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Polysulphone and Polyethersulphone Hollow Fiber Membranes with Developed Inner Surface as Material for Bio-medical Applications

ANDRZEJ CHWOJNOWSKI*, CEZARY WOJCIECHOWSKI, KONRAD DUDZIŃSKI, EWA ŁUKOWSKA

Institute of Biocybernetic and Biomedical Engineering, Polish Academy of Sciences, Warsaw, Poland

A method of obtaining hollow fibers with developed internal surface has been elaborated. As materials were selected synthetic polymers, namely polysulphone Udel P-1700 and polyethersulphone Ultrason E2020P. This method enables the obtaining of such membranes by means of a spinneret with smooth walls and the installation for spinning hollow fibers. A mechanism of the formation of corrugations on the membrane internal surface has been proposed. The effect of spinning parameters on membrane formation has been described. An explanation of the reasons of formation of defects on the external skin layer has been proposed.

K e y w o r d s: Polysulphone membranes, polyethersulphone membranes, hollow fiber membrane

1. Introduction

Many different types of semipermeable hollow fibers have been prepared using the well known dry or wet spinning techniques [1–8]. For membranes preparation, various polymers were used and the effect of various parameters involved in the spinning process was studied [1–16]. In the dry/wet spinning technique, coagulation of the internal surface of the nascent fiber starts immediately after extrusion from the spinneret, whereas the external surface experiences coalescence and orientation of polymer aggregates through the spinning line before gelation in the external coagulation medium [15]. When a polymer solution is extruded through a tube in the spinneret orifice, shear stress is induced within the thin annular of the spinneret. It was

* Correspondence to: Andrzej Chwojnowski, Institute of Biocybernetic and Biomedical Engineering, Polish Academy of Sciences, ul. Ks. Trojdena 4, 02-109 Warsaw, Poland, e-mail: achwoj@ibib.waw.pl
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reported in various studies that the stress affects dramatically the polymer molecular orientation and relaxation at the outer surface of the nascent fiber. If there is an air gap before coagulation, the effects of elongation and relaxation will play important roles. The induced elongation stresses outside the spinneret from gravity and spin line stresses complicate the kinetics and dynamics of the phase inversion process [16]. Lately, it was reported that molecular orientation induced by shear stress within the spinneret might relax in the air gap region if the elongation stress along the spin line is small as spinning solution is a visco-elastic fluid, or enhance if the spin line stress is high [14, 17]. In fact, elongation stress caused by gravity becomes more pronounced with increasing air gap. In membrane literature, various studies were carried out on polymeric hollow fiber preparation and characterization [1–23]. All studied fibers were prepared mostly in air or in a humid air spinning line [1–26].

The prepared hollow fibers are being applied in various processes such as gas separation, ultrafiltration, reverse osmosis, dialysis, etc. Membrane technology is of major importance in medical applications, in particular in a number of life saving treatment methods. Membranes are used in drug delivery, artificial organs, tissue regeneration, diagnostic devices, as coatings for medical devices, bio-separations, etc. The total membrane area produced for medical applications almost matches all industrial membrane applications together [26]. In fact, in fiscal terms, the value of medical membrane products is far larger than all other applications combined [26, 27]. At present, in medical and biotechnological applications greater and greater attention is drawn to the development of Bio-Artificial-Organs (BAO), which can be a chance of temporary supplementing the lost or miss-functioning parts of an organism [28, 29].

The possibility of obtaining developed surfaces of hollow fiber membranes seems to be very interesting. An increase in the exchange surface should cause an increase in the permeability of membranes [30–33]. Ceramic multi channel membranes produced and delivered by Fairey Filtration Systems Ltd. are an example of membranes of increased internal surface. The internal surface of channels in these ceramic membranes has a developed, corrugated surface. Recently, two patents and a work describing the method of obtaining hollow fibers of developed internal and external surfaces by means of specially designed spinnerets have been published [34–36]. However, this method has some limitations resulting from technological reasons when making the spinneret. Technological difficulties limit the size of corrugating the hollow fiber surface. The obtaining of internal corrugation above 200 μm is sufficient, when only an increase in the surface is concerned, but too large for cell cultivation. However, when utilizing the method called phase separation micromolding it was possible to obtain flat scaffolds with corrugation every 20–50 μm [37–38]. This is a value satisfactory in cell cultivations.

The purpose of the work was to work-out a method of obtaining semi-permeable hollow fiber membranes of developed internal surface. These membranes we intended to obtain by means of a typical spinneret used in the preparation of typical classic cylindrical fibers. We decided to select only appropriate conditions of hollow fiber spinning.

We believed that it will be possible to achieve a required effect without the necessity of using micro-engineering techniques in designing the spinnerets. These membranes were predicted for biotechnological applications, especially for cell cultivation. The membranes developed by us can be used as a synthetic carrier playing a supporting role for biological components (e.g. hepatocytes). We also see their application in the design of bio-artificial organs. The developed, corrugated internal structure should permanently facilitate the placing of cells on the surface of the membrane.

2. Experimental

2.1. Materials and Methods

In Table 1 all materials used in our work and molecular weight for polymers and proteins are given.

Table 1. Materials list

Substance type	Molecular weight (MW) [g/mol]	Supplier
Polysulfone (PSF) UDEL 1700 NT LCD	70.000	Dow Corning
Polyethersulfone (PESF) Ultrason E2020P	42.000	BASF
Polyvinylpyrrolidone (PVP)	10.000	Sigma
	40.000	
	55.000	
Polyethylene glycol (PEG)	15.000	Sigma
	35.000	
Albumin from chicken egg white (CEA)	45.000	Sigma
Bovine serum albumin (BSA)	67.000	
Innulin	5.000	
N,N-dimethylformamide (DMF)	–	MERCK
N-methyl-2-pyrrolidone (NMP)	–	
N,N-dimethylacetamide (DMA)	–	
Glycerol	–	POCH

All solvents and polymers were dried and stored under dry argon or nitrogen. Membrane forming mixtures were prepared in a dry inert gas atmosphere (argon or nitrogen) in amber glass flasks. Membrane forming mixtures were heated up to 39–41°C and stirred with a magnetic stirrer up to 48 hours.

Determination of the cut-off point was made by transferring aqueous solutions of markers of 1 g/dm^3 concentrations through a hollow fiber module at continuous circulation, at trans-membrane pressure of 0.10 MPa. The concentration measurements were carried out every 0.5 hour during 4 hours.

The concentrations were determined spectrometrically by means of a UV-VIS HITACHI – 3010 spectrophotometer. The membrane images were taken with a HITACHI TM1000 and HITACHI N-3500 scanning electron microscope, without coating by conductor.

2.2. Preparation of Hollow Fiber Membranes

Membranes were made of polysulfones and polyethersulfones. Polymer solutions were prepared by dissolving PSF or PESF in one of the listed in Table 1 solvents. Different amounts of pore forming agents (PVP of various MW) were added to the PSF or PESF solutions. The concentrations of membrane forming polymers and PVP depended on the properties of membranes we wanted to achieve, such as cut-off point, fiber diameter and wall thickness. The solutions were prepared in an atmosphere of dry gas such as air, argon or nitrogen.

The hollow fiber membranes were prepared by means of a home-made device with replaceable spinnerets. The membrane formation was computer controlled by special software enabling quick change of the process parameters. In the coagulation and washing baths during membrane formation and washing process constant water flow was maintained.

The polymer solution was delivered from a chamber to the external spinneret nozzle by a spinning pump, whereas the core fluid (water) to the central nozzle under the pressure of nitrogen from the cylinder (666.6–4444 Pa or 5–40 mmHg). The size of the air gap was 13–29 cm from the water level. The temperature of the membrane forming mixtures, air and spinneret was 21–22°C. The temperature of water in the coagulation and washing baths was 20±1°C. Relative humidity of air in the air gap was controlled in the range from 60 up to 99%.

For obtaining membranes with a corrugated internal surface, very small pressures of the core liquid were applied. It was also necessary to experimentally determine the air gap. The hollow fiber, after going through subsequent rinsing baths was spinned onto a receiving reel and rinsed for about 4 hours in water. The final stage consisted in rinsing in 10% aqueous glycerol solution for 1 hours and drying. Glycerol remaining in the pores assured hydrophility of the membranes.

For comparison purposes, hollow fibers of identical inner diameter and similar average thickness of the inner wall undeveloped structure were made. These membranes were made from the same membrane-forming solutions as membranes with a developed surface.

From the membranes obtained modules of 25 cm^2 surface were made for further studies. For all the membranes, the ultrafiltration coefficient (UFC), defined as the volume of water penetrating through the hollow fiber walls in a time unit at a given constant pressure, was determined. For all membranes the molecular weight cut off was also determined, equal to the molar mass of the compound stopped by the membrane in 90%.

3. Results and Discussion

By experimentally setting the air gap size and core fluid pressure it is possible to obtain a hollow fiber with developed internal surface with the aid of a typical spinneret of smooth walls. When operating only with spinning parameters, utilizing the same apparatus and the same membrane-forming mixture, we obtained hollow fiber membranes of various internal wall structure. These can be both membranes of smooth walls (Fig. 1a) as well as membranes of developed internal surface (Fig. 1b). The size of corrugation of the membrane inner side depends on the core liquid pressure. This relationship is inversely proportional to the core liquid pressure. However, this dependence covers only a relatively narrow range of pressures 666.6–6666 Pa (5–50 mmHg). At pressures above 4444 Pa (40 mmHg) the inner wall is already

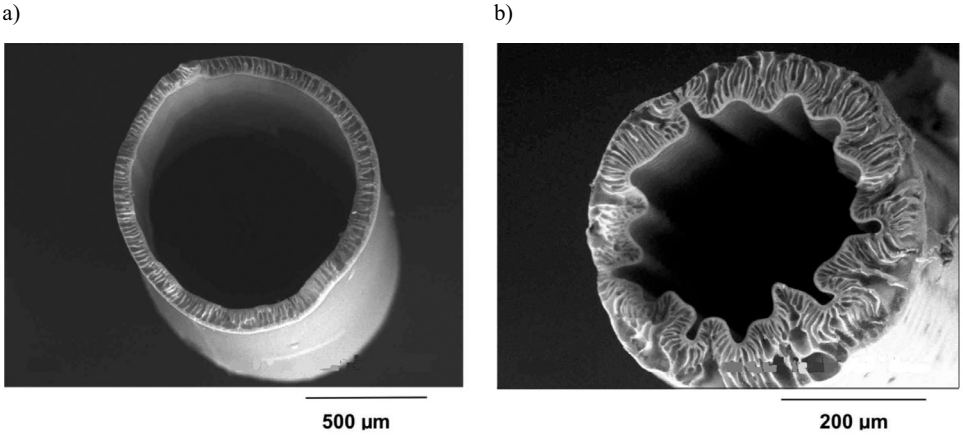

Fig. 1. SEM photomicrograph of polysulfone membranes a) smooth walls, b) developed internal surface

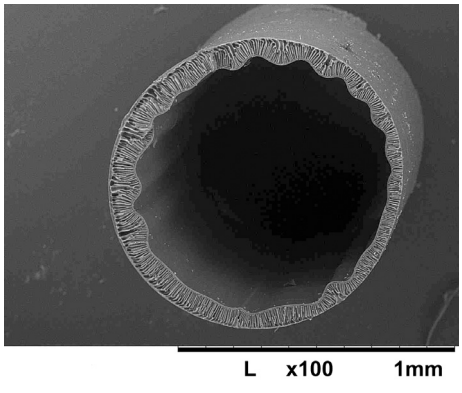

Fig. 2. SEM photomicrograph of polysulfone membrane, magnification ×100. Slight corrugation of the inner wall is visible

nearly flat (Fig. 2). At pressures lower than 666 Pa (5 mmHg) it is not possible to obtain a correct hollow fiber. Thus, it is necessary to maintain the core liquid pressure in the given range.

It was found that the relative humidity of air in the air gap is of fundamental importance when obtaining hollow fibers with developed inner surface. Humidity measurements were carried out at a distance not greater than 40 cm from the spinneret and air gap. Humidity should be as high as possible, but always above 90%. At such high humidity the skin layer on the hollow fiber outer surface is smooth and uniformly formed (Fig. 3a). When lowering humidity below 90%, longitudinal cracks start to appear (Fig. 3b). At humidity below 75% the hollow fibers look as if the longitudinal strips on the outer side of hollow fibers were completely devoided of the skin layer. Open macropores are clearly visible (Fig. 3c). The inner side of the hollow fibers was, however, always formed correctly. Hear never a lack of covering of the inner surface with a skin layer was observed.

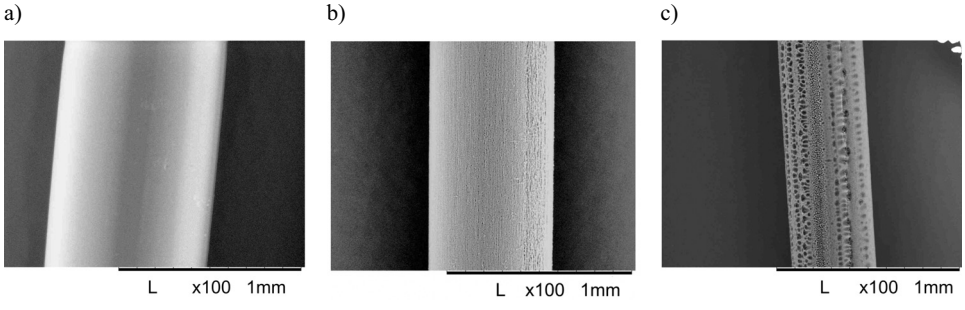

Fig. 3. SEM photomicrograph of the outer side of polysulfone membranes obtained in: a – high humidity (above 90%); b – some lower humidity (below 90%); c – humidity below 75%

The formation of hollow fibers without the skin layer, both on the inner and outer surface, was never observed when obtaining membranes of classical structure. Classical membranes were obtained many times at various air humidity (40 – 99%), various spinning rate and with the use of various spinnerets.

These observations inclined us to suggest the following mechanism of forming a developed internal surface during spinning hollow fibers. When forming hollow fibers, first external and internal skin layers are formed. At that time the pressure of the membrane-forming mixture is decisively higher than that of the core liquid (Fig. 4). The external skin layer being formed as a result of very high humidity achieves sufficient resistance not to undergo cracking. Simultaneously, the pressure of the membrane-forming mixture causes the formation of corrugation of the inner skin layer. Minimal pressure of the core liquid is not capable to prevent this process. As a result, the internal side of the membrane is formed into folds. This state is retained in the gelating bath.

However, when the air humidity in the air gap is too low, the formed skin layer is too thin to withstand the membrane-forming mixture internal pressure. We then observe cracking of the skin layer (Fig. 5 and 3c), and on the hollow fiber surface stripes appear lacking of the typical skin. If during the same spinning process we increase the relative humidity in the air gap, e.g. by forced water vapor flow, a suitable skin appears.

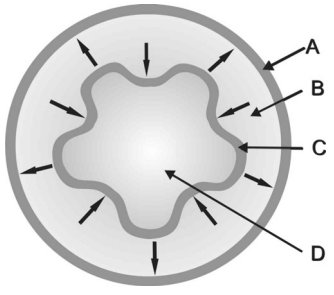

Fig. 4. Suggestion of the mechanism of hollow fibers with developed inner surface formation. The arrows between skin layers represent directions of pressure effect. A) external skin layer, B) liquid membrane forming mixture, C) internal skin layer, D) core liquid. See Fig. 3a and 8 also

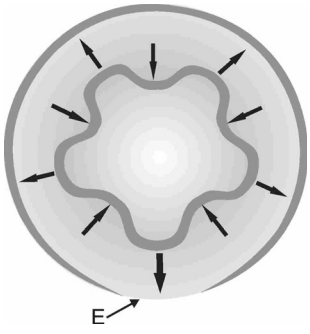

Fig. 5. Suggestion of the mechanism of hollow fibers with cracked skin formation. The place showing cracking and "separation" of the skin layer is marked E. It appears when the air humidity in the air gap is too low. The formed skin layer is too thin to withstand the membrane-forming mixture internal pressure. See Fig. 3c also

Studies of the basic properties of the membranes obtained showed some general features. When maintaining gelating temperatures, the membrane cut-off points depended only on membrane-forming mixture composition. They did not depend, however, on the internal surface shape. Molecular weight cut off (MWCO) was identical for membranes of developed and classical (cylindrical) surfaces made from the same solution or solutions of the same composition. What is more important, this regularity was maintained even for membranes of defected outer skin layer.

The degree of damage of the external skin layer did not affect the cut-off point. Also, measurements of the greatest pore by the "bubble point" method did not show

essential differences between classical membranes and those with a developed surface, providing they were made from the same membrane-forming mixture. However, the differences in water permeability for classical membranes and those of developed surface were considerable. The following assumptions were made to obtain the most similar geometrical parameters:

- only membranes made from the membrane-forming mixture of identical composition and membranes of the most similar internal diameter are to be compared,
- membranes of the most similar wall thickness are to be compared,
- membranes on non-defected external skin layer are to be compared.

It was very difficult to select appropriate membrane pairs. It was, therefore, assumed that the classic membrane wall thickness should be included between the smallest thickness of the corrugated membrane and average thickness of that membrane. Then, the ratio of the internal surface to the outer one for all the hollow fibers was calculated. This ratio was denoted with the symbol χ (see Table 2). It is a good indicator of the membrane internal surface increase and useful indicator when comparing classical membranes and those with developed surface.

Table 2. Molecular weight cut-off, circumferences of membranes and hydraulic permeability coefficient for polysulfone (PSF) and polyethersulfone (PESF) hollow fibers. χ – internal surface/external surface

Sample No	MWCO [kD/mol]	External circumference [μm]	Internal circumference [μm]	χ	UFC [$cm^3 \cdot min^{-1} \cdot m^{-2} \cdot mmHg^{-1}$]	% increase UFC
PSF 1-1	*21*	*1797*	*1580*	*0.713*	*2.1±0.1*	–
PSF 1-2	**22**	**1696**	**1548**	**0.913**	**3.0**±*0.1*	**42**±*0.5*
PSF 2-1	*32*	*1539*	*1099*	*0.717*	*2.3±0.1*	–
PSF 2-2	**32**	**1477**	**1570**	**1.063**	**3.8**±*0.1*	**65**±*0.5*
PSF 3-1	*42*	*1561*	*1052*	*0.714*	*3.1±0.1*	–
PSF 3-2	**42**	**1445**	**1550**	**1.072**	**4.9**±*0.1*	**58**±*0.5*
PSF 4-1	*45*	*1766*	*1285*	*0.724*	*3.8±0.1*	–
PSF 4-2	**45.5**	**1813**	**1720**	**0.949**	**5.6**±*0.1*	**47**±*0.5*
PSF 5-1	*58*	*3145*	*2251*	*0.716*	*6.1±0.1*	
PSF 5-2	**58**	**2890**	**3109**	**1.076**	**9.3**±*0.1*	**52**±*0.5*
PSF 6-1	*65*	*2310*	*1955*	*0.846*	*9.1±0.1*	–
PSF 6-2	**65**	**2480**	**2865**	**1.155**	**12.6**±*0.1*	**38**±*0.5*
PESF 1-1	*48*	*1539*	*1260*	*0.731*	*3.0±0.1*	–
PESF	**48**	**1636**	**1795**	**1.116**	**4.7**±*0.1*	**57**±*0.5*
PESF	*69*	*1774*	*1297*	*0.732*	*10.4±0.1*	–
PESF	**68.5**	**1822**	**1799**	**0.987**	**14.5**±*0.1*	**39**±*0.5*
PESF	*138*	*2824*	*2371*	*0.890*	*12.9±0.1*	–
PESF	**139**	**2890**	**2832**	**0.979**	**18.3**±*0.1*	**42**±*0.5*

Italic – membranes with flat inner surface
Bold – membrane with developed inner surface

When studying the hydraulic permeability it appeared that development of the internal surface is of essential importance in the membrane permeability. Membranes of greater internal surface showed greater hydraulic permeability. This, as expected tendency, was maintained irrespective of the cut-off point. Also, the material of which the membrane was made did not change this tendency. It was observed as well as for polysulfone and polyethersulfone. Also, the addition of polyvinylpyrrolidone as a pores precursor, irrespective of the PVP molecular weight, did not affect the tendency observed.

Figure 6 shows a comparison of UFC values of the membranes obtained. This figure clearly shows the remarkable effect of the membrane internal surface corrugation on the membrane hydraulic permeability. This effect is most visible for lower cut off values. Despite this, both for the lowest and highest cut off values that effect is of a really essential value.

Figure 7 shows the UFC increase for membranes of developed surface in comparison to that of classical ones. This increase has been presented as a function of the difference in the χ parameter value between the corrugated membrane and compared with a classical membrane. Unfortunately, no general regularity for the hydraulic permeability percentage increase was found. However, the considerable differences in the UFC values between the classical membranes and those of developed surface are clearly visible here and also how this increase is remarkably affected by an increase in the membrane internal surface is visible.

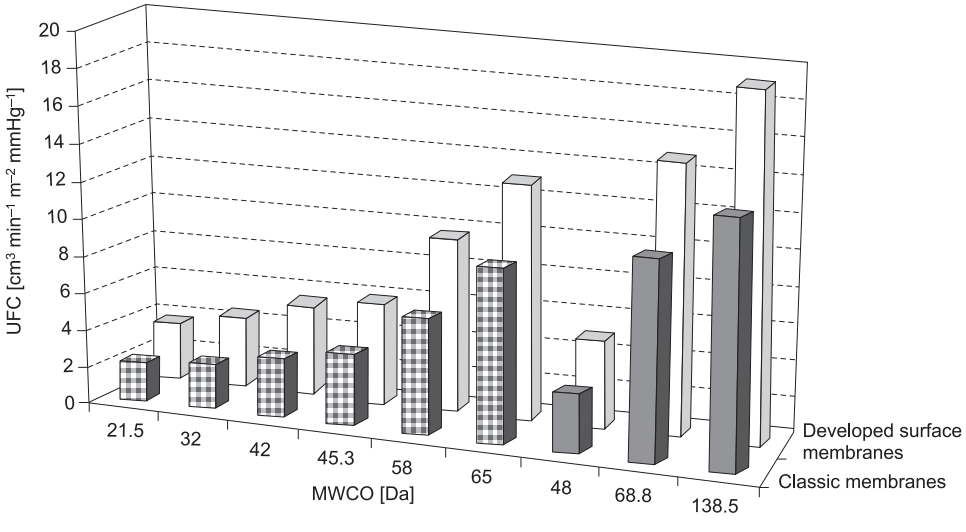

Fig. 6. Dependence of UCF on the membrane structure for membranes of various cut off point. Membranes are collected in pairs for subsequent MWCO. Bright – PSF membranes, dark – PESF membranes

Another purpose was the development of membranes intended specially for cell cultivation. Examples of such membranes are shown in Figs. 8 and 9. These are membranes of very developed internal surface. The development of this surface has the form of regular corrugations along the whole hollow fiber length. The appearance of the internal surface is also shown in Figures 7 and 8. The size of corrugations seems to be appropriate for the cell cultivations carried out both for medical and biotechnological purposes. It is interesting that the appearance and size of the corrugations obtained are similar to the results obtained by other methods in flat scaffolds [37–39], also intended for cell cultivations. Membranes obtained from polysulfones and polyethersulfones are not cyto-toxic, as was checked many times by us previously. This permits to assume that they will be perfectly suitable for biotechnological and medical purposes, and especially for macro-encapsulation.

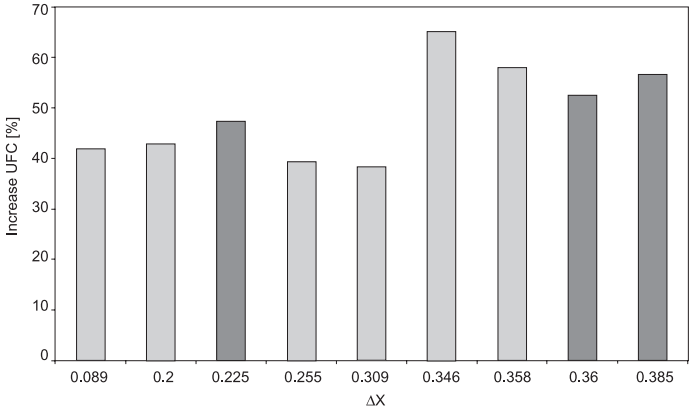

Fig. 7. Percentage increase of UFC as a function of $\Delta\chi$ (χ of corrugated membrane – χ of classical membrane). Dark – PESF membranes, Bright – PSF membranes

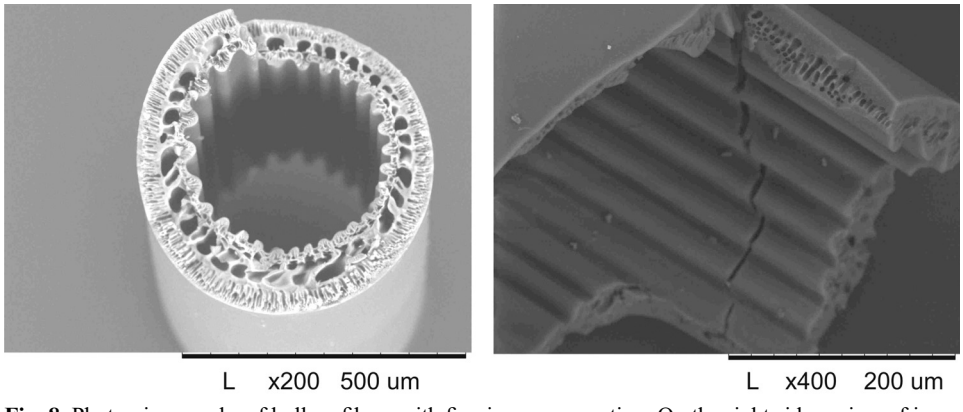

Fig. 8. Photomicrographs of hollow fibers with fine inner corrugation. On the right side – view of inner corrugations. This membrane seems to be a good one for cell micro-encapsulation

4. Conclusion

By selecting appropriate parameters of the spinning process it is possible to obtain semipermeable hollow fibers of developed inner surface by means of standard spinnerets. The key parameters are: core liquid pressure, membrane-forming mixture pressure, air gap size, relative humidity in air gap and stable temperature. By appropriate selection of these parameters the formation of the membrane inner corrugation can be controlled. There is a possibility of obtaining membranes with very dense and fine corrugation as well as membranes with several larger corrugations. Membranes with developed inner surface have greater hydraulic permeability than that of classical cylindrical membranes. This is caused by the increase in the membrane hollow fiber internal surface and hence skin layer inner surface. Since the membrane skin layer has an essential effect on the formation of the hydraulic resistance, then an increase in the surface results in a flow increase.

Since polysulfone membranes can be obtained in non-cytotoxic and bioconformity versions, they can be used for both biomedical and biotechnological applications. The membranes with developed inner surface have increased permeability in comparison to that of classical ones. It may be a very valuable and required property especially in cases when the use of as low as possible trans-membrane pressures is necessary.

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References

1. Aptel P., Abidine N., Ivaldi F., Lafaille J.P.: Polysulfone hollow fibres—effect of spinning conditions on ultrafiltration properties. J. Membr. Sci. 1985, 22, 199–215.
2. Pesek S.C., Koros W.J.: Aqueous quenched asymmetric polysulfone hollow fibers prepared by dry/wet phase separation. J. Membr. Sci. 1994, 88, 1–19.
3. He T., Versteeg L.A.M., Mulder M.H.V., Wessling M.: Composite hollow fiber membranes for organic solvent-based liquid–liquid extraction. J. Membr. Sci. 2004**,** 234, 1–10.
4. Idris A., Ismail A.F., Noordin M.Y., Shilton S.J.: Optimization of cellulose acetate hollow fiber reverse osmosis membrane production using Tagushi method. J. Membr. Sci. 2002, 205, 223–237.
5. Khayet M.: The effects of air gap length on the internal and external morphology of hollowfiber membranes. Chem. Eng. Sci. 2003, 58, 3091–3104.
6. Khulbe K.C., Feng C., Matsuura T., Kapantaidakis G.C., Wessling M., Koops G.H.: Characterization of polyethersulfone–polyimide hollow fiber membranes by atomic force microscopy and contact angle goniometry. J. Membr. Sci. 2003, 226, 63–73.
7. Yang Q., Chung T.S., Santoso Y.W.: Tailoring pore size and pore size distribution of kidney dialysis hollowfiber membranes via dual-bath coagulation approach. J. Membr. Sci. 2007, 290, 153–163.
8. Lee S.H., Kim J.J., Kim S.S., Kim U.Y.: Morphology and performance of polysulfone hollow fiber membrane. J. Appl. Polym. Sci. 1993, 49, 539–548.

9. Khayet M., Garcia-Payo M.C., Qusay F.A., Khulbe K.C., Feng C.Y., Matsuura T.: Effects of gas gap type on structural morphology and performance of hollow fibers. J. Membr Sci. 2008, 311, 259–269.
10. Wang K.Y., Matsuura T., Chung T.S., Guo W.F.: The effects of flow angle and shear rate with the spinneret on the separation performance of poly(ethersulfone) (PES) ultrafiltration hollowfiber membranes. J. Membr. Sci. 2004, 240, 67–79.
11. McKelvey S.A., Clausi D.T., Koros W.J.: A guide to establishing hollow fiber macroscopic properties for membrane applications. J. Membr. Sci. 1997, 124, 223–232.
12. Khayet M., Feng C.Y., Khulbe K.C., Matsuura T.: Study on the effect of a non-solvent additive on the morphology and performance of ultrafiltration hollow-fiber membranes, Desalination 2002, 148, 31–37.
13. Qin J., Chung T.S.: Effect of dope flow rate on the morphology, separation performance, thermal and mechanical properties of ultrafiltration hollow fiber membranes. J. Membr. Sci. 1999, 157, 35–51.
14. Ismail A.F., Mustaffar M.I., Illias R.M., Abdullah M.S.: Effect of dope extrusion rate on morphology and performance of hollow fibers membrane for ultrafiltation. Sep. Purf. Technol. 2006, 49, 10–19.
15. Mok S., Worsfold D.J., Fouda A.E., Matsuura T., Wang S., Chan K.: Study on the effect of spinning conditions and surface treatment on the geometry and performance of polymeric hollow-fibre membranes. J. Membr. Sci. 1995, 100, 183–192.
16. Chung T.S.: The limitations of using Flory–Huggins equation for the states of solutions during asymmetric hollow fiber formation. J. Membr. Sci. 1997, 126, 19–34.
17. Chung T.S., Xu Z.L., Lin W.: Fundamental understanding of the effect of air-gap distance on the fabrication of hollow fiber membranes. J. Appl. Polym. Sci. 1999, 72, 379–395.
18. Chung T.S., Hu X.: Effect of air gap distance on the morphology and thermal properties or polyethersulfone hollow fibers. J. Appl. Sci. 1997, 66, 1067–1077.
19. Qin J.J., Gu J., Chung T.S.: Effect of wet and dry-jet wet spinning on the shear-induced orientation during the formation of ultrafiltration hollow fiber membranes. J. Membr. Sci. 2001, 182, 57–75.
20. Tsai H.A., Huang D.H., Fan S.C., Yang Y.C., Li C.L., Lee K.R., Lai J.Y.: Investigation of surfactant addition effect on the vapor permeation of aqueous ethanol mixtures through polysulfone hollow fiber membranes. J. Membr. Sci. 2002, 198, 245–258.
21. Miao X., Sourirajan S., Zhang H., Lau W.W.Y.: Production of polyethersulfone hollowfiber ultrafiltration membranes. Part I. Effects ofwater (internal coagulant) flow rate and length of air gap. Sep. Sci. Technol. 1996, 31, 141–156.
22. Feng C.Y., Khulbe K.C., Chowdhury G., Matsuura T., Sapkal V.C.: Structural and performance study of microporous polyetherimide hollow fiber membranes made by solvent-spinning method. J. Membr. Sci. 2001, 189, 193–203.
23. Khulbe K.C., Feng C.Y., Hamad F., Matsuura T., Khayet M.: Structural and performance study of micro porous polyetherimide hollowfiber membranes prepared at different air-gap. J. Membr. Sci. 2004, 245, 191–198.
24. Kapantaidakis G.C., Koops G.H., Wessling M.: Effect of spinning conditions on the structure and the gas permeation properties of high flux polyethersulfone–polyimide blend hollow fibers. Desalination 2002, 144, 121–125.
25. Tsai H.A., Kuo C.Y., Lin J.H., Wang D.M., Deratani A., Pochat-Bohatier C., Lee K.R., Lai J.Y.: Morphology control of polysulfone hollow fiber membranes viawater vapor induced phase separation. J. Membr. Sci. 2006, 278, 390–400.
26. Baker R.W.: Membrane Technology and Applications,Wiley&Sons Ltd., Chichester, England, 2004.
27. Stamatialis D.F., Papenburg B.J., Gironés M., Saiful S., Srivatsa N.M.B., Schmitmeier S., Wessling M.: Medical applications of membranes: Drug delivery, artificial organs and tissue engineering. J. Membr. Sci. 2008, 308, 1–34.

28. Mazariegos G.V., Patzer J.F., Lopez R.C., Giraldo M., Devera M.E., Grogan T.A., Zhu Y., Fulmer M.L., Amiot B.P., Kramer D.J.: First clinical use of a novel bioartificial liver support system (BLSS). Am. J. Transplant. 2002, 2, 3, 260–266.
29. Nyberg S.L., Shatford R.A., Payne W.D., Hu W.S., Cerra F.B.: Primary culture of rat hepatocytes entrapped in cylindrical collagen gels: an in vitro system with application to the bioartificial liver. Rat hepatocytes cultured in cylindrical collagen gels. Cytotechnology 1992, 10, 3, 205–215.
30. Granicka L.H., Kawiak J., Snochowski M., Wójcicki J.M., Sabalińska S., Weryński A.: Polypropylene hollow fiber for cells isolation. methods for evaluation of diffusive transport and quality of cells encapsulation. Artificial Cells, Blood Substitutes and Immobilization Biotechnology 2003, 31, 3, 251–264.
31. Granicka L., Weryński A., Kawiak J.: Membrane for immunoisolation: Properties before and post implantation. preliminary report. Artificial Cells, Blood Substitutes and Immobilization Biotechnology 2004, 32, 4, 1–10.
32. Granicka L. H., Wdowiak M., Kosek A., Świeżewski S., Wasilewska D., Jankowska E., Weryński A., Kawiak J.: Survival analysis of Escherichia coli encapsulated in hollow fibre membrane in vitro & in vivo. Preliminary report. Cell Transplantation 2005, 14, 323–330.
33. Ellis M.J., Chaudhuri J.B.: Poly(lactic-co-glycolic acid) hollow fibre membranes for use as a tissue engineering scaffold. Biotechnol. Bioeng. 2007, 96, 1, 177–187.
34. Nijdam, W., de Jong, J., van Rijn, C.J.M., Visser, T., Versteeg, L., Kapantaidakis, G., Koops G.-H., Wessling M.: High performance micro-engineered hollow fiber membranes by smart spinneret design. J. Membr. Sci. 2005, 256, 209–215.
35. Herczeg A.: Pat. US 2003, 0140790 A1.
36. Van R., Cornelis J.M., Vogelaar L., Nijdam W., Barsema J.N., Wessling M.: Pat. US 2004, 0028875 A1.
37. Papenburg B.J., Vogelaar L., Bolhuis-Versteeg L.A.M., Lammertink R.G.H., Stamatialis D., Wessling M.: One-step fabrication of porous micropatterned scaffolds to control cell behavior. Biomaterials 2007, 28, 1998–2009.
38. Vogelaar L., Barsema J.N., Rijn C.J.M.V., Nijdam W., Wessling M.: Phase separation micromolding--PS_M. Adv. Mater. 2003, 15, 16, 1385–1389.
39. De Jong J., Ankone B., Lammertink R.G.H., Wessling M.: New replication technique for the fabrication of thin polymeric microfluidic devices with tunable porosity, Lab on a Chip; Miniatur. Chem. Biol. Bioeng. 2005, 5, 11, 1240.