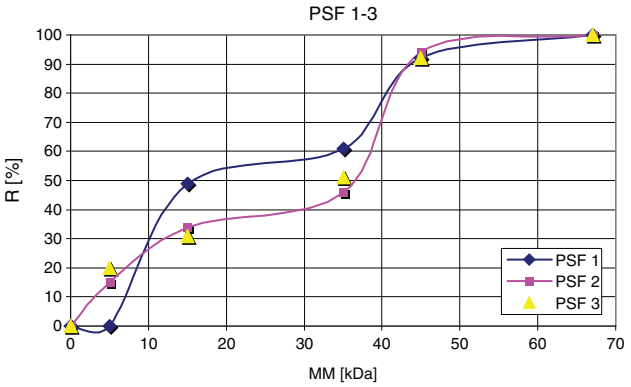

Fig. 1. Characterizations of membranes PSF 1–3.

Using an experimental method, suitable solvents and efficient composition of penetrate mixture were chosen for every membrane. Then the procedure of the treatment process was formulated. The same volume of the penetrate mixture was set at 160 cm^3 for every measurement while the content of the solvent in solution varied. Conducting the process under the constant pressure, the solution is let through to the capillaries, which significantly increases the flux of the solution at the end of the process, and causes an evident increase in porosity (as result of slight dissolution of the membrane structure), which often leads to damaging the membranes. That is why during the process, the pressure was reduced to eliminate the rapid changes of the flux at the end of the process, and for the whole process to run in the same time for all the measurements.

200 cm^3 of ethanol, 160 cm^3 of solvent-ethanol penetrate mixture, and at the end - 400 cm^3 of ethanol, were let through the capillary module in succession (Fig. 2). All the liquids were administered to the inside of the capillary module under initial pressure of 0.02 MPa and through the membranes' walls to the outside of the module. The flux of the penetrate mixture increased from 2–4 to 15 cm^3/min at the end of the process. The ethanol added after the treatment was to rinse the residue of the solvents and the polymer from the capillaries and module dissolved in them. Then the membranes were rinsed in 500 cm^3 of clear water in order to completely remove the solvents and ethanol.

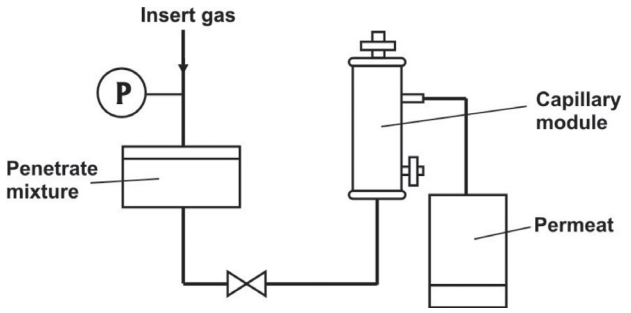

Fig. 2. Scheme of membranes' treatment.

2.3. Investigation of separation macromolecules on treatment membranes from human blood serum

Experimentally, optimal parameters of the treatment process were chosen, that is: solvent concentration in penetrate mixture, the time of the flux, and pressure under which the process took place.

Table 2 presents the composition of the penetrate mixture of constant volume of 160 cm^3 and varied solvent concentrations. For the PSF membrane the first solvent was EMK, for the other - EA (both dissolved in ethanol). Then, there are: the duration of the process, the pressure at the beginning and end of the process (column 3). The next columns show the changes of UFC before and after the treatment of membranes.

Human blood serum was used to determine the retention of high-molecular markers on membranes. The serum was let through the modules with the membranes after the treatment process, the retention values of the following markers: (tab. 2) albumin [69 kDa], immunoglobulin IgG [150 kDa], cholesterol HDL [125–320 kDa], immunoglobulin IgM [900 kDa] and cholesterol LDL [23000–27000 kDa].

The concentration of immunoglobulin IgG and IgM in the serum at the entrance to the module and in the filtrate was indicated on the Turbox analyzer by nephelometry method. Albumin and cholesterols HDL and LDL were indicated with colorimetric method using spectrophotometer HITACHI U-3010.

3. Results

3.1. Separation macromolecules from human blond serum

The disadvantage of using protein markers, especially macromolecules is that they settle on the membranes' walls (so-called fouling), which results in clogging the pores and obstructing the solutions. In order to see how the retention of macromolecules changes during the process, their retention values were marked each 30 min during 3 h.

The UFC of membranes after the treatment is higher than those than don't undergo such process. It applies to all of the tested membranes. The smallest increase of the UFC is noted for the PSF 1 membrane where EMK had been used as a solvent. For other membranes where the solvent had been EA, the increase of UFC is significant and it rises further with the increase of the concentration of EA in the treatment solvent. In the membranes treated with 31% EA solution, UFC increases from 2–3

Table 2
Parameters of treatment process, UFC and retentions value of macromolecules from human blood serum

Membrane	Solvent's concentration in treatment solution	Parameters of treatment Time [min] Pressure [mmHg]	UFC before treatment	UFC after treatment	Albumin R [%]	HDL R [%]	IgG R [%]	IgM R [%]	LDL R [%]
PSF 1	EMK (56%)	Time-18 Pressure-120	1.1	2.8 ± 1	45–95	75–100	65–96		
PSF 2-1	EA (50%)	Time-22 Pressure-110	2	60 ± 8					10-0
PSF 2-2	EA (50%)	Time-36 Pressure-110	2	30 ± 6				0	5
PSF 2-3	EA (31%)	Time-34 Pressure-120	2	4.2 ± 1	7–1				52-34
PSF 3-1	EA (50%)	Time-16 Pressure-200-120	3	20 ± 3		0		0	10
PSF 3-2	EA (50%)	Time-18 Pressure-200-90	3	40 ± 4	0			0	10
PSF 3-3	EA (50%)	Time-15 Pressure-200-90	3	15 ± 2	5				5
PSF 3-4	EA (50%)	Time-18 Pressure-200-140	3	22 ± 2	0				0
PSF 3-5	EA (38%)	Time-16 Pressure-200-110	3	33 ± 2	10–40			20–60	100
PSF 3-6	EA (31%)	Time-15 Pressure-200-170	3	8.0 ± 1	83	100	93		

before the treatment to 4,2 (PSF 2–3) and 8 (PSF 3–8) [$cm^3 \cdot min^{-1} \cdot m^{-2} \cdot mm\,Hg^{-1}$] after the treatment. The cause of the difference is that, these are two different membranes and various parameters of the treatment process were used for each of them. As for the membranes treated with 50% EA solution, UFC is in the range of 15 to 60 [$cm^3 \cdot min^{-1} \cdot m^{-2} \cdot mm\,Hg^{-1}$] after the treatment, which is a major increase in comparison to UFC ranging 2–3 [$cm^3 \cdot min^{-1} \cdot m^{-2} \cdot mm\,Hg^{-1}$] before the treatment.

The PSF 1 membrane (Fig. 3), was the only one for which EMK was used as a polymer solvent in the penetrate mixture. The retention was marked for albumin, IgG and HDL. After every 30 min it amounts to 45, 65 and 75%. After 120 min, the retentions of the above mentioned compounds were in the 95–100% range. This is a typical case of fouling. Further attempts at using EMK as a solvent for that and other two membranes gave similar results. That is why in the next tests EA was used as a polymer solvent.

Two other membranes: PSF 2-1 and PSF 2-2 (Figs. 4 and 5) were treated similarly (the same composition of the penetrate mixture). The retentions of the markers for

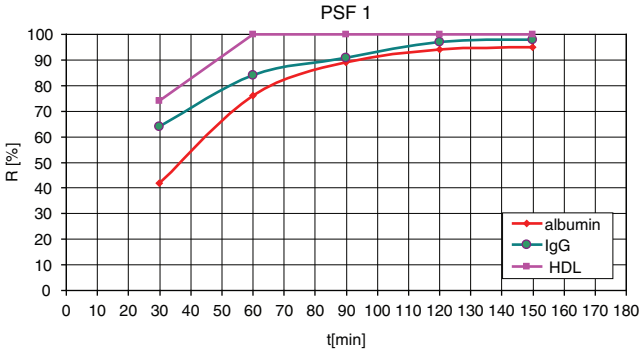

Fig. 3. Retentions of albumin, IgG and HDL from separation time on membrane PSF 1.

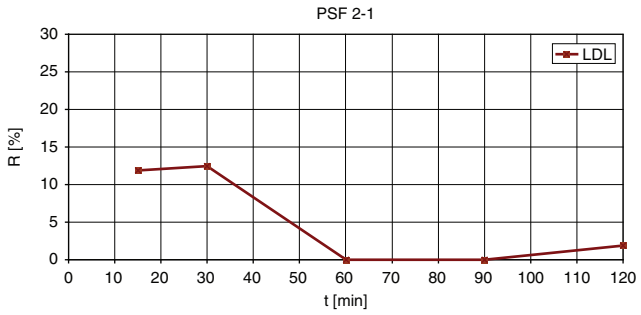

Fig. 4. Retentions of LDL from separation time on membrane PSF 2-1.

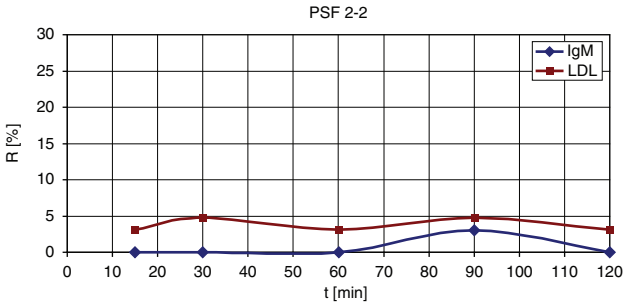

Fig. 5. Retentions of IgM and LDL from separation time on membrane PSF 2-2.

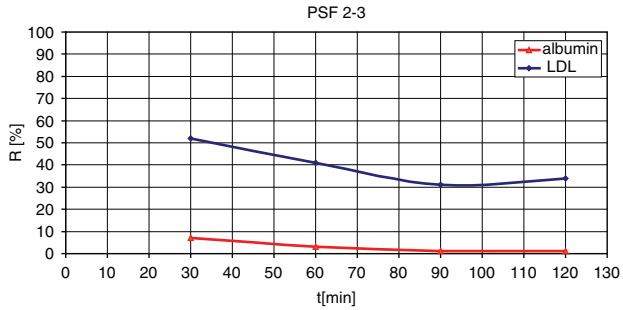

Fig. 6. Retentions of albumin and LDL from separation time on membrane PSF 2-3.

each of them are low in the time they were measured (15–120 min). Membrane PSF 2–3 (Fig. 6) was treated with a solution having a lower concentration of the solvent in the treatment solvent than the other two, and its UFC is considerably lower (Table 4). The retention of albumin decreases during the measurement from 7 to 1%, whereas for LDL in decreases from 52 to 34%. This significant difference in retention between the albumin and LDL enables partial separation of these two compounds from the blood serum.

The membrane PSF 3 (Figs. 7–12) underwent eight treatment processes and separation measurements. The first four PSF 3 (1–4) were treated with solution of the

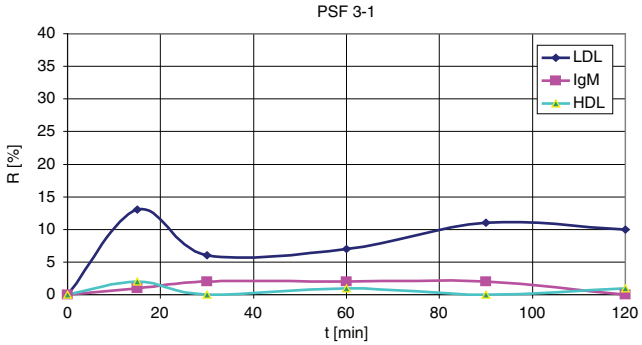

Fig. 7. Retentions of HDL, IgM and LDL from separation time on membrane PSF 3-1.

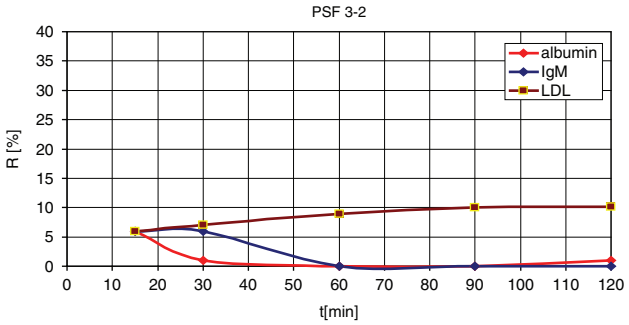

Fig. 8. Retentions of albumin, IgM and LDL from separation time on membrane PSF 3-2.

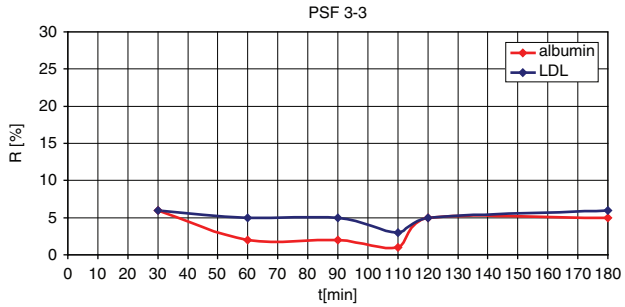

Fig. 9. Retentions of albumin and LDL from separation time on membrane PSF 3-3.

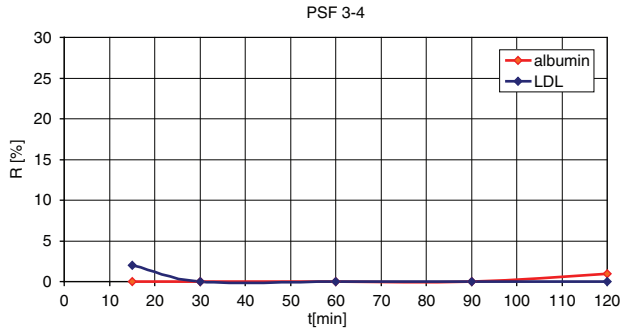

Fig. 10. Retentions of albumin and LDL from separation time on membrane PSF 3-4.

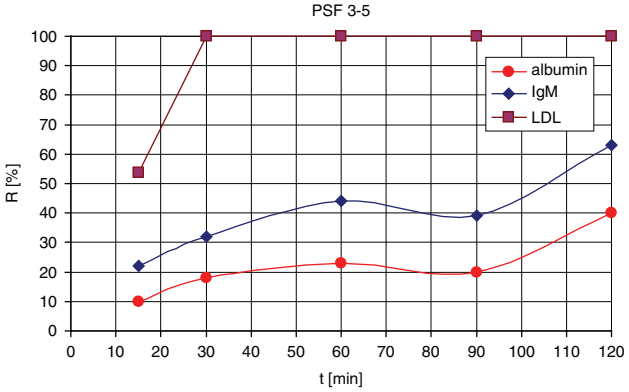

Fig. 11. Retentions albumin, IgM and LDL from separation time on membrane PSF 3-5.

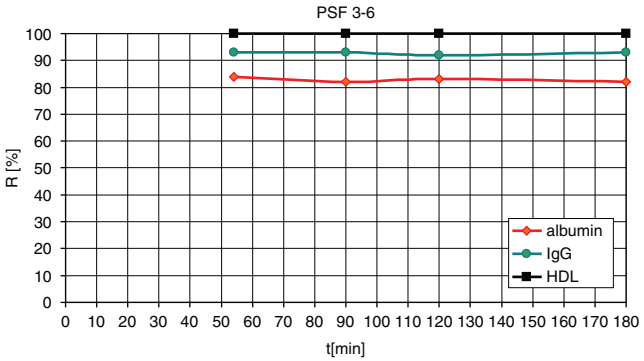

Fig. 12. Retentions of albumin, IgG and LDL from separation time on membrane PSF 3-6.

highest concentration of solvent (50%). All the compounds from serum, LDL included were let through these membranes. The PSF membranes 3–5 were treated with concentration of 38% solvent in the etching solution. Retention for LDL after 30 min amounted to 100% and remained unchanged through the whole separation process. For albumin it increased from 10 to 40%, and for IgM from 20 to 60% during the process. The difference between the LDL retention, and albumin and IgM retentions, enables conducting complete separation of LDL from the serum on this membrane, especially in the time range of 20–90 min, when retention for the highest of the other IgM compounds was in the range of 40%. The last membrane (PSF 3–6) was treated with a solution with the lowest concentration of the solvent in the etching solution (31%). The retention values are following: for albumin - 83%, IgG - 93% and HDL - 100% and they are stable during the measurement time, the membrane is resistant to fouling, but it almost thoroughly retains the above mentioned markers.

3.2. Measurements mass and flame analysis of membranes

In order to see if the treatment with solvents causes part of the membrane material from the membrane to rinse out, and to what extent, the membranes' masses were measured before and after the treatment process.

The membranes were placed in modules and treated with solutions of following compositions: for PSF 1 – EMK (56%), for PSF 2 – EA (50%), for PSF 3 – EA (31%) and PSF 3 – EA (50%), these are the same as the ones used treating the membranes when testing compounds in the blood serum. The measurements were done twice for each membrane. The results are as shown in Table 3.

For the PSF 1 membrane the loss in mass is the smallest, comparing to others. It is due to greater resistance to the solvent, which was EMK. This resulted in high retentions of the compounds let through the membrane. (Fig. 3), while the increase of UFC in this membrane after the treatment is the lowest in comparison.

For PSF 2 membrane the loss in mass is significant – 18.6%. The result is complete permeability to IgM and LDL (Figs. 4 and 5) and high increase of UFC.

Measurement of mass for PSF 3 membrane was done in two cases. For the membrane treated with 31% OE – the loss is slight, comparable to PSF 1 membrane, and the retention values of the marked compounds are high as well (Fig. 12). In the second case, the membrane was treated with 50% OE (Figs. 7–10), the loss in mass is very significant (25.7 %). That is why permeability of all of the marked compounds is almost complete.

We can conclude that the loss in mass of the treated membranes depends on the kind of solvent and its concentration. It increases with its concentration in the etching solution. Retention of these compounds decreases with the rise of the difference in loss in the mass of the membranes after the treatment.

PVP was the porophor for all the casting solutions, from which the membranes were obtained. In order to see what is rinsed out from the membrane – is it only PSF, or is it PSF with PVP, and at what rate, non-modified and modified membranes, as well as the dry filtrate residue (of solvent after the membranes' treatment) underwent flame analysis, on analyzer CHNS. Analysis of PVP and PSF contents are based on marking sulphur and nitrogen in the material of the membrane. PSF 2 and PSF 3 membranes underwent analysis before and after the solvent treatment (treated exactly as described above). The percentages of the marked chemical elements were converted to PSF and PVP, as shown in Table 4. To obtain an adequate amount of the material, etching solution filtrate was gathered from several treatment processes and evaporated to dry matter.

Table 3
Measurements mass of membranes before and after treatment

Membrane	Mass before treatment [g]	Mass after treatment [g]	Difference of mass [g]	Difference of mass [%]
PSF 1 (EMK-56%)	0.0595	0.0566	0.0029	4.9
PSF 2 (EA-50%)	0.1138	0.0926	0.0212	18.6
PSF 3 (EA-31%)	0.1682	0.1569	0.0113	6.7
PSF 3 (EA-50%)	0.1656	0.1229	0.0427	25.7

Table 4
Flame analysis of membranes and filtrate

Membrane	Contents of PSF (%)		Contents of PVP (%)	
	Before treatment	After treatment	Before treatment	After treatment
PSF-2	97.5	98	2.5	2.0
PSF-3	98.8	98.8	1.2	1.2
Dry remains of filtrate		98.7		1.3

In PSF 2 and PSF 3 membranes, the PSF and PVP content is the same before and after the treatment process. It means that both compounds are rinsed evenly. In the dry remains of the filtrate, the composition of the compounds in percentage is almost the same as in those membranes. In the rinsed material from PSF membrane, it constitutes 90% of the mass, and PVP - 2%.

3.3. Scanning electron microscopy (SEM) membranes

Photographers of outer surface of PSF 2 and PSF 3 membranes (photo 1,2) were taken to determine the changes in the membrane structure before and after the modification by the etching solution.

Photo 1. Outer surface of membrane PSF 2 before (photo A) and after treatment (photo B). Magnification 5000x.

Photo 2. Outer surface of membrane PSF 3 before (photo A) and after treatment (photo B). Magnification 5000x.

In the photo 1A and 2A on the left, there is an image of outer surface of PSF 2 and PSF 3 membranes before the treatment. The surface of their outer skin layer is even and consists of pores similar in size. In the picture 1B and 2B the same membranes are shown under identical magnification after the treatment. The ”black holes” on their surfaces are the result of the treatment process. These are macropores of 4–6 μm diameters, and they are linked to even greater pores under the skin layer. These kinds of damages are the most probable cause of the increased membrane permeability. It is also possible that the links between the pores inside the membrane undergo similar changes, and it creates an opening of inner canals which brings about the increase of the flux.

4. Conclusions

During our search on the topic we haven't found a satisfactory method which modifies the structure of PSF membranes increasing their cut-off point, enabling the separation of macromolecules' compounds from the blood serum. The new method was suggested. After selecting the polymer solvents of the membranes, the etching solvents were put through the membrane, which caused partial dissolving of the polymer, increasing its pore size. This way their filtration and separation capabilities were more efficient. The modified membranes have high hydraulic permeability. The membranes before the treatment had low cut-off points of 44 kDa, and they didn't let through even BSA (67 kDa). Depending on the method of treatment (solvent concentration, process parameters) we can receive membranes of different retention of macromolecules compounds – from the ones entirely retaining them to the ones letting through all the marked compounds in the blood serum, including LDL (23000–27000 kDa).

The presented modification method doesn't require complicated apparatus, or expensive materials. The solvents are low-cost and non-toxic, and the treatment set-up is easy to make. The duration of the modification process is short and its effect is permanent longstanding. There are no limitations to the scale of the process. It is imperative though, to use modifications in the membranes' modules which are resistant to solvents (glass, teflon, steel). The following parameters of the treatment process: concentrations of the solvent in the ethanol solution, time of the flux through the module, and the pressure, have to be precise and carefully considered. The slightest changes in the solvent concentration or flux time cause considerable alternations in the membranes' permeability.

References

[1] J. Wolff, H. Steinhauser and G. Ellinghorst, Tailoring of ultrafiltration membranes by plasma treatment and their application for the desalination and concentration of water-soluble organic substances, J. Membr. Sci., 36 (1988) 207–214.
[2] M.L. Steen, L. Hymas, E.D. Havey, N.E. Capps, D.G. Castner and E.R. Fisher, Low temperature plasma treatment of asymmetric polysulfone membranes for permanent hydrophilic surface modification, J. Membr. Sci., 188 (2001) 97–114.
[3] F.F. Stengaard, Characteristics and performance of new types of ultrafiltration membranes with chemically modified surfaces, Desalination, 70 (1988) 207.
[4] A. Higuchi, N. Iwata and T. Nakagawa, Surface-modified polysulfone hollow fibers. II. Fibers having $CH_2CH_2CH_2SO_3^-$ segments and immersed in HCl solution, J. Appl. Polym. Sci., 40 (1990) 709.
[5] Y. Liu, G.H. Koops and 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.
[6] B. Chakrabarty, A.K. Ghoshal and M.K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, J. Membr. Sci., 309 (2008) 209.
[7] J.H. Kim and K.H. Lee, Effect of PEG additive on membrane formation by phase separation, J. Membr. Sci., 138 (1998) 153.

[8] J.F. Li, Z.L. Xu and H. Yang, Microporous polyethersulfone membranes prepared under the combined precipitation conditions with non-solvent additives, Polym. Adv. Technol., 19 (2008) 251.
[9] S.J. Shin, J.P. Kim, H.J. Kim, J.H. Jeon and B.R. Min, Preparation and characterization of polyethersulfone microfiltration membranes by a 2-methoxyethanol additive, Desalination, 186 (2005) 1.
[10] T.S. Chung, S.K. Teoh and X. Hu, Formation of ultrathin high performance polyethersulfone hollow fibre membranes, J. Membr. Sci., 133 (1998) 161.
[11] P. Aptel, N. Abidine, F. Ivaldi and J.P. Lafaille, Polysulfone hollow fibres ± effect of spinning conditions on ultrafiltration properties, J. Membr. Sci., 22 (1985) 199–215.