

MEMBRANES FROM POLYSULFONE/*N,N*-DIMETHYL- ACETAMIDE/WATER SYSTEM; STRUCTURE AND WATER FLUX

Vladimir KAISER and Črtomir STROPNIK

*University of Maribor, Faculty of Chemistry and Chemical Engineering,
Smetanova 17, 2000 Maribor, Slovenia*

Received 04-02-2000

Abstract

Polymeric membranes were prepared by the wet-phase separation method from solutions of different contents of polysulfone in *N,N*-dimethylacetamide; solutions were cast in different thickness before immersion into the pure water coagulation bath. Two main processes take place during the formation of membranes: nucleation and growth of the polymer lean phase with subsequent solidification of the polymer rich phase, and the formation of channels, macrovoids and mega-macrovoids. By the first process a cellular structure is formed whilst the second process connects the cells by opening the space between them. The degree of interconnectedness is an additional factor that affects the pure water flux. By changing the cast solution compositions and/or their cast thickness the interconnectedness of the cells can be controlled.

Introduction

Polysulfone (PSf) is a well-known material in the field of polymeric membranes. It is used in different types of membranes from flat sheets to hollow fibbers, mostly for microfiltration and ultrafiltration separation techniques.^{1,2}

The usual method for preparing polysulfone membranes is wet phase separation.³⁻⁹ A thin layer of PSf solution in an appropriate solvent is immersed into the nonsolvent coagulation bath. Many solvents can be used for this: *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), morpholine (MP), *N*-methylpyrrolidinone (NMP), etc. Also, different nonsolvents are used as coagulants: water, methanol, propanol, etc.

Because of the important role polymeric membranes play in separation technology many studies of membrane formation mechanisms by wet-phase separation of different ternary systems (polymer/solvent/nonsolvent) were carried out.^{3-6,8-12} PSf was examined

among many other polymers. The membrane formation mechanism of PSf/DMA/water and PSf/NMP/water ternary systems was studied by Wijmans et al.⁵ Similar studies of PSf/DMF/water have been done by Broens et al.⁶ These two works have shown that PSf membranes are consolidated by nucleation and growth of the polymer lean phase. Some precipitation paths of the PSf/DMA/propanol system were calculated by using the mass transfer model for early stages of phase inversion proposed by Radovanovic et al.⁷ Examination of PSf/DMA/water ternary system was part of work that led Ray et al.¹³ to their macrovoid formation theory. As macrovoids have a great influence on the performance of membranes, several studies were made in order to understand the phenomena of macrovoids formation.^{3,9,14-17}

In this study the polysulfone/*N,N*-dimethylacetamide/water ternary system is investigated. Systematic work was performed regarding cast thickness and concentration of PSf in the cast solution. The influences of variation of these two parameters on membrane morphology and especially on membranes' pure water flux, were examined. Beside the turbidity phenomena, taking place during the transformation of the cast solution to a membrane, the shrinkage of the cast solution to a membrane was also studied.

EXPERIMENTAL

Polysulfone (PSf) was supplied by Aldrich (18,224-3). The weight-average molecular weight of PSf was 22,000. The solvent, *N,N*-dimethylacetamide (DMA) was purchased from Riedel–de Haën (60145). PSf and DMA were used as received. The nonsolvent, pure water was deionised.

7,5 wt.%, 12,5 wt.%, 18,0 wt.% and 25,0 wt.% solutions of PSf in DMA were prepared by weighing solid polymer (PSf) and the solvent (DMA), and stirring them (24–48h) to get a clear solution.

Solutions with different content of PSf in DMA were cast on the grinded glass plate by knives with exactly dimensioned slits (80µm, 150µm, 300µm).^{11,12} The glass plate with the cast solution was immersed into the coagulation bath with pure deionised water.

During the formation of the membrane the onset, grow rate and maximal value of the turbidity of the cast solution/membrane system were measured by a turbidity measurement set-up.^{4,7} The formed membrane was left in a coagulation bath for 10 min. Afterwards it was transferred to a container with a large quantity of water where it remained for the next 24 – 48 h.

The thickness of the membranes was measured by a magnetic measuring probe (Minimer HD1) in 10 different points and the average value was calculated.

The membrane pure water flux was determined by measuring the water flux trough the membrane in the AMICON 8400 cell.

The cross-section morphology was observed by scanning electron microscopy (SEM, JEOL JSM-840A). To prepare samples the membranes were dried for at least 48 h between sheets of filter paper, frozen in liquid nitrogen, broken, mounted into the sample holder, dried in a desiccator for the next 24 h, gilded, and examined with SEM.

Results and discussion

In Figure 1 time dependencies of turbidity for different PSf/DMA/water membrane forming systems are presented. Their main characteristics are instantaneous appearance of the turbidity and its very high rate of growth. Immediately after the contact of the PSf/DMA solution with the coagulation bath, namely pure water, white to pale yellow colour of the membrane appears. Turbidity growth is so rapid that the ultimate membrane colour is seen already after some seconds. These properties are characteristic of all examined PSf/DMA/water membrane forming systems. Such behaviour is the consequence of nucleation and growth of the polymer lean phase.^{5,11,12}

In the schematized PSf/DMA/water ternary phase diagram the changes in composition after the immersion of the PSf/DMA solutions into the coagulation bath of pure water are also presented schematically with the broad arrow (Figure 2).

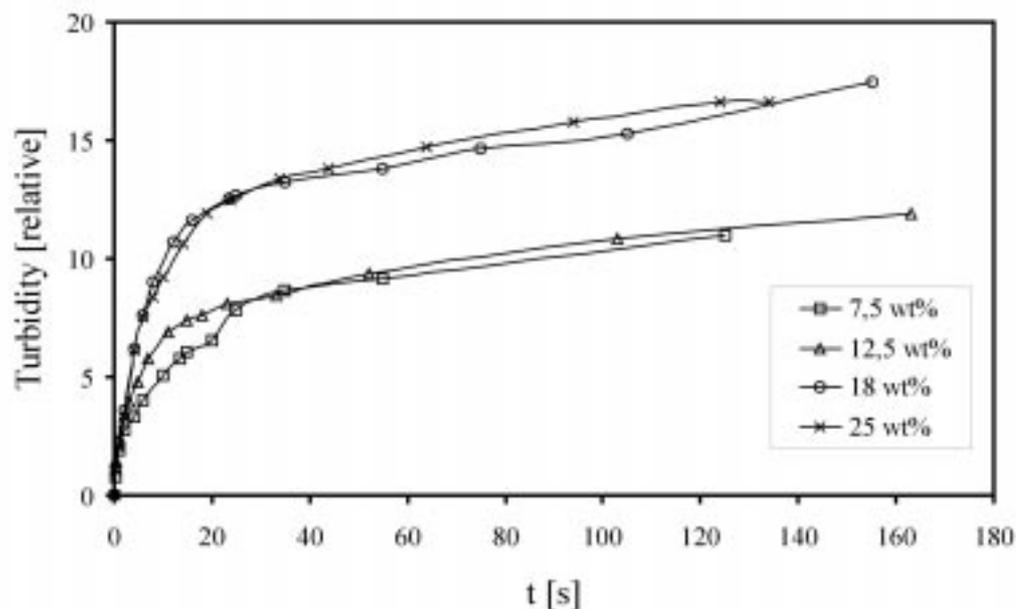


Figure 1: Time dependencies of turbidity for PSf/DMA:water systems; nominal cast thickness is 300 μm .

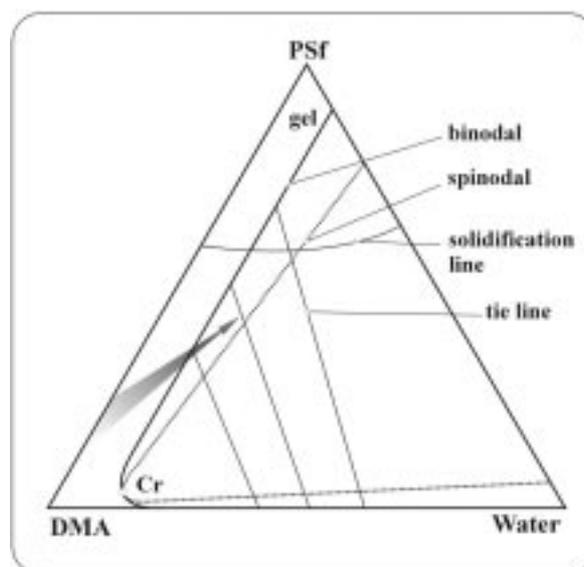


Figure 2: Schematized ternary phase diagram with schematized composition path.

It represents all the examined membrane forming systems. By solvent–nonsolvent mass exchange the stable one-phase system is converted into the metastable system. To reach new thermodynamic stability it takes phase separation by nucleation and growth of the

polymer lean phase; its concentration is in the ternary phase diagram presented by the intersection of the tie lines with the binodal at its "down side" with respect to the critical point.^{11,12} Many forming and growing nuclei of the polymer lean phase form a lot of phase boundaries on which light is scattered; this is the reason for appearing turbidity.

By the solidification of the polymer rich phase, which surrounds the growing nuclei, the solid membrane with a cellular structure is formed. Such a morphological structure can be found on every scanning electron micrographs of cross-section morphology of all examined membranes (Figure 3 and 4).

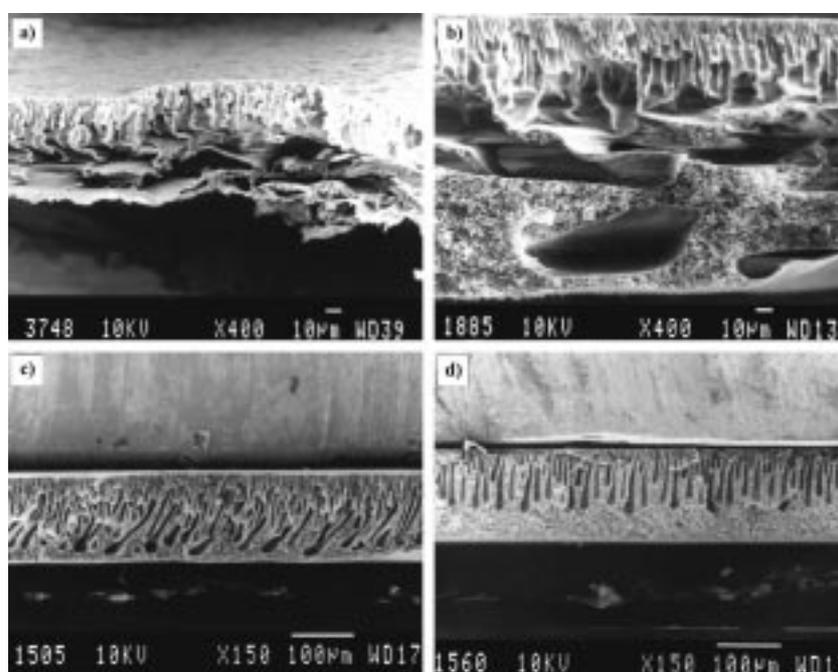


Figure 3: Scanning electron micrographs of cross section morphology. Nominal cast thickness is 300 μm ; cast solutions concentration: a) 7,5 wt%, b) 12,5 wt%, c) 18 wt% and d) 25 wt%.

Beside macrovoids and channels, emerging beneath the membranes' upper surface, cellular structure is the most distinguishing feature of the membranes' cross section morphology. Quite remarking are the differences in cross section morphology when we change the cast solution composition and cast thickness. Membranes prepared from the solutions with lower PSf content (7,5 and 12,5wt%) have long channels with very great macrovoids (mega-macrovoids) while membranes prepared from the PSf/DMA solutions with higher PSf content have shorter, tear-like macrovoids. The

interconnectedness of cells by channels and mega-macrovoids is much more pronounced in the former case.

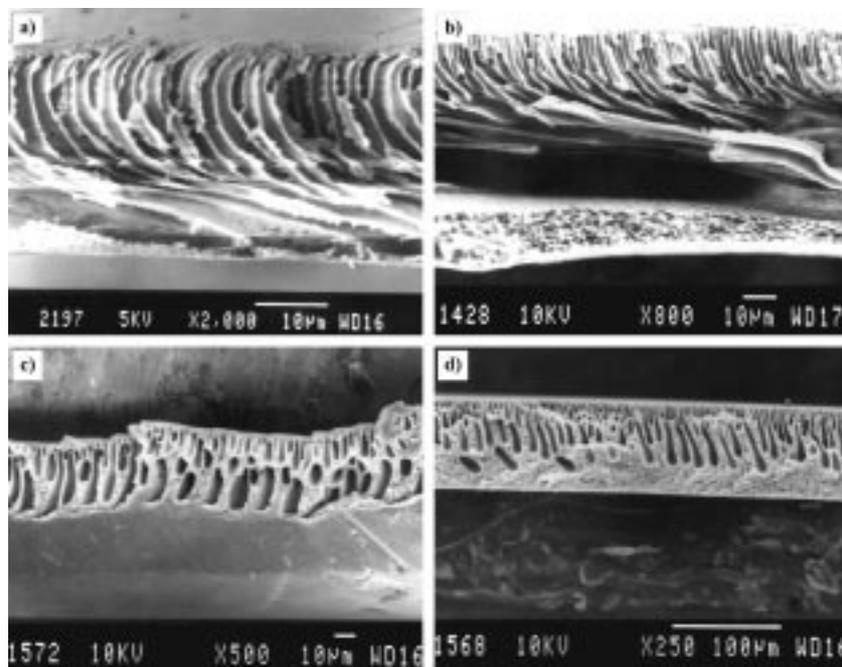


Figure 4: Scanning electron micrographs of cross section morphology. Cast solution concentration and nominal cast thickness: a) 12,5wt%/80 μm , b) 12,5wt%/150 μm , c) 25wt%/80 μm and d) 25wt%/150 μm .

This interconnectedness is also reflected by the pure water flux (PWF) through the membranes (Table 1).

Table 1: Pure water fluxes

Cast thickness [μm]	Concentration of PSf/DMA solution [wt.%]			
	7,5	12,5	18	25
	Pure water flux [$\text{l}/\text{m}^2\text{h}$] ([bar)]*			
80	391,8 (2) *	882,8 (2)	163,0 (2)	0,0 (2)
		1263,0 (4)	298,8 (4)	8,3 (4)
			543,2 (6)	12,3 (6)
150	540,2 (2)	488,9 (2)	6,5 (2)	0,0 (2)
		624,7 (4)	13,6 (4)	0,0 (4)
		724,3 (6)	25,0 (6)	0,0 (6)
300	626,84 (2)	163,0 (2)	0,0 (2)	0,0 (2)
		190,1 (4)	0,0 (4)	0,0 (4)
		210,5 (6)	0,0 (6)	0,0 (6)

* transmembrane pressure

Generally speaking, in the membrane formed only by the process of nucleation and growth of the polymer lean phase with subsequent solidification of the polymer rich phase, individual cells are not interconnected and the decisive mechanism of water permeation through the membrane is the solution/diffusion mechanism where water has to pass the dense polymeric continuous matrices of the solidified polymer rich phase. Membranes, prepared from the PSf/DMA solutions with high PSf content (25wt%) and from the thick cast solutions (300 μm) have a lot of such non-connected cellular structure, especially at their lower part. Their PWF under ultrafiltration conditions is practically zero (Table 1). Quite opposite is the situation when the cellular interconnectivity is enhanced by channels and mega-macrovvoids. Namely, membranes, prepared from the PSf/DMA solutions with low PSf content (7,5 and 12,5wt%) and from the thin cast solutions (80 and 150 μm) have (very) high PWF under ultrafiltration conditions (Table 1). In this case mass transport is decisively carried out by the hydrodynamic flow mechanism where water passes through the space, formed by channels, macrovoids and mega-macrovvoids.

Such a consistent picture of PWF and PSf membranes cross section morphology is something new in the consideration of PSf membrane water flux. The skin of the membrane is always considered to be (completely) responsible for high or low PWF of the PSf membranes.¹⁸ We think that the influence of the membrane skin on the PWF cannot be avoided although there is practically nothing known or cited in the literature about its thickness and structure. But the contribution of cellular structure interconnectedness by channels, mega- and macrovoids in the PSf membranes to the PWF can not be neglected.

Shrinkage of the PSf/DMA cast solution into the membrane¹² during the immersion in the coagulation bath (Table 2) is also in accordance with the cellular/macrovvoid structure and PWF. Membranes, prepared from the PSf/DMA solutions with higher contents of PSf and from the thicker cast layer are thicker and their PWF is practically zero. It is opposite in the case when the membranes are prepared from the PSf/DMA solutions with lower contents of the PSf and from the thinner cast solutions: membranes are thinner and they have a (very) high PWF.

Table 2: Membrane thickness

Cast thickness [μm]	Concentration of PSf/DMA solution [wt.%]			
	7,5	12,5	18	25
	Membrane thickness [μm]			
80	25,2	24,7	30,8	39,1
150	22,0	53,4	63,9	75,1
300	46,9	115,9	130,5	139,8

Conclusions

Polymeric membranes were prepared by wet-phase separation by immersing of different polysulfone solutions in *N,N*-dimethylacetamide into the coagulation bath consisting of pure water. Nucleation and growth of the polymer lean phase and subsequent solidification of the polymer rich phase are processes which form the cellular structure of the membranes. Channels, macrovoids and mega-macrovoids, present in the membrane structure, interconnect the so formed cells. The pure water flux of PSf membranes is determined by the interconnectedness of the cells; in the non-connected cellular structure the solution/diffusion mass transport takes place, whereas in the connected cellular structure the much greater hydrodynamic mass transport takes place. Membranes, prepared from the solution with a lower content of PSf have long channels and mega-macrovoids, extending practically through their whole cross section and consequently a high pure water flux. Membranes, prepared from the solutions with a higher content of PSf have tear-like macrovoids only in the upper part of the membrane and practically zero PWF under ultrafiltration conditions. By controlling the intercellular connectedness very different membranes can be prepared from the PSf/DMA:water system.

References and Notes

1. P. M. Bungay, H. K. Lonsdale, M. N. de Pinho (Eds.), *Synthetic membranes: science, engineering and applications*; D. Riedel Publishing Company, Dordrecht, 1983, pp 254-261.
2. K. Schott, *Handbook of Industrial Membranes*; Elsevier, Oxford, 1997, pp 28-30.
3. H. Strathmann, K. Kock, P. Amar, *Desalination* **1975**, *16*, 179 - 203.
4. A. J. Reuvers, *Membrane formation diffusion induced demixing processes in ternary polymeric systems*, Ph. D. Thesis; Twente University of Technology, The Netherlands, 1987, pp 8 - 10.
5. J. G. Wijmans, J. P. B. Baaij and C. A. Smolders, *J. Memb. Sci.* **1983**, *14*, 263 - 274.

6. L. Broens, F. W. Altena, C. A. Smolders, *Desalination* **1980**, 32, 33 - 45.
7. P. Radovanovic, S. W. Thiel and S.-T. Hwang, *J. Memb. Sci.* **1992**, 65, 213 - 229.
8. I. M. Wienk, R. M. Boom, M. A. M. Beerlage, A. M. W. Bulte, C. A. Smolners, H. Strathmann, *J. Memb. Sci.* **1996**, 113, 361 - 371.
9. S. A. McKelvey, W. J. Koros, *J. Memb. Sci.* **1996**, 112, 29 - 39.
10. F. G. Paulsen, S. S. Shojaie, W. B. Krantz, *J. Memb. Sci.* **1994**, 91, 265 - 282.
11. C. Stropnik, L. Germic, B. Zerjal, *J. Appl. Polym. Sci.* **1996**, 61, 1821 - 1830.
12. C. Stropnik, L. Germic, *Polimeri* **1996**, 17, 137 - 142.
13. R. J. Ray, W. B. Krantz and R. L. Sani, *J. Memb. Sci.* **1985**, 23, 155 - 182.
14. C. A. Smolders, A. J. Reuvers, R. M. Boom and I. M. Wienk, *J. Memb. Sci.* **1992**, 73, 259 - 275.
15. R. Matz, *Desalination* **1972**, 10, 1 - 15.
16. Y. Termonia, *J. Polym. Sci.: Polym. Phys. Ed.* **1995**, 33, 279 - 288.
17. M. A. Frommer and R. M. Messalem, *Ing. Eng. Chem. Prod. Res. Develop.* **1973**, 12, 328 - 333.
18. Mulder, *Basic Principles of Membrane Technology*, Dordrecht: Kluwer Academic Publishers, 1996, pp 12-13, pp 293-294.

Povzetek

Polimerne membrane smo pripravili z metodo mokre fazne inverzije iz raztopin z različno vsebnostjo polisulfona v *N,N*-dimetilacetamidu, spreminjali pa smo tudi debelino nanosa raztopine pred potopitvijo v koagulacijsko kopel iz čiste vode. Med formiranjem membrane sta potekala dva osnovna procesa: nukleacija in rast s polimerom revne faze s posledičnim nadaljnim strjevanjem s polimerom bogate faze ter nastanje kanalov, makrovoidov in mega-makrovoidov. S prvim procesom nastaja celična struktura z izoliranimi in nepovezanimi celicami, medtem ko drugi proces povzroči povezovanje celic z odpiranjem praznega prostora med njimi. Stopnja takšne povezanosti celic je eden od faktorjev, ki določajo pretok čiste vode skozi membrano. S spreminjanjem sestave in/ali debeline nanosa raztopine lahko vplivamo na stopnjo povezanosti celic.