PREPARATION AND CHARACTERIZATION OF MICRO- AND ULTRAFILTRATION MEMBRANES

G.H. Koops
Department of Chemical Technology, University of Twente, The Netherlands

Keywords : Ultrafiltration, Materials, Hydrophilicity, Hydrophobicity, Geometries, Substrate, Ceramic Membranes

Contents

Summary

In this chapter the reader can find extensive and useful information regarding the

preparation and characterization of different types of microfiltration and ultrafiltration membranes. State-of-the-art preparation and characterization methods are discussed, as well as somewhat newer and more exotic methods. A complete as possible overview is tried to be given. The chapter is supported by 30 illustrative figures and tables and more than 130 references. Much information in this chapter originates form a selected number of handbooks (Microfiltration and Ultrafiltration, Principles and Application by Zeman and Zydney, 1996, Handbook of Industrial Membranes by Scott, 1995, Ultrafiltration and Microfiltration Handbook by Cheryan, 1998 and Basic principles of Membrane Technology by Mulder, 1996) and the author would recommend these books as a good reference for further and even more extensive information regarding microfiltration and ultrafiltration membranes and membrane processes.

1. Preparation of Micro-and Ultrafiltration Membranes

1.1. Classification of Micro- and Ultrafiltration Membranes

Microfiltration and ultrafiltration membranes can be classified according to their different characteristics. Most of these characteristics apply to both types of membranes, e.g. type of material (ceramic or polymer), membrane geometry (hollow fiber, capillary, tubular, flat sheet), hydrophilicity (hydrophilic or hydrophobic), reinforced or unsupported, etc.

Only one characteristic, the pore size, is used to make a distinction between micro- and ultrafiltration membranes. Microfiltration membranes generally have pore diameters larger than 50 nm, while ultrafiltration membranes have typical pore diameters between 2 nm and 50 nm, according to IUPAC and the European Membrane Society (EMS) standards (Koops 1995). The pore diameter is the parameter used to specify microfiltration membranes. Ultrafiltration membranes are normally specified by a so-called Molecular Weight Cut-off (MWCO) value, representing the molecular weight of a species that is retained for 90 per cent by the membrane. An exception to this rule is made by the manufacturers of ceramic membranes, who also specify ultrafiltration membranes by pore size. As well as the larger pore size, the surface and volume (or bulk) porosity of microfiltration membranes are also generally larger.

1.1.1. Materials

Both types of membranes can be made from different materials e.g. polymers, ceramics, metals or glasses. By far the most commercial membranes are made of polymers followed by ceramics and very few, mostly small scale membranes, are made of metal or glass. Ceramic microfiltration and ultrafiltration membranes are two to four times as expensive as polymeric membranes, but possess excellent chemical, temperature and mechanical stability. The better stability results in a longer life time, which compensates partly for the higher prices per square meter of membrane area. Polymeric micro- and ultrafiltration membranes have reported life times, dependent on the application, of more than five years. Table 1 contains a listing of the most commonly applied membrane materials, where a distinction is made between micro- and ultrafiltration membranes.

Material	**Membrane Process**	
Cellulose acetate	MF	UF
Cellulose nitrate	MF	
Cellulose	MF	UF
Poly(sulfone)	MF	UF
Poly(ethersulfone)	MF	UF
Poly(sulfone)/poly(vinylpyrrolidone)	MF	UF
Poly(ethersulfone)/poly(vinylpyrrolidone)	MF	UF
Poly(vinylidenefluoride)	MF	UF
Poly(tetrafluoroethylene)	MF	
Poly(acrylonitrile)		UF
Poly(ethylene)	MF	
Poly(propylene)	MF	
Poly(imide)		UF
Poly(amide)	MF	UF
Al_2O_3	MF	
γ-Al_2O_3/α-Al_2O_3		UF
Zirconia/alumina	MF	
Zirconia/carbon	MF	UF
Zirconia/stainless steel		UF
Silica	MF	UF
Type 316 stainless steel.	MF	

Table 1. The most commonly used materials in commercially available micro- and ultrafiltration membranes.

1.1.2. Hydrophilicity and Hydrophobicity

Another distinction that can be made and which is directly related to the membrane material is the measure of hydrophilicity/hydrophobicity. Hydrophilic membrane surfaces are less susceptible to adsorption of species like proteins, bacteria, colloids, etc. and consequently less sensitive to fouling. Generally, hydrophilic polymers show a rather poor chemical and thermal stability, which explains why hydrophobic polymers are mainly used as a basic material for membranes. In order to introduce some hydrophilicity to a membrane several techniques can be distinguished:

- Hydrophobic polymers can be chemically modified by the introduction of polar functional groups, e.g. the introduction of SO_3H-groups in poly(sulfone), poly(ethersulfone) or poly(ether ether ketone) (Noshay and Robeson 1976; Drzewinski and Macknigth 1985; Brousse et al. 1976; Bailly et al. 1987; Jin et al. 1985; Ogawa and Marvel 1985) or the introduction of COOH-groups in poly(sulfone) by carboxylation.
- Copolymers consisting of hydrophobic and hydrophilic blocks can be used as membrane material, e.g. ethylene and vinylalcohol or ethylene and vinylacetate. This way hydrophilicity can be combined with good chemical and temperature stability.

- Hydrophobic membranes can be treated to introduce hydrophilic functional groups at the membrane surface. Techniques used for surface modification are: (i) chemical modification (Stengaard 1988), where functional groups, like carbonyl- amino- and hydroxyl-groups or even ionic groups like sulfonic acid, carboxylic acid and quaternary ammonium groups are covalently bonded to the membrane surface by chemical reaction; (ii) plasma treatment (Wolff et al. 1988; Krakelle and Zdrahala 1989), where specific functional groups can be introduced by using NH_3, N_2 or CO as discharge gases; (iii) coating, where a hydrophilic layer is applied by interfacial polymerization or adsorption coating; and (iv) grafting.
- Hydrophobic polymers that serve as the basic material can be mixed with small amounts of a hydrophilic polymer. A polymer combination has to be found that results in a homogenous solution when dissolved (Paul and Newman 1978). Heterogeneous blends normally result in heterogeneous membrane structures with insufficient mechanical stability. Examples of homogenous blends of a hydrophobic and a hydrophilic polymer are (i) poly(sulfone) and poly(vinylpyrrolidone) (Tweddle et al. 1983; Aptel et al. 1985); (ii) poly(ethersulfone) and poly(vinylpyrrolidone) (Wienk 1993; Wienk 1995a; Boom et al. 1993; Boom et al. 1994a; Boom et al. 1994b); (iii) poly(etherimide) and poly(vinylpyrrolidone) (Roesink 1991); (iv) cellulose and poly(acrylonitrile) and cellulose and poly(vinylbutyrate) (Grinsgpan et al. 1986).

1.1.3. Geometries

Microfiltration and ultrafiltration membranes are available in different geometry's. Polymeric membranes are manufactured as (i) flat sheets, which are then applied in plate-and-frame modules, pleated in cartridges or packed in spiral wound modules; (ii) hollow fibers, which are characterized by outside diameters smaller than 1.5 mm; (iii) capillaries, which are characterized by outer diameters of 1.5-5 mm; and (iv) tubular membranes, which are characterized by outer diameters larger than ±5 mm (Koops 1995).

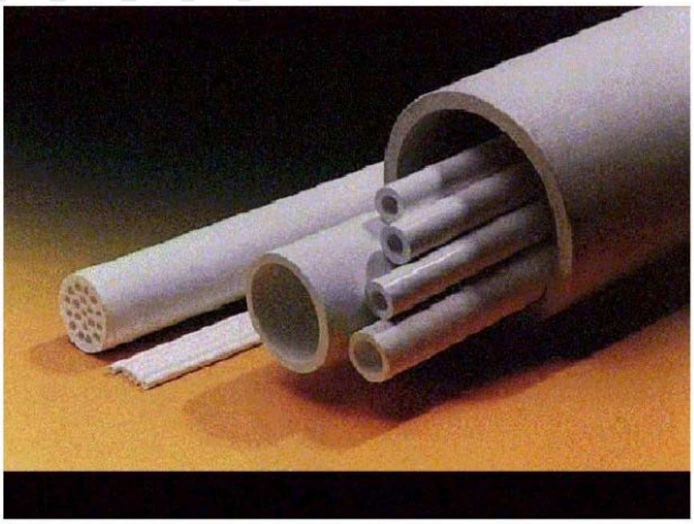

Figure 1. Several ceramic tubular geometries; assortment of ECN Petten, The Netherlands, ceramic membrane products. (Printed with permission of ECN)

Flat sheet ultrafiltration membranes are often reinforced by highly porous nonwoven or macro-porous webs. The same is true for polymeric tubular membranes, while hollow fiber and capillary membranes are self-supporting. Inorganic membranes are manufactured as disks, tubes, multi-channel tubes and honeycomb monoliths, examples of tubular ceramic membranes can be seen in Figure 1.

1.1.4. Structures

As well as having a different geometry the membrane structure itself can be quite different. A homogenous membrane consists of one and the same material, while a composite membrane is made up of two different materials, where a thin layer responsible for the separation is applied on top of a porous support layer, e.g. γ-aluminum on top of an α-aluminum support layer (see Figure 2). Looking at the cross section of a membrane the structure can be either symmetric (or isotropic), with a homogeneous structure throughout the membrane thickness, or asymmetric (or an-isotropic), with a thin top layer of small cell/pore sizes at the feed side and a gradually increasing cell/pore size towards the permeate side(see Figure 3). Asymmetric structures are typically formed in the so-called phase-inversion process developed by Loeb and Sourirajan (1962).

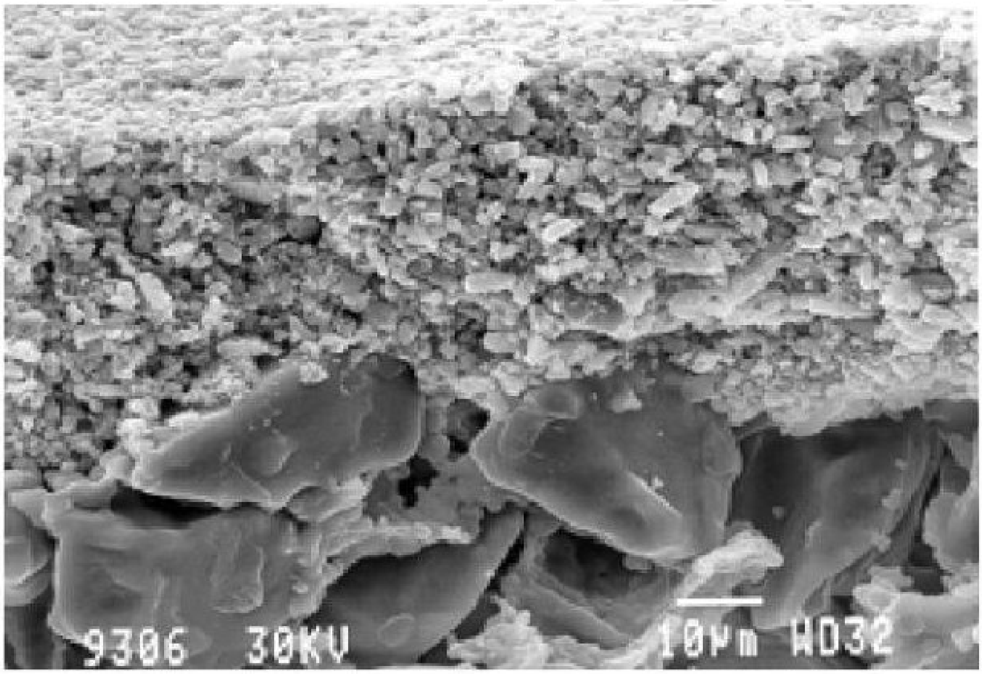

Figure 2. Cross section of a microfiltration ceramic composite membrane; γ-aluminum on top of an α-aluminum support. A product from Velterope B.V., The Netherlands. (Printed with permission of Velterop)

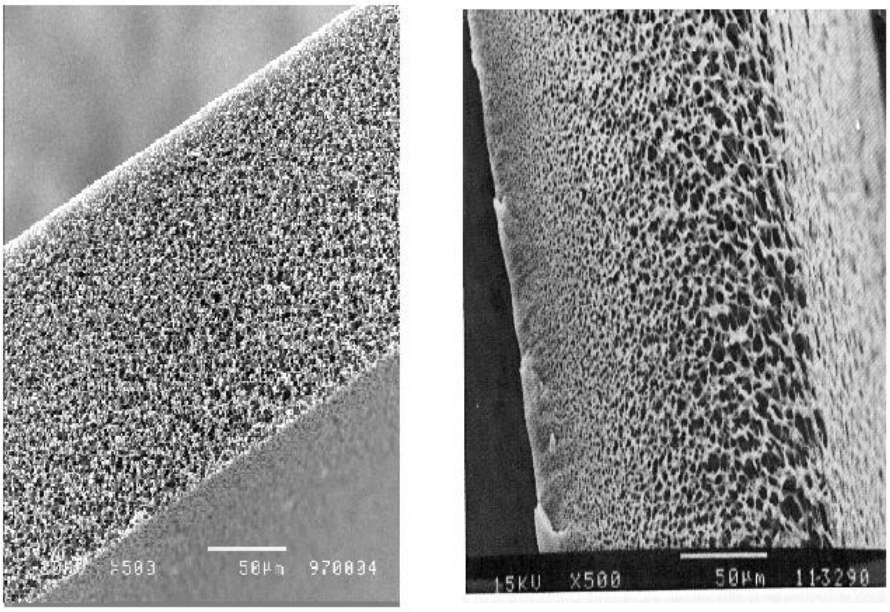

Figure 3. Cross section a symmetric membrane structure (Sartorius) (left) and an asymmetric membrane structure (University of Twente) (right).

1.1.5. Surface Charge

Another classification of micro- and ultrafiltration membranes can be made in relation to the surface charge of the membrane; it can have a positive charge, a negative charge or as in most commercial micro- and ultrafiltration membranes be neutral.

1.2. Preparation of Filtration Membranes

The different membrane geometries discussed earlier imply different manufacturing techniques. Flat sheet polymeric membranes are cast as self-supporting sheets or on top of a non-woven or other support for extra mechanical strength (see Figure 4). Hollow fiber membranes are manufactured by a spinning process (see Figure 5), where a polymer solution is extruded through a nozzle and ceramic tubular membranes are prepared by extrusion of a ceramic paste.

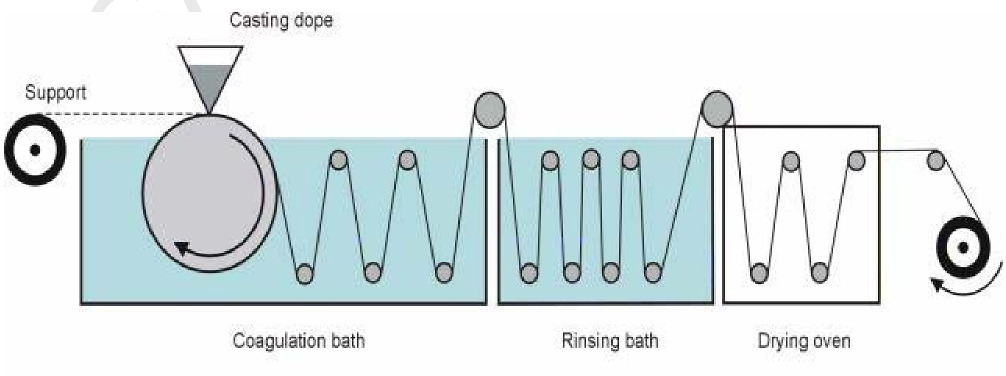

Figure 4. Schematic representation of the membrane casting process.

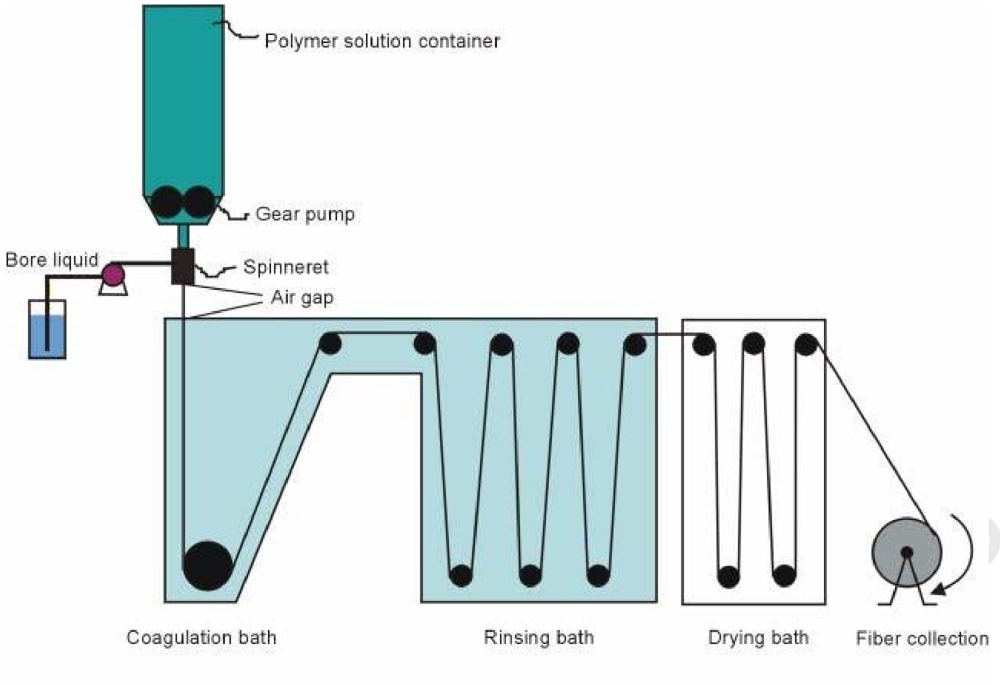

Figure 5. Schematic representation of a hollow fiber spinning process.

For the preparation of flat sheet porous membranes different structure formation techniques can be distinguished, e.g. the phase-inversion process, the track-etch process, two dimensional stretching of a film, etc.

Hollow fibers, capillaries and tubular polymeric membranes are generally formed by a phase inversion process, while the ultimate ceramic membranes structures are formed by a sinter process. Most of the commercial membranes on the market today are produced according to a phase-inversion process (see later).

To influence a membrane structure, such as pore size and porosity (overall as well as surface porosity) or membrane nature (hydrophilicity, chemical stability, etc.) all kinds of additives are used in the polymeric solution. Salts are added to enhance the porosity, weak nonsolvents are added to obtain spongy structures (suppress macrovoids) and influence the porosity and small amounts of hydrophilic polymer are added to enhance wettability and suppress macrovoids.

-
-
-

Bibliography and Suggestions for further study

Altena F W and Smolders C A (1982) Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and a nonsolvent. *Macromolecules* 15, 1491.

Andrianne J. and Alardin, F. (2002) Thermal and membrane processes economics: Optimised selection for seawater desalination, Desalination, 153, p. 305-311.

Aptel P, Abidine N, Ivaldi F and LaFaille JP (1985) Polysulfone hollow fibers, effect of spinning conditions on ultrafiltration properties. *Journal of Membrane Science* 22, 199.

Ayse Asatekin, Adrienne Menniti, Seoktae Kang, Menachem Elimelech, Eberhard Morgenroth, and Anne M. Mayes (2006),Antifouling Nanofiltration Membranes for Membrane Bioreactors from Self-Assembling Graft Copolymers, Journal of Membrane Science 285 ,81-89.

Bailly C, Williams D J, Karasz F E and Macknight W J (1987) The sodium salts sulfonated poly(aryl-ether-ether-ketone): preparation and characterization. *Polymer* 28, 1009-1016.

Bargeman D, Vugteveen E, te Hennepe J, van't Hof J.A. and Smolders C A (1987) Thermoporometry applied to membrane characterisation. *Synthetic Polymeric Membranes* (ed. B Sedlack and J Kahovec), p. 637. Berlin: Walter de Gruyter.

Boer de J H (1958) *The Structure and Properties of Porous Materials* (eds DH Everett and FS Stone), p. 68. London: Butterworth.

Bonekamp B C (1996) Preparation of asymmetric ceramic membrane supports by dip-coating. *Fundamentals of Inorganic Membrane Science and Technology*, *Membrane Science and Technology Series 4* (eds AJ Burrggraaf and L Cot), p. 141. The Netherlands: Elsevier Science BV.

Boom R M, Boomgaard Th van den and Smolders C A (1994a) Equilibrium thermodynamics of a quaternary membrane forming system with two polymers. I, Theory. *Macromolecules* 27, 2034-2040.

Boom R M, Boomgaard Th van den and Smolders C A (1994b) Equilibrium thermodynamics of a quaternary membrane forming system with two polymers. II, Experiments. *Macromolecules* 27, 2041-2044.

Boom R M, Rolevink H W W, Boomgaard Th van den and Smolders C A (1993) Microscopic structures in phase inversion membranes: the use of polymeric blends for membrane formation by immersion precipitation. *Markromolkulare Chemie, Macromolecular Symposiums* 69, 133-140.

Brinker C J and Scherer G (1990) *Sol-Gel-Science*. New York: Academic Press.

Broens L, Bargeman D and Smolders C A (1978) Proceedings of the 6th International Symposium on Fresh Water from the Sea, vol. 3, 165.

Brousse Cl, Chapurlat R and Quentin J P (1976) New membrane for reverse osmosis I. characteristics of the base polymer: sulfonated polysulfones. *Desalination* 18, 137-153.

Brun M A, Quinson J F, Spitza R and Bartholin M (1982) Structural characterization of swollen resins by thermoporometry and by nitrogen adsorption-desorption. *Makromelekulare Chemie* 183, 1523 - 1531.

Brun M, Lallemand A, Quinson J F and Eyraud Ch (1973) *Journal Chimique Physique* 70, 973.

Brun M, Lallemand A, Quinson J F and Eyraud Ch (1977) A new method for the simultaneous determination of the size and shape of pores: thermoporometry. *Thermochimica Acta* 21, 59-88.

Burggraaf A J and Cot L (1996) General overview, trends and prospects. *Fundamentals of Inorganic Membrane Science and Technology*, *Membrane Science and Technology Series 4* (eds A J Burggraaf and L Cot), pp. 1-20. The Netherlands: Elsevier Science BV.

Burggraaf A J and Keizer K (1991) Synthesis of inorganic membranes. *Inorganic Membrane Synthesis, Characterization and Applications* (ed. R R Bhave), pp. 10-63. New York: van Nostrand Reinhold.

Cabasso I, Klein E and Smith J K (1976) Polysulfone hollow fibers. I Spinning and properties. *Journal of Applied Polymer Science* 20, 2377.

Cabasso I, Klein E and Smith J K (1977a) Polysulfone hollow fibers. II. Morphology. *Journal of Applied Polymer Science* 21, 165.

Cabasso I, Robert K Q, Klein E and Smith J K (1977b) Porosity and pore size determination in polysulfone hollow fibers. *Journal of Applied Polymer Science* 21 (7),1883.

Cadotte J E (1985) Evolution of composite reverse osmosis membranes. *Materials Science of Synthetic Membranes* (ed. D R Lloyd), pp. 273-294. Washington DC: ACS.

Cao G Z, Meijerink J, Brinkman H W and Burggraaf A J (1993) Permporometry study on the size distribution of active pores in porous ceramic membranes. *Journal of Membrane Science* 83, 221-235.

Capanelli G, Becchi I, Bottion A, Moretti P and Munari S (1988) *Computer driven porosimeter for UF membranes, characterization of porous solids*. (eds K K Unger et al.), pp. 238-294. Amsterdam: Elsevier.

Capanelli G, Vigo F and Munari S (1983) UF membranes - characterization methods. *Journal of Membrane Science* 15, 289-313.

Cheryan M (1998) *Ultrafiltration and Microfiltration Handbook*, pp. 71-112. Lancaster, United States: Technomic Publishing Company.

Cohen C, Tanny G B and Prager S (1979) Diffusion controlled formation of porous structures in ternary polymer systems. *Journal of Polymer Science, Polymer Physics Edition* 17, 477.

Cuperus F P, Bargeman D and Smolders C A (1987) Thermoporometry and permporometry applied to UF - membranes characterization. *Characterization of Ultrafiltration Membranes* (proceedings of Symposium, Sweden, 1987), pp. 115.

Cuperus F P, Bargeman D and Smolders C A (1991) Characterization of an-isotropic UF membrane: Top layer thickness and pore structure. *Journal of Membrane Science* 61, 73-83.

Cuperus F P, Bargeman D and Smolders C A (1992a) Permporometry. The determination of active pores in UF membranes. Journal of Membrane Science 71, 57-67.

Cuperus F P, Bargeman D and Smolders C A (1992b) Critical points in the analysis of membrane pore structure by thermoporometry. *Journal of Membrane Science* 66, 45-53.

Dietz P, Hansma P K, Inacher O, Lehmann H-D and Herrmann K-H (1992) Surface pore structures of micro- and ultrafiltraton membranes imaged with the atomic force microscope. *Journal of Membrane Science* 65, 101-111.

DiLeo A J and Philips M W (1994) Integrity test for membranes. US Patent 5282380.

DiLeo A J, Allergrezza A E and Burke E T (1991) Membrane, process, and system for isolating virus from solution. US Patent 5,017,292.

Drioli E., Romano M.,((2001), Progress and new perspectives on integrated membrane operations for sustainable industrial growth, Ind. Eng. Chem. Res. 40 , 1277-1300

Drzewinski M and Macknight W J (1985) Structure and properties of sulfonated polysulfone ionomers. *Journal of Applied Polymer Science* 30, 4753-4770.

Durin M L, Loft J T and Plovan S G (1974) Novel open-celled microporous film. US Patent 3,801,404.

Eyraud C, Betemps M and Quinson J F (1984) Determination of pore radius distribution in an ultrafilter. *Bulletin de la Societe Chimique de France* 9-10, 1-238.

Fane A G, Fell C J D and Waters A G (1981) The relationship between membrane surface pore characteristics and flux for ultrafiltration membranes. *Journal of Membrane Science* 9, 245-262.

Fleischer R L, Price P B and Walker R M (1969) Nuclear tracks in solids. *Scientific American* 220, 30.

Flory P J (1953) *Principles of Polymer Chemistry*. New York: Cornell University Press.

Fritzsche A K Arevalo A R, Moore M D, Weber C J, Elings V B, Kjoller and Wu C M (1992c) Image enhancement of polyethersulfone ultrafiltration membrane surface structure for atomic force microscopy. *Journal of Applied Polymer Science* 46, 167.

Fritzsche A K, Arevalo A R, Connely A F, Moore M D, Elings V B and Wu C M (1992b) The structure and morphology of the skin of polyethersulfone ultrafiltration membranes: a comparative atomic force microscope and scanning electron microscope study. *Journal of Applied Polymer Science* 45, 1945.

Fritzsche A K, Arevalo A R, Moore M D and O'Hara C (1993) The surface structure and morphology of polyacrylonitrile membranes by atomic force microscopy. *Journal of Membrane Science* 81, 109-120.

Fritzsche A K, Arevalo A R, Moore M D, Elings V B, Kjoller K and Wu C M (1992a) The surface structure and morphology of polyvinylidene fluoride microfiltration membranes by atomic force microscopy. *Journal of Membrane Science* 68, 65-78.

Germic L, Ebert E, Bouma R H B, Borneman Z, Mulder M H V and Strathman H (1997) Characterization of polyacrylonitrile ultrafiltration membranes. *Journal of Membrane Science* 132, 131-145.

Goel V, Accomazzo M A, DiLeo A J, Meier P, Pitt A and Pluskal M (1992) Deadend microfiltration: applications, design, and cost. *Membrane Handbook* (eds W S W Ho and K K Sirkar), pp. 506-570 New York: Van Nostrand Reinhold.

Gore R W (1976) Process for producing porous products. US Patent 3,953,566.

Gore R W (1977) Very highly stretched PTFE and process thereof. US Patent 3,962,153.

Gregg S J and Sing K S W (1982) *Adsorption, Surface Area, and Porosity*. New York: Academic Press.

Grinshpan D D, Savitskaya T A, Makarevich S E and Koputskii F N (1986) Kinetic stability and viscosity of cellulose-synthetic polymer blends in a common solvent. *Acta Polymerica* 37, 670.

Guizard C (1996) Sol-gel Chemistry and its application to porous membrane processing. *Fundamentals of Inorganic Membrane Science and Technology*, *Membrane Science and Technology Series 4* (eds A J Burggraaf and L Cot), pp. 227-258. The Netherlands: Elsevier Science BV.

H. Mehdizadeh, (2006), Membrane desalination plants from an engery-exergy viewpoint, Desalination 191, , 200-209.

Hsu C C and Prausnitz J M (1974) Thermodynamics of polymer compatibility in ternary systems. *Macromolecules* 7, 320-324.

J. Koschikowski, M. Wieghaus, M. Rommel: (2003),Solar thermal-driven desalination plants based on membrane distillation, Desalination, 295-304, 156

Jin X, Bishop M T, Ellis T E and Karasz F E (1985) A sulphonated poly(aryl ether ketone). *British Polymer Journal* 17, 4-10.

Joseph A. Cotruvo, (2007),World Health Organization Guidance on Desalination for a Safe Water Supply: Health and Environmental Aspects Applicable to Desalination) and Health Factors Related to the Composition of Desalinated Water

Julbe A and Ramsay J D F (1996) Methods for the characterization of porous structure in membrane materials. *Fundamentals of Inorganic Membrane Science and Technology*, *Membrane Science and Technology Series 4* (eds A J Burggraaf and L Cot), pp. 67-118. The Netherlands: Elsevier Science BV.

Kamusewitz H, Keller and Paul D (1995) Membrane characterization by means of pneumatic scanning force microscopy. *Thin Solid Films* 264, 184-193.

Katz M and Baruch G (1986) New insights into the structure of microporous membranes obtained using a new pore size evaluation method. *Desalination* 58, 119.

Katz M G (1982a) Measurement of pore size distribution in microporous filters and membranes. Harnessing theory for practical application. Proceedings of the 3rd World Filtration Congress, p. 508, Croydon: The Filtration Society, Uplands Press.

Katz M G (1982b) Method of measurement of pore size distribution in microporous ultrafilters and membranes. Israel Patent Application No. 66,672.

Kim K J, Fane A G, Ben Aim R, Liu M G, Jonsson G, Tessaro I C, Broke A P and Bargeman D (1994) A comparative study of techniques used for porous membrane characterization: Pore characterization. *Journal of Membrane Science* 87, 35-46.

Kim K J, Fane A G, Fell C J D and and Joy D C (1992) Fouling mechanism of membranes during protein ultrafiltration. *Journal of Membrane Science* 68, 79-91.

Kim K J, Fane A G, Fell C J D, Suzuki T and Dickson M R (1990) Quantitative microscopic study of surface characteristics of ultrafiltration membranes. *Journal of Membrane Science* 54, 89-102.

Kimmerle K and Strathmann H (1990) Analysis of the structure-determining process of phase inversion membranes. *Desalination* 79, 282-302.

Kimura K., Hane Y., Watanabe Y., Amy G., Ohkuma N.,(2004), Irreversible membrane fouling during ultrafiltration of surface water, Water Res. 38 (2004) 3431–3441

Kools W F C, Boomgaard Th van den and Strathmann H (accepted in 1998) A systematic study of equilibrium thermodynamics of a quaternary membrane forming system with three low molecular weight components and one polymer. *Macromolecules* (in press).

Kools W F C, Boomgaard Th van den and Strathmann H (accepted in 1998) A morphological study of membranes obtained from immersion precipitation in quaternary systems with three low molecular weight components and one polymer. *Journal of Polymer Science* (in press).

Koops G H (1995) Nomenclature and Symbols in Membrane Science and Technology. Enschede, The Netherlands: European Society of Membrane Science and Technology (EMS).

Koutake M, Uchida Y, Kimura T, Sagara Y, Watanabe A and Nakao S (1985) Observation of UF membrane pores through a scanning electron microscope and their pure water fluxes. *Maku* 10, 310-312.

Krakelle M and Zdrahala (1989) Membranes for biomedical applications: utilization of plasma polymerization for dimensionally stable hydrophilic membranes. *Journal of Membrane Science* 41, 305.

Krantz W B, Ray R J, Sani R L and Gleason K J (1986) Theoretical study of the transport processes occurring during the evaporation step in asymmetric membrane casting. *Journal of Membrane Science* 29, 11-36.

Kulkarni S S, Funk E W and Li N (1992) Membrane Handbook (eds W S W Ho and K K Sirkar), pp. 506-570. New York: Van Nostrand Reinhold.

Kupcu S, Sara M and Sleytr U B (1993) Influence of covalent attachment of low M_W substrates on the rejection and adsorption properties of crystalline proteinaceous UF membranes. *Desalination* 90, 65-76.

Lafreniere L Y, Talbot F D F, Matsuura T and Sourirajan S (1987) Effect of polyvinylpyrrolidone additive on the performance of polyethersulfone ultrafiltration membranes. *Industrial and Engineering Chemistry Research* 26, 2385.

Larbot A (1996) Ceramic processing techniques of porous support systems for membranes synthesis. *Fundamentals of Inorganic Membrane Science and Technology*, *Membrane Science and Technology Series 4* (eds A J Burggraaf and L Cot), pp. 119-140. The Netherlands: Elsevier Science BV.

Lee H K, Meyerson A S and Levon K (1992) Non-equilibrium liquid-liquid phase separation in crystallizable polymer solutions. *Macromolecules* 25, 4002-4010.

Lee S., Cho J., Elimelech M., (2005) , Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling, Journal of Membrane Science 262,27-41

Li S, Koops G H, Mulder M H V, van den Boomgaard Th and Smolders C A (1994) Wet spinning of integrally skinned hollow fiber membranes by a modified dual-bath coagulation method using a triple-layer spinneret. *Journal of Membrane Science* 94, 329-340.

Livage J, Henry M and Sanchez C (1988) Sol-gel chemistry of transition metal oxides. *Progress Solid State Chemistry* 18, 259.

Lloyd D R, Kim S S and Kinzer K E (1991) Microporous membrane formation via thermally induced phase separation. II. Liquid-liquid phase separation. *Journal of Membrane Science* 64, 1-11.

Lloyd D R, Kinzer K E and Tseng H S (1990) Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation. *Journal of Membrane Science* 52, 239-261.

McHugh A J and Yilmaz L (1985) The diffusion equations for polymer membrane formation in ternary systems. *Journal of Polymer Science, Polymer Physics Edition* 23, 1271-1274.

McHugh A J and Yilmaz L (1989) Further comments on the diffusion equations for membrane formation. *Journal of Membrane Science* 43, 319-323.

Merin U and Cheryan M (1980) Ultrastructure of the surface of a polysulfone ultrafiltration membrane. *Journal of Applied Polymer Science* 25, 2139-2142.

Mey-Merom A and Katz M (1986) Measurement of the active pore size distribution of microporous membranes. A new approach. *Journal of Membrane Science* 27, 119.

Mulder M H V (1996) Basic Principles of Membrane Technology, Second Edn, Dordrecht, The Netherlands: Kluwer Academic Publishers.

N. Hilala, H. Al-Zoubia, N.A. Darwishb, A.W. Mohammac, c and M. Abu Arabi (2004) ,A Comprehensive Review of Nanofiltration Membranes." Desalination 170 , 281-308.

Nakao S-L (1994) Review: determination of pore size and pore size distribution 3. Filtration membranes. *Journal of Membrane Science* 96, 131-165.

Noshay A and Robeson L M (1976) Sulfonated polysulfone. *Journal of Applied Polymer Science* 20, 1885-1903.

Nyström M, Pihlajamäki A and Ehsani N (1994) Characterization of UF membranes by simultaneous streaming potential and flux measurements. *Journal of Membrane Science* 87, 245-256.

Ogawa T and Marvel C S (1985) Polyaromatic ether-ketones and ether-ether-keto-sulfones having various hydrophilic groups. *Journal of Polymer Science, Polymer Chemistry Edition* 23, 1231-1241.

Paul D R and Newman S (1978) *Polymer blends*. New York: Academic Press.

Pearce G., (2007),The case of UF/MF pretreatment to RO in seawater applications, Desalination 203 , 286-295

Peeters J M M, Mulder M H V and Strathmann H (1999) Streaming potential measurements as a characterization method for nanofiltration membranes. *Colloids and Surfaces*, *A. Physicochemical Engineering Aspects* 150,247-259.

Philips M W and DiLeo A J (1996) A validation porosimetric technique for verifying the integrity of virus-retentive membranes. *Biologicals* 24, 243-253.

Pilat B.,(2001), Practice of water desalination by electrodialysis, Desalination 139 . 385-392

Pilat B.V.,(2003), Industrial application of electrodialysis reversal systems, Desalination 158 , 87-89

Porter M C (1974) A novel membrane filter for the laboratory. *American Laboratory* Nov.

Porter M C (1979) Membrane Filtration. Handbook of Separation Techniques for Chemical Engineers (ed. P A Schweizer) New York: MacGraw-Hill Book Co.

Price P B and Walker R M (1967) Molecular sieves and methods for producing same. US Patent 3,303,085.

Radovanovic Ph, Theil S W and Hwang S-T (1992a) Formation of asymmetric polysulfone membranes by immersion precipitation. Part I: Modeling mass transport during gelation. *Journal of Membrane Science* 65, 213.

Radovanovic Ph, Thiel S W and Hwang S-T (1992b) Formation of asymmetric polysulfone membranes by immersion precipitation. Part II: The effects of casting solution and gelation bath compositions on membrane structure and skin formation. *Journal of Membrane Science* 65, 231.

Reuvers A J and Smolders C A (1987b) Formation of membranes by means of immersion precipitation. II. The mechanism of formation of membranes prepared from the system cellulose acetate-acetone-water. *Journal of Membrane Science* 34, 67.

Reuvers A J, van den Berg J W A and Smolders C A (1987a) Formation of membranes by means of immersion precipitation. I. A model to describe mass transfer during immersion precipitation. *Journal of Membrane Science* 34, 67.

Riemersma M.C., Post J.W.,(2003) Hydraulically optimised design increases productivity and reduces cost, The International Desalination & Water Reuse ,13/2, 26-29

Rijn van C J M and Elwenspoek M C (1995) Microfiltration membrane sieve with silicon machining for industrial and biomedical applications. Micro Electro Mechanical Systems (Proceedings IEEE Amsterdam, 1995).

Roesink H D W, Beerlage M A M, Potman W, Boomgaard Th van den, Mulder M H V and Smolder C A (1991) Characterization of new membrane materials by means of fouling experiments. Adsorption of BSA on polyethermide-polyvinylpyrrolidone membranes. *Colloids and Surfaces* 55, 231-243.

Sara M and Sleytr U B (1987) Production and characterization of UF membranes with uniform pores from two-dimensional arrays of proteins. *Journal of Membrane Science* 33, 27-49.

Sara M, Kupcu S and Sleytr U B (1990) Crystalline bacterial cell surface layers used as UF membranes and immobilization matrix. *Genetic Engineer and Biotechnologist* Mar./Apr., 10-13.

Schnabel R (1976) Separation membranes from porous glass and methods to produce them. German Patent 2,454,111.

Scott K (1995) *Handbook of Industrial Membranes*. Oxford, UK: Elsevier Advanced Technology.

Seacord T.F., Coker S.D., MacHarg J.,(2006) Affordable Desalination Collaboration 2005 results, The International Desalination & Water Reuse 16/2 , 10-22

Skapski A, Billups R and Rooney A (1957) *Capillary-cone method for determination of surface tension of solids*. *Journal of Chemical Physics* 26, 1350.

Smith A W (1973) Porous anodic aluminum membrane. *Journal of the Electrochemical Society* 120(8), 1068-69.

Smith A W (1974) Process for producing an anodic aluminum oxide membrane. US Patent 3,850,762.

Smith K A, Colton C K, Mernill E W and Evans L B (1968) Convective transport in a batch dialyzer: determination of true membrane permeability from a single measurement. *Chemical Engineering Progress Symposium Series* 64, 45-58.

Smolders C A and Vugteveen E (1985) New characterization methods for asymmetric UF membranes. *Materials Science of Synthetic Membranes* (ed. D R Lloyd), pp. 327-338. Washington DC: ACS.

Stengaard F F (1988) Characterization and performance of new types of ultrafiltration membranes with chemically modified surfaces. *Desalination* 70, 207.

Strathmann H., Giorno L., Drioli E.,(2006), An introduction to membrane science and technology, Publisher CNR Roma,

Tan L, Greenberg A R and Krantz W B (1993) Laser interferometry studies of polymeric film and membrane formation via evaporation casting. *Polymer Preprints* 34(1), 902-903.

Tanny G (1984) Method for manufacturing microporous membrane. US Patent 4,466,931.

Tomi Y. et. al.,(2005), Evolution of RO Membrane for Seawater Desalination, International Forum on Water Industry Qingdao 2005, China, , 92- 97.

Tompa H (1956) *Polymer Solutions*. London: Butterworth.

Tsay C S and McHugh A J (1990) Mass transfer modeling of asymmetric membrane formation by phase inversion. *Journal of Polymer Science*, *Polymer Physics Editions* 28, 1327.

Turek M.,(2003) Cost effective electrodialytic seawater desalination, Desalination 153 , 371-376

Tweddle T A, Kutowy O, Thayer W L and Sourirajan S (1983) Polysulfone ultrafiltration membranes. *Industrial and Engineering Chemistry*: *Product Research and Development* 22, 320.

Vadalia H C, Lee H K, Meyerson A S and Levon K (1994) Thermally induced phase separation in ternary crystallizable polymer solutions. *Journal of Membrane Science* 89, 37-50.

Van der Bruggen, B.; Vandecasteele, C. (2002) Distillation vs. Membrane filtration: overview of process evolutions in seawater desalination. Desalination 143, 207-218.

Venkataraman K, Choate W T, Torre E R, Husung R D and Batchu H R (1988) Characterization studies of ceramic membranes. A novel technique using a Coulter® Porometer. *Journal of Membrane Science* 39, 259-271.

Vilensky Al, Oleinikov V A Markov N G, Mchedlishvili B and Dontzova E P (1994) Polyimide track membranes for UF and MF (in Russian). *Vysokomlekulyyarnye Soedineniya Seriya A* 36(3), 475-485.

Villa Sallangos O.L.,(2005),Operating experience at the Dhekelia seawater desalination plant using an innovative energy recovery system, Desalination 173 , 91-102

Wesselingh J A and Krishna (1990) *Mass Transfer*. New York: Ellis Horwood.

Wienk I M, Folkers B, van den Boomgaard Th and Smolders C A (1994a) The formation of nodular structures in the top layer of ultrafiltration membranes. *Journal of Applied Polymer Science* 53, 1011-1023.

Wienk I M, Folkers, B, van den Boomgaard Th and Smolders C A (1994b) Critical factors in the determination of the pore size distribution of UF membranes using a liquid displacement method. *Separation Science and Technology* 29, 1433-1440.

Wienk I M, Meuleman E E B, Borneman Z, van den Boomgaard Th and Smolders C A (1995b) Chemical treatment of membranes of a polymer blend: mechanism of the reaction of hypochloride with poly(vinyl pyrrolidone). *Journal of Polymer Science*: *Part A: Polymer Chemistry* 33, 49-54.

Wienk I M, Olde Scholtenhuis F H A, van den Boomgaard Th and Smolders C A (1995a) Spinning of hollow fiber ultrafiltration membranes from a polymer blend. *Journal of Membrane Science* 106, 233-243.

Wienk I M, Teunis H A, van den Boomgaard Th and Smolders C A (1993) A new spinning technique for hollow fiber ultrafiltration membranes. *Journal of Membrane Science* 78, 93-100.

Wijmas J G, Altena F W and Smolders C A (1984) Diffusion during the immersion precipitation process. *Journal of Polymer Science*, *Polymer Physics Edition* 22, 519-524.

Wolff J, Stenihauser H and Ellinghorst G (1988) Tailoring of ultrafiltration membranes by plasma treatment and their application for the desalination and concentration of water soluble organic substances. *Journal of Membrane Science* 36, 207.

Yi Hua Ma (1996) Adsorption phenomena in membrane systems. *Fundamentals of inorganic membrane science and technology, Membrane Science and Technology Series 4* (ed. A J Burggraaf and L Cot), pp. 35-66. The Netherlands: Elsevier Science BV.

Yilmaz L and McHugh A J (1986) Modelling of asymmetric membrane formation. I. Critique of evaporation models and development of a diffusion equation formation for the quench period. *Journal of Membrane Science* 28, 287-310.

Zeman I and Denault L (1992a) Characterization of microfiltration membranes by image analysis of electron micrographs. Part I. Method development. *Journal of Membrane Science* 71, 221-231.

Zeman L (1992b) Characterization of microfiltration membranes by image analysis of electron micrographs. Part II. Functional and morphological parameters. *Journal of Membrane Science* 71, 233-246.

Zeman L and Tkacik G (1985) Pore volume distribution in UF membranes. *Materials Science of Synthetic Membranes* (ed. D R Lloyd), pp. 339-350. Washington DC: ACS.

Zeman L, Tkacik G and Parlouer Le P (1987) Characterization of porous sublayers in UF membranes by thermoporometry. *Journal of Membrane Science* 32, 329-337.

Zsigmondy R and Bachmann R (1922) Filter and method of producing same. US Patent 1,421,341.

Zularisam A.W., Ismail A.F., Salim R.,(2006), Behaviours of natural organic matter in membrane filtration for surface water treatment — a review, Desalination 194 , 211–231