MEMBRANE CHARACTERIZATION

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Contents

Glossary
Bibliography and Suggestions for further study
Biographical Sketches

Summary

Nowadays, many researchers are working on membrane development, either for membrane water treatment or membrane gas separation. Many of them are attempting to find the cause and affect relationship between membrane fabrication-membrane morphology-membrane performances. The ultimate goal of the research is to provide a rational guideline for membrane fabrication conditions to achieve some specific membrane morphology, which enables the desired separation performance. For this reason, membrane morphology characterization is one of the indispensable components of membrane research.

Membrane manufacturers should also specify the membranes they provide by various characterization parameters such as pore size and pore size distributions and solute and particle rejections. By knowing these parameters, membrane users are able to choose conveniently those membranes that satisfy their requirements and to decide the conditions under which the membranes are used. It is needless to say that the ideal characterization method should be non-destructive, accurate, and repeatable and fast and also should give a maximum possible number of data. To this end, many methods have been devised.

This chapter focuses on the methods to characterize membranes for pressure driven processes such as reverse osmosis, nano-filtration, ultrafiltration, microfiltration, membrane gas and vapor separation, pervaporation etc. The examples shown in the article are mostly for the characterization of synthetic polymeric membranes but the applications of the methods are not necessarily limited to those.
Even though there are many characterization methods available, they are generally classified into the following categories

- Conventional physical methods to determine pore size and pore size distribution
- Micrographic methods to have photographical images
- Spectroscopic methods to know the membrane structure in its molecular level
- Methods to obtain bulk properties of membranes such as thermal and mechanical properties
- Other methods such as contact angle and zeta potential measurement

In this chapter, attempts are made to show principles and examples for each method.

1. Introduction

The development of asymmetric membranes for seawater desalination with a thin selective layer supported by a porous layer opened up a new avenue in membrane separation technology by Loeb and Sourirajan during the nineteen sixties [1]. Over the past 50 years membrane separation technology has grown into an annual several billion-dollar industry world wide. There are a number of membrane separation processes

currently being used. Typical examples are: reverse osmosis (RO), microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), forward osmosis (FO), pervaporation (PV), vapor separation (VP), membrane gas separation and membrane distillation.(MD).

Nowadays, many researchers are working on membrane development, either for membrane water treatment or membrane gas separation, and all of them attempt to find the cause and affect relationship between membrane fabrication-membrane morphology-membrane performances. The ultimate goal of the research is to be able to choose fabrication conditions to achieve membrane morphology, which is designed to enable the desired separation performance. In this regard, membrane morphology characterization is one of indispensable components of membrane research.

There are a number of methods to specify the membrane morphology. The classical way of characterizing the membrane is to determine pore size and pore size distribution of the membrane. The pore sizes determined by different methods do not necessarily agree with each other but they usually show some common trends. Currently, with the advancement of sophisticated physical instrument, researchers tend to identify the environment of the permeating molecules more on a molecular level. As the digital quantification of the instrument progresses in sub-nano scale, the difference between measurement of pore size and specification of the segmental distance in macromolecules is disappearing. In other words, the measurement of sub-nano scale pore size is generally accepted.

Another important trend in membrane characterization is that emphasis is more on the characterization of membrane surface morphology. It is in a way natural since membrane separation is fundamentally the reflection of surface phenomena, as manifested by the structure of integrally skinned asymmetric membranes and thin-film composite membranes. This trend has also been enhanced by the advancement of modern physical instrument such as atomic force microscopy (AFM) and X-ray photoelectron microscopy (XPS).

Yet, characterization of bulk membrane properties by conventional methods should not be ignored. The thermal, mechanical and chemical properties are examples of those.

The objective of this chapter is to make a comprehensive overview of different membrane characterization methods. For each method, the principle, instrumental method and examples that are particularly relevant to the membrane characterization are shown.

2. Pore Size Distribution Measurement

2.1. Bubble Gas Transport Method

This method is based on the measurement of the pressure necessary to blow air through a water-filled porous membrane [2]. The method so developed has been thoroughly used to characterize membranes and also is called the *bubble point* method. This method is only able to discriminate maximum pore size present in the pore distribution, corresponding to the minimum pressure necessary to blow the firstly observed air

bubble.

Figure 1 shows a schematic drawing of the test apparatus and the principle of the bubble-point method is depicted schematically in Figure 2, from which it can be seen that the liquid on the top of the membrane wets the latter. The bottom of the membrane is in contact with air and the air pressure is gradually increased until bubbles of air penetrate through the membrane at a certain pressure.
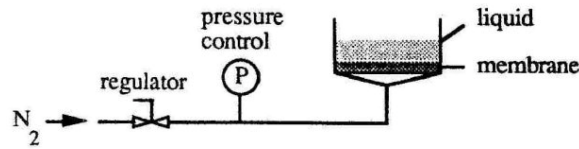
Figure1. Schematic drawing of a bubble-point test apparatus
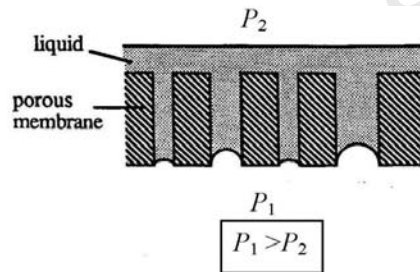
Figure2. The principle of the bubble-point method

An air bubble will penetrate through a pore of radius r_P when the transmembrane pressure difference $\Delta P = P_1 - P_2$ given by the following Laplace equation is reached.

$$r_P = \frac{2\gamma \cos\theta}{\Delta P} \tag{1}$$

In Eq. (1), γ is the surface tension at the liquid/air interface and θ is the contact angle. When a commercial wetting fluid Galwick^{TM} (Porous Materials Inc. USA) is used, the pore is wetted spontaneously and the contact angle of 0° can be assumed. The surface tension of the liquid is 15.9 x 10^{-3} N/m.

When $\theta = 0^o$, the Laplace equation is reduced to

$$r_p = \frac{2\gamma}{\Delta P} \tag{2}$$

which is called Cantor's equation.

Penetration will first occur through the largest pores and since the pressure difference is known, the pore radius can be calculated from Eq. (1). It is also possible to obtain pore

size distribution by performing this technique by a stepwise increase of pressure. This will be explained later on as permporometry.

Using water as wetting fluid, the pressure that corresponds to the pore radius of 0.01 µm, will become 145 bar because the surface tension of water is as high as 72.3 x 10^{-3} N/m (and assuming 0° contact angle). To avoid these high pressures, Bechhold [3] and Erbe [4] used two different liquids, instead of an air-liquid interface, reducing appreciably the surface tension. For example, using isobutyl alcohol-water interface, the measurement of pore sizes 40 times lowers is achieved, as compared with air-water interface. (This method is explained more in detail as liquid displacement method later on.) The method has been improved for both liquid-gas interfaces [5], and liquid-liquid ones [6], allowing the evaluation of pore sizes corresponding to a range of porous material, and is very well commercialized. The bubble point method is an easy, fast and inexpensive method to determine the maximum pore size and pore size distribution of membranes.

2.2. Mercury Intrusion Porosimetry

Mercury intrusion porosimetry is used extensively for the characterization of various aspects of porous media, including porous membranes and powders. Mercury porosimetry is applicable to pores from 30 Å up to 900 Å in diameters. It is well commercialized. Mercury intrusion porosimetry involves placing the sample in a special sample cup (penetrometer), surrounding the sample with mercury. Mercury is a non-wetting liquid to most materials and resists entering voids, doing so only when pressure is applied. The pressure at which mercury enters a pore is inversely proportional to the size of the opening to the void. As mercury is forced to enter pores within the sample material, it is depleted from a capillary stem reservoir connected to the sample cup. The incremental volume depleted after each pressure change is determined by measuring the change in capacitance of the stem. This intrusion volume is recorded with the corresponding pressure or pore size. By this technique, both pore size and pore size distribution can be determined.

The relationship of pressure and pore size is given by the Laplace equation (1). As mercury does not wet the membrane (since its contact angle is greater than 90° and $\cos\theta$ will have a negative value), Eq. (1) is modified as follows:

$$r_{p} = -\frac{2\gamma\cos\theta}{P} \tag{3}$$

The contact angle of mercury with polymeric material is often 141.3^{o} and the surface tension at the Hg/air interface is 0.48 N/m. Hence Eq. (3) will be

$$r_{p} = \frac{7492}{P} \tag{4}$$

where r_{p} is expressed in nm and P in bar.

Since the volume of mercury can be determined very accurately, pore size distributions

can be determined quite precisely. In Eq. (4), it is assumed that the membranes have capillary pores. As in general, it is not always right, morphology constant must be introduced. Furthermore, very high pressures should be avoided since these may damage the porous structure and lead to an erroneous pore size distribution.

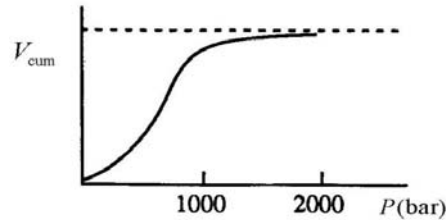Figure 3 gives a schematic drawing of the results of mercury intrusion experiment.

Figure. 3 Cumulative volumes (V_{cum}) as a function of the applied pressure

There are few disadvantages of this technique: i) it is expensive and not widely used. ii) it needs high pressure which could damage the surface, and iii) it measures all the pores present in the structure, including dead end pores.

2.3. Adsorption-Desorption Method (Barett-Joyner-Halenda (BJH) Method) [7]

Gas adsorption is a popular and commonly used method for characterization of surface and structural properties of porous materials allowing the determination of their surface area, pore volume, pore size distribution and adsorption energy distribution. Nitrogen is often used for the adsorbent gas but other adsorbents such as argon and benzene are also used. According to this method adsorption-isotherm (amount of adsorbed gas versus relative pressure (pressure/saturation vapor pressure of the adsorbent)) is drawn and the data are analyzed by assuming capillary condensation.

The vapor pressure, p, of the adsorbent liquid in the pore of radius r_{p} is given by the following Kelvin equation,

$$\ln \frac{p}{p_0} = -\frac{2\gamma V}{r_{\text{p}} RT} \cos \theta \tag{5}$$

where p_0 is the saturation vapor pressure, γ is the surface tension of the adsorbent liquid, V is the molar volume of the adsorbent liquid, R is the universal gas constant, T is absolute temperature and θ is the contact angle. Assuming $\theta = 0^{\circ}$, the above equation becomes for the liquid nitrogen,

$$r_{\text{p}} = -\frac{4.1}{\log \dfrac{p}{p_0}} \tag{6}$$

Assuming further all the pores whose radii are smaller than r_p are filled at a given relative pressure p/p_0, the cumulative pore volume curve versus r_p can be drawn. Often, the thickness of adsorbed layer t is added to r_p obtain above to calculate more precise pore radius.

In reality, the sorption-desorption curves are different due to hysteresis, depending on the pore structure. During analysis it is necessary to decide which branch of the isotherm to use, the adsorption or desorption branch. BJH method was modified by Kruk and Jaroniec in 2000 [8]. This method also is well documented in literature and university text books [2] and well commercialized.

2.4. Gas Liquid Equilibrium Method (Permporometry)

This method is based on the phenomenon of capillary condensation of liquids in micropores, which is the basis of one of the most popular methods for the characterization of the pore size distribution in porous media. Permporometry is the only method known so far [9] suitable for the determination of size distribution of the active pores with diameters ranging from about 1.5 nm to 0.1 µm in porous media, particularly those with an asymmetric and/or composite structure. This method is relatively new technique, is based on the controlled blocking of the pores by capillary condensation and simultaneous measurement of the gas diffusion flux through the remaining open pores. There are two different approaches of the method [10].

2.4.1. Liquid Displacement Permporometry (LDP) [11]

The liquid displacement method is commonly used to determine pore sizes and pore size distributions of a membrane because it is close to (ultra)filtration practice: dead-end pores are not evaluated; the membrane is characterized in wet conditions; in addition the pressure is kept as low as possible and thus no alteration of the membrane occurs [12].

This method was first described by Erbe [4] and Kesting [13] and further developed by Capannelli et al. [11, 14]. It is based on the measurement of the flux of a displacing liquid through the membrane as a function of the pressure applied. Thus, this method is similar to the bubble point method but a liquid in the pore is displaced by another liquid instead of gas. From the flux-pressure curve the pore size distribution is calculated using the Hagen-Poiseuille equation. Following assumptions are used for the calculation of pore size distribution.

a. The pores are cylindrical.
b. The pores are parallel to each other and not interconnected and thus are straight through the whole membrane layer.
c. The pores all have length l, where l is usually taken to be the thickness of the membrane (or thickness of the membrane skin layer in the case of an asymmetric membrane).

With assumption A and B, pore density function $N(r_p)$ can be calculated from the

increase in the measured flux ($d\varphi_s$) upon the increase in transmembrane pressure ($d\Delta P$) using the following Hagen-Poiseuille equation.

$$N(r_p) = \frac{8\eta l}{\pi r_p^4} \frac{d\varphi_s}{d\Delta P} \tag{7}$$

where η is the viscosity of the displacing liquid. If l is not known, a relative pore size distribution can be calculated.

The results obtained by the liquid displacement become incorrect if the pores are connected to each other or if there is a resistance against flow in membrane sub-layer or in the measurement apparatus. As a result of the additional resistance, the estimated pore size distribution shifts toward smaller pores and a larger number of pores. To overcome this, two methods have been suggested by Gijsbertsen-Abrahamse et al. [15]: either by estimating the sub-layer resistance by determining the number of active pores or by repeated measurement of the flux-pressure curves with different levels of coverage of the membrane surface.

2.4.2. Diffusional Permoporometry (DP) [17]

Diffusional permoporometry (DP) was first used by Katz [16, 17]. Later on, refinements to the technique have been suggested by many authors [9, 10, 18]. In this method, the Kelvin equation given in Section 1.3 is used combined with the diffusive vapor transport through the open pores. The measurement starts from the relative vapor pressure $p/p_0 = 1$, where all the pores are filled with liquid and the vapor transport is impossible. By reducing the vapor pressure progressively, more pores will be emptied and become available for vapor transport. Thus, measuring vapor flow rates at progressively decreasing vapor pressures, pore size distribution can be obtained.
In this method, a fluid "A", which completely wets the membrane, is used to fill the pores. A second fluid "B" (gas), immiscible in the "A", is then permeated through the membrane. The permeate flow rate is measured at various transmembrane pressures. Thus, this is an extension of the bubble point method.

Again the pore size and the transmembrane pressure difference are related to each other by Cantor's equation. Again the Hagen-Poiseuille equation is used to calculate the pore density function.

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Bibliography and Suggestions for further study

1. Loeb, S., Sourirajan, S., (1962)."Sea Water Demineralization by Means of an Osmotic Membrane", *Advances in Chemistry Series, 38,* 117

2. Mulder, M., Dordrecht, (1996). "*Basic Principles of Membrane Technology*", 2nd ed., Boston : Kluwer Academic Publishers.

3. Bechhold, H. Schlesinger, M., Silbereisen, K., Maier, L., Nurnberger, W., (1931)."Pore diameters of ultrafilters", Kolloid Z., 55, 172

4. Erbe, F., (1933). "Die Bestimmung der Porenverteilung Nach Ihrer Groe in Filtern und Ultrafiltern", *Kolloid-Zeitschrift*, 63, 277

5. Pereira Nunes, S., Peinemann, K. V., (1992). "Ultrafiltration Membranes from PVDF/PMMA Blends", *J. Membrane Sci.,* 77, 25

6. Munari, S., Bottino, A., Moretti, P., Capannelli, G., Becchi, I., (1989) "Permoporometric study on ultrafiltration membranes", *Journal of Membrane Science* 41(15), 69-86.

7. Barrett EP, Joyner LG, Halenda PP. (1951). "The determination of pore volume and area distribution in porous substances. I. Computations from nitrogen isotherms", *J Am Chem Soc.* 73, 373–80.

8. Kruk M**.,** Jaroniec M**.,** (2002) "Determination of Mesopore Size Distri- butions from Argon Adsorption Data at 77 K," *J. Phys. Chem. B*, 106, 4732–4739

9. Cao G. Z., J. Meijerink, H. W. Brinkman, A. J. Burggraaf, (1993). "Permporometry Study on the Size Distribution of Active Pores in Porous Ceramic Membranes," *J. Membrane Sci.*, 83 221-235

10. Hazri, A., Vaidya, A. M., (1995) "A new computational technique for the analysis of diffusion permoporometric data for asymmetric membranes", *Journal of Membrane Science* 101(1-2), 61-66.

11. Capannelli, G., Vigo F., Munari, S. , (1983) "Ultrafiltration membranes — characterization methods", *Journal of Membrane Science,* 15(3), 289-313

12. Nakao, Shin-ichi (1994). "Determination of pore size and pore size distribution: 3. Filtration membranes" *Journal of Membrane Science.* 96(1-2), 131-165

13. Kesting, R. E., (1971).Synthetic Polymeric Membranes, McCraw Hill, New York.

14. Capannelli, G., I. Becchi, A. Bottino, P. Moretti, S. Munari, (1987) "Computer Driven Porosimeter for Ultrafiltration Membranes," *Proc. Studies in Surface Science and Catalysis*, 283.

15. Gijsbertsen-Abrahamse, A.J., Boom, R.M., Padt, A. van der, (2004). "Why liquid displacement methods are sometimes wrong in estimating the pore-size distribution". *AIChE Journal* 50, ISSN 0001-1541, 1364 – 1371.

16. Katz,M.G., Baruch, G., (1986) "New Insights Into The Structure Of Microporous Membranes Obtained Using A New Pore Size Evaluation Method", *Desalination,* 58, 199-211

17. Katz MG, (1982) "Measurement of Pore Size Distribution in Microporous Filters and Membranes" In R. J. Wakeman (Ed.) Congress III, *The Filtration Society, Uplands Press, Croydon ,* Vol. II, 508.

18. Cuperus, F.P., Bargeman, D., Smolders, C.A. (1992) "Permporometry: the determination of the size distribution of active pores in UF membranes*", Journal of Membrane Science*, 71 (1-2), 57-67.

19. Brun, M., Lallemand, A., Quinson, J.F., Eyraud, C. (1977) "A new method for the simultaneous determination of the size and the shape of pores: the thermoporometry", *Thermochim. Acta* 21, 59.

20. Smolders, C.A., Vugteveen, E., (1985) "New characterization methods for asymmetric ultrafiltration membranes". *Mater. Sci. Synth. Membr.*, 327–338.

21. Zeman, L., Tkacik, G., Le Parlouer, P., (1985) "Pore volume distribution in UF membranes", *Mater. Sci. Synth. Membr.* p. 339.

22. Landsry, MR., (2005) "Thermoporometry by differential scanning calorimetry: experimental considerations and applications" *Thermochimica Acta* , 433(1-2), 27-50.

23. Altena, F.W., Knoef, H.A.M., Heskamp, H., Bargeman, D., Smolders, C.A. (1983) "Some comments on the applicability of gas permeation methods to characterize porous membranes based on improved experimental accuracy and data handling" *Journal of Membrane Science,* 12(3), 313-322.

24. Michaels, A.S., (1980). "Analysis and prediction of sieving curves for ultrafiltration membranes: a universal correlation", *Sep. Sci. Technol.* 15, 1305.

25. Singh S, Khulbe KC, Matsuura T, Ramamurthy, P., (1998). "Membrane characterization by solute transport and atomic force microscopy", *Journal Of Membrane Science* 142(1), 111-127.

26. Khulbe KC. Matsuura T. (2000) "Characterization of Synthetic membranes by Raman ... and atomic force microscopy; a review", *Polymer*; 41, 1917-1935.

27. Kesting, R.E., Engdahl, M., Stone Jr., W., (1969). "The application of scanning electron microscopy to membrane morphology", *J. Macromol. Sci.* A3 (1),157-167.

28. Patterson, D.A., Havill, A., Costello, S., See-Toh, Y.H., Livingston, A.G., Turner A., (2009) "Membrane Characterisation by SEM, TEM and ESEM: The Implications of Dry and Wetted Microstructure on Mass Transfer through Integrally Skinned Polyimide Nanofiltration Membranes", *Separation and Purification Technology,* 66, 90-97.

29. Riley, R., Gardner, J.O., Merten, U. (1964). "Cellulose acetate membranes: Electron microscopy of structure" *Science* 143(3608), 801-803.

30. Merin, U., Cheryan, M. (1980) "Ultrastructure of the surface of a polysulfone ultrafiltration membrane", *J. Appl. Polym. Sci. 25,* 2139-2142.

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

32. Zeman, Leos., Denault, Lauraine (1992) "Characterization of microfiltration membranes by image analysis of electron micrographs Part I. Method development" *Journal of Membrane Science* 71(3), 221-31.

33. Zeman L, Denault, Lauraine (1992) "Characterization of microfiltration membranes by image analysis of electron micrographs. Part II. Functional and morphological parameters" *J. Membrane Sci.* 71. 233.

34. Schossig-Tiedemann, M., Paul, D. (2001) "Improved preparation of membrane surfaces for field-emission scanning electron microscopy" *Journal of Membrane Science* 187(1-2), 85-91.

35. Kesting, R. E. (1990) "The four tiers of structure in integrally skinned phase inversion membranes and their relevance to the various separation regimes ", *Journal of Applied Polymer Science* 41(11-12), 2739–2752.

36. Wienk, I. M., van den Boomgaard, Th., C. Smolders, A. (1994) "The formation of nodular structures in the top layer of ultrafiltration membranes" *Journal of Applied Polymer Science,* 53(8), 1011–1023.

37. Khulbe KC, Feng CY, Matsuura (2008) "Synthetic Polymeric Membranes: Characterization by Atomic Force Microscopy" *Springer*.

38. Binnig, G., Quate C. F. (1986) "Atomic Force Microscope" *Phys. Rev. Lett.* 56, 930–933.

39. Albrecht, T.R., Dovek, M.M., Lang, C.A., Grutter, P., Quate, C.F., Kuan, S.W.J., Frank, C.W., Pease, R.F.W. (1988) "Imaging and modification of polymers by scanning tunneling and atomic force microscopy" *J. Appl. Phys.* 64, 1178.

40. Hirose M, Itoh H, Minamizaki Y, Kamiyama Y (1996) "Proceedings of the International Congress on Membranes and Membrane Process", Yokohama, Japan 18-23 August, pp 178.

41. Elimelech M, Zhu X, Childress AE, Hong S (1997). "Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes" *J Member Sci.,* 127, 101-109.

42. Khulbe KC, Matsuura T, Lamarche G, Kim HJ, (1997). "The morphology characterisation and performance of dense PPO membranes for gas separation" *J Membr Sci* 135, 211-223.

43. Bessieres A, Meireles M, Coratger R, Beauvillain J, Sancbez V (1996). "Investigations of surface properties of polymeric membranes by near field microscopy" *J Membr Sci.,* 109,271-284.

44. Bowen, WR, Hilal, N, Lovitt, RW, Williams, PM. (1996) "Atomic force microscope studies of membranes: Surface pore structures of Cyclopore and Anopore membranes" *J Membr Sci.,* 110, *233-238.*

45. Kunal Pal, Ajit K. Banthia, Dipak K. Majumdar. (2007) "Preparation and Characterization of Polyvinyl Alcohol–Gelatin Hydrogel Membranes for Biomedical Applications" *AAPS PharmSciTech*; 8 (1) Article 21.

46. Belfer S, Fainchtain R, Purinson Y, Kedem OJ. (2000) "Surface characterization by FTIR-ATR spectroscopy of polyethersulfone membranes-unmodified, modified and protein fouled" *J Membr Sci.* 172,113-124.

47. Sloan, James M (2004) "Characterization of the transport properties in elastomeric polymer membranes by FT-IR-ATR ", *ANTEC Conference Proceedings* vol. 2, pp. 2386-2389.

48. DAI, Qing Wen, XU, Zhi Kang, WU, Jian (2004) "A Novel Approach for the Surface Modification of Polymeric Membrane with Phospholipid Polymer" *Chinese Chemical Letters* Vol. 15, No. 8, pp 993-996.

49. Gall, M.J., Hendra, P.J., Peacock, C.J., Cudby, M.E.A., Willis, H.A. (1972) "Laser-Raman spectrum of polyethylene: Part 1. Structure and analysis of the polymer", *Polymer*, 13(3), 104-108.

50. Zubov, P.I., Voronkov, V.A., Sukharev, L.A. (1968) "Effect of solvent and polymer solid interactions on the structure and properties of polystyrene", *Vysokomol Soedin Ser. B* 10 (2) 92–95 (C.A. 68, 3606g)

51. K. C. Khulbe, B. Kruczek, G. Chowdhury, S. Gagné, T. Matsuura, S. P. Verma (1996) "Characterization of membranes prepared from PPO by Raman scattering and atomic force microscopy" *Journal of Membrane Science,* 111(1), 57-70.

52. Khulbe KC, Matsuura T, Kim HJ (2000) "Raman scattering of PPO membranes J Appl Polym Sci". *Journal of Applied Polymer Science* 77(11), 2558-2560.

53. Carrington A (1962) "The Principles of Electro-spin Resonance" *Endeavour* 21, 51-57.

54. Khulbe, K. C. , Chowdhury, G. , Matsuura, T. Lamarche, G. (1997) "Characterization of PPO [poly(phenylene oxide)] powder and membranes from it by ESR technique" *Journal of Membrane Science,* 123(1), 9-15.

55. Stone, T. J., Buckman, T., Nordio, P. L., McConnell, H. M. (1965) "Spin-labeled biomolecules". *Proc. Natl. Acad. Sci. U.S.A.*, 54, 1010-1017.

56. Miller WG (1976) "Spin Labeled Synthetic Polymers. Molecular Biology Spin Labeling II:Ttheory and Application" *Academic Press*, New York, pp 173.

57. Khulbe, K. C., Chowdhury, G., Kruczek, B., Vujosevic, R., Matsuura, T. Lamarche G. (1997) "Characterization of the PPO dense Membrane prepared at different temperatures by ESR, atomic force microscope and gas permeation" *Journal of Membrane Science* , 126(1), 115-122.

58. Khulbe, K. C. , Matsuura, T. , Feng, C. Y. , Lamarche, G., Lamarche, A. -M. (2002) "Characterization of ultrafiltration membrane prepared from poly ethersulfone by using electron spin resonance technique" *Separation and Purification Technology* 29(1), 15-22.

59. Griffith, O. Hayes, Waggoner, A. S. (1969) "Nitroxide free radicals: spin labels for probing biomolecular structure" *Acc. Chem. Res.*, *2* (1), 17–24.

60. Sheldon F. Oppenheim, Garry R. Buettner, Jonathan S. Dordick, V.G.J. Rodgers (1994) "Applying electron paramagnetic resonance spectroscopy to the study of fouling in protein ultrafiltration" *Journal of Membrane Science* , 96(3), 289-297.

61. Gary C. Rex, Shulamith Schlick (1987) "Study of polymer gels using paramagnetic probes: E.S.R. spectra of Cu^{2+} in reversible polyacrylamide gels" *Polymer* 28(12), 2134-2138.

62. Kim, Soon Sam, Yavrouian, Andre H., Liang, Ranty H., (1993) "Segmental mobility and free-volume decay of poly(phenyl methacrylate). An EPR study" *Journal of Polymer Science Part B: Polymer Physics* 31, 495–499.

63. Patrick A. C. Gane, Cathy J. Ridgway, Esa Lehtinen, Rustem Valiullin, Istvan Furó, Joachim Schoelkopf, Hannu Paulapuro, John Daicic (2004)."Comparison of NMR Cryoporometry, Mercury Intrusion Porosimetry, and DSC Thermoporosimetry in Characterizing Pore Size Distributions of Compressed Finely Ground Calcium Carbonate Structures" *Ind Eng Chem Res* 43(24),7920-7927.

64. Christopher L. Glaves, Gregory C. Frye, Douglas M. Smith, C. Jeffery Brinker, Abhaya Datye, Antonio J. Ricco, Stephen J. Martin (1989) "Pore structure characterization of porous films" *Langmuir* 5(2), 459-466.

65. A. Viallat - M.M. Margulies (2000) "Porous structure of membranes of an acrylonitrile copolymer. Porosity, ^{1}H-NMR permeability" *Eur. Phys. J. E,* 2, 117-123.

66. Davis, P.J., Smith, D.M. (1989) "Using NMR Spectroscopy to Analyze the Pore Structure of Coatings", *TAPPI. Journal*, 72(5), 85-89.

67. Khulbe, K. C., Matsuura, T., Lamarche, G., Lamarche, A. -M. (2000) "X-ray diffraction analysis of dense PPO membranes" *Journal of Membrane Science* 170(1), 81-89.

68. Kim, T. H., Koros, W. J., Husk, G. R., O'Brien, K. C. (1988) "Relationship between gas separation properties and chemical structure in a series of aromatic polyimides" *Journal of Membrane Science*, 37(1), 45-62.

69. Suk D, (2005) "Development of Surface Modifying Macromolecule Blended Polyethersulfone Membranes for Vacuum Membrane Distillation" *Ph.D. Thesis, Department of Chemical Engineering, University of Ottawa*.

70. Yi Fang, Vu Anh Pham, Takeshi Matsuura, J. P. Santerre and Roberto M. Narbaitz (1994) Effect of surface-modifying macromolecules and solvent evaporation time on the performance of polyethersulfone membranes for the separation of chloroform/water mixtures by pervaporation J Appl Polym Sci Volume 54 issue 12 pages 1937–1943.

71. Ho J., Santerre, J.P., Matsuura, T., (2000) "The effect of Fluorinated Surface Modifying Macromolecules on Polyethersulfone Membranes", *J. Biomat. Sci., Polym. Ed.*, 11 (10), 1085-1105.

72. Wang Y, Yin S, Ren L, Zhao L. (2009) "Surface characterization of the chitosan membrane after oxygen plasma treatment and its aging effect". *Biomed Mater.* 4(3), 035003.

73. Kulkarni, Sandeep, Krause, Sonja, Wignall, G. D. (1994) "Investigation of the Pore Structure and Morphology of Cellulose Acetate Membranes Using Small-Angle Neutron Scattering (SANS). 2. Ultrafiltration and Reverse-Osmosis Membranes" *Macromolecules*, 27 (23), 6785–6790.

74. Kulkarni, Sandeep, Krause, Sonja, Wignall, G. D., Hammouda, B. (1994) " Investigation of the Pore Structure and Morphology of Cellulose Acetate Membranes Using Small-Angle Neutron Scattering. 1. Cellulose Acetate Active Layer Membranes" *Macromolecules*, 27 (23), 6777–6784.

75. Satyanarayana, S.V., Subrahmanyam, V.S., Verma, H.C., Sharma, A., Bhattacharya, P.K. (2006) "Application of positron annihilation: Study of pervaporation dense membranes" *Polymer* 479(4), 1300-1307.

76. Malcolm L. Williams, Robert F. Landel, John D. Ferry (1955) "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids" *J. Am. Chem. Soc.*, 77 (14), 3701–3707.

77. Jean YC, Malton PE, Schrader DM (2003) "Principles and Applications of Positron and Positronium Chemistry", *World Scientific Publishers*, New Jersey.

78. Nakanishi H, Wang SJ., Jean YC. (1988) "Positron Annhilation studies of fluids" in *Sharma SC. Editor, Singapore , world scientific*. p292.

79. Tao SJ. (1972) "Positronium annihilation in molecular substance", *J. Chem. Phys.* 56, 5499-5510.

80. Wang, Y. Y., Nakanishi, H., Jean, Y. C., Sandreczki, T. C. (1990) "Positron annihilation in amine-cured epoxy polymers—pressure dependence" *J Polym Sci, Polym Phys B* 28 (9), 1431–1441.

81. Hill, A. J., Weinhold, S., Stack, G. M., Tant, M. R. (1996) "Effect of copolymer composition on free volume and gas permeability in poly(ethylene terephthalate)-poly(1,4 cyclohexylenedimethylene terephthalate) copolyesters" *European Polymer Journal* 32(7), 843-849.

82. Yin, Htwe Htwe, Yin, Zejie, Ma Weitao, Zhu, Daming (2005) "A Review of Studies of Polymeric Membranes by Positron Annihilation Lifetime Spectroscopy" *Plasma Science & Technology*, 7(5), 3062-3064.

83. Chen, Hongmin, Hung, Wei-Song, Lo, Chia-Hao, Huang, Shu-Hsien, Cheng, Mei-Ling, Liu, Guang, Lee, Kueir-Rarn, Lai, Juin-Yih, Sun, Yi-Ming, Hu, Chien-Chieh, Suzuki, R., Ohdaira, T., Oshima, N., Jean, Y. C. (2007) "Free-Volume Depth Profile of Polymeric Membranes Studied by Positron Annihilation Spectroscopy: Layer Structure from Interfacial Polymerization" *Macromolecules* 40(21), 7542–7557.

84. Tung, Kuo-Lun, Jean, Yan-Ching, Nanda, Dipankar, Lee, Kueir-Rarn, Hung, Wei-Song, Lo, Chia-Hao, Lai, Juin-Yih (2009) "Characterization of multilayer nanofiltration membranes using positron annihilation spectroscopy" *Journal of Membrane Science* 343(1-2), 147-156.

85. Shantarovich, P., Azamatova, Z. K., Novikov, Yu. A., Yampolskii, Yu. P. (1998) "Free-Volume Distribution of High Permeability Membrane Materials Probed by Positron Annihilation" *Macromolecules*, 31(12), 3963–3966.

86. Shantarovich, V. P., Kevdina, I. B., Yampol'skii, Yu. P. (2000) "Evaluation of nonuniformity of polymeric membrane materials by positron annihilation technique" *High Energy Chemistry* 34, 265-272.

87. Katleen Boussu, Jérémie De Baerdemaeker, Charles Dauwe, Marc Weber, Kelvin G. Lynn, Diederik Depla, Steliana Aldea, Ivo F. J. Vankelecom, Carlo Vandecasteele, Bart Van der Bruggen. (2007) "Physico-Chemical Characterization of Nanofiltration Membranes" *ChemPhysChem* 8(3), 370–379.

88. Li, Jianxin, Sanderson, R. D., Jacobs, E. P. (2002) "Non-invasive visualization of the fouling of microfiltration membranes by ultrasonic time-domain reflectometry" *Journal of Membrane Science* 201(1-2), 17-29.

89. Reinsch, Veronika E., Greenberg, Alan R., Kelley, Stephen S., Peterson, Rorik Bond, Leonard J. (2000) "A new technique for the simultaneous, real-time measurement of membrane compaction and performance during exposure to high-pressure gas" *Journal of Membrane Science* 171(2), 217-228.

90. Cosentino C, Amato F, Ferrari M (2007) in "BioMEMS and Biomedical Nano Technology", *eds. Ferrari M, Lee AP, Lee J, Springer* US, , pp. 203.

91. Tomás E. Gómez Álvarez-Arenas (2003) "Air-coupled ultrasonic spectroscopy for the study of membrane filters" *Journal of Membrane Science* 213(1-2), 195-207.

92. Haines, N.F., Bell, J.C., McIntyre, P.J., (1978) "The application of broadband ultrasonic spectroscopy to the study of layered media". *J. Acoust. Soc. Am* 64, 1645–1651.

93. Keurentjes, J. T. F., Harbrecht, J. Brinkman, G., D., Hanemaaijer, J. H., Cohen Stuart, M. A., van't Riet, K. (1988) "Hydrophobicity measurements of microfiltration and ultrafiltration membranes" *Journal of Membrane Science* 47(3), 333-344.

94. Rosa, M.J., de Pinho, M.N. (1997) "Membrane surface characterisation by contact angle measurements using the immersed method" *Journal of Membrane Science* 131(1-2), 167-180.

95. Rafat, Mehrdad, De, Dibyendu, Khulbe, K. C., Nguyen, Thanh, Matsuura, T. (2006) "Surface characterization of hollow fiber membranes used in artificial kidney" *J Appl Polym Sci*. 101(6), 4386-4400.

96. Elimelech, M., Chen, W.H., Waypa, J.J. (1994). "Measuring the zeta (electrokinetic) potential of reverse osmosis by a streaming potential analyzer", *Desalination*, 95, 269–286.

97. Moore, Theodore T., Koros, William J. (2005) "Non-ideal effects in organic–inorganic materials for gas separation membranes" Journal of Molecular Structure 739(1-3), 87-98.

98. Chung, T. S., Jiang, L. Y., Li, Y., Kulprathipanja, S., (2007) "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation" *Prog. Polym. Sci.* , 32, 483-507.

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