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HIGH PERFORMANCE BLENDED MEMBRANES USING A NOVEL PREPARATION TECHNIQUE

(MEMBRAN CAMPURAN BERPRESTASI TINGGI MENGGUNAKAN TEKNIK NOVEL)

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ABSTRACT

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The possibility of applying novel microwave (MW) technique in the dissolution of polyethersulfone (PES) and lithium halides in aprotic solvent is studied. The lithium halides additives used are lithium fluoride (LiF), lithium bromide (LiBr) and lithium chloride (LiCl) and a comparison is made with conventional method. PES was dissolved in dimethylformamide (DMF) in the single solvent whilst for the double solvent (DS); PES was dissolved in a mixture of two different solvents DMF and acetone. The concentrations of lithium halide in both solvents were varied from 1 to 5 wt%. In order to illuminate the mechanism through which lithium halide influences the kinetic membrane performance in both techniques, rheological, FTIR, contact angle and water uptake analysis were performed. The performances of the membranes were evaluated in terms of pure water permeation (PWP), permeation rate (PR) and separation rates of various polyethylene glycols. Result revealed that the hollow fiber MW membrane with the 3 wt% LiBr additive exhibits both high permeation rates of 222.16 $Lm^{-2}hr^{-1}$ and separation rates of 99% and molecular weight cutoff (MWCO) of 2.6 kDa. In general, the MW membranes exhibited higher permeation and separation rates compared to conventional electrothermal heating (CEH) membranes. The FTIR, contact angle and water uptake measurement revealed that the LiCl and LiBr have enhanced the hydrophilic properties of the PES membranes thus producing membrane with high permeation and separation rates.

(Keywords: microwave, hollow fiber membranes, lithium halide, polyether sulfone)

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ABSTRAK

MEMBRAN CAMPURAN BERPRESTASI TINGGI MENGGUNAKAN TEKNIK NOVEL

Kajian telah dilakukan untuk melarutkan poliethersulfona (PES) dan lithium halide di dalam pelarut aprotic melalui pengapilaksian kaedah microwave baru(MW). Bahan penambah lithium halide yang digunakan adalah lithium flouride (LiF), lithium bromide (LiBr) dan lithium cloride (LiCl) di mana perbandingan turut dilakukan terhadap kaedah konvesional (CEH). PES telah dilarutkan di dalam dimethylformamide (DMF) untuk larutan tunggal (SS), manakala bagi larutan berganda (DS), PES telah dilarutkan di dalam campuran dua pelarut iaitu DMF dan aceton. Kepekatan lithium halide bagi kedua-dua pelarut tersebut divariasikan antara 1 hingga 5 wt%. Bagi mengenalpasti pengaruh lithium halide terhadap prestasi membran di dalam teknik microvawe baru (MW) dan teknik konvensional (CEH), analisa terhadap rheological, FTIR, sudut sentuhan dan ketelapan air oleh membran telah dijalankan. Prestasi membran melalui ketelapan air tulen (PWP), kadar ketelapan (PR) dan kadar pemisahan pelbagai polyethilene glicol. Keputusan ujian menunjukkan bahawa membran MW dengan 3 wt% LiBr menghasilkan kadar permeasi yang tinggi serta kadar pemisahan pada 181 $Lm^{-2}hr^{-1}$ dan berat molekul *cut off* (MWCO) pada 2.6 kDa. Secara amnya, membran MW menghasilkan kadar ketelapan dan pemisahan yang lebih tinggi berbanding membran CEH. Keputusan yang diperolehi pada FTIR, sudut sentuhan dan ketelapan air oleh membran membuktikan bahawa LiCl dan LiBr telah meningkatkan keupayaan membran PES sekaligus menghasilkan membran yang mempunyai kadar ketelapan dan pemisahan yang tinggi

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CHAPTER 1

INTRODUCTION

1.1 Overview

Almost every chemical process involves at least one separation or purification step and the chemical industry has developed a range of separation techniques to facilitate recovery of the required products. In recent years, membranes and membrane separation techniques have grown from laboratory tool to an industrial process with considerable technical and commercial impact. In many cases, membrane processes are faster, more efficient and economical than conventional separation techniques. With membranes, the separation is usually performed at ambient temperature, thus allowing temperature-sensitive solutions to be treated without the constituents being damaged or chemically altered. This is important in the food and drug industry and in biotechnology where temperature-sensitive products have to be processed (Porter, 1990). Amongst all the membranes process, ultrafiltration has the largest variety of applications in various industries, because it is as a separation technology of high efficiency and low energy consumption (Nunes and Pienemann, 2006).

The beginnings of ultrafiltration (UF) are coincident with that of reverse osmosis (RO) around 1960. The term “ultrafiltration” first appeared in the colloid literature toward the end of the last century. Since Bechhold's original membranes, there has been continuous effort to develop new ultrafiltration membranes which has resulted in many diverse types of such membranes (Allegrezza *et al*., 1989). Today, the membrane that predominate commercially are asymmetric membranes made from synthetic polymers, co-polymers or blends by the phase-inversion method.

Phase inversion process is one of the most important means to prepare asymmetric membrane. The preparation of membrane structures with controlled pore size involves several techniques with relatively simple principles, but tricky. The material is usually cast into flat sheet or fine hollow fibers. In comparison with the tubular, plate frame, spiral-wound and capillary modules, the hollow fiber modules are generally compact and have a high packing density up to 3000 m^2/m^3 (Ani *et al.,* 2002a).

Membrane research is still apprehensive with the development of new techniques and the comprehension of the phenomena in membrane formation across the world. This is due to the difficulties to obtain membranes with the desired properties, i.e., ultra-thin and defect-free dense skin (Cristina *et al*., 2003). Different methods of polymer membrane preparation have been covered in several reviews (Nunes and Pienemann, 2006). The asymmetric membranes combine high permeant flow, provided by a very thin selective top layer and a reasonable mechanical stability, resulting from the underlying porous structure (Nunes and Pienemann, 2006). Asymmetric membranes are characterized by a non uniform structure comprising of an active top layer, or skin, supported by a porous support or sub-layer. Usually asymmetric membrane has long finger-like pores that reach to one surface of the membrane, while towards the outer surface of the membrane the pores become much smaller and a thin skin layer can be detected (Scott, 1995). Asymmetric membranes with thin top layers such as cellulose acetate, polysulfone or polyethersulfone membranes prepared by phase inversion generally achieve the required objective (Kim *et al.,* 1996). However they do have certain limitations, certain polymers are not soluble in the preferred solvents (Scott, 1995). Hence, to overcome these problems composite membranes have also been developed for UF (Allegrezza *et al.,* 1989). An asymmetric structure characterizes most of the presently commercially available membranes, which are now produced from a wide variety of polymers.

Materials used for the membranes cover a wide range, from organic polymeric materials to inorganic materials. New materials, products and processes continue to emerge as membrane scientists strive to enhance separation speed and selectivity and improve membrane properties for non-separating purposes (Gobina, 2004). Numerous polymers such as cellulose and its derivatives such as, cellulose acetate (CA), cellulose triacetate (CTA), cellulose butyrate (CB), cellulose nitrate (CN), polysulfone (PSf), sulfonated or carboxylated polysulfone (CPSf) and polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), poly(vinyl chloride) (PVC) and polyetherimide (PEI) could be used to prepare ultrafiltration membranes by phase inversion separation method (Jian and Xu, 2002).

The cellulose acetate (CA) membrane was the first high performance asymmetric membrane material. It has been widely used for reverse osmosis (RO), ultrafiltration (UF) and gas separation. CA membranes have been prepared by many of the membrane researchers and characterized for their compaction, hydraulic permeability, and osmotic permeability (Prabhaker and Misra, 1986). CA membranes have excellent hydrophilicity that is very important in minimizing fouling, good resistance to chlorine and solvent (Ashraf, 2002). A regenerated CA membrane that was hydrolyzed from cellulose acetate has significantly improved solvent-resistance and thermo stability (Yun, *et al*., 2002) Asymmetric ultrafiltration membranes based on CA were prepared and studied extensively as a function of casting solution composition and membrane formation mechanism (Kunst and Vajnaht, 1977). Modification of CA has been carried out by diisocyanate, characterized and applied to solute rejection at different operating pressures (Hseih *et al*., 1989). However, application of cellulose acetate membrane to processes which involve increasingly diversified macromolecular components requires the modification of cellulose acetate with a balanced hydrophilic–hydrophobic moiety (Ani and Iqbal, 2007a). The hydrophilic/hydrophobic balance, as well as the physicochemical properties, of a membrane system can be easily changed if the membrane is prepared from multicomponent polymer mixture blends (Ani and Iqbal, 2007a). The structural, kinetic and thermodynamic parameters of cellulose acetate membranes have been determined at controlled casting conditions and different annealed conditions (Uemura *et al*., 1980).

While polysulfone (PSf) and polyethersulfone (PES) materials have long been used for making porous supports for reverse osmosis membranes, they are now being used increasing in asymmetric membranes for direct use as UF/RO membranes (Tweddle *et al*., 1983). This is because PSf and PES has superior properties such as chemical, mechanical, and thermal resistance, wide pH tolerances and fairly good chlorine resistance. They are also easy to fabricate into a wide variety of configurations and modules with wide range of pore sizes available for UF applications ranging from 10 Å to 0.2 μm and good chemical resistance to aliphatic hydrocarbons, alcohols and acids (Cheryan, 1998b). PSf and PES are considered the ideal candidate in the membrane industry. However polysulfone is uncharged and hydrophobic in nature. Research on improvement of its flux and retention behavior started early in the early 1980s. One of the method used to improve the structure and performance of the membrane is to introduce low molecular weight organic additives having different functional groups in the polymer solution. (Kesting and Irvine, 1985).

The studies on sulfonated or carboxylated - polysulfone and polyethersulfone membranes have proved that the structure and performance are dependent on the composition of both the casting solution and the nascent membrane at the instant of gelation (Kinzer *et al*., 1985). Sulfonated polysulfone membranes have already been prepared and studied for water permeability, salt permeability, and water regain studies (Brousse *et al*., 1976). Asymmetric RO and ultrafiltration (UF) membranes were also prepared using sulfonated polysulfone (SPS), and the effect of various parameters such as casting solution composition, viscosity, solvent evaporation time, and precipitation bath composition on the usage as ultrafiltration membranes has been described (Kesting and Irvine, 1985).

In order to increase the usefulness of the hydrophobic PES and PSf membranes, hydrophilicity or surface wettability is an important membrane characteristics which need to be improved. Based on the fundamental concept that the surface layer of the asymmetric polymeric membrane is strongly influenced by the additives or that of their aggregates which are in the casting solution, there is always an ongoing research in finding new suitable additives for membrane making. In brief, additives used in the fabrication of PES membranes can be broadly categorized into polymeric additives such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and weak solvents such as glycerol. In fact the addition of PVP and PEG has become a standard method or approach to obtain ‘hydrophilized’ membranes (Ani and Iqbal, 2008b). Organic acid such as acetic acid, propionic acid causes macrovoid formation (Ani and Iqbal, 2007b and Lee *et al.*, 2002). Other less common additives used are low-molecular-weight inorganic salts such as lithium chloride (LiCl), zinc chloride ($ZnCl_2$), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), magnesium perchlorate ($Mg(ClO_4)_2$) and calcium perchlorate $Ca(ClO_4)_2$ (Ani and Iqbal, 2008b).

Additionally for polymeric membrane production the most frequently used polar and dipolar solvents are N-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetone, γ-butyrolactone and ε-caprolactam acid solvents such as acetic acid and formic acid (Ani and Iqbal, 2007b). The coagulation bath is often water or a mixture of water and solvent. The use of two solvents for polymeric membrane dope solution has also been reported. Baker (1971) prepared the first high flow polysulfone anisotropic membranes from a mixture of two solvents. It was reported that a mixture of polar, aprotic and volatile solvent such as dioxane and acetone causes rapid evaporation on the surface, leading to the formation of a dense layer on the surface. The use of solvent/non-solvent mixture changes the solubility parameter of the solvent system which in turn changes the polymer–solvent interaction in the ternary-phase polymer system. Subsequently, these changes have altered the polymer morphology of the surface layer and sub-layer (Yanagishita *et al.,* 1994).

1.2 Background of the Problem

Generally polymeric membranes production is a complicated process since it involved many steps namely; material selection, drying process, dope solution preparation, casting or hollow fiber spinning, phase inversion process, and post treatment. These steps are illustrated in Figure 1.1. Amongst the various steps, the dope dissolution process of membranes production is expensive and time consuming;

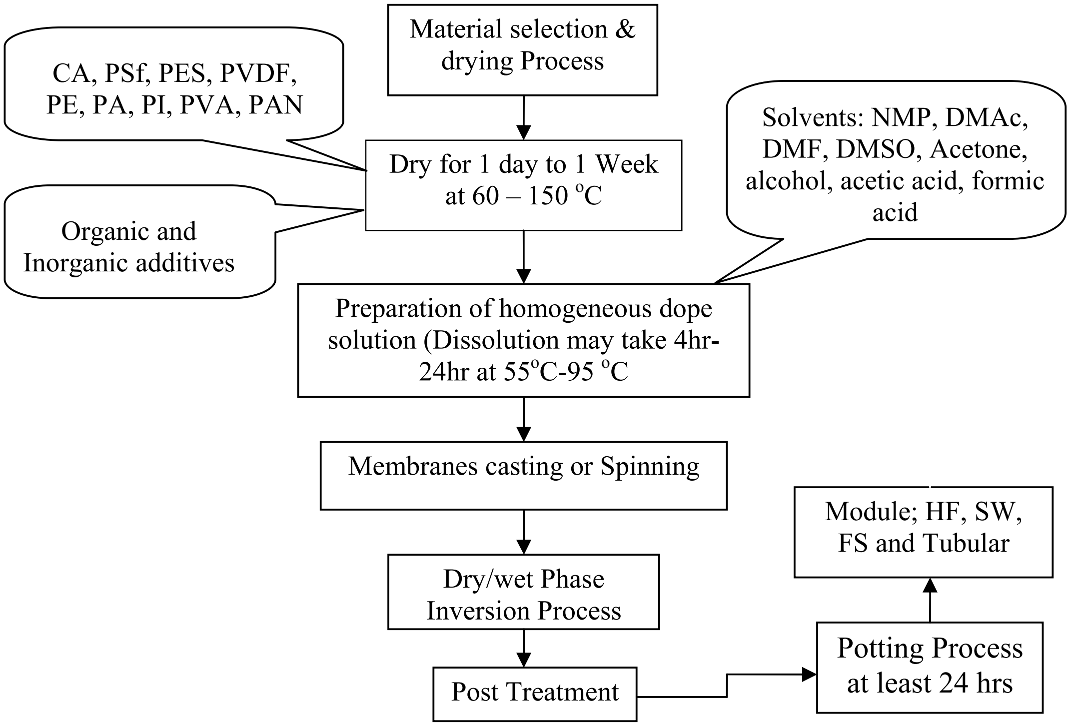


Figure 1.1: Membranes preparation process (Ani and Iqbal, 2007c)

particularly when membranes are prepared from glassy amorphous polymers such as PVDF, PSf, PES, PI, PA, PP and polyetherketone.

The dissolution of a polymer in a pair of nonsolvent was first observed in the 1920s during research related to cellulose nitrate solution systems. It was then found that solvent and nonsolvent for a polymer, when mixed in some specific compositions, might actually function as a solvent for that polymer (Cheng *et al.,* 2000). Generally the dissolution of polymer solids or powder samples are usually carried out in reaction vessels containing the sample volume of polymer solution, typically at laboratory level of 200 to 1000 ml. Traditionally, the mixture is heated for long periods of time using a hot plate, heating mantle, or oven. Normally as the temperature of a casting solution increases so does the average diameter of the pores in the resulting membrane, all other variables being constant (Wrasidlo, 1986). If the temperature of a casting solution is too high or low, the resulting membrane can have undesirable characteristics.

Besides, the frequently available dope solution methods for membrane fabrication, the equipment, man power and energy required to exercise an effective control and minute observation regarding their much needed properties put the most common methods for making microporous membrane beyond reality and financial reach (Wrasidlo, 1986). These traditional heating techniques are slow and time-consuming, and sometimes can lead to overheating and decomposition of the substrate and product. Heating is terminated when the analyst decides that the dissolution of the polymer is sufficiently complete. This type of reaction vessel digestion has many drawbacks, which include the use of large volumes (and multiple additions) of materials, a large potential for contamination of the sample by materials and laboratory environment (Richter, 2003). While the dissolving rate can be increased either by the use of high temperatures or intense agitation, these practices are undesirable. If high shear agitation is employed to enhance dissolving rate, the shearing forces can rupture or break the polymer chains thus reducing the molecular weight of the polymer in solution (Hadermann *et al*., 1985).

In cases, when multi solvents and additives are used the dissolution process becomes even more difficult. The dissolution of amorphous polymers becomes more difficult by physical media at the presence of inorganic salts. These low molecular weight inorganic salt additives in casting solution are considered to change the solvent properties and/or the interaction between the macromolecule chains of polymer. These low molecular weight inorganic salts are particularly interesting as additives for membrane casting solutions because it interacts strongly to form complexes with solvents commonly used for membrane preparation (Bottino *et al.,* 1988; Kraus *et al.,* 1979; Shibata *et al.,* 2000; Tweddle *et al.,* 1983 and Wang *et al.,* 2000b). This strong inorganic–solvent interaction would increase the viscosity of the casting solution but reduce the solvency power (Phadke *et al.,* 2005). However in practice, the addition of inorganic salts to casting solutions was reported to be very effective to prepare membranes with higher performance (Bottino *et al.,* 1988; Kraus *et at.,* 1979 and Tweddle *et al.,* 1983). Besides that the addition of cosolvents induces the change in the solvent quality, which would affect the interaction between polymer and solvent (Wang. 1999). Therefore the use of multisolvent and additives are motivated by several factors such as to reduce the cost and improve the membranes performance. Thus in this study the use of microwave technique is proposed so as to reduce the amorphous polymer dissolution time.

Since the mid-1980s, the applications of microwaves in chemical synthesis have been widely investigated. Many inorganic (Komarneni *et al*., 1992) and organic (Baghurst and Mingos, 1992) reactions could proceed under microwave radiation at a much higher rate than conventional methods. Besides the rapid reaction rate, microwave heating has some other advantages (Mingos, 1994). Molecular sieve membranes consisting of NaA zeolite crystals have been successfully synthesized on symbol α-Al_2O_3 substrate by means of microwave heating and membranes obtained are stable and dense, and their thickness is well controlled (Han *et al.,* 1999). Bryjak *et al*. (2002) has produced plasma treatment of porous polymer membranes by microwave technique. While Boey and Yap, (2001) has used microwave technique for curing epoxy-amine system.

As far as the synthesis of zeolite is concerned, microwave heating is commonly applied to obtain pure and perfect crystals of uniform size with different Si/Al ratios. Many kinds of zeolite such as A, X, Y, ZSM-5 (Arafat *et al.,* 1993), and $AlPO_4$-5 (Girnus *et al*., 1995) have been successfully synthesized by using microwave heating. Xu *et al*. (2001) has found that by using microwave heating, he could synthesized NaA zeolite membranes in just 15 min to achieve high hydrogen permeance up to 106 mol $m^{-2}s^{-1}Pa1^{-1}$ and have good H_2/*n*- C_4H_{10} permselectivity. Arafat *et al*. (1993) have prepared zeolite Y crystallites in a microwave oven in 10 min, whereas 10–50 hours is required by conventional heating techniques depending upon the lattice of Si/Al ratio. Relatively high Si/Al ratios, up to 5, were obtained from hydrogels containing low aluminum content without crystallization of undesired phases. ZSM-5 could also be synthesized in 30 min at 140°C using this technique.

Thermoplastic polymers such as PES constitute of long chains with a large number of segments, forming tightly folded coils which are entangled to each other. Numerous cohesive and attractive both intra and intermolecular forces hold these coils together, such as dispersion, dipole-dipole interaction, induction, and hydrogen bonding. Based on these features, one may expect noticeable differences in the dissolution behavior shown by polymers. Due to their size, coiled shape, and the attractive forces between them, polymer molecules dissolved quite impulsively by microwave irradiation than conventional. Billmeyer (1984) pointed out that there are two stages involved in physical media process: i) the polymer swelling and ii) the dissolution step itself. Moreover the trend in material development for better solid liquid separation membranes is mainly towards improving the properties of existing polymers, which is attained via chemical and/or physical modification of the polymers to favor the transport properties of the solvents of interest.

Up to this date, no work has been reported on the use of microwave irradiation for preparing polymeric membrane solution except on its application for the surface modification of polymers for other applications. Thus, in this study the microwave irradiation technique is used for the polymer dissolution process involving the use of a series of monovalent lithium halides such as lithium bromide (LiBr), lithium chloride (LiCl) and lithium fluoride (LiF) anhydrous additive and two solvents systems, DMF and acetone, for the preparation of UF membranes. The performance of these membranes are then compared to those prepared using the conventional electro thermal heating (CEH). Both membranes are prepared by the dry/wet phase inversion method.

1.3 Objectives of the Study

The objective of this thesis is to produce both high rejection and flux ultrafiltration polyethersulfone (PES) asymmetric membranes using three different monovalent lithium halide additives (lithium fluoride, lithium bromide and lithium chloride anhydrous). Also, this research involves the use of the microwave technique for the dissolution process. In addition the effect of single solvent, dimethylformamide (DMF) and double solvent consisting of DMF and acetone were investigated.

1.4 Scope of the Study

In order to achieve the objectives, the following factors were investigated.

1) To study the influence of monovalent LiBr, LiCl and LiF additives on the rheological properties of the dope solutions and the performance of the flat sheet membranes.
2) To study the effect of the microwave technique on the dope solution rheological properties and the performance of the flat sheet membranes. In order to study this effect, the dope solutions were also prepared using the conventional electrothermal heating.
3) The performance of membranes were evaluated in terms of permeation and separation rates of various molecular weight polyethylene glycol (PEG) solutions. Subsequently, the molecular weight cut off (MWCO), mean pore size and pore size distribution are determined.
4) To determine the membrane surface property such as hydrophilicity and wetability properties by performing contact angle and water uptake measurement. In addition the membrane morphology is examined using scanning electron microscope (SEM).
5) To correlate membrane performance with the different lithium halides and dissolution technique using Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray (EDX).
6) Finally the best formulated solution was spun into the hollow fiber membranes and their performance were once again evaluated.

1.5 Significance of the study

The properties of membrane are known to be dependent on many factors amongst which are membrane formulation, phase inversion parameter and rheological conditions. Besides these, the method of membrane preparation and the type of additives used are other aspects that have always be considered by membranologist if the membrane performance is to be heightened beyond the recognized intrinsic value of the particular polymer.

Thus in this study, the influence of additives on the phase inversion and the membrane dissolution method will be systematically studied for UF membranes. Although research on PEG and polyvinylpyrrolidone (PVP) additives have been performed (Lafreniere, *et al.,* 1987 and Kim and Lee, 1998), the additives (LiBr, LiCl and LiF) in this study has not been used for PES except for LiCl. In addition, the use of microwave technique for the polymer dissolution process has never been reported. Therefore, the objective of this study is to produce a novel membrane using microwave technique that exhibits both high rejection and flux rates.

1.6 Methodology

The achievement of the objectives set forth requires the adherence to a well thought methodology as outlined in the following.

1) Modification of the domestic microwave which involved the assembling of reaction vessel and stirring setup in such a way that the dissolution of polymeric resins and additives can be performed. The dope solution temperature is continuously controlled and measured by a pico meter so as to ensure no overheating occurred.

2) Three different lithium halides, LiBr, LiCl and LiF additives are used and their concentration is varied from 1-5 wt%. Two types of solvent system i) single solvent, DMF and ii) double solvent DMF and acetone were used for the PES polymer.

3) Various PES/lithium halides in DMF and DMF/acetone dope solution were prepared for the hollow fiber UF membrane using two different techniques;
   i) Conventional electrothermal heating (CEH)
   ii) Microwave heating (MW)

4) The membrane morphology was characterized using SEM whilst the membrane surfaces were characterized using FTIR. The hydrophilic property of the membrane is determined using the contact angle measurement and swelling characterization.

CHAPTER 2

MICROWAVE MODIFICATION FOR POLYMER DISSOLUTION

Membranes fabrication involved a series of process as mentioned earlier. Along with these process the preliminary preparation process which involves the polymer dissolution is very time consuming and expensive. Currently the conventional electrothermal heating (CEH) is used to dissolve polyethersulfone for membrane fabrication. This CEH requires a duration of 6 to 8 hrs at temperatures of 80 to 95 ^{0}C and can lead to polymer degradation due to oxygen in the solvent. In this chapter, an attempt was made to use the microwave technique (MW) for polymer dissolution process in making membrane and this involved modification of the domestic microwave oven. Fortunately most of the synthetic polymeric membrane materials are polar which is a very important factor in microwave. This fact is a prospective approach for an efficient interaction between the electromagnetic field and dipolar materials for membrane process. The efficiency of the modified microwave is determined by microwave power absorbance, dielectric loss and volume rate of heat generation for PES/DMF.

2.1 Introduction

There are several published methods for the safe modification of domestic microwave ovens as described in many papers. The advantage of modifying an oven in this way is that the reaction vessel is neither sealed nor directly open to the microwave oven; thus reactions can be conceded out using a flask attached to a reflux condenser (Caddick*,* 1995). These MW ovens are available in various rated power out put ranging from 600 - 1100 (240V~50 H_Z), with operation frequency of 2450 MHz.

There are several advantages of using such modified microwave oven. An extensive variety of solvents can be used because the fire risk is extensively reduced compared to an open vessel system. Reactions can be carried out under inert conditions. Most of the modified microwave systems are involved in the synthesis of organic chemistry. Cablswki *et al.* (1994) and Chen *et al.* (1990) detailed the use of continuous microwave reactors for organic transformations. Recently Cao *et al*., 2001; Cai Ge *et al*., 2005 and Huacai *et al*., 2006 modified safe domestic microwave for graft polymerization of chitosan blend. Huacai *et al.* (2006) modified the microwave in such a manner that so as to provide the inlet and outlet for synthesizing the grafting. The modification is performed such that; $\lambda < 12$ cm in order to ensure safety of operator.

Thus, the objective of this chapter is to modify the MW oven so that the dissolution of polymer and additives in solvent can be performed safely. The modified microwave irradiation with closed heating system for preparation of polymeric membrane solution has never been investigated. In addition the use of microwave irradiation technique can also be used for drying and membrane post-treatment process. In addition the objective of this chapter is to determine the microwave power absorbed by the polymer solution. In order to determine the microwave power absorbed, the dielectric constant, dielectric loss and volume rate of heat generation must be calculated.

2.2 Microwave Modification

To accomplish microwave modification several factors must be considered such as the selection of multi mode cavity of the lowest cost commercial microwave oven with rated power of 900 watts (240V~50 H_Z) which includes the various microwave pulse levels. The MW oven must have a flat roof cavity gap with upper cover and multi mode cavity.

Multi mode cavity is a sort of box and is the part of the oven where microwaves interact with the chemical system. Therefore the selection of multi mode and position of magnetron inside the cavity is very important for microwave modification. The microwave oven selected cavity is constructed to distribute a specific frequency (2.45 GHz in most cases) and power inside cavity. A control unit regulates the power value introduced into the cavity in each pulse through an automatic on/off cycle of the magnetron. A typical energy output in a microwave system is 900 Watts in 5 min irradiation which is approximately 43000 cal are delivered into the cavity (Fini and Breccia, 1999).

In order to increase the possibility of interaction between the dope solution ingredients and the microwaves and to maximize absorption, the sample is placed in reaction vessel which is continuously stirred. The multi mode cavity walls reflect the microwaves which are coming from magnetron, until it hits the sample and is absorbed. Besides that the reflective walls are necessary to prevent leakage of radiation and to increase the efficiency of the oven. There is rarely perfect match between the frequency used and the resonant frequency of the load, so if the energy is reflected by the walls, absorbance is increased because the energy more often pass through the sample and can be partially absorbed on each passage. This can be particularly important if the sample volume is dimensionally small. If too much energy is reflected back into the wave guide the magnetron may be damaged. To prevent the magnetron from exposure to excess wall reflected waves, a beaker of water should always be placed inside the cavity, which acts as a dummy load. In this manner the magnetron and also the operator is protected from the reflected power (Mingos and Baghurst, 1991).

In order to perform polymer dissolution under microwave irradiation the multi mode cavity of domestic microwave ovens was modified. Figure 2.1 shows the schematic modification cavity details of National domestic microwave oven model: NN-5626F used in this study. The details of the National domestic microwave oven were described in Table 2.1. The magnetron position inside the multi mode cavity was placed according to our experimental requirements. The objective of such size of domestic microwave is to generate as much disarray as possible inside the cavity. The greater the chaos, the higher is the dispersion of radiation, which increases the area that can cause effective heating inside the reaction vessel. As a result, a multi-mode microwave heating apparatus can accommodate a number of samples simultaneously for heating.

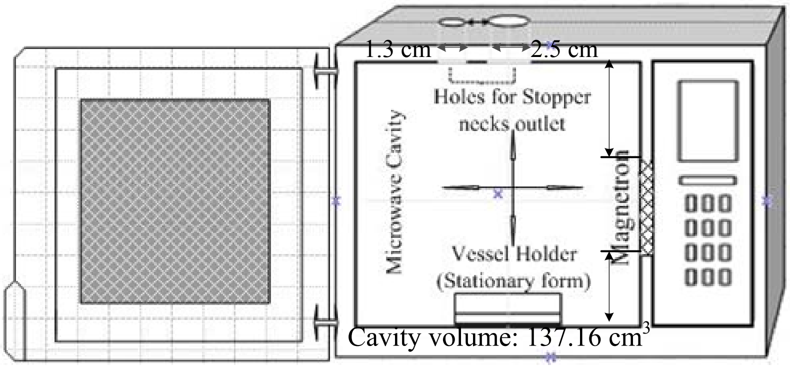


Figure 2.1: Modified multi mode cavity of National domestic microwave oven model: National domestic microwave oven NN-5626F

Table 2.1: Details of the National domestic microwave oven NN-5626F

Frequency	2450 MHz.
Power consumption	220 V~ 50Hz
Power outlet	900 Watt
Pulsed level	Low, Medium low, Medium, Medium high and High
Power level (watts)	360-900
Cavity dimensions	25.5 cm (H) * 32 cm (W) * 30.2 cm (D)
Exterior dimensions	30.40 cm (H) * 51 cm (W) * 37.9 cm (D)
Oven capacity	2700 cm^3

2.2.1 Microwave Closed Heating System

The retrofitted microwave apparatus provides a simple and inexpensive assembly to prepare a polymeric membrane dope solution in which polymeric material and additives are dissolved in selected solvent. The retrofitted microwave apparatus is to provide an apparatus assembly which employs dielectric heating via microwave to dissolve the high and low glass transition temperature (T_g) polymeric material into the selected solvent. Furthermore this microwave closed heating system offer an apparatus to perform membrane dope dissolution to achieve significant heating in a short duration thus lowering the incurred cost of laboring in membrane manufacturing. However in conventional method the dissolution techniques used for aromatic polymeric materials in an aprotic solvent involve a time-consuming digestion because they involve multi-step and labor intensive procedures.

Microwave assisted high glass transition polymer dissolution for membrane fabrication under the appropriate conditions can be carried out using the new closed heating system as described in Figure 2.2. This closed heating system for polymer dissolution can be performed at high temperatures of 250 ^{0}C and pressure of ~ 4 bars in fluid sealed systems. The vessel is made of quartz glass with 0.5 cm glass thickness and fluid sealed stirring assembly which is made of Teflon and high density polyethylene (HDPE) materials which can tolerate high speed agitation (~ 1200 rpm).

It is known in the art that the microwave irradiation of the microwave oven is generated through magnetron fixed within the oven and the irradiation is directed to the cavity. The assembled and disassembled closed system improved domestic microwave heating of thermoplastic dipolar polymers with additives and solvents. The closed system consists of a transparent high pressure and high temperature quartz glass reaction vessel clamp with two necks quartz glass stopper which is teflon coated placed in a microwave cavity. The vessel is placed in a manner such that the two necks are out side the cavity. Thus holes are made at the microwave roof such that the microwave wave length must be kept to $\lambda < 5$cm Debye.

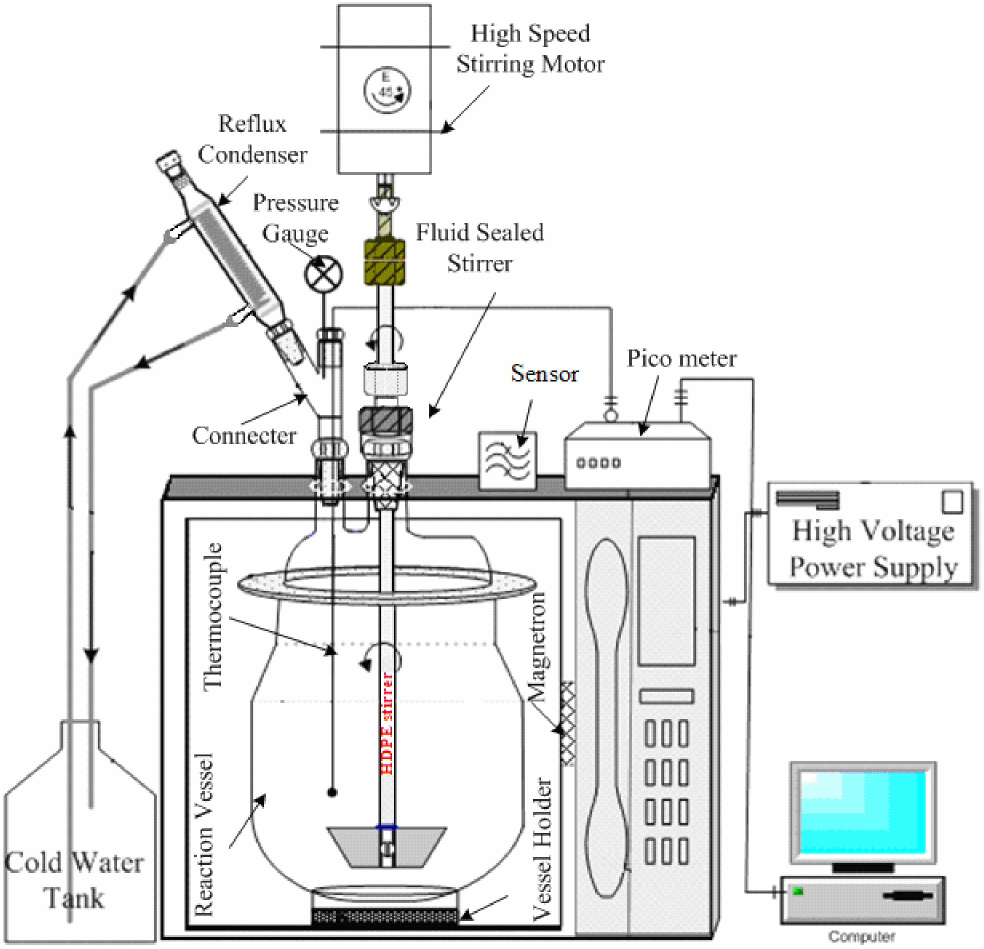


Figure 2.2: Microwave experimental setup diagram for dope solution preparation (Ani and Iqbal, 2008c).

The magnetron which is the source of domestic microwave radiation is directed into the cavity. The exterior of the stopper which is inside the cavity is Teflon coated so as to prevent the microwave irradiation from heating the materials. Teflon fluid seal is used to put the stirring rod in place inside the cavity and to absorb microwave radiations substantially in the horizontal rotary or oscillating rotary motion. The stirrer shaft is driven by a high speed motor. The fluid seal which is made of teflon material acts as bush or buffer between the neck aperture and the stirrer rod. The stirrer rod is made of high density polyethylene shaft located at the central stopper neck; the teflon assemblies consist of the teflon cylinder which is tapered. It is fixed by means of a flange and bolt. Rubber fluid seal is located at the end of the HDP stirrer connecting it to the housing of the motored mixer. It is assembled such that it passes through a neck holder, high pressure and temperature fluid seals, and an external teflon fluid seal.

The fluid seals are placed such that it allows free rotation of the rod but at the same time maintains a substantially fluid-tight chamber. The fluid seals are also adapted such that it can absorb the vibrations caused by the radial and axial motion between the stationary part and the rotatable shaft. A quartz glass y-shape teflon coated connecter is locked to the teflon coated two neck quartz glass vessel stoppers. The reflux condenser is attached to one of the y-shape openings and a thermocouple to the other. In some instances, it can also act as a hopper for materials addition. The materials to be heated are placed in the vessel during microwave heating and the stirrer is used to ensure homogeneity of the solution. The Y-shape connecter is used as the reflux condenser connecter and is also attached to the thermocouple.

The vessel stopper exterior is coated with teflon paint, the central neck is meant for the HDPE stirrer rod which is then connected to the motor. The system must be well enclosed such that it represents an almost closed system. Thus the solvent temperature can be raised to their boiling points and their vapor condensed back to the reaction vessel. In this manner, loss of solvents is negligible during the dissolution process. The transparent reaction vessel wall is made of microwave permeable material so that the microwave radiation from the source of radiation can be transmitted to dope polymer solution in the container through the wall.

2.3 Experimental

2.3.1 Materials

Microwave-assisted polymer dissolution procedures involve the stepwise, sequential dissolution of polyethersulfone with a series of anhydrous lithium halides in anhydrous form like lithium fluoride (LiF), lithium bromide (LiBr) and lithium chloride (LiCl) in aprotic solvents dimethylformamide and DMF/acetone mixed solvent system. PES (Ultrasont E 6020P); weight-average molecular weight (Mw) 58,000, weight-average molecular weight/number-average molecular weight (Mw/Mn) 3.6 was procured from BASF. Analytical grade N, N-dimethylformamide DMF [HCON (CH3)2, M=73.10 g/mol] were purchased from Merck (Merck Germany). Inorganic additive lithium bromide anhydrous (86.85) and lithium fluoride anhydrous (25.93) analytical grade were procured from Acros Organic, the anhydrous lithium chloride (42.4) of analytical grade, was procured from BDH, and commercial grade acetone was used without further purification.

2.3.2 Calibration of Modified Microwave Closed System

The modified microwave closed system was calibrated before preparing the dope solutions. The advantage of this calibration is to avoid assumptions of instrument linearity, and it provides engineering feedback about the contribution to calibration error of each functional dope solution preparation within the instrument. Therefore retrofitted microwave apparatus were calibrated at low to high pulse using distilled water of quantity 500 gm. The measurements of absorbing performance of water were kept at low to high pulse. A thermocouple which is connected to the Pico meter and voltage regulator is used to measure the temperature of each pulsed power level with respect to time. The microwave operating frequency pulse have five levels as depicted in Table 2.2. Thus each experiment were run at low to high cycle pulse for 10 to 60 seconds interval of time. The measurement results calibrated by this method are quite closed to the results measured by time domain measurement method.

2.3.3 Calibration Procedure

Calibration techniques are necessary to understand and control microwave ovens for microwave-accelerated laboratory procedures (Cheng *et al.,* 2006 and Login *et al.,* 1998). Upon assembling the set setup as shown in Figure 2.2, calibration was performed. The nominal power of existing microwave oven was 900 W as given by the manufacturer. It is necessary to determine the actual output power which is different from the declared capacity by the manufacturers due to modifications process. Calorimetric method is widely used for the measurement of output power in a microwave oven both by manufacturers and researchers, and was adopted in this study. The sample used in this experiment was the distilled water with the initial temperature of 25 ± 2 ^{0}C. Distilled water of 500 g was poured into the vessel. The water was stirred before noting the initial temperature. Both initial and final temperatures were recorded using thermocouple fiber optic instrument which can be equipped to an analog digital meter. This thermocouple can also be equipped with computer or temperature recorder digital meter. In this research, all the temperatures were recorded by digital meter at atmospheric pressure during the dissolution process. The water was continuously stirred and the final temperature was read. Table 2.2 showed the power distribution of magnetron for each pulse. The power absorbed, $P_{absorbed}$, was calculated using Equation 2.37 for the various heat pulses. These values are tabulated in Table 2.3.

Table 2.3 shows the calibration of this modified microwave closed system containing 500 gm water. In all the tests, the input power was noted at low – high pulse. Calibration as each pulse level was carried out in triplicate and the mean value was recorded. The source input voltage was 220 V at 50 Hz. The experimental results show the maximum output power of existing microwave oven to be 870 W, which is 93.4% of nominal value of 900 W. It was also observed that, the rates of

Table 2.2: National domestic microwave NN-5626F power distribution

Power level Heat Pulses (watts)	Low 250	Med. Low 400	Medium 550	Med. High 700	High 900
Total Pulse Per 60 (sec)	3	3	3	3	Full
Radiation time per pulse (sec)	4	8	12	16	60
Total heat ^{0}C/60 sec.	12	24	36	48	60
Off Time per pulsed (sec)	16	12	8	4	0
Total off time in 60 sec	48	36	24	12	0

Table 2.3: Calibration of modified microwave to heating the water (500gm) at 26 ^{0}C

Heat Pulses	**Time, *t* (Sec.)**	**Initial Temp. T_o (^{0}C)**	**Final Temp. T_f (^{0}C)**	**ΔT ^{0}C**	**$\Delta T/t$ ^{0}C/sec**	**P_{absorb} Watts**
Low	60	26	30	4	0.066	138.03
Med. low	60	28	36	8	0.133	278.15
Med.	60	35	47	12	0.2	418.27
Med. high	60	45	62	17	0.283	591.85
High	60	60	85	25	0.416	870.01

temperature change with time increases at higher pulses. The results were expected since the dielectric loss of water is small.

2.6 Conclusion

The concept of modified microwave based closed heating system and the acquisition of its efficiency by the preparation of PES/DMF dope solution was successfully achieved for the fabrication of membranes. Experimental evaluation shows that, this modified closed heating system is efficiently designed as it can be precisely assembled and disassembled inside the microwave cavity, easy to deliver the materials into the reaction vessel from out side the oven. The performance of the modified microwave closed heating apparatus was clearly shown by the demonstration of PES/DMF dope solutions which shows the decreases in digestion and dissolution time. It may be noted that simultaneous effect of microwave closed heating system is equally efficient in heterogeneous media (solid/liquid) as well as for homogeneous liquid media. The results showed that dissolution of PES in DMF is performed in less than 6 hours as compared to the conventional electrothermal heating dope solution.

CHAPTER 3

ASSESSMENT OF MICROWAVE ASSISTED FLAT SHEET MEMBRANES PERFORMANCE

The objectives of this chapter are to examine the influence of anhydrous form monovalent lithium halides; lithium bromide (LiBr), lithium chloride (LiCl) and lithium fluoride (LiF) and the microwave preparation technique (MW) on the performance of flat sheet ultrafiltration membranes. The flat sheet polyethersulfone (PES) asymmetric membrane was prepared by the dry/wet phase inversion process. In order to compare the MW and CEH dissolution techniques membranes prepared using conventional electrothermal heating (CEH) technique were also casted. The dope solutions were prepared concentration of 20 wt% PES through out the study. The dope solutions prepared in Chapter 4 were casted into flat sheet membranes. Membrane performance were characterized in terms of pure water permeation (PWP), permeation rate (PR) and solute separation of polyethylene glycols (PEG) of various molecular weight cut off (MWCO) ranging from 600 – 36000 Daltons. Polyethylene glycol in the feed and permeate samples were then analyzed spectrophotometrically. Subsequently the mean pore size and pore size distribution of the UF membranes were determined.

3.1 Introduction

Ultrafiltration (UF) is a process of separating extremely small particles and dissolved macromolecules from fluids using asymmetric membranes of surface pore size in the range of 50 to 1 nm and often operated in a tangential flow mode where the feed stream sweeps tangentially across the upstream surface of membranes as filtration occurs, thereby maximizing flux rates and membrane life. It imposes specific requirements on the membrane material and membrane structure, and the efficiency of UF is determined by the porosity and the pore size of the membrane (Jönsson and Trägårdh, 1990).

Recent literature survey indicated that an ever increasing number of polymers, copolymers and blends are being considered as potential membrane materials. In addition, the selection of appropriate solvent and the additive are among the many factors that have a great influence on the final membrane morphology (Lloyd*,* 1985). The efficiency as well as the economics of the various industrial processes can be greatly improved if the membrane processes are suitably integrated in the exiting process, particularly, to control membrane structure and membrane performance. This objective is not easy to achieve because membrane structure and performance depend on different factors such as polymer choice, solvent and nonsolvent choice, composition and temperature of coagulant, and casting solution (Xu *et al.,* 2004). Solvent/non-solvent mixture changes the solubility parameter of the solvent system thus changing the polymer–solvent interaction in the ternary-phase polymer system, which changes the polymer morphology of surface layer and sub-layer (Yanagishita *et al.,* 1994).

Additives such as non solvents, inorganic salts and surfactants are always used to tailor the membrane properties. The presence of the additives in the dope not only changes the thermodynamic state of the dope but also influences the conformation and dynamics of the polymer. This in turn, affects the kinetics of phase separation hence influence the performance of membranes. In the search for an alternative dope solution preparation, the use of a microwave oven for rapid sample dissolution in a closed system seemed to be an attractive procedure. Previous reports on the use of microwave irradiation for organic membrane applications are for polymer surface modification and enhancement of permeability of cellulose acetate membranes (Nakai *et al.,* 2002). The use of microwave technique as a replacement for conventional heating has already been applied in inorganic membranes for biochemical and gas separation processes but not for polymeric membranes (Arafat *et al.,* 1993). However, that finding seems to have been treated as a novelty of little practical value for inorganic membranes. In the case of organic polymeric membranes, no study has been conducted on the use of microwave technique for their preparation of polymeric membranes. Thus, the microwave irradiation technique is used for the polymer dissolution process involving the use of anhydrous monovalent lithium halides additive in single solvent and two solvent systems, DMF and acetone, for the preparation of UF membranes. The performance of these membranes are then compared to those prepared using the conventional electro thermal heating (CEH). Both membranes are prepared by the dry/wet phase inversion method.

3.2 Experimental

3.2.1 Materials and Dope Solution Preparation Techniques.

Materials and dopes solution preparation by MW and CEH were described in chapter 3 and chapter 4. The formulation for the various membrane dope solutions are listed in Table 4.1. Different dope solutions were prepared by MW and CEH. The polymer concentration was fixed at 20 wt% as shown in Table 4.1 chapter 4. The single solvent system consisted of 20 wt% PES and the solvent DMF. The double solvent system contained 20 wt% PES and two solvents; DMF and acetone, and the ratio of these solvents were kept to 3.47 just to avoid gelation of the solution. In both cases, the amount of LiBr was varied from 1 to 5 wt%. In addition, membrane with additives LiCl and LiF containing 20 wt% PES in single solvent (DMF) was prepared. The concentration of the LiCl and LiF was varied from 1-5 wt%. Polyethylene glycols (PEG) with different molecular weight ranging from 200 to 36,000 Daltons purchased from Fluka were used as solutes. Feed solutions were prepared using distilled water. Other chemicals used were sodium iodide (KI) purchased from SureChe Products Ltd, barium chloride ($BACl_2$) from Labguard, iodine (I_2) from Emory and hydrochloric acid (HCl) from Merck.

3.2.2 Membrane Casting

The dope solution was poured onto a clean glass plate at room temperature and casted on a glass plate using a casting knife with a thickness of 200 μm. Immediately after casting, the glass plate with the casted film was dipped into ordinary tap water at room temperature. After few minutes, a thin polymeric film separated out from the glass plate due to the phase inversion process. The membrane was washed with distilled water and transferred to another container ready to be tested. All flat sheet membranes were visually inspected for defects and only good areas were chosen for membrane evaluation.

3.2.3 Post Treatment of Membranes

In order to remove the additives from the membrane, the cast asymmetric membranes were post treated by microwave technique. The membranes were washed with de-ionized water and then immersed in a 500 ml beaker of de-ionized water covered with aluminum foil for 30 minutes in a microwave oven. The conductance of the de-ionized water was measured by a standardized digital conductivity meter of type Hanna instrument Model H18633 to make sure that the excessive additive inside the membrane pores is totally removed. The treated membranes were then rinsed again in de-ionized water until conductance readings reached values equivalent to pure de-ionized water conductance. The membranes were then ready for testing.

3.2.4 Membrane Evaluation

The performances of the various lithium halides flat sheet membranes were evaluated in terms of pure water permeation fluxes (PWP), solute permeation fluxes (PR) and solute rejection rates (SR) in a stainless steel cross flow test cell at 3.5 bars as depicted in Figure 3.1. All the experiments were conducted at room temperature of 25-26 ^{0}C. Membrane sample with an area of 2.0×10^{-3} m^2 was placed in the cross flow filtration test cell with the active skin layer facing the incoming feed. A minimum of three flat sheet samples were prepared for each condition so as to ensure the reproducibility and the average value was tabulated. Pure water permeation experiments were performed using double distilled deionized water. Pure water permeation fluxes (PWP) and solute permeation fluxes (PR) of membranes were obtained as follows:

$$J = \frac{Q}{\Delta t \times A} \tag{3.1}$$

where J is the permeation flux for PEG solution (Lm^{-2}h^{-1}) or pure water, Q is the volumetric flow rate of permeate solution and Δt is the permeation time (hr).

Solute rejection of membranes were evaluated with various molecular weight PEG solutions ranging from 200 to 36,000 Daltons at 3.3 bar. The concentration of PEG solution used was 500 ppm (Sabde *et al.,* 1997). The concentration of the feed

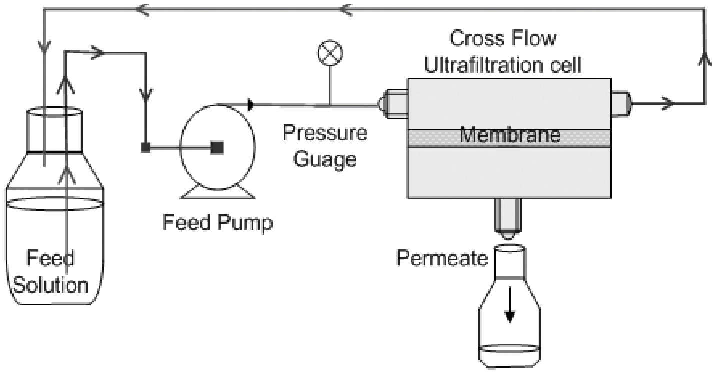


Figure 3.1: Schematic diagram of cross flow ultrafiltration cell for membrane testing.

and permeate solution were determined by the method described by Sabde e*t al.* (1997). The membrane solute rejection (*SR*) is defined as in equation 2.13.

3.2.4.1 Polyethylene glycols (PEG) Concentration Analysis

Concentrations of polyethylene glycols with molecular weight distribution range from 600 to 36,000 Daltons were analyzed using the method by Sabde *et al*. (1997) as described as follows:

5% (w/v) $BaCI_2$ is dissolved in 1N HCI (100 ml) and 2% (w/v) KI is diluted 10 times. Four milliliters of sample solution was added to 1 ml 5% (w/v) $BaCI_2$ in 1N HCl. To this mixture, 1 ml of solution prepared by dissolving 1.27g 1_2 in 100 ml 2% KI (w/v) solution was added which is further diluted 10 times. Color was allowed to develop for 15 min at room temperature. The absorbance was read using the spectrophotometer (Shidmazu UV-160) at a wavelength of 535 nm against reagent blank.

3.2.5 Pore Size and Pore Size Distribution

The pore size of PES membrane was determined using transport data as derived by Singh *et al*. (1998). Solute diameter is given by equation 2.12 and 2.14. The mean pore size (μ_p) and standard deviation (σ_p) of the membranes are determined from the solute separation curve plotted. Solute separation is plotted against solute diameter on log normal graph. The mean pore size, d_s, corresponding to $R = 50\%$ on the linear regression line was determined. The standard deviation was calculated from the ratio d_s at $R = 84.13\%$ and 50%. Thus, MWCO can be measured from the regression line at $R = 90\%$.

3.3 Results and Discussion

3.3.1 Performance of MW and CEH PES/DMF/LiBr Membranes

3.3.1.1 Pure Water and PEG Permeation Rate

The pure water permeation (PWP) of the membranes produced from various dope solutions of PES/DMF/LiBr are depicted in Figure 3.2. The presence of LiBr has a large influence on the PWP and PR of membranes. It is observed that as the concentration of LiBr increases, the PWP increases. However when the concentration of LiBr is increased beyond 3 wt% the PWP rates begin to decrease. The highest PWP rate is obtained when LiBr concentration is at 3 wt% for both MW and CEH prepared membranes. In general, the MW prepared membranes have higher PWP compared to the CEH membranes. These results apparently seem to indicate that the MW prepared membranes are more hydrophilic. The differences could be due to different solubility parameters as well as salt solvent interaction. A similar trend is also observed for the PEG permeation rates (PR) as shown in Figure 3.3. The

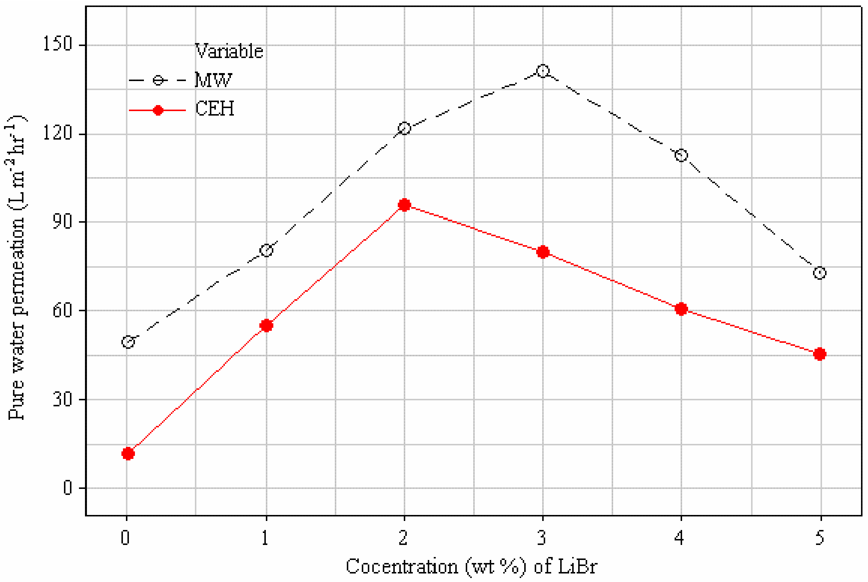


Figure 3.2: Pure water permeation rates versus concentration of LiBr of for PES/DMF/LiBr membranes prepared using MW and CEH.

presence of additives has improved the PR of MW and CEH membranes. Highest PR was obtained when LiBr concentration was at 3 wt%.

In general, the MW membrane containing LiBr has higher PR compared to the CEH membranes with LiBr and this is observed in Figure 3.3. The results clearly indicate that LiBr when used as additive has enhanced the hydrophilic properties of the membranes and this is displayed by the improved PWP and PR rates. The permeation rates for membranes with LiBr are approximately 83.9% higher than those without LiBr. Permeation rates of 5.26 fold - 3.8 fold increments are achieved when 3 wt% and 4 wt% LiBr are used for MW and CEH membranes respectively and this means increase in productivity. With the participation of LiBr which has high swelling properties, the PES becomes more hydrophilised and this hydrophilicity become more pronounced at 3 wt% LiBr in both the MW and CEH prepared membranes. There is the possibility that at this concentration, the balance of the hydrophilic and hydrophobic moieties has prevailed.

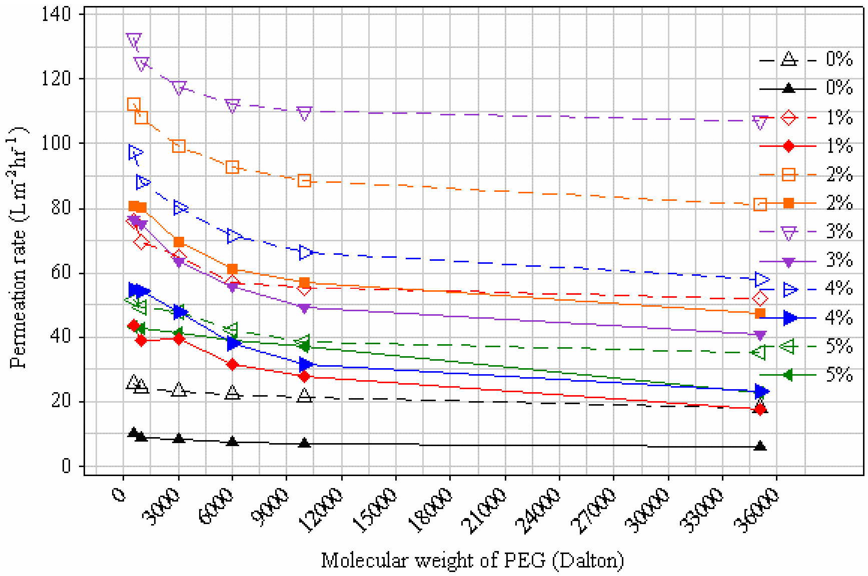


Figure 3.3: Permeation rates of the MW (---) and CEH (—) Membranes with various concentration of LiBr

3.3.1.2 Rejection Rates of Membranes

The PES/DMF membranes in the absence of LiBr prepared by both MW and CEH yielded the lowest separation of PEG and this is shown in Figure 3.4 and 3.5. The presence of LiBr has not only improved the permeation rates but also the rejection rates. When the LiBr concentration is increased to 3 wt% the membrane rejection increases however a further increase beyond this value does not increase the rejection rates. The MWCO of the MW membranes at 90% rejection rate for the 3 wt% LiBr is 2.8 kDa with permeation rates of 118 $Lm^{-2}hr^{-1}$ for PEG 3000. A different phenomenon is observed for the CEH membranes instead of 3 wt% LiBr the maximum rejection is observed at 2 wt% LiBr concentration with permeation rates of 90.2 $Lm^{-2}hr^{-1}$ and its MWCO is at slightly greater 2.93 kDa.

The results clearly showed that MW assisted membranes exhibited higher rejection and permeation performance than CEH assisted membranes. Figure 3.4 shows the rejection performance of MW assisted PES membranes composition with various concentration of LiBr. Similar PEG rejection trends were also observed in Figure 3.5 for CEH assisted membranes respectively. However, a comparison of

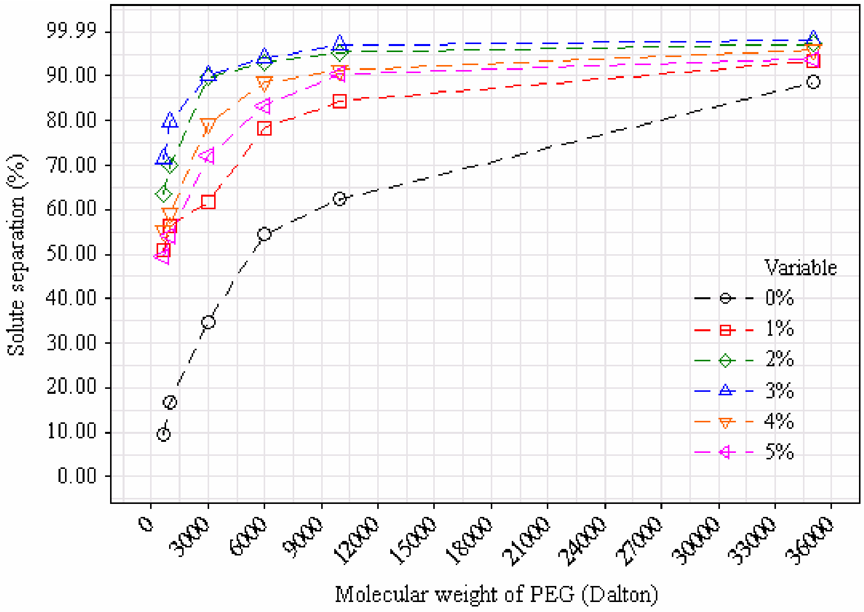


Figure 3.4: Molecular weight cutoff profile of MW assisted PES/DMF membranes with various concentrations of LiBr.

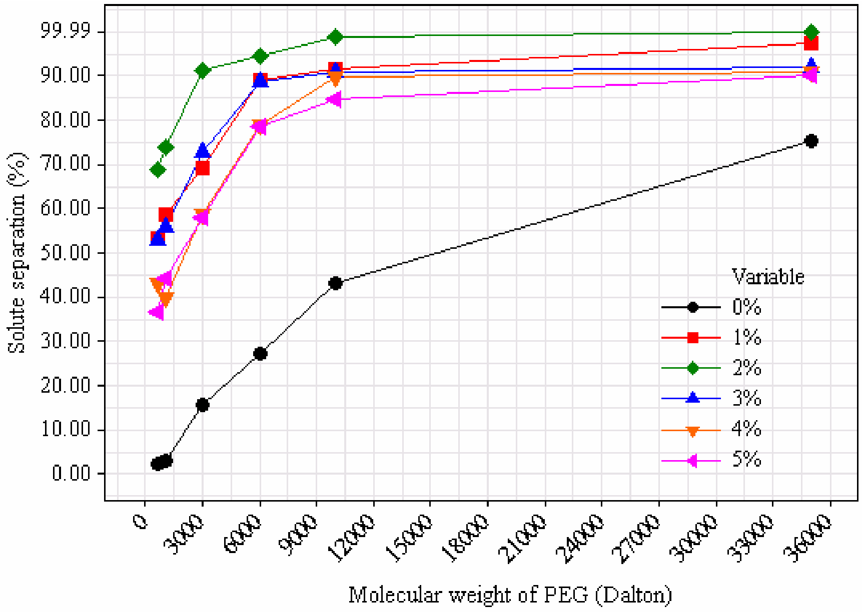


Figure 3.5: Molecular weight cutoff profile of CEH prepared PES/DMF membranes with various concentrations of LiBr. "●" represents PES/DMF membranes without LiBr

Figures 3.4 and 3.5 showed that MW assisted membranes has higher PEG rejection rates compared to all CEH assisted membranes. This higher PEG rejection with increasing LiBr content in PES might be due to the good homogeneity or best solubility arising as a result of the LiBr content creating hydrophilicity in the PES membranes due to the nucleophilic substitutions which is carried by electrophilic dipolar solvent (DMF).

3.3.1.3 Molecular Weight Cutoff Profiles

By definition, molecular weight cut off is molecular weight at which 90% of solutes was rejected by the membrane (Causserand *et al.,* 2002). MWCO is a pore characteristic of the membranes and it is related to rejection for a given molecular weight of solutes. The molecular weight cut off has linear relationship with pore size of the membranes (Wang *et al.,* 2004). It is observed that all PES ultrafiltration membranes perform scatter profile. MW assisted PES ultrafiltration membrane with

3 wt% LiBr as additive exhibits the lowest MWCO, whilst for the CEH membranes the 2 wt% LiBr exhibits the lowest MWCO. As demonstrated in Figures 3.4 and 3.5, the MW assisted PES ultrafiltration membranes with 3 wt %, 4 wt% and 5 wt% LiBr exhibit lower MWCO compared to CEH ultrafiltration membrane.

However, these results are contradictory to the fact that the inorganic additive leaches out of the membrane during the precipitation of the polymer solution and, acts as a "pore former", as sometimes referred to in literature (Huang *et al.,* 1995). From the viewpoint of thermodynamics, it can be assumed that the addition of LiBr causes the water required to phase-separate the casting solution, to decrease thereby resulting in a change in the porosity of the membrane due to its high nucleophilicity property. It can also be analyzed that the pore size on the surface of the membrane becomes smaller because the LiBr gives rise to an association between the moieties units of PES, note that nucleophilicity is greater in dipolar aprotic solvents like dimethyl sulfoxide and dimethylformamide than in protic solvents like water or alcohols. For this reason, DMF is often participating as a solvent for carrying out nucleophilic substitutions of Br^{-1} ions thereby decreasing the mobility of the polymer chain.

Therefore, in MW casted solution the LiBr additive acted as a "pore inhibitor" rather than a pore former leading to the simultaneous decrease of pore size and increase of hydrophilicity. When the LiBr concentration in the casting solution was increased from 5 wt% in MW membranes and 3-5 wt% in CEH, both the permeation and rejection rate decreased as observed in Figures 3.4 and 3.5. The reason for this may be that the membrane hydrophilicity significantly decreases at higher concentration of LiBr because the packing density in the polymer matrix becomes significantly higher in both techniques. The experimental results seem indicate to that the increasing membrane pore density was the major factor, and decreasing membrane pore radius is the secondary factor.

3.3.1.4 Membranes Characterization Using Solute Transport Data

Log normal plots of solute separation versus solute diameter for MW and CEH PES ultrafiltration membranes with additives of different molecular weights are presented in Figure 3.6 and 3.7. Regression line was drawn with high correlation coefficient (r^2 = 0.98). The Stokes diameter d_s can be determined using equation 2.14. The value of mean pore size (μ_p), standard deviation (σ_p) and MWCO of the PES ultrafiltration membranes were calculated from solute separation curves and the results are given in Table 3.1. The mean pore size is calculated with d_s corresponding to solute separation R = 50%. PES ultrafiltration membranes without additive exhibited MWCO of 35.78 kDa with mean pore size of 3.346 nm and 36.503 kDa MWCO and 3.498 nm mean pore size for MW and CEH membranes respectively. The results also show that increase in LiBr concentrations to 3 wt% and more, increase mean pore sizes from 0.252 to 8.926 nm for MW prepared membranes. The molecular weight cut off is measured to be around 2.814 to 9.748 kDa. The results revealed that the membrane with high LiBr concentrations greater than 3 wt% LiBr has the large pore radius, but PWP and permeation rate were low. MWCO acts as guidance for pore sizes of the membranes where large MWCO implies pore size of the membrane are large. PES MW prepared UF membrane with 3 wt% of LiBr as

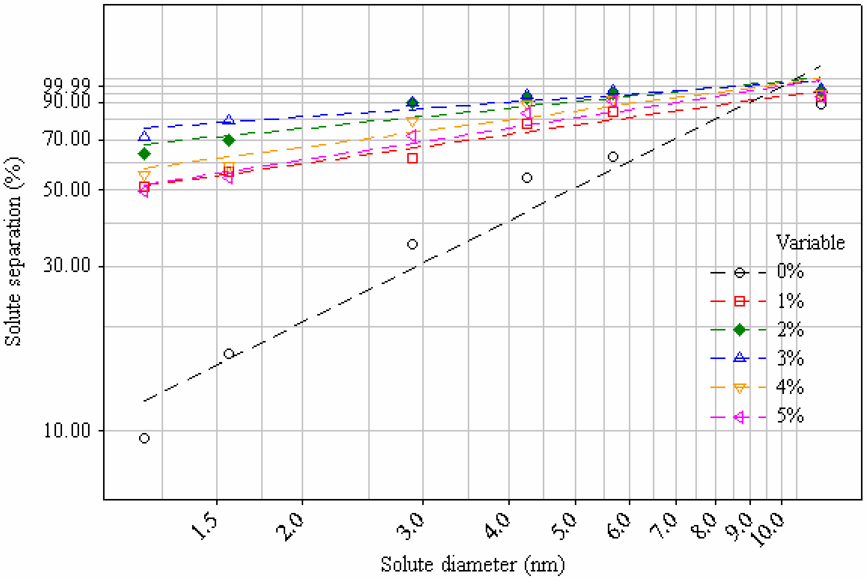


Figure 3.6: Pore size distribution of MW prepared PES/DMF membranes with various LiBr concentrations.

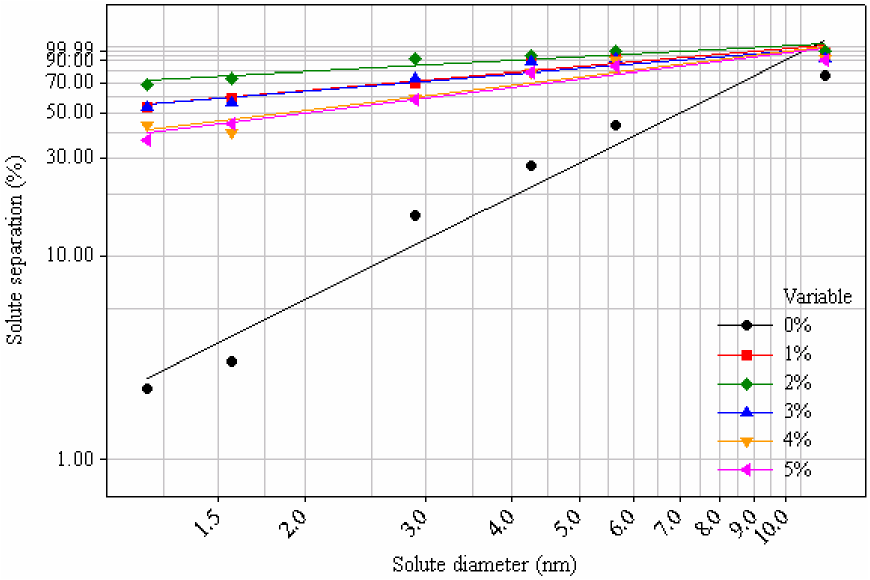


Figure 3.7: Pore size distribution of CEH prepared PES/DMF membranes with various LiBr concentrations

Table 3.1: Mean pore size, standard deviation and molecular weight cut-off of the MW and CEH with and without LiBr membranes

Membr. No.	**Microwave Irradiation**			**Conventional. Electro Thermal heated**		
	MWCO (kDa)	*μ_p (nm)	*σ_p	MWCO (kDa)	*μ_p (nm)	*σ_p
0	35.71	3.34	4.56	36.5	3.4	5.37
1	25.38	2.45	4.49	7.35	0.69	0.28
2	3.5	0.42	0.30	2.93	0.24	0.30
3	2.81	0.25	0.41	9.04	0.85	0.65
4	8.05	0.71	0.34	16.45	1.47	1.3
5	9.72	0.92	0.68	34.49	2.4	2.1

*μ_p – mean pore size, *σ_p – standard deviation

additive has small pore sizes of 0.25 nm and low MWCO the region of 2.81 kDA. This explained for the good separation rates. This study also revealed that MW membranes with 3 wt% LiBr has not only high rejection rates but also high flux. For the CEH membranes, the 2 wt% LiBr exhibits both high rejection and flux rates with MWCO of 2.93 kDa and reasonable flux rates but not higher than those prepared using the MW technique. Adding low molecular weights salt additives allows production of membranes with different pore sizes thus allowing for many applications. When the concentration of LiBr increases beyond 2 wt% the mean pore size and MWCO of CEH membrane increases.

3.3.2 Performance of MW and CEH PES/DMF/Acetone/LiBr Membranes

3.3.2.1 Pure Water and PEG Permeation Rates

The pure water permeation rates (PWP) of the membranes produced from the various solutions are depicted in Table 3.2. It is observed that as the concentration of LiBr additive increases, the PWP rates increases. However when the concentration of LiBr is increased beyond 3 wt% LiBr, PWP rate begins to decrease. The highest PWP rate is obtained when LiBr concentration is 3 wt% for both MW and CEH prepared membranes. In general, the MW prepared membranes have slightly higher PWP rates and this is observed in Table 3.2.

The permeate rates (PR) of the MW and CEH prepared membranes are shown in Table 3.3. The 3 wt% LiBr concentration exhibits highest permeation rates when separating various PEG solutions. Both the MW membranes and CEH membranes containing 3 wt% LiBr exhibits the highest PR at approximately 39 L m^{-2} hr^{-1} when separating PEG 600 solutions. In general the MW membranes containing LiBr has higher PR compared to the CEH membranes and this can also be observed in Table 3.3. The results clearly indicate that LiBr when used as additive enhanced the hydrophilic properties of the membrane and this is displayed by the improved PWP and PR rates. With the participation of LiBr which has high swelling properties, the PES becomes ‘hydrophilic’ and this hydrophilicity becomes more pronounced at 3 wt% LiBr in both the MW and CEH prepared membranes. There is the possibility that at this concentration, the balance of the hydrophilic and hydrophobic moieties has prevailed

In addition, permeation rates for the MW membranes are slightly higher compared to the CEH membranes. During MW irradiation the heat transfer occurring is through volumetric heating, thus the temperature can be increment to 25 ^{0}C higher

Table 3.2: Pure water permeation rates of the MW and CEH membranes

No	**Dope comp. (wt.%)**	**PWP$_{(MW)}$** (Lm^{-2}hr^{-1})	**PWP$_{(CEH)}$** (Lm^{-2}hr^{-1})
0	PES/DMF/Ace.	12.8	9.0
1	PES/DMF/Ace/LiBr (1%)	19.7	18.6
2	PES/DMF/Ace/LiBr (2%)	20.4	19.3
3	PES/DMF/Ace/LiBr (3%)	41.6	40.6
4	PES/DMF/Ace/LiBr (4%)	24.7	19.2
5	PES/DMF/Ace/LiBr (5%)	23.2	17.9

Table 3.3: Permeation rates of the PES/DMF/acetone membranes produced using both MW and CEH techniques

Memb. No.	**PR (Lm^{-2}hr^{-1}) of MW membranes**					
	PEG 600	PEG 1000	PEG 3000	PEG 6000	PEG 10000	PEG 35000
0	7.8	7.3	7.0	6.8	6.2	6.0
1	17.3	17.1	15.2	14.0	12.6	10.2
2	18.0	17.7	17.0	16.4	16.1	15.8
3	39.0	38.3	33.7	29.1	26.3	21.2
4	19.1	17.7	15.3	15.0	12.5	11.3
5	19.0	18.7	17.5	17.0	16.9	15.7
Memb. No.	**PR (Lm^{-2}hr^{-1}) of CEH membranes**					
	PEG 600	PEG 1000	PEG 3000	PEG 6000	PEG 10000	PEG 35000
0	5.5	5.3	5.2	5.0	4.8	4.6
1	15.3	15.3	15.0	14.7	13.6	12.6
2	15.2	18.5	18.5	17.4	18.0	17.7
3	39.0	39.3	38.3	30.0	28.5	27.2
4	19.1	17.8	17.2	17.0	16.5	15.3
5	17.0	16.4	16.0	15.7	14.6	14.2

than the temperature of 65 ^{o}C used in the CEH (Baghurst and Mingos, 1992 and Gabriel *et al.,* 1998). Such volumetric heating increases the energy levels which can cause molecules to transit from a strongly bound and almost totally ionic state to a nonionic repulsive state. Such volumetric heating under irradiation probably promotes formation of LiBr and DMF/acetone complexes which create the hydration effect and subsequently cause swelling of the polymer gel due to presence of acetone. The formation of such salt-solvent complexes have been reported and explained by Kesting, (1965) for cellulose acetate using inorganic salt additives. Similar results on the influence of inorganic additives such as $ZnCl_2$ and LiCl on permeation properties of PSf (Bottino *et al.,* 1988 and Kim *et al.,* 1996) and polyamide (Kraus *et al.,* 1979) membranes have also been disclosed.

However the presence of acetone has resulted in lower permeation rates compared to membranes prepared using the single solvent DMF. Highest permeation rates achieved was only 39 $Lm^{-2}hr^{-1}$ while for the single solvent membranes, the flux rates obtained as three times more at 130 $Lm^{-2}hr^{-1}$. When using the double solvent the viscosity of the dope solution is lower that of the single solvent dope solution as reported in Chapter 3. The low viscosity solution influences the rate exchange between solvent mixture and water during the precipitation process. The slow diffusion rate of solvent mixture and water exchange makes the precipitation rate slower and this results in the formation dense skinned membranes and this is exhibited by the low flux rates.

3.3.2.2 Molecular Weight Cut Off Profile of PES/DMF/Acetone/LiBr

Figures 3.8 and 3.9 show the rejection rates of the MW and CEH membranes for the various PEG solutions. The presence of LiBr has not only improved the permeation rates but also the rejection rates. When the LiBr concentration is increased to 2 wt% the membrane rejection increases, however a further increase beyond this value does not increase the rejection rates. The MWCO of the MW membranes at 90% rejection rates for the 2 wt% LiBr is 7.5 kDa with permeation rates of 18 $Lm^{-2}hr^{-1}$ for PEG600 solutions. A similar phenomenon is observed for the CEH membranes. Maximum rejection rates are also observed at 2 wt% LiBr concentration with permeation rates of 19 $Lm^{-2}hr^{-1}$, but its MWCO is slightly greater at 9.57 kDa. A further increase in LiBr does not improve its rejection rates although its permeation rate is increased.

Another observation is the good and improved rejection rates observed for all the MW membranes compared with the CEH membranes. In the microwave membranes high rejection rates are probably contributed to the smaller pore size membranes produced.

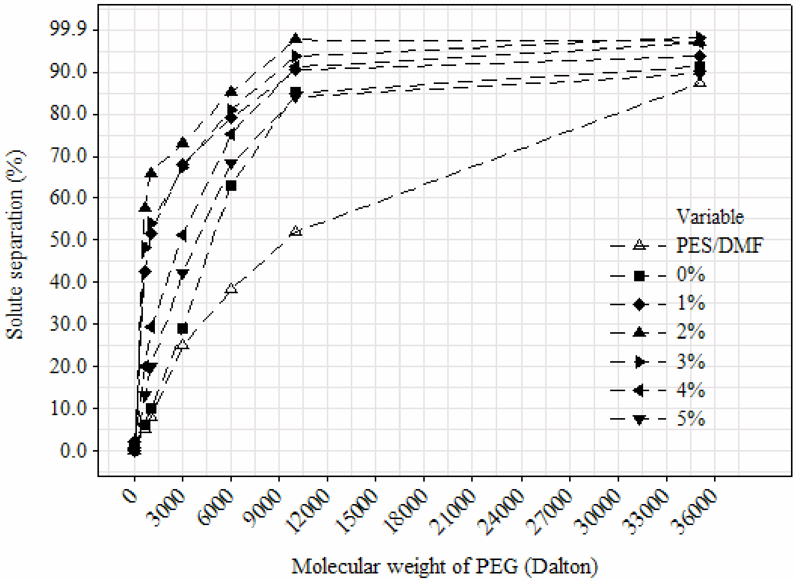


Figure 3.8: Solute separation of MW prepared PES/DMF/Acetone membranes with various concentrations of LiBr.

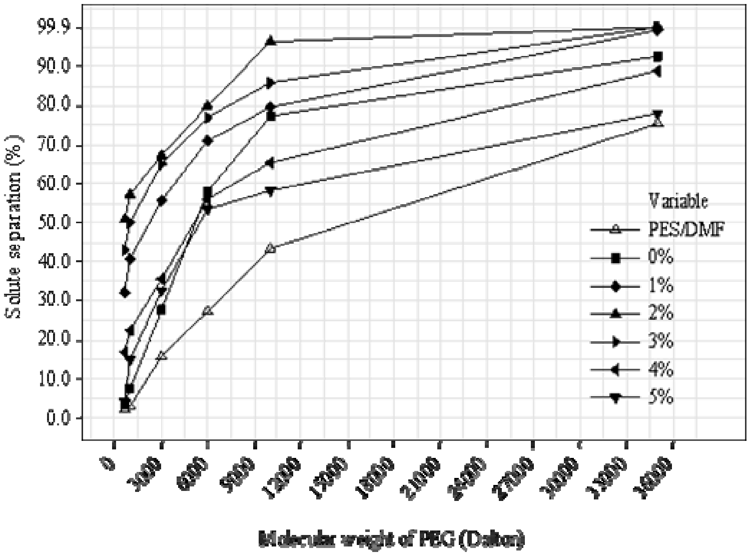


Figure 3.9: Solute separation of CEH prepared PES/DMF/Acetone membranes with various concentrations of LiBr

3.3.2.3 Membrane Characterization Using Solute Transport Data

The long normal plots of solute separation verses solute diameter for MW and CEH PEH UF membrane are illustrated in Figures 3.10 and 3.11. In the single solvent system the MW membranes without LiBr exhibited MWCO equivalent to 35.7 kDa whilst in double solvent system the MWCO was 19.1 kDa with mean pore sizes of 3.34 nm and 1.77 nm respectively. Whilst, CEH membranes without LiBr exhibited MWCO equivalent to 36.5 kDa whilst in double solvent system the MWCO was 31 kDa with mean pore sizes of 3.4 nm and 2.72 nm As the concentration of LiBr is increased, the MWCO and the pore diameter decreased until LiBr concentration reached 3 wt%. The smallest pore size was observed in both single and double solvent membranes prepared by MW and CEH containing 3 wt% of LiBr as shown in Table 3.4, thus, explaining for its excellent separation efficiency.

Further increase in LiBr concentration did not result in reduction in the MWCO and mean pore diameter. In general upon comparing the separation rates of the double solvent system PES/DMF/acetone and single the solvent system PES/DMF membranes with and with out LiBr in both techniques, it was observed that the membranes produced from the double solvent systems exhibits better separation and lower MWCO. As we can see from Table 3.1 and 3.4, pore sizes of

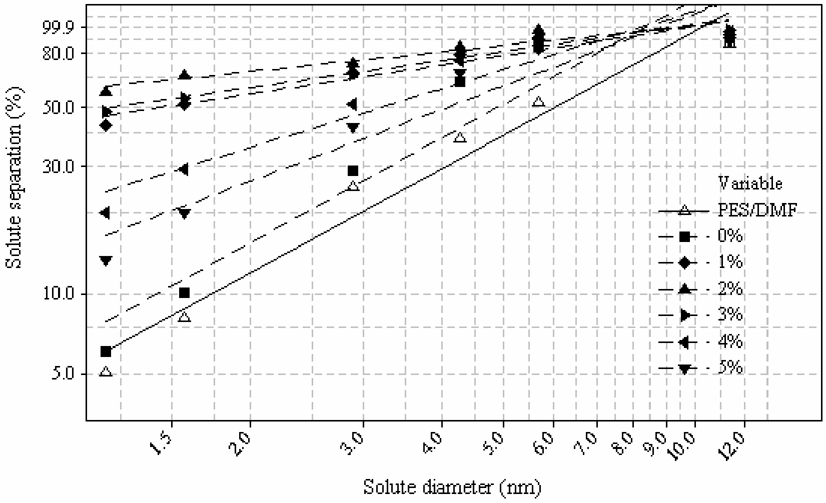


Figure 3.10: Pore size distribution of MW prepared PES/DMF/Acetone membranes with various LiBr concentrations.

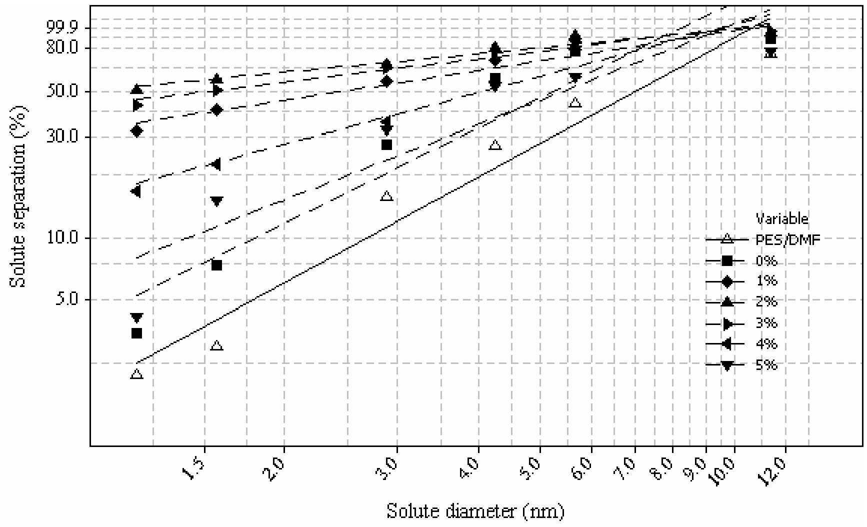


Figure 3.11: Pore size distribution of CEH prepared PES/DMF/Acetone membranes with various LiBr concentrations.

Table 3.4: Mean pore size, standard deviation and molecular weight cut-off of the PES/DMF/Acetone MW and CEH membranes

Memb. No.	**Microwave Irradiation**			**Conventional. Electro heated**		
	MWCO (kDa)	*μ_p (nm)	*σ_p	MWCO (kDa)	*μ_p (nm)	*σ_p
2	19.1	1.771	0.953	31.0	2.727	2.664
3	9.2	1.089	0.677	23.5	2.324	0.665
4	7.5	0.778	0.475	8.3	0.811	0.494
5	8.9	0.836	0.615	17.5	1.831	2.882
6	10.0	0.982	0.59.	35.0	3.256	4.882
7	27.0	2.754	3.129	38.0	3.526	4.563

*μ_p – mean pore size, *σ_p standard deviation

the membranes prepared from the double solvent systems are smaller, thus explaining for the lower MWCO and better separation.

In general the MW prepared membranes has smaller pore sizes thus explaining for the higher rejection rates as show in Table 3.1 and 3.3. It appears that the presence of LiBr has improved the hydrophilic properties of the membrane thus improving not only the permeation rate but also the rejection rates of the membranes. It seems that LiBr acts as a pore reducer observed by the reduction in the MWCO of the membranes and smaller pore sizes. The swelling property of both the DMF and LiBr is balanced by the introduction of acetone thus producing membranes with excellent rejection rates and reasonably high flux. In addition the production cost of the membranes is lower because acetone is a cheaper solvent compared to DMF.

3.3.3 Influence of LiCl Additives on the PES/DMF Membranes

3.3.3.1 Pure Water and PEG Permeation Rate

The pure water permeation (PWP) rates of the membranes produced from the various solutions are depicted in Figure 3.12. The results revealed that the presence of LiCl improves the PWP rates of the PES membranes produced from both techniques. As can be observed when the concentration of LiCl additive increases, the PWP rate increases. It is usually impractical to increase the concentration of a salt in the polymer solution beyond a certain value because of solubility and dissolution time limitations (Kraus *et al.,* 1979) in CEH method. As illustrated in Figure 3.12 the PWP for membranes prepared by MW dope solution was higher than the CEH prepared membranes. This trend observed is different from the influence of LiBr

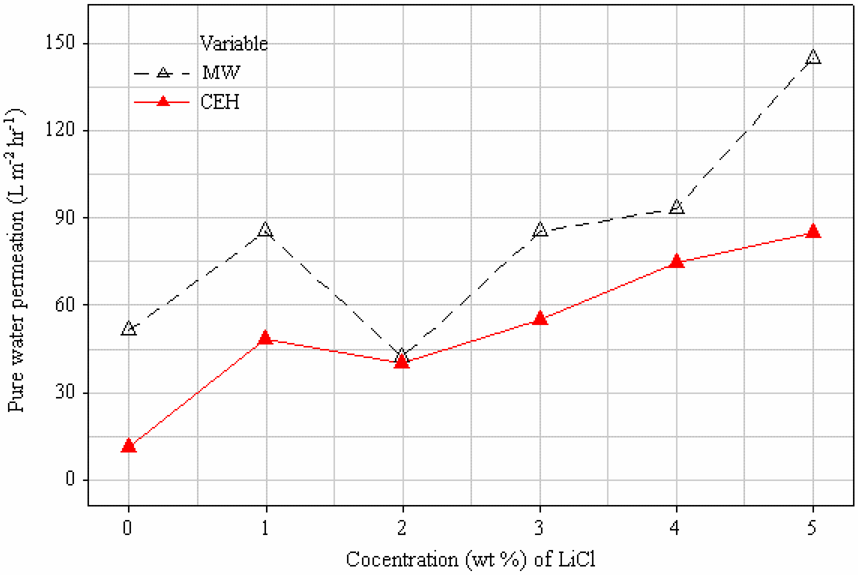


Figure 3.12: Pure water permeation rates of the MW and CEH membranes

additive in PES membranes where PWP declines after a certain high salt concentration. It appears that LiCl presence attributed to relative nucleophilicities which change rapidly in an aprotic solvent under magnetic oscillation.

However, nucleophilicity is often solvent-dependent and the relationship is a complex one and depends on a number of different factors; for example, the relative nucleophilicities substitutions of the halide ions in dimethylformamide are $Cl^{-1} > Br^{-1} > I^{-1}$ (Miller *et al.,* 1999). Thus it can be possible that due to higher nucleophilic tendency of LiCl in DMF, higher hydrophilic PES membranes were produced. This trend observed could be related to the viscosity of the solution as described in Chapter 4, section 4.4. It is believed that the higher viscosity of the MW solution compared to CEH solution leads to different rates of exchange between solvent and non solvent during the precipitation process. The high viscosity solutions tend to promote delayed demixing and this feature decreases the membrane resistance and increases the PWP.

The solute permeation rates (PR) of MW and CEH membranes are shown in Figure 3.13. For the MW membrane, the 1 wt% LiCl concentration exhibits the highest PR which is approximately 158 $Lm^{-2}hr^{-1}$ while in CEH membrane, the 5 wt% LiBr exhibits highest PR. In both cases the presence of LiCl has increase the PR many folds compared to PES/DMF membrane without LiCl. The results clearly indicate that LiCl when used as an additive enhances the hydrophilic property of the membrane and this is displayed by the improved PWP and PR. The solute permeation rates for the MW membranes are also higher than the CEH membranes. The formation of the LiCl and DMF complexes creates a hydration effect and causes swelling in polymer gel. Similar findings were reported by Kesting (1965) in the effect of inorganic salt additives on the formation and properties of cellulose acetate membranes where it was revealed that the permeation rate of cellulose acetate membranes significantly increases when salts are added to the casting solutions. According to Kesting (1965) the increase in water permeation rate is attributed to the following factors; first, a complex between the salt cations and the non-solvent water molecules in the casting solution is formed (i.e. a hydration effect). Second, this complex caused subsequent swelling of the polymer gel structure. Other membranes

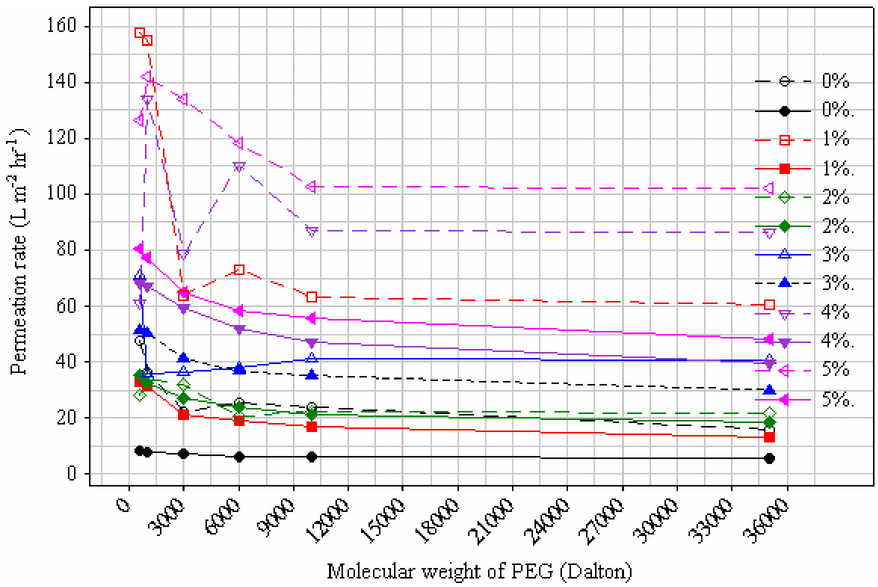


Figure 3.13: Permeation rates of the MW (---) and CEH (—) membranes with various concentration of LiCl

whose permeation properties are also strongly influenced by the addition of inorganic salts include aromatic polyamide, (Kraus *et al.,* 1979), PVDF (Bottino *et al.,* 1988) and polysulfone (Kim *et al.,* 1996).

3.3.3.2 Molecular Weight cut Off Profiles of PES/DMF/LiCl

Figure 3.14 and 3.15 show the rejection rates of the MW membranes for various PEG solutions. The presence of LiCl increases both the PR and rejection rates. Increase in LiCl concentration up to a maximum of 3 wt% increased the rejection rates of the membranes. Beyond this LiCl concentration, the rejection rate of the membrane decreases. The MWCO of the MW membranes at 90% rejection rates for 3wt% LiCl is 2.236 kDa with permeation rates of 35 Lm^{-2}hr^{-1}. Figure 3.15 demonstrates different observation for CEH membranes. Maximum rejection rates are observed at 2 wt% LiCl concentration. Further increase in LiCl beyond 2 wt% did not improve the membrane rejection rates although its permeation rate is increased. The optimum concentration of LiCl for the CEH membranes is 2 wt% with permeation rates of 34.89 Lm^{-2}hr^{-1} and its MWCO is 9.161 kDa. As illustrated

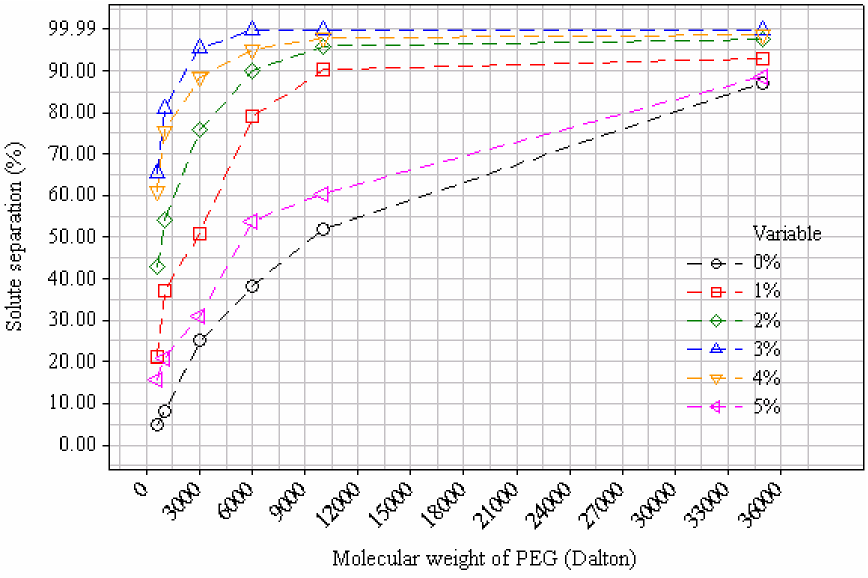


Figure 3.14: Solute separation of MW (---) prepared PES/DMF membranes with various concentrations of LiCl.

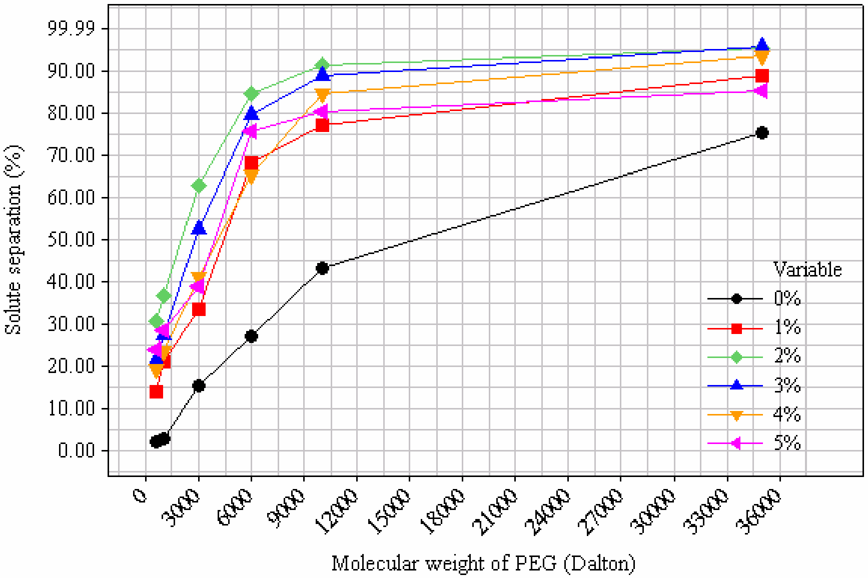


Figure 3.15: Solute separation of CEH (—) prepared PES/DMF membranes with various concentrations of LiCl.

in Figure 3.14 the prepared MW membranes indicates better rejection rates than all CEH membranes. The MW and CEH membranes without LiCl additive exhibit MWCO which is approximately 35 kDa and 36 kDa respectively. It appears that the LiCl strongly interacts with PES and enhances the membrane properties thus improving not only the permeation rates but also the rejection rates of the membranes. LiCl probably interacts with PES and acts as a charged pendant group for the polymer. This is similar to the findings reported by Kim *et al.* (1996) in his work with $ZnCl_2$. The nucleophilicity or substitution property of both the DMF and LiCl is stabilized by the introduction of OH^- to PES bridge moiety, thus, producing membranes with excellent rejection rates and high flux by MW. It is believed that the high viscosity solutions lead to a decrease in membrane resistance and an increase in water flux through the membrane. This view is also shared by Schmid *et al.* (1991). In addition, the viscosity of the solution also influences the rate of exchange between solvent and not solvent during the precipitation process. As a result, this can affect the skin layer thickness of the membranes.

3.3.3.3 Membrane Characterization Using Solute Transport Data

Log normal plots of solute separation versus solute diameter for the MW and CEH assisted membranes with the various concentrations of LiCl additive are displayed in Figure 3.16 and 3.17. As the concentration of LiCl increases the MWCO and the pore diameter of the MW membranes decreases but up to 3 wt% of LiCl as depicted in Table 3.5. It is evident that as further increase beyond 3 wt% LiCl does

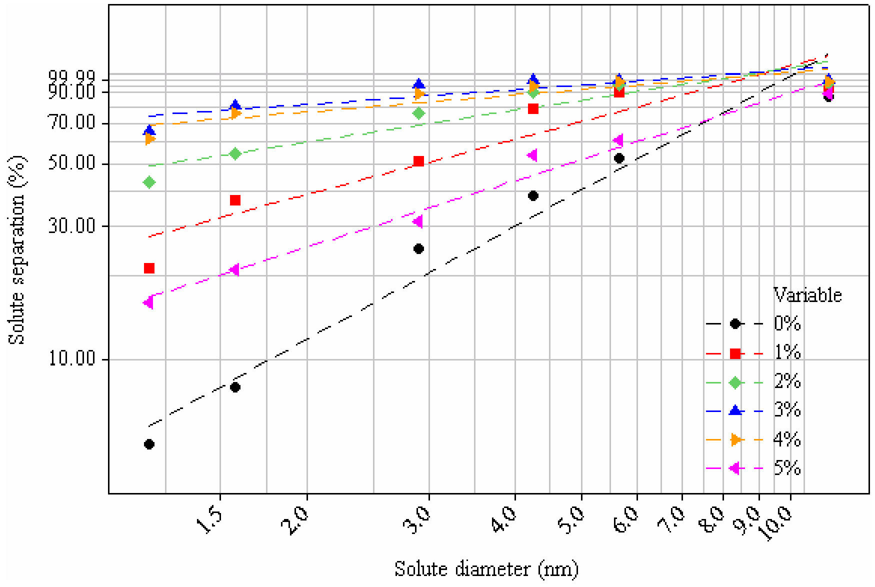


Figure 3.16: Pore size distribution of MW (---) prepared PES/DMF membranes with various LiCl concentrations.

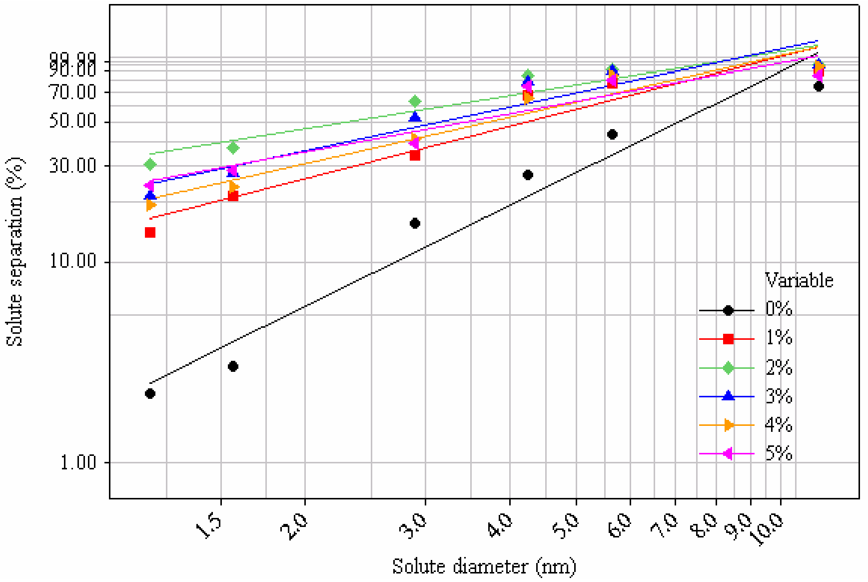


Figure 3.17: Pore size distribution of CEH (—) prepared PES/DMF membranes with various LiCl concentrations.

Table 3.5: Mean pore size, standard deviation and molecular weight cut-off of the MW and CEH membranes

Conc. of LiCl	**Microwave Irradiation**			**Conventional. Electro heated**		
	MWCO (kDa)	$^*\mu_p$ (nm)	$^*\sigma_p$	MWCO (kDa)	$^*\mu_p$ (nm)	$^*\sigma_p$
0%	35.325	3.497	6.625	35.835	3.467	2.142
1%	10.133	0.9597	0.8996	35.185	2.687	2.263
2%	6.185	0.5879	0.5129	9.161	0.762	0.8229
3%	2.236	0.2193	0.2083	12.263	1.071	1.185
4%	3.686	0.2512	0.26	23.974	2.266	2.135
5%	35.175	2.835	2.57	35.487	3.457	4.625

$^*\mu_p$ – mean pore size, $^*\sigma_p$ – standard deviation

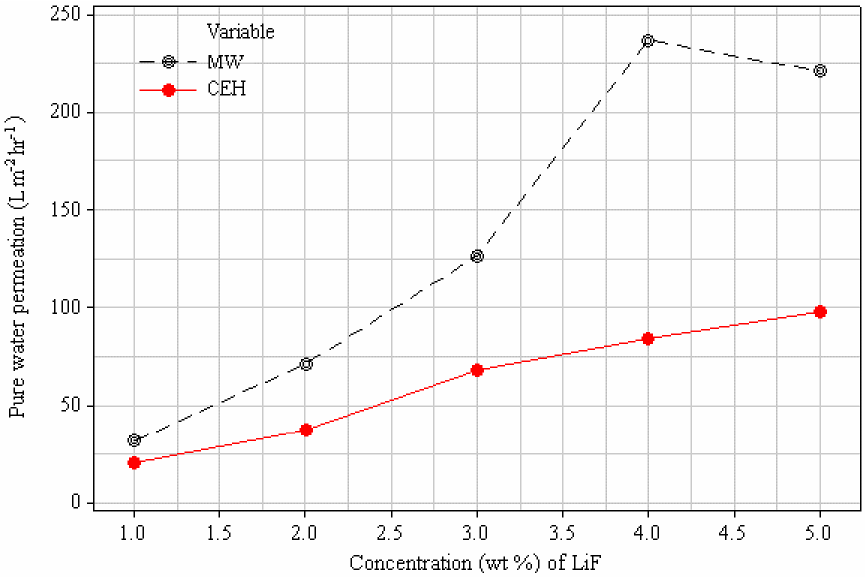
not result in reduction in the MWCO and mean pore diameter. A similar trend is observed for CEH membranes. MWCO acts as guidance for pore sizes of membranes where small MWCO implies small pore size of the membranes. The separation efficiency in MW membranes is better than in CEH membrane due to its finer mean pore size.

3.3.4 Influence of LiF Additive on PES/DMF Membranes

3.3.4.1 Pure Water and PEG Permeation Rates

The influence of LiF concentration, on the PWP of PES membranes prepared by both MW and CEH is shown in Figure 3.18. As can be seen from the graphs, it is evident that the MW membranes show higher PWP rates compared to the CEH membranes. It can also be observed that increase in LiF concentrations increase the PWP rates. A similar trend is also observed in Figure 3.19 for PEG permeation rates; increase in permeation rates is observed as LiF concentration in membrane is increased. In most cases, the MW prepared membranes exhibit higher permeation rates. Apparently, it appears that LiF has improved the hydrophilic properties of the membranes. The concentration of LiF was not further increased to 6 wt% due to the solubility problems.

Amongst all the lithium halides; LiBr, LiCl and LiF, LiF has the lowest molecular weight and has very low solubility in polar and dipolar solvents. LiF has the lowest molecular weight and has very low solubility in polar and dipolar solvents. These properties were observed to influence the viscosity, whish in turn affects the phase inversion process occurring thus affecting the performance of the



3.18: Pure water permeation rates of the MW and CEH membranes.

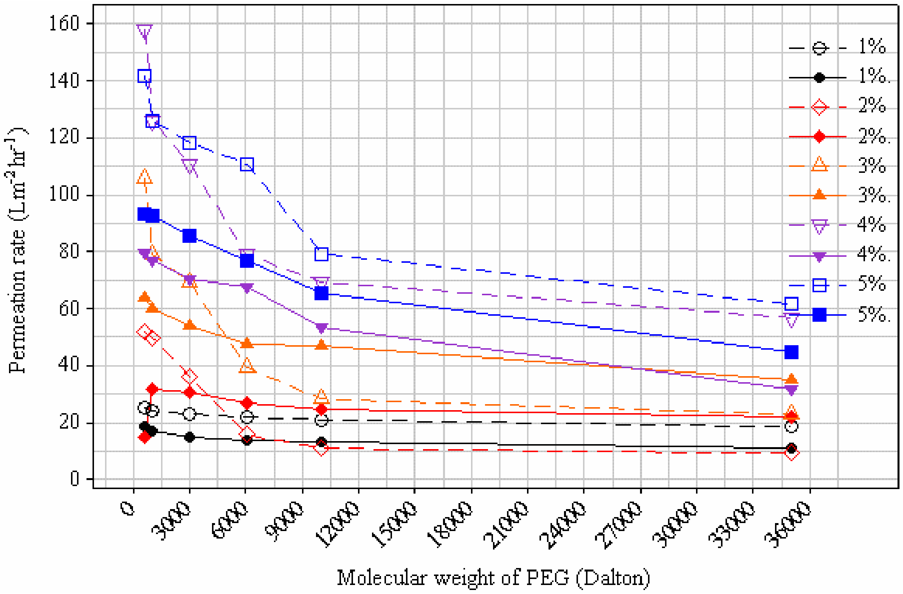


Figure 3.19: Permeation rates of the MW (---) and CEH (—) Membranes with various concentration of LiF

membranes. The low viscosity produced by the presence of LiF results in rapid diffusion rates occurring between the polymer solution and water, thus promotes the formation of macrovoids and porous substructure and this improves both PR and PWP of membranes.

3.3.4.2 Molecular Weight cut Off Profiles of PES/DMF/LiF

The separation data for the UF membrane samples namely, MW and CEH membranes for the various PEG 600 – 36000 Daltons feed solutions is presented in figures 3.20 and 3.21. It can be seen that the separation increases with increase in molecular weight of PEG solute and the profiles attained for the MW membranes are sharper as compared to CEH membranes which tend to be gradual and diffused. As illustrated in Figure 3.20, for the MW membranes, if the concentration of LiF is increased beyond 3 wt%, the separation rates of the membranes will start to decline. This trend is also observed for the CEH membranes, but maximum separation is observed when LiF concentration is at 2 wt%. By using the MW techniques, higher LiF concentrations can be used and separation performance can be improved but

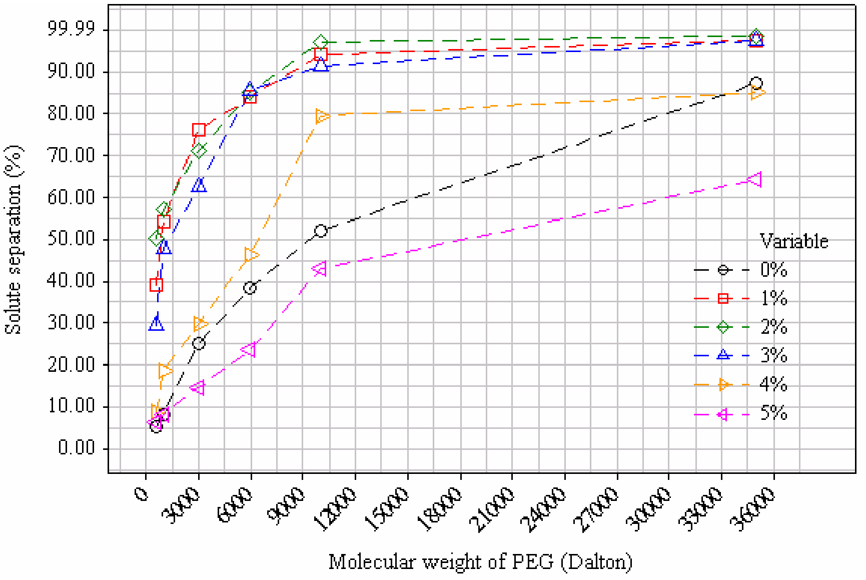


Figure 3.20: Solute separation of MW prepared PES/DMF membranes with various concentrations of LiF.

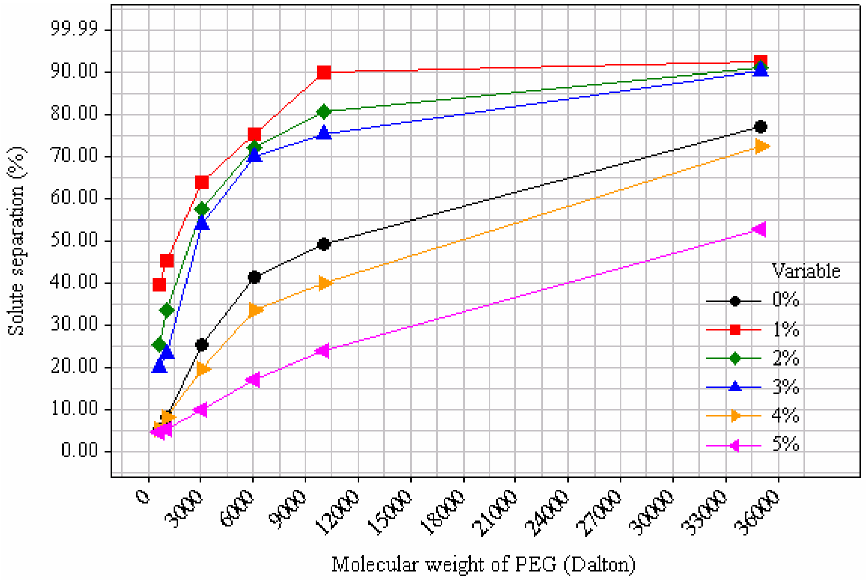


Figure 3.21: Solute separation of CEH prepared PES/DMF membranes with various concentrations of LiF.

only up to a certain limit. For the MW membranes exceeding concentration of 3 wt% LiF will no doubt increase the permeation rates but do not improve the separation rates. For the CEH membranes, the LiF concentration should not exceed 1 wt% because separation rates will decline despite improvements in PR rates. The results seem to suggest that the low molecular weight, LiF, probably diffused rapidly thus promotes the macrovoid formation and also acts as pore former during the phase inversion process.

3.3.4.3 PES Membranes Characterization using Solute Transport Data

Figure 3.22 and 3.23 demonstrates the log normal plots of solute separation versus solute diameter for PES MW and CEH membranes containing 0 - 5 wt% LiF. In contrast to the membranes without additives, the presence of LiF decreases the pore size of membranes but only up to a certain limit. For the MW prepared membranes, increase concentrations of LiF to more than 2 wt% will decrease the pore size of membranes and thus reduce the MWCO. However for the CEH membranes increase of LiF beyond 1 wt% do not further decrease the pore size of membranes. Thus the results indicated only small amounts LiF additive is recommended to improve membrane performance having both high separation and permeation rates.

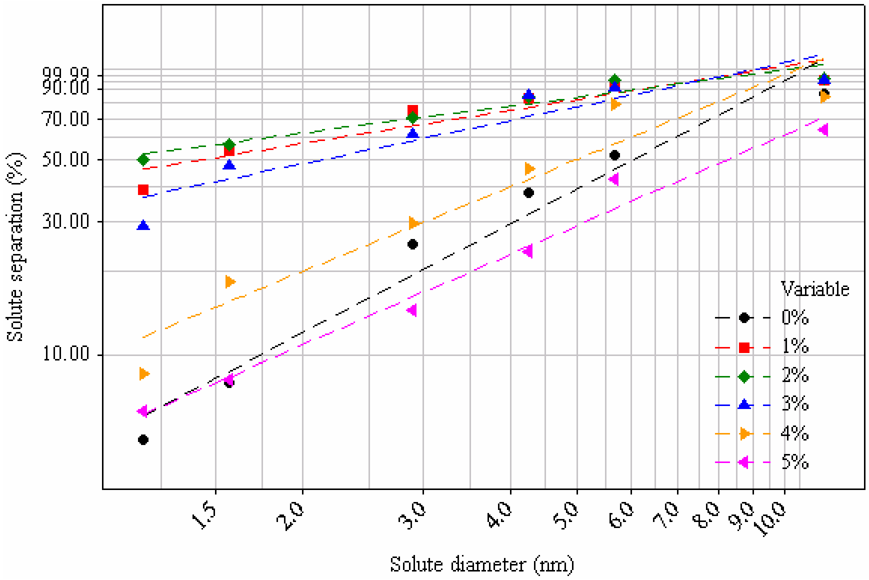


Figure 3.22: Pore size distribution of MW prepared PES/DMF membranes with various LiF concentrations.

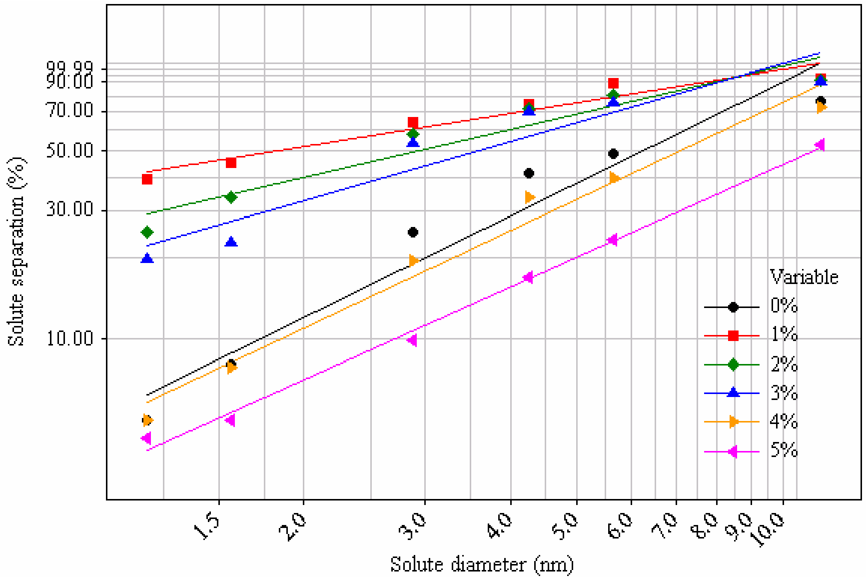


Figure 3.23: Pore size distribution of CEH prepared PES/DMF membranes with various LiF concentrations.

As illustrated in Table 3.6 the membrane without additive has 35 kDa MWCO and 3.75 nm mean pore size. As for the MW membranes containing 1, 2 and 3 wt% LiF, results show that the MWCO of membranes are 8.1 kDa, 7.1 kDa and 8.45 kDa and the mean pore size were 0.884 nm, 0.649 nm and 1.043 nm respectively. These values displayed a linear relationship between the mean pore size and MWCO. Smaller pore size of 1 wt% and 2 wt% LiF membrane contributed to low flux although the rejection rate is high. While 4 wt% LiF membrane has high flux but less rejection. The pore sizes obtained in Table 3.6 further explains the performance of the membranes. Increasing LiF concentration to more than 2 wt% will not reduce the pore size of membranes. Thus the best concentration of LiF that should be used is 3 wt% as the membranes produced has small pore sizes which displays high rejection rate and permeate rates.

Table 3.6: Mean pore size, standard deviation and molecular weight cut-off of the MW and CEH membranes

Conc. of LiF	**Microwave Irradiation**			**Conventional. Electro heated**		
	MWCO (kDa)	$*\mu_\rho$ (nm)	$*\sigma_\rho$	MWCO (kDa)	$*\mu_\rho$ (nm)	$*\sigma_\rho$
0%	39.68	2.72	2.35	36.83	2.61	4.16
1%	11.09	1.12	0.81	10.99	1.8	0.94
2%	7.60	0.80	0.58	32.40	2.90	1.03
3%	9.17	0.84	0.55	35.02	3.58	1.85
4%	39.90	4.8	4.94	38.70	7.05	0.82
5%	41.61	6.37	4.68	41.61	10.95	0.94

$*\mu_\rho$ – mean pore size, $*\sigma_\rho$ – standard deviation

3.4 Comparisons of the Various Additives

This comparison section brings together all the results on the influence of LiBr, LiCl and LiF on the performance of the casted membranes. As revealed on the PWP and PR of PEG plots in Figure 3.2, 3.3, 3.12, 3.18 and 3.19, LiBr exhibits the highest rejection rates at 3 wt% compared to the other lithium halides. The presence of the other additives, LiF and LiCl have also improved the PWP and PR of membranes but PES/DMF/LiBr membrane exhibits the highest PEG permeation rates of .134.171 Lm^{-2}hr^{-1} The PES/LiCl/DMF and PES/LiF/DMF membranes have almost similar PEG permeation rates as the range of 12.69 – 80.73 Lm^{-2}hr^{-1} LiBr seemed to have improved the hydrophilic properties of the PES membranes. The use of the microwave technique has in fact improved both the PWP and PR of the PES/DMF/LiBr membranes to further limits.

Results revealed that the membrane with LiBr additive at a concentration of 3 wt% not only exhibits good permeation but also excellent separation with high rejection rates. The results also indicated that a PES/DMF/LiBr membrane has a MWCO of 2.82 kDa and pore size of 0.2466 nm with standard deviation of 0.3012 when LiBr concentration is at 3 wt%. This explains for the highest separation rate obtained. This is followed by LiCl and LiF membranes with MWCO of 9.161 and 10.992 kDa respectively.

Amongst the lithium halides, LiBr, LiCl and LiF, LiBr has the highest molecular weight of 86.845 g/mol, followed by LiCl, 42.39 g/mol and LiF, 25.94 g/mol. Unlike LiF and LiCl, which leaches out of the membrane during the precipitation of the polymer solution and acts as a pore former (Huang *et al.,* 1995), LiBr seems to behave differently. Viscosity data revealed that amongst the three dope solutions containing LiBr, LiCl and LiF, the dope solution containing LiBr has a moderate viscosity between LiF and LiCl and this is clearly observed in Chapter 4.

The pore size on the surface of the membrane becomes smaller because the LiBr gives rise to an association between the moieties units of PES, and its nucleophilicity is greater in dipolar aprotic solvents like dimethylformamide than in aprotic solvents like water or alcohols. For this reason, DMF participates as a solvent for carrying out nucleophilic substitutions of Br^{-1} ions thereby decreasing the mobility of the polymer chain. Therefore, the LiBr additive acted as a pore inhibitor rather than a pore former leading to the simultaneous decrease of pore size and increase in hydrophilicity as depicted in Figure 3.6. However when the LiBr concentration in the casting solution increased to more than 3 wt% both the permeation and separation rates declined as shown in Figure 3.3 and 3.4. This is probably attributed to the increase in packing density in the polymer matrix at higher concentrations of LiBr. The experimental results indicated that the increasing membrane pore density is the major factor, and decreasing membrane pore radius is the secondary factor.

3.5 Conclusions

Ultrafiltration asymmetric membranes with various MWCO in the range of PEG 200-35000 Dalton can be prepared by microwave technique from polyethersulfone polymer with proper adjustment of solvents and lithium halides additives. The nature of solvents and additives monovalent lithium halides in anhydrous form is found to play a significant role in microwave technique to achieve high performance UF membrane. The electrophilic nature of dipolar dimethylformamide and nucleophilic nature of the monovalent lithium halides enhanced the hydrophilicity of the PES casting solution as well as the water permeation rate of the resultant membranes. The main finding are listed below

1. The membranes prepared from the microwave casting solutions exhibited good rejection and permeation rates. In fact their performances were superior compared to the ones prepared from CEH solutions with lower MWCO, smaller pore sizes and high flux. The enhancement of permeability is probably due to polar functional groups which is attached to the polymer structure during dope solution preparation. Minor chain scissions occurring during MW irradiation could have promoted the attachment of the polar functional groups in the polymeric membranes.

2. Amongst LiCl, LiF and LiBr additives, LiBr additive enhanced the performance of the PES membranes both in terms of high separation and high permeation rates.

3. The MW casting solutions using LiBr as additives in single solvent for PES ultrafiltration membranes produced the lowest MWCO membranes and high flux values. The results indicated that during phase inversion process acetone reduces the PES hydrophilicity and increased the solute rejection with low flux.

CHAPTER 4

SPINNING OF MICROWAVE POLYETHERSULFONE HOLLOW FIBER MEMBRANES CONTAINING LITHIUM BROMIDE AND LITHIUM CHLORIDE AS ADDITIVES

In the previous chapter it was observed that the performance of the microwave membranes prepared from dope solutions are far more superior than those prepared from CEH dope solutions. In addition, the LiBr and LiCl additives exhibit excellent additive affects producing membranes with both high separation and flux rates. Hence in this chapter hollow fibers are spun and their performance evaluated in terms of PWP, PEG permeation and separation rates. In addition, a novel post treatment method is introduced to enhance membranes performance. The hollow fibers were characterized in terms of scanning electron microscope to indicate the membrane morphology.

4.1 Introduction

Addition of inorganic additives such as monovalent, divalent, or trivalent salts in the dope solutions of various polymers to improve the permeability and selectivity of ultrafiltration membranes have been investigated (Shinde *et al.,* 1999). Bottino *et al.* (1988) used lithium chloride doped casting solutions to prepare poly(vinylidene fluoride) hollow fiber membranes with higher porosity and better overall performance than the salt free dope solution. Kim *et al.* (1996) observed the electroviscous behavior caused by adding zinc chloride in polysulfone/NMP solutions and interpreted this behavior in terms of interactions between salt and polymer. The formed membranes were reported to exhibit an increased rejection rate and a decreased molecular weight cut-off. Instead of using pure salt, Kraus *et al.* (1979) studied the influence of salt mixtures in aromatic polyamide/dimethylacetamide solutions and results revealed that the membrane structure and performance is very influenced by its performance. Wang *et al.* (2000b) used nonsolvent/LiCl mixture as an additive and produced PVDF hollow fibers with improved permeability and good mechanical strength. Salt additives were also used to prepare membranes for certain separation purposes; e.g. Lai *et al.* (1992) prepared ($PMMA/CH_2Cl_2$)/DMF/$CuCl_2{\cdot}2H_2O$) complex membranes for separation of oxygen from nitrogen. Lee *et al.* (2000 and 2002) reported the solution properties of poly (amic acid)–NMP containing LiCl and their effects on membrane morphologies. Besides that, such additives may interact with either the solvent or the polymer or both N,N-Dimethylformamide .

Annealing reduces a substrate’s pore size and improves selectivity. Without annealing, the inventors could not produce useful membranes. The annealing technology was probably developed 30 years ago for polybenzimidazole (PBI) membranes in RO applications (Porter, 1990). Without annealing in hot chemical solution such as, ethylene glycol, sodium hypochlorite, glycerin and surfactant at 95–180 $^{\circ}$C, polymeric membranes exhibit a poor performance in terms of rejection rates. This technology was extended by Cabasso and Tamvakis (1979) for the development of polyethyleneimine/polysulfone (PS) hollow fibers for RO. They observed intrusion of a polymeric solution into pores to a depth as great as 0.5 cm. They contracted surface pore sizes and reduced intrusion by means of annealing microporous PSf hollow fibers at 110–150 ^{0}C for less than 30 min.

The annealing post-treatment process was found to be compulsory for membranes. The annealing of the membranes in hot water led to permanent changes in properties concerning water permeability and salt rejection values. The annealing post-treatment provide thermal energy to the polymeric matrix of the membranes, which gives rise to translational movements of the macromolecules of polymeric membranes, resulting in the approaching of the polar groups, allowing for the formation of hydrogen bonds.

Thus in this chapter, the best formulated membranes were spun into hollow fibers. Only dope solutions prepared by the MW technique were spun into hollow fibers because the results from previous chapters revealed that the membranes produced are far more superior in terms of permeation and rejection rates.

4.2 Experimental

4.2.1 Materials and Dope solution preparation Techniques.

In this section of the thesis, only two types of additives are used: LiBr and LiCl. The solvent used is DMF. Materials and dopes solution preparation by MW and CEH were described in chapter 3.

4.2.2 Spinneret Concentricity for Hollow Fiber

In this study a conical spinneret was used for the hollow fiber spinning process. The polymer extrusion flow angle was 60^{o} and the complexity of the hollow fiber spinneret design is shown in Figure 4.1. This alignment are based on compression of gasket or O-ring between the surface of a two-piece spinneret, one body for the lumen "needle" and one for the polymer "bore" as shown in Figure 4.1. With this design spinneret concentricity can be set or offset to the desired amount by compressing the gasket or O-ring unevenly to produce concentric hollow fiber membranes. The polymer outlet bore diameter is approximately 0.6 mm whilst the needle outer diameter is approximately 0.25 mm.

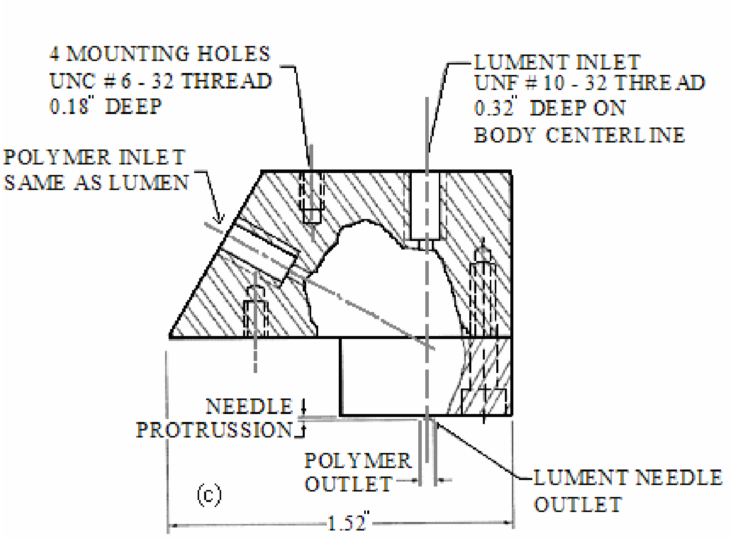


Figure 4.1: Schematic diagrams of concentricity spinnerets for hollow fiber spinning

4.2.3 Preparation of PES Hollow Fiber Membranes

All PES hollow fiber membranes were spun via the dry-wet phase inversion method. The equipment used to spin hollow fibers is illustrated in Figure 4.2. The dope solution was placed in a 1 litre pressure vessel that was subsequently pumped to the spinneret concentricity by gear pump. The dope reservoir was kept at 1 atm. The gear pump used was 30 watts motor and was capable of delivering 0.3 cm^3 rev. The motor had a double gear reduction so as to give steady rotation even at lower speed. This system ensures that the dope was smoothly conveyored to the spinneret at the desired dope extrusion

For the spinning process the spinnerets with flow angles of 60^o were used in hollow fiber spinning process and their schematic diagram of the spinning rig is presented in Figure 4.1. The internal coagulant was pumped to the tube side of the spinneret using a high pressure precision metering pump (ISCO Model 500 D; series D). The nascent fiber emerging from the spinneret was partially solidified by the internal coagulation fluid. The spinneret was positioned above the coagulation bath so that the outer surface of the fiber was exposed to air for partial evaporation of solvent before being immersed in the coagulation bath, where coagulation occurred on the outer surface of the membrane due to solvent-nonsolvent exchange. As a result, asymmetric hollow fibers could be obtained. The hollow fiber filament then passed through a series of rollers in the coagulation bath. It was passed through the washing and treatment bath. The fully formed fiber was then continuously collected onto a wind up drum of diameter 35 cm. The fibers remained in the water bath so as to complete the coagulation process before being taken out. During the coagulation period, most of the LiBr and LiCl additive leached out from the membrane. Hollow fiber spinning conditions are listed in Table 4.1

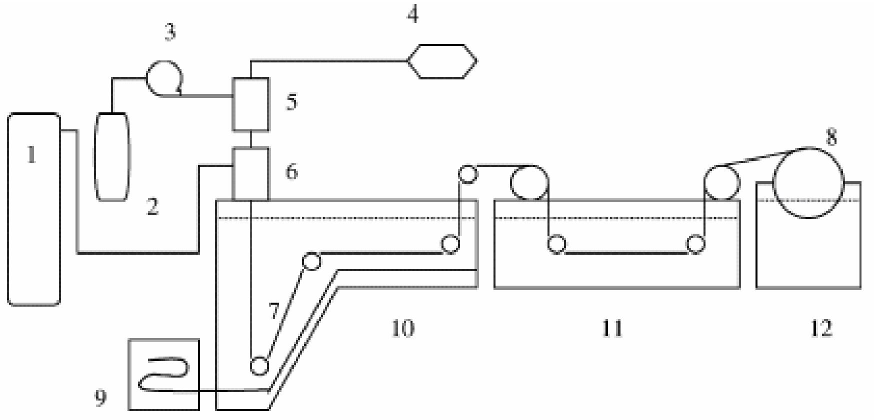


Figure 4.2: Hollow fiber spinning system: (1) nitrogen cylinder; (2) dope vessel; (3) gear pump; (4) syringe pump; (5) spinneret; (6) forced convective tube; (7) roller; (8) wind up drum; (9) refrigeration/heating unit; (10) coagulation bath; (11) washing bath/treatment bath; (12) wind up drum Ani *et al.* (2002a).

Table 4.1: Spinning conditions of hollow fiber membranes.

Spinning Condition	
Internal bore fluid rate	2 ml/min
Fiber take-up speed	6.5~7.78 m/min
Fiber take-up roller diameter	35 cm
Air gap between spinneret and coagulant bath	3.0 cm
Dope Extrusion rate	3.95 - 4.0 ml/min
Dope solution temperature	25 ^{0}C
Relative humidity	60-70%
Spinning temperature	22 ^{0}C

4.2.4 Cloud Point Measurements

Cloud point data to determine the binodal composition of the PES/lithium halides/DMF system were measured by means of a titration method as illustrated in Figure 4.3. The cloud points were determined visually at 25 ^{0}C by titrating 10 gm of homogeneous solutions of PES in DMF with homogeneous solutions of PES/lithium halide in DMF or vice versa (Silva *et al.,* 2003). Pure water was slowly added to a solution of polymer and solvent. The solution continuous stirred using a magnetic bar. Every drop of water added to the solution caused local coagulation.

Further addition of water was performed after the solution became homogeneous again. This procedure was continued until permanent turbidity was detected visually. Since water was added drop wise, with one drop of water amounting to approximately 7 mg, the titration process was tedious, but this method

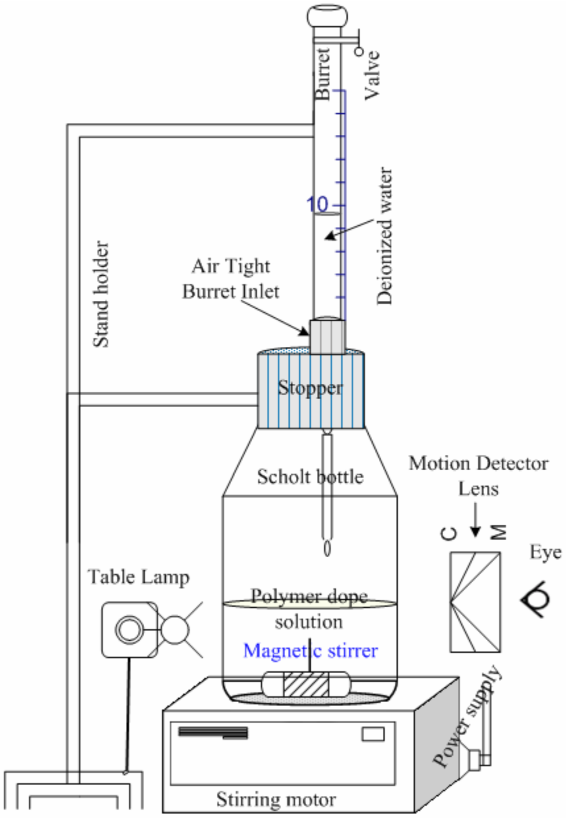


Figure 4.3: Schematic diagram of turbidimetric titration setup for polymer cloud point experiment

allowed for systematic treatment of many samples without significant overshooting of the end points. An analytical balance was used to weigh the amount of water that was put into the solution. To stop the surrounding contaminant i-e humidity and the solution evaporation, small mouth glass wares and air tight caps were utilized during the titration process. In this study, the effects of lithium halides additives at 25 ^{0}C on the polymer precipitation were also studied. At the onset of turbidity, the volume fractions of nonsolvent, solvent, and polymer represent the cloud point in a ternary phase diagram. The obtained cloud-point curve was used to represent the binodal curve. In the preparation of polymeric membranes normally a homogeneous polymer solution is used. Therefore, smaller amounts of water necessary to cause phase separation are added to the dope solution used in membrane preparation. The ratio of water added and the amount required to reach phase separation is defined as the coagulation value.

4.2.5 Post-Treatment Protocols

Two post-treatment protocols were used in order to remove the excess solvent and additives from the membranes structure and surface of resultant hollow fiber polyethersulfone membranes. The spun hollow fiber membranes were rinsed thrice with de-ionized water and then post treated using 2 methods detailed as follows:

i) Microwave method – The spun hollow fibers were immersed in de-ionized water in a glass container covered with aluminum foil. The glass container was then placed in a microwave oven for 10 minutes at medium high pulse with the temperature controlled at 90 $\underline{+}$ 5 ^{0}C using a Pico data logger. The conductance of the de-ionized water was measured by a standardized digital conductivity meter of type Hanna instrument Model H18633 so as to ensure excess additive inside the membrane pores was totally removed. The treated fibers were then rinsed again in de-ionized water until conductance readings reached values equivalent to pure de-ionized water conductance. The membranes were then ready for testing.

ii) Thermal annealing method – The spun hollow fibers were immersed in a deionized water bath and the temperature of the water bath was kept at 90 $\pm$ 5 ^{0}C and annealed for 30 minutes. After annealing the hollow fibers were immersed in distilled water at 25 ^{0}C for 24 hours. Similarly, the conductance of the deionized water was measured by the method described in (i).

4.2.6 Potting Hollow Fiber Membranes

After post-treatment, the hollow fiber membranes were dried for 24 hrs at room temperature. The hollow fiber membranes were then potted in bundles of about 30 fibers each with a 30 cm length. A high fiber packing density is needed in PES hollow fiber membranes to minimize any axial diffusional effects and channeling. A tight bundle of 30 fibers of PES hollow fibers were therefore housed in a 7 cm long stainless steel hollow pipe of 2 cm diameter then the concentric annular space between the steel pipe and fiber bundle was filled with epoxy resin. One end of the hollow fiber membranes were sealed in aluminum caps. The geometrical characteristics of the permeator are given in Table 4.2

Table 4.2: Geometrical Characteristics of the hollow fiber module

Geometrical Characteristics	
Total number of fiber	30
Average fiber outer diameter (mm)	0.619 ± 0.6375
Average fiber inner diameter (mm)	0.31813 ± 0.3015
Potted length (mm)	200
Total permeation volume area (mm)^3	1859
Packing Fraction	0.954

4.2.7 Membrane Evaluation

The ultrafiltration hollow fiber membranes experiments were performed in a stainless steel cross flow test cell at 3-3.5 bars as illustrated in Figure 4.4. Hollow fiber membrane samples with area of 6.0×10^{-4} m^2 were placed in the hollow fiber test cell with the active skin layer facing the feed direction. The membranes were tested for pure water permeation fluxes (PWP) using distilled water. Then, the rejection rates of the membranes were determined by separation experiments using various molecular weight polyethylene glycol (PEG) solutions with concentration of 1000 ppm. The volume of permeate was collected and measured so as to determine the solute permeation rates (PR) at 3-3.5 bars. The concentration of feed and permeate solutions were also measured so as to determine the solute rejection rate (SR). A minimum of three hollow fiber modules were prepared for each condition and the average data was tabulated so as to ensure reproducibility. Pure water permeation (PWP) and solute permeation rate (PR) of the membranes were obtained as follows:

$$Flux = J = \frac{Q}{A\Delta P} = \frac{Q}{N\pi\, d_O\, l\, \Delta P} \qquad (4.1)$$

where Q is the volume flow rate of permeate ($Lm^{-2}h^{-1}$), A the effective membrane area (m^2), ΔP the transmembrane pressure (bar), N the number of fibers, d_o the outer diameter of fiber (m), and l the effective length of fiber (m). Solute

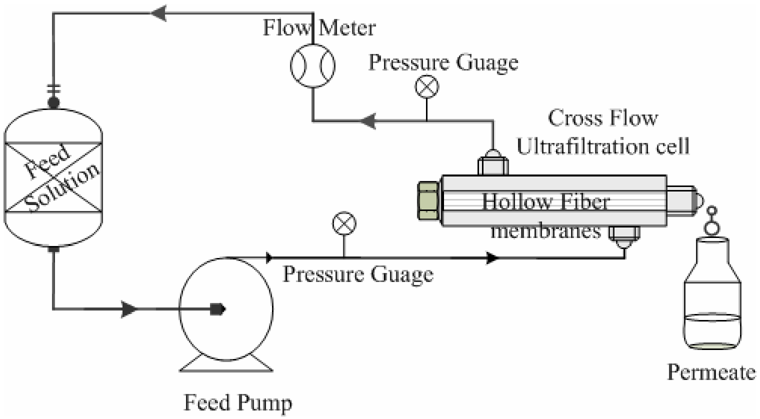


Figure 4.4: Schematic diagram of hollow fiber (out to in) cross flow filtration cell

rejection of membranes were evaluated with various molecular weight PEG solutions ranging from 200 to 36,000 Dalton. The concentration of the feed and permeate solutions were determined by the method described in Chapter 5. The absorbance was measured using the spectrophotometer (Shidmadzu UV-160) at a wavelength of 535 nm against a reagent blank. The membrane solute rejections (SR) were determined from Equation 5.2, Chapter 5.

4.2.8 Scanning Electron Microscope Analysis

The membranes were snapped in liquid nitrogen so as to give a generally clean break. These samples were then placed onto carbon holders and sputtered with gold to prevent charging up of the surface by the electron beam. Cross sections of the hollow fiber membranes images were obtained using the SUPRA 35VP FESEM.

4.3 Results and Discussion

4.3.1 Cloud Points of Polymer with Lithium Halides Additives

Ternary membrane forming systems consisting of PES/DMF/Lithium halides and nonsolvent (water) are characterized by a liquid-liquid (L–L) demixing gap (Laninovic, 2005). The boundary of this gap is called binodal, which is determined experimentally by cloud point titration at isothermal phase as shown in Figure 4.5. As observed from Figure 4.5, the L–L demixing in ternary systems generates a polymer-lean phase (PLP) and a polymer-rich phase (PRP). The tiny droplets of the PLP formed during the L–L demixing process are surrounded by a PRP, which solidifies in the precipitation process. Whether the droplets of the PLP coalescence and form a porous structure before solidification of the PRP takes place strongly depends on the composition of the PES/DMF/Lithium halides solution at the moment of onset of L–L demixing (Witte *et al.,* 1996). When the onset of the demixing

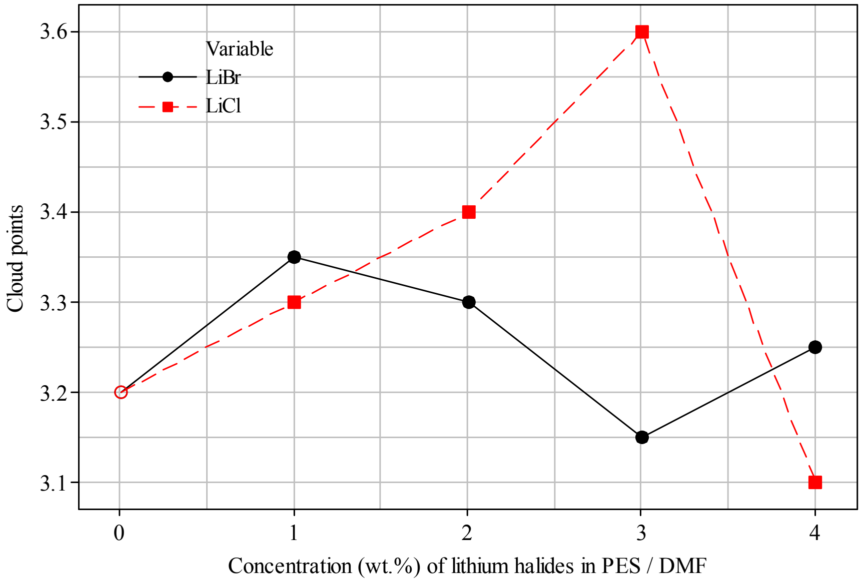


Figure 4.5: Clouding points of polymer solutions with various concentrations of lithium halides. "O" represents pure polymer solution.

process is delayed, the composition of the PES/DMF solution remains in the single-phase region of the phase diagram for a certain period of time. This period is called the delay time. During the delay time, the composition of the polymer solution gradually shifts to higher nonsolvent concentrations until finally the demixing gap is entered. At this moment the nuclei of the PLP start to form and turbidity of the polymer solution appears. Experimentally determined isothermal phase process of the systems PES/DMF/LiBr and PES/DMF/LiCl are presented in Figure 4.5. It can be observed that the cloud point curve approaches the PES–(DMF-lithium salts) axis with the addition of nonsolvent additives (LiBr and LiCl) in the polymer solution, hence reducing the single-phase region. This brings the initial composition of the polymer solution nearer to the precipitation point.

The influence of LiBr and LiCl on cloud points of polymer solutions was depicted in the cloud point versus concentration of lithium halides plot in Figure 4.5. As illustrated in Figure 4.5, the dope solution containing LiBr can tolerate only a small amount of water before precipitation while those with LiCl can tolerate more water. In other words, LiBr bring the polymer solution closer to the cloud points compared to LiCl. It is observed that polymer solution containing 3 wt% LiBr required the smallest water to precipitate which indicates that at this concentration, LiBr facilitates liquid – liquid demixing and bring the solution very close to the cloud point. On the other hand the phase separation data shows that the polymer solution containing 4 wt% LiCl required a smallest amount of water to precipitate than did the polymer solution without LiCl. The presence of LiCl facilitates liquid-liquid demixing of the solution during phase inversion. This results in a reduction in the polymer solubility (Huang and Feng, 1995). Luccio *et al.* (2002) also noticed that the addition of LiCl to a polycarbonate/NMF system would significantly decrease the miscibility gap of the system. While the presence of 1 – 3 wt% LiCl additive increases the amount of water imbibed in the polymer system, which tends to increases the porosity of the membrane, the additive also contributes to the formation of pores in the membrane after it leaches out of the polymer during polymer precipitation.

As an inorganic salt, LiBr dissociated in the aqueous solution, which would enhance the formation of polymer aggregates due to the existence of a charge transfer complex between the ether units of PES. In part, this is attributed due to the complex formation through the coordinating DMF methylene units. In the case of anions such as Cl^{-1} increase of the cloud points while Br^{-1} anions decreases the cloud point as reported by Scott (1995). This ionic effect breaks the solvent structure or accumulation around the polymer molecules hence, leading to decrease in solvent power (Shinde *et al.,* 1999).

Hence, the LiBr and LiCl have two opposite effects on the membrane structure from a thermodynamic point of view. Subsequently, the resulting membrane morphology will be influenced by the two opposing effects simultaneously.

4.3.2 Effect of Lithium Halides on the Performance of Membranes

The pure water permeation (PWP) rates of the hollow fiber membranes produced from the dope solutions are depicted in Table 4.3. Results revealed the PES membranes with out additives show low flux values. However, membranes prepared

Table 4.3: Pure water permeation rates of the PES/DMF with various concentrations of LiBr and LiCl membranes

Lithium Halides Concentration (wt %)	**PWP$_{LiBr}$ Lm^{-2}hr^{-1}**	**PWP$_{LiBr}$ Lm^{-2}hr^{-1}**
0	51.32	
1	125.58	119.58
2	179.34	67.89
3	230.1	73.58
4	119.01	98.67

with additives showed the better pure water permeation flux values. Apparently the membranes containing LiBr additives exhibits very high flux rates compared those containing LiCl additives.

In the case of PES/DMF/LiBr membranes as the concentration of LiBr increases PWP rate increases until concentration of LiBr reaches 3 wt%, after which the flux decreases. This phenomenon observed seem to suggest that the 3 wt% LiBr facilitates the liquid - liquid demixing and brings the solution very close to the cloud point thus promoting instantaneous precipitating to occur resulting in a very thin asymmetric skin layer which results in the high rejection rates of the membranes. Unlike LiBr, LiCl does not bring the polymer solution very close to the cloud point at the concentration of 2 – 3 wt%. The solution is closest to the cloud point at 1 wt% which explains for the membranes high permeation. With PES/DMF/LiCl membranes a 1 wt% LiCl increases the PWP, beyond this value, the flux decreases.

A similar trend was observed for the permeation rates when using various molecular weight PEG solutions (1000 ppm) as the feed solution. As observed from Figure 4.6 hat the permeation rates for all lithium bromide membranes were 2.3 – 4.4 times greater than the membrane without LiBr. The PR of PES/DMF/LiCl membranes also increased but increment is about 1.9 – 2.3 times higher than the membranes without LiCl. The permeation rates increase when the amount of lithium halides is increased until 3 wt% LiBr is reached and highest permeation rate was observed only at 1 wt% LiCl. In all cases the presence of LiBr has increased the permeation rates by many folds compared to the pure PES and LiCl. The results

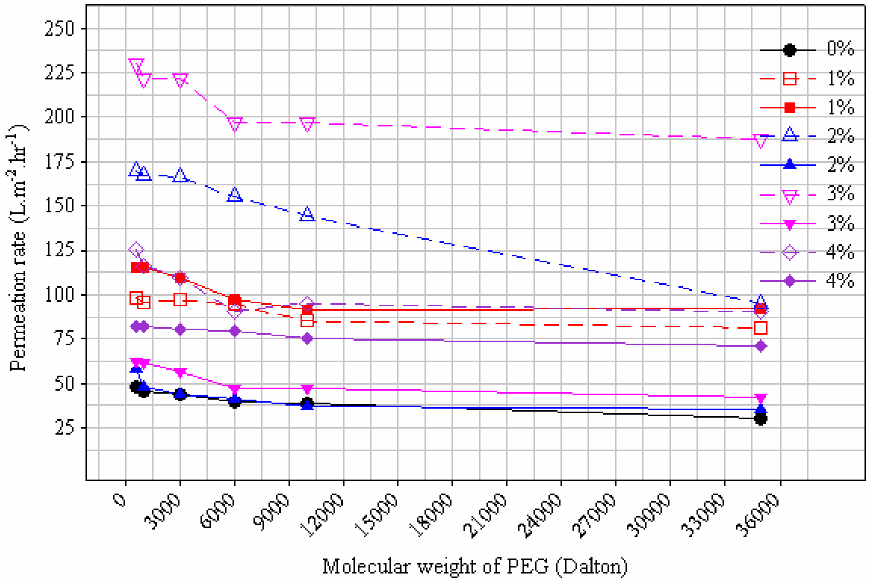


Figure 4.6: Permeation rates of PES/DMF (●) with various concentration of LiBr (---) and LiCl (—) Membranes

clearly indicated that LiBr when used as an additive enhanced the hydrophilic property of the membrane and this is displayed by the improved permeation rates. The permeation rates for the best membranes with LiBr were approximately 4 times higher than those without LiBr and 3 times higher than the membranes with above 1 wt% LiCl. Permeation rates of 3 fold increments were achieved when 3 wt% and 4 wt% of LiBr is added which means increase in productivity. With the participation of LiBr and LiCl which has high swelling properties, the PES becomes hydrophilised. For the membranes with LiBr hydrophilicity becomes more pronounced with membranes containing 3 wt% LiBr. The higher hydrophilicity is in good agreement with higher nucleophilicity of LiBr over LiCl in liquid dope solution under microwave irradiation (Miller *et al.*, 1999). There is the possibility that at this concentration the balance of the hydrophilic and hydrophobic moieties has prevailed. Details related to the changes in hydrophilicity caused by the incorporation of LiBr would be described in the contact angle, FTIR and water uptake analysis section in Chapter 7.

As described in Chapter 4 that this trend observed could also be related to the viscosity of the solution and polymer hydrophilicity. It was reported that the presence of 3 wt% LiBr does not result in very viscous dope solutions especially when prepared by MW as depicted in chapter 4. The low viscosity is believed to lead to different rates of exchange between solvent and non solvent during the precipitation process. The low viscosity solutions tend to promote instantaneous demixing and this decrease membrane resistance and increase both the pure water permeation and permeation rates of the membranes. Compared to PES/DMF/LiBr, PES/DMF/LiCl solution, have higher viscosity and thus tend to promote delayed demixing.

The superior hollow fiber membranes obtained from casting solutions containing LiBr and LiCl additives were probably due to the increased swelling of the membrane. In addition, the higher solute permeation rates for PES with 3 wt% LiBr membranes could be due to the formation of the LiBr and DMF complexes that creates a hydration effect and causes swelling of the polymer gel. Watson *et al.* (1965) has also reported similar results and was particularly concerned with the effects of water and salts such as $ZnCl_2$ and $Mg(C1O_4)_2$ in casting solutions of cellulose acetate and acetone.

Figure 4.7 shows the rejection rates of the PES hollow fiber membranes with and with out lithium halides for the various PEG solutions. The presence of lithium halides has not only improved the permeation rates but also the rejection rates. Increase in LiBr and LiCl concentration up to a maximum of 4 wt% increased the rejection rates of the membranes. The MWCO at 90% rejection rate for membranes with 3 wt% LiBr is 2.83 kDa LiBr and 4.210 kDa with 3 wt% LiCl. However, without lithium halides in PES for membranes, the rejection rate of the membrane was extremely low with high MWCO of 34.936 kDa. A further increase of LiBr concentration above 3 wt% of LiBr in PES does not improve both the membrane rejection and permeation rates. It appears that the LiBr strongly interacts with PES and enhances the membrane properties thus improving not only the permeation rates but also the rejection rates of the membranes. The 3 wt% LiBr has brought the polymer very close to cloud point, thus promotes instantaneous demixing. Such phenomenon results in the formation of very thin skin layer which not only offers very low resistance to flow but also improves the separation rates of membrane. Shinde *et al.* (1999) has also reported similar finding that the addition of different salts to the PAN/DMF casting solution results in membranes with higher rejection for various solutes (BSA, lysozyme, PEG-9000) and with relatively high flux. In

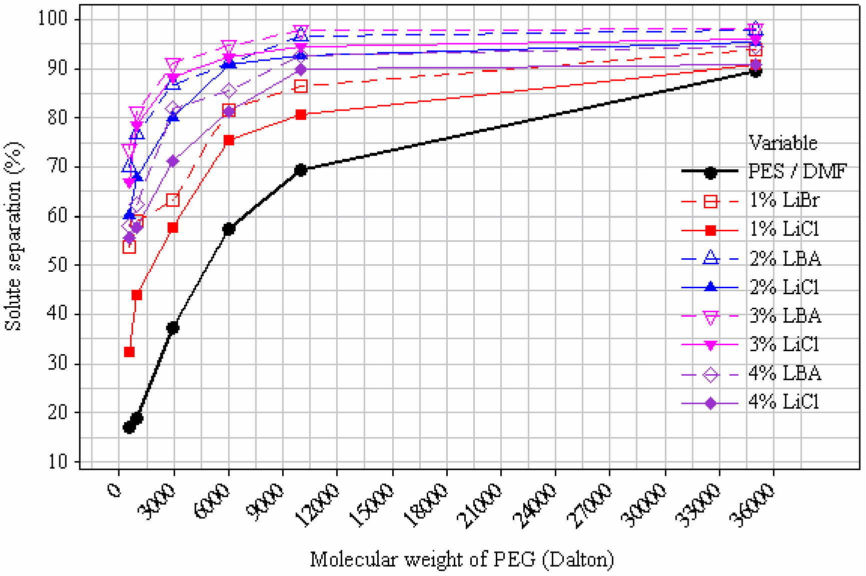


Figure 4.7: Solute separation of PES/DMF with various concentration of LiBr (---) and LiCl (—) Membranes

addition, the low viscosity solution of LiBr produced promotes instantaneous demixing to occur during the solvent exchange process. The LiBr probably interacts with PES and act as a charged pendant group for the polymer. Similar findings Botvay *et al.* (1999) have been reported during preparation of brominated polyethersulfone.

4.4 Membrane Morphology

The membrane morphology is strongly affected by the amount of nonsolvent additives. Botvay *et al.* (1998) has reported that appropriate amount of nonsolvent salts additives enhanced the formation of macrovoids (finger-like pores) while too much nonsolvent suppressed their formation (Bottino *et al.*, 1991; Lai *et al.*, 1996; Pinnau and Koros, 1993 and Smolders *et al.*, 1992). For the microwave synthesized hollow fiber membranes discussed in this paper, additives such as LiBr and LiCl can successfully increase the PES membrane hydrophilic properties. In fact, not only the hydrophilicity but also the membrane morphology is influenced by the addition of lithium halides. Figure 4.8 shows the cross-sectional morphologies of membranes

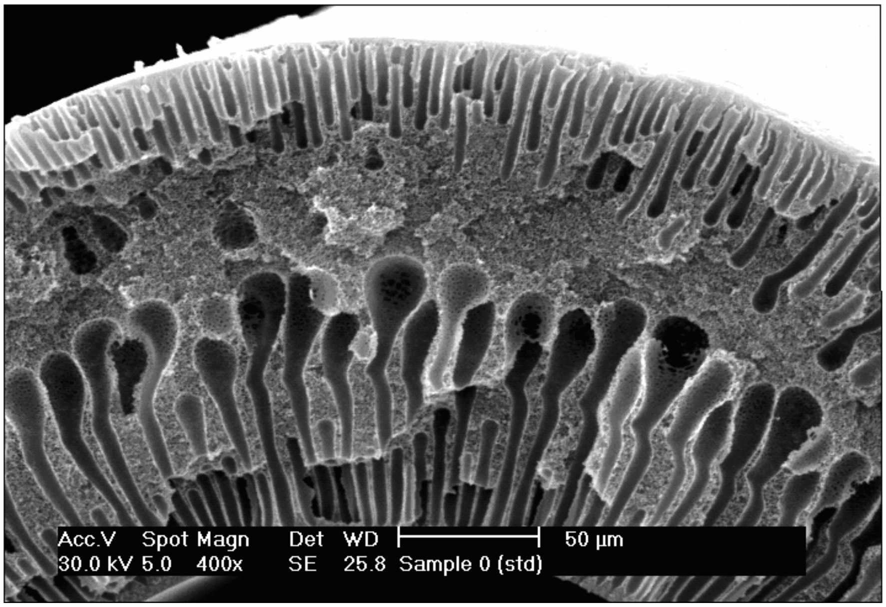


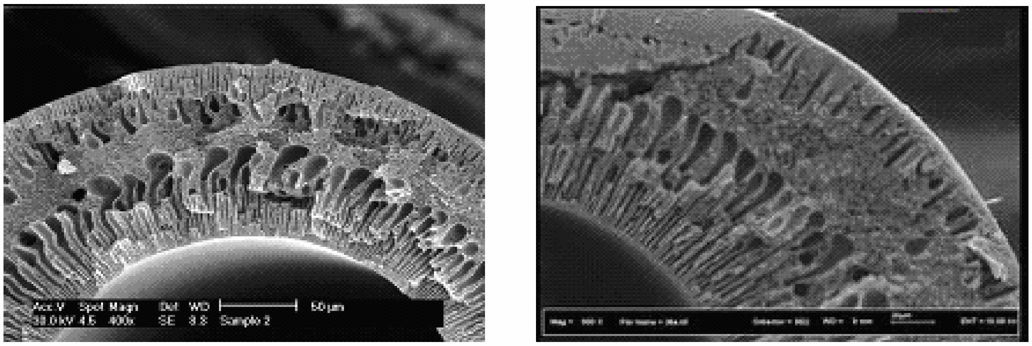
Figure 4.8: SEM pictures of the PES/DMF hollow fiber membranes

prepared PES/DMF solution without any additive. The prepared membranes exhibited the typical asymmetric structure. It is obvious that membrane without lithium halide has a dense sponge like structure pitted between the two layers of finger like structure and thick asymmetric skin layer.

4.4.1 Influence of LiBr and LiCl on Membrane Morphology

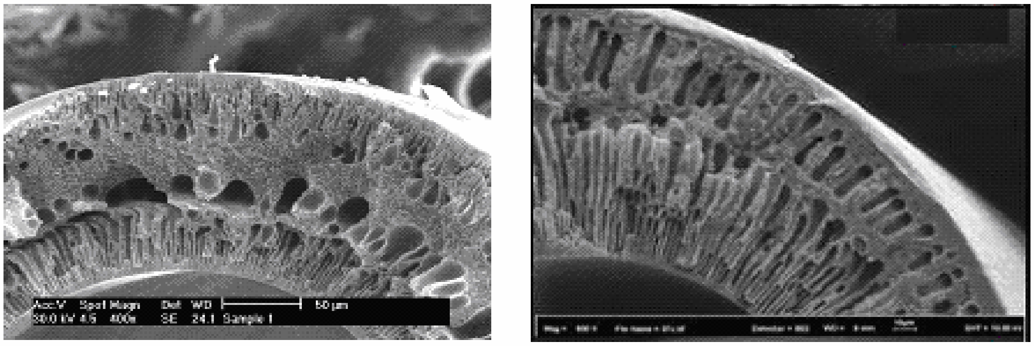
Figure 4.9 (a-d) shows the SEM images of the membranes prepared containing LiBr additive. Images indicate the presence of two dense layers both on the bore side and on the shell side of the hollow fiber. It is also interesting to note that there is a boundary between the region of small finger-like voids and that of moderate finger-like voids near the shell side surface of the hollow fiber. This is considered to be the boundary where the flows of the gelation media by diffusion from the bore side and from the shell side meet.

As the amount of LiBr increases, the dense spongy boundary region is slowly replaced by more porous macrovoids. At 3 wt% LiBr, the porous macrovoids totally replaced the dense spongy structure and the asymmetric skin layer becomes very thin



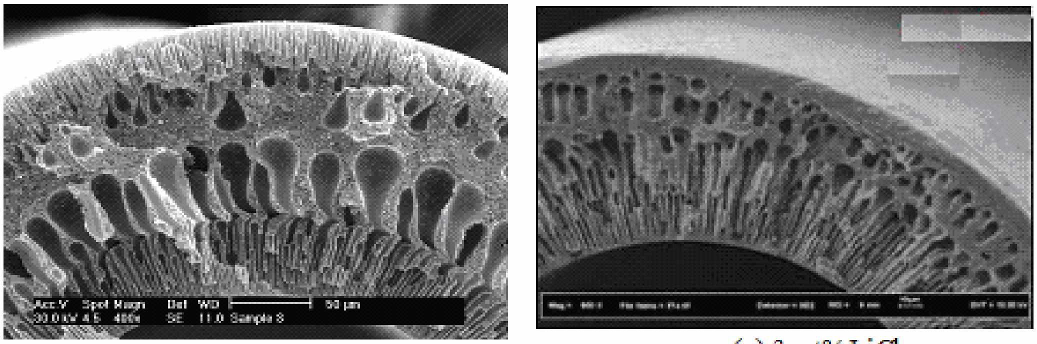
(a) 1 wt% LiBr

(e) 1 wt% LiCl



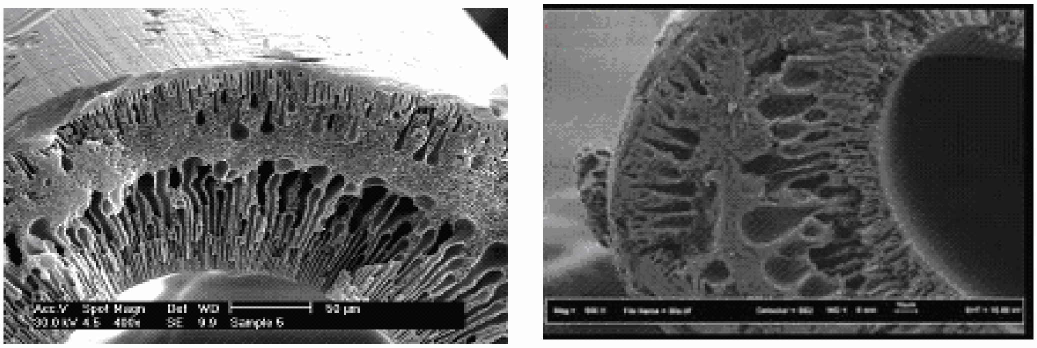
(b) 2 wt% LiBr

(f) 2 wt% LiCl



(c) 3 wt% LiBr

(g) 3 wt% LiCl



(d) 4 wt% LiBr

(h) 4 wt% LiCl

Figure 4.9: Cross-sectional morphologies of hollow fiber membranes; from PES/DMF with various concentrations of LiBr and LiCl.

until its hardly visible. Apparently such morphology seems to increase flux rates and improve the separation efficiency.

The presence of LiBr has brought the solution closer to the cloud point and this case instant mixing to occur and thus promote rapid exchange between water and solvent. Such rapid solvent exchange promotes the formation of macrovoids and results in the formation of the thin layer. Figure 4.9 (c) also indicates that more space is occupied by the finger-like voids and the front of the finger advances more towards the shell side surface when the LiBr content is at 3 wt% in the casting solution. Wang *et al.* (2000a) also reported similar results, where it was revealed that the morphology and transport properties of membranes were much controlled by the solution viscosity and movement during phase inversion. The advantage of this novel process is to control the membrane structure, from dense to porous one, including selective skin formation simply through the chemical gelation by MW irradiation of solution prior to the spinning process and immersion into the coagulant medium.

Figure 4.9 (e-h) denotes the SEM images of the cross sections of LiCl hollow fibers prepared under the same conditions of LiBr. For the PES/DMF/LiCl membranes, a thick asymmetric skin is observed and macrovoids formation mostly occurs at 4 wt% LiCl. This probably explains for their low permeation and separation rates compared to LiBr. The morphology results agree with cloud points results whereby, when the polymer solutions are very close to the cloud points instantaneous demixing tend to occur and thus macrovoids formation is promoted. In the case of LiBr, the polymer closest to the binodal region occurred at 3 wt% concentration whilst for the LiCl at 4 wt% concentration

For LiCl, the thick asymmetric layer and very fine finger like structure is attributed to the slow solvent-nonsolvent exchange caused by partial evaporation of solvent when the fibers pass the air gap, during which period the local polymer concentration on the external surface increases. As illustrated in Figure 4.5, unlike LiBr, LiCl does not bring the solution too close to the cloud point except when its concentration is at 1 wt%. Thus delay demixing seems to have occurred. Lin *et al.* (2003) has also reported same results in PVDF/LiCl gas separation membranes.

4.5 Effect of Microwave Post-Treatment on LiBr Membranes Performance

4.5.1 Effect of Microwave Post-Treatment on PWP and PR

Figure 4.10, show the effect of the post treatment and post treatment methods such as microwave and thermal annealing in water on the PWP of PES/DMF/LiBr membranes for various concentration of LiBr. Results revealed the PES membranes without annealing show extremely low PWP values. However, membranes without additives but post treated using either the microwave and thermal annealing technique showed better pure water permeation flux values of 58 $Lm^{-2}hr^{-1}$ and 49.63 $Lm^{-2}hr^{-1}$ respectively. It is observed that the flux increases as the LiBr concentration increases from 2 wt% to 3 wt% and the highest pure water permeation rate is achieved at 3 wt% LiBr concentration for both post treated techniques. The pure water permeation rates and the permeation rates of the microwave post-treated polyethersulfone hollow fiber membranes exhibit higher permeation rates compared to the thermal annealing post treatment membranes and this is clearly shown in Figure 4.10 and Figure 4.11. Highest PWP rate of approximately 222.1 ($Lm^{-2}hr^{-1}$) is obtained with the 3 wt% LiBr additive post treated by the microwave method which

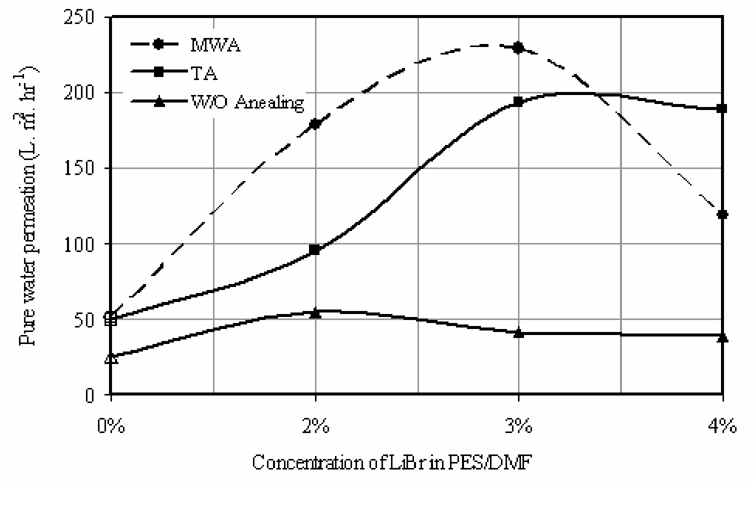


Figure 4.10: Pure water permeation of PES/LiBr UF hollow fiber membranes post-treated with microwave and traditional method. O and Δ are showing to PES with out additive

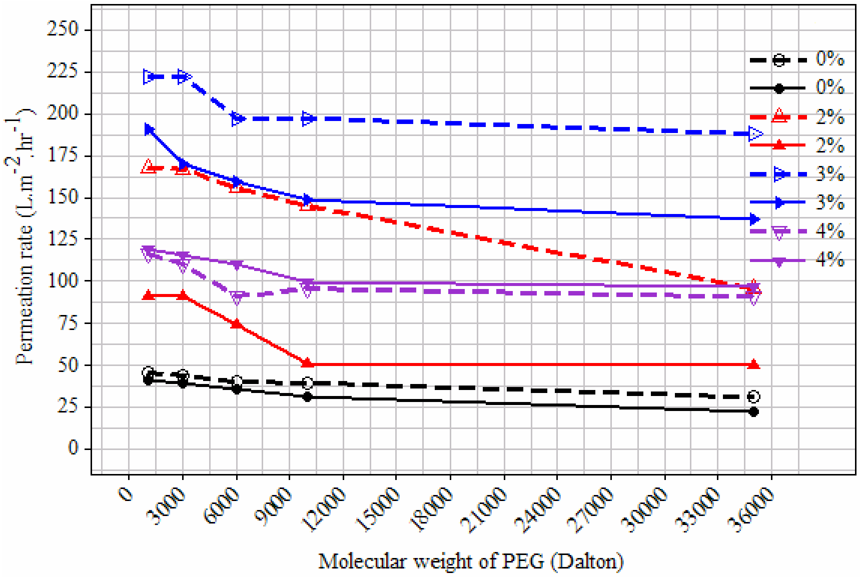


Figure 4.11: Permeation rates of PES/LiBr UF hollow fiber membranes post-treated with microwave (- - -) and traditional method. (—), O and ● are PES without additive

is 23% higher than the thermal annealed post treated membranes. A similar trend was observed for the permeation rates when using various molecular weight PEG (1000-35000 Dalton) solutions as the feed solution and this is clearly shown in Figure 4.11. Higher permeation rates are observed for microwave treated membranes.

Figure 4.12 shows the rejection rate for the membranes post treated using the microwave technique are slightly higher; with MWCO profiles are slightly lower than those treated using the thermal annealing method. The MWCO for the microwave post treated PES membranes at 90% rejection rates for the 3 wt% LiBr is 2.63 Dalton with permeation rates of 222.16 ($Lm^{-2}hr^{-1}$).

Although LiBr can decrease the pore size of the PES membrane, the post-treatment is desired to shrink the pore size even further. Among all the amorphous polymers, PES has the highest glass transition temperature of about 230 ^{0}C and also contains an abundance of polar sulfonyl (SO_2) side groups. This means that with microwave post treatment at medium low pulse, the polar sulfonyl (SO_2) side groups which have low dielectric loss and high heat penetration depth (Nilsson, 1990) are hindered sterically. Due to this hindrance, the dipole repulsed each other and thus

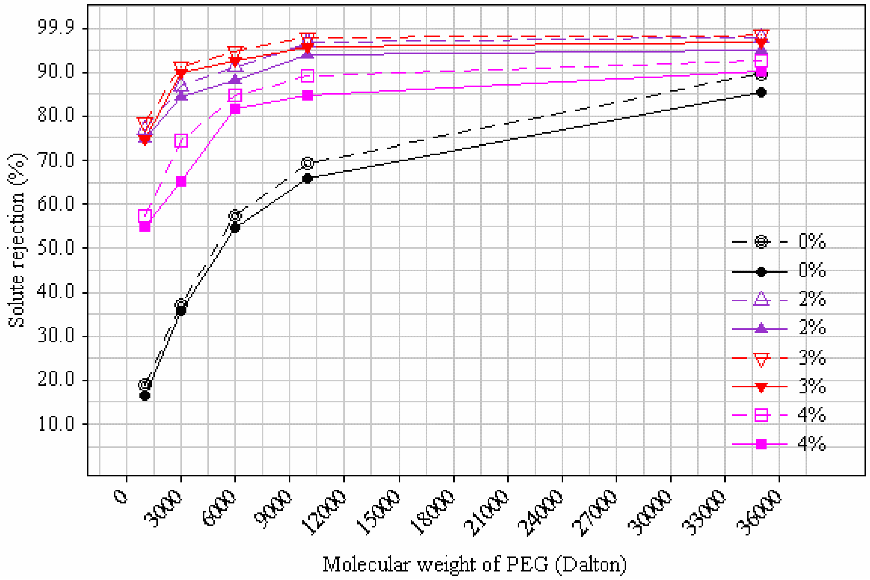


Figure 4.12: Solute rejection of PES/DMF/LiBr UF hollow fiber membranes post-treated with microwave (- - -) and traditional method (—), O and ● are PES with out additive

generates heat. This makes the molecule rod-like and therefore PES molecules can fit into a fairly regular crystalline structure. There is also the possibility that under microwave irradiation, the water molecules in the water bath vibrates rapidly and absorbed energy into heat rapidly and thus results in very rapid diffusion of excess solvents from the membrane.

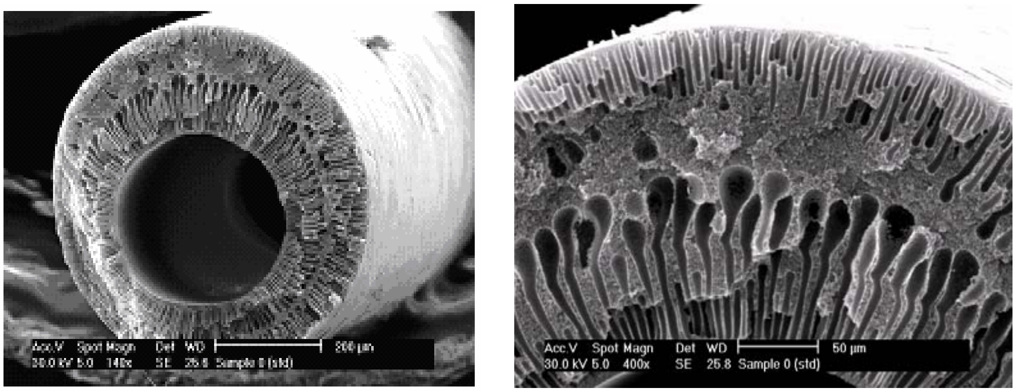
This probably altered the surface polymer concentration and caused greater surface modification and better wettability of the membranes. In addition such solvent transport phenomena may result in the stereo-regular polar PES polymers to rearrange and pack themselves in a more crystalline and structured manner. All these phenomena could contribute to the enhanced rejection rates and also increased permeation rates about 23% higher than the ones prepared using the thermal annealing method. In the thermal annealing process, the rate of solvent diffusion occurring is probably much slower and less compared to the microwave method thus contributing to the much reduced surface modification.

4.5.2 Effect of Microwave Post-Treatment on Membranes Morphology

The SEM photographs of hollow fiber PES ultrafiltration membrane without LiBr not post treatment are shown in Figure 4.13. It is obvious that membranes without LiBr has sponge like structure pitted between the two layers of finger like structure as shown in Figure 4.13 (a) and (b). When LiBr is added, the sponge like structure layer in the middle tend to reduce but the finger like structure elongates and extends through the sponge like structure as shown in Figure 4.14.

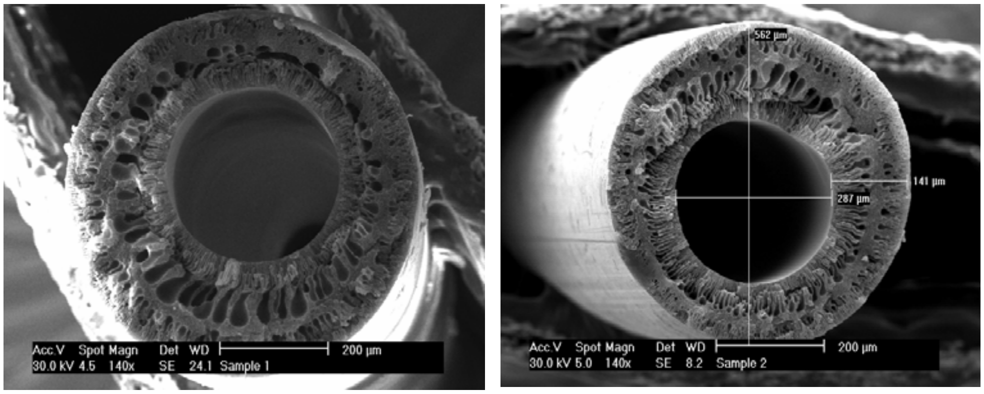
Such membrane morphology changes are very much related to the viscosity of the solutions. When an amount of LiBr is increased, the viscosity also increases as reported in chapter 4. Such high viscosity solutions hinder the diffusional exchange rate of solvent (DMF) and nonsolvent (water) in the sublayer, which makes the precipitation rate of sublayer become slower. Such rapid penetration of non solvent at the sublayer cause the formation of large macrovoids that almost penetrates the middle spongy layer as observed in Figure 4.14 (a-c) and Figure 4.14 (d-f). Such morphological change improved the flux rates of the membranes.

We would expect that such macrovoid formation would no doubt increase the flux but will decrease the rejection rate. However in this particular case this did not occur because of the effective post treatment performed. In fact the microwave post treatment method produced both membranes which have both high rejection rates

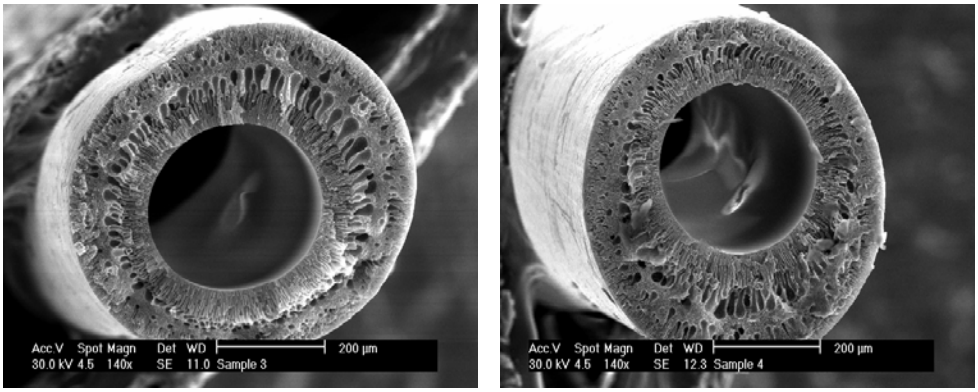


(a) (b)

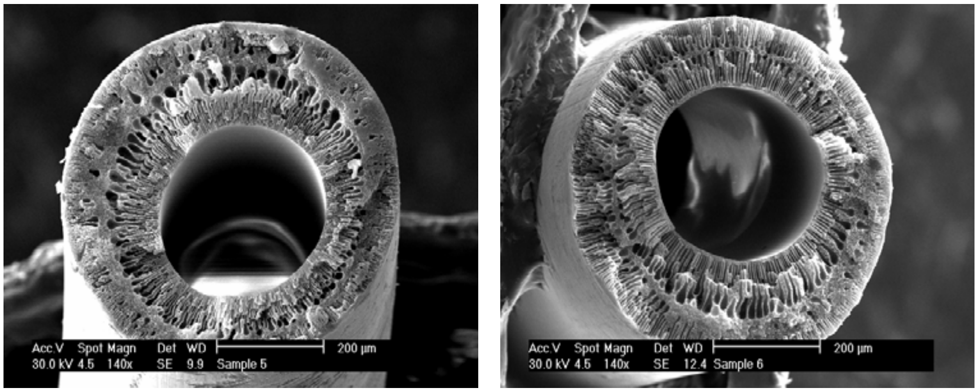
Figure 4.13: PES membranes without LiBr and not post treated (a) full cross section (b) segment of cross section.



(a) 2 wt% LiBr (d) 2 wt% LiBr



(b) 3 wt% LiBr (e) 3 wt% LiBr



(c) 4 wt% LiBr (f) 4 wt% LiBr

Figure 4.14: SEM morphologies of post treated hollow fiber membranes from PES/DMF/LiBr; (a-c) post treatment by MW and (d-f) post treatment by CEH

and high flux as shown earlier. Morphology differences are observed upon comparing microwave post treated and thermal annealed membranes as exhibited in Figure 4.14 (a-c) and Figure 4.14 (d-f). Respectively, such differences could be probably due to the solvent transport phenomena occurring when the membrane was post treated differently. Under microwave irradiation rapid diffusion of excess solvents from the membrane occurs and creates surface modification. Microwave heating can achieve very uniform and rapid heating through a self heating process that arises from the direct adsorption of microwave energy into the bulk of materials rather than being conducted from the outside. Unlike microwave post treatment, the rate of solvent diffusion still occurs during the thermal annealing process but at a much slower rate thus results in minor surface modification and this explains for the lower flux and rejection rates.

4.6 Conclusion

In summary the hollow fiber membranes spun from LiBr additive doped solutions are superior in terms of permeation and rejection rates compared to those membranes prepared from LiCl additives. The 3 wt% LiBr concentration apparently brings the solution very close to the cloud point and this facilitates liquid – liquid demixing, which tends to promote instantaneous precipitation to occur. Such phenomenon results in macrovoids formation and very thin asymmetric skin being formed which subsequently enhanced both the permeation and rejection rates of the hollow fiber membrane. Unlike LiBr, the presence of LiCl seem to promote delayed demixing at low concentrations of 1-3 wt% and thus explain for thick asymmetric skin layer, which subsequently produced membranes with lower permeation and separation rates.

Results also revealed that the new microwave post treatment method is capable of enhancing membrane performance in a very short time. The permeation rates of the microwave post treated membranes are much higher by at least 20% with MWCO of 2.63 kDa than the membranes post treated using the thermal annealing method. Thus in this study microwave irradiation was not only used for the polymer dissolution but also in the pretreatment process. In the microwave technique solvents are irradiated thus contributing to rapid dissolution of polymers during dope preparation without deteriorating the membrane performance. In addition, the microwaves result in rapid and uniform heat transfer which accelerates the molecules vibration thus speeds up diffusion of residual solvent during the microwave post treatment process. The microwave method has proven to be a rapid and an economical process for polymeric membrane production replacing the conventional heating process.

CHAPTER 5

GENERAL CONCLUSIONS AND RECOMMENDATIONS

In the last decade, ultrafiltration (UF) has been successfully developed from a useful laboratory tool to an industrial process. The costs of polymeric membrane filtration are for a large part determined by the cost of the membranes. So it is important to minimize the required polymeric membrane processing cost, operating with high performance membranes. In view of this fact, a new modified microwave system is designed and used in dissolving PES in single solvent and double solvent with various concentrations of monovalent lithium halides such as LiBr, LiCl and LiF additives. This study was a step forward to study the influence of the microwave technique on the overall performance of PES ultrafiltration membranes using lithium halide additives as compared to conventional technique. This was achieved through a detailed analysis of characterization and performance measurements of polymer solutions and UF membranes. It was found that the solubility, rheological and cloud point parameters provide useful information for characterizing MW and CEH assisted dope solutions.

The results shows that microwave closed heating system can reduce the dope preparation time which contributes to the high cost and polymer dissolution can be achieved in a very short time, as quick as 15 minutes for 1 wt% LiBr. In fact the 3 wt% LiBr takes almost 24 hrs to dissolve with CEH versus less than 1 hr for the MW technique. Results showed that the microwave closed heating system, provides an energy field that is very homogeneous for dope solution inside the modified cavity to achieve reproducible and uniform energy for about 510.27 J.sec^{-1} under mode of continuous stirrers, temperature differences of as much as 59.33% can be observed in identical vessels within the microwave cavity. Thus PES dissolution rate was increased by an order of magnitude over the conventional method, and the loss of organic solvents could be reduced due to the short exposure time of only about 12 minutes. While under traditional heating conditions, the PES dissolution time is at least 6 hrs under thermal heat exposure time of 90-95 ^{0}C with continuous stirring. This means the microwave irradiation can enhance PES dissolution rate by 30 times over the traditional heating method. Generally microwave is volumetric heating and microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces, and it is possible to achieve rapid and uniform heating of high temperature materials.

The performance evaluation of the membranes revealed the membranes prepared from the microwave casting solutions exhibits higher permeation and separation rates. Amongst the LiBr, LiCl and LiF additives membranes with the 3 wt% LiBr additive exhibits highest PWP, PR and separation rates. In addition all the membranes prepared using the MW technique exhibits higher performance in terms of PWP, PR and separation rates LiBr has a higher nucleophilic nature and thus under microwave radiation might have caused some chain scission to occur and thus enhanced the hydrophilic properties of the PES.

FTIR, contact angle and water uptake measurements provide evidence that the presence of LiBr and LiCl has improved the hydrophilic properties of the membranes. The emergence of peaks OH, C = O and C – O groups found in the MW prepared membranes suggest that chain scission may have occurred and thus indirectly enhanced the hydrophilic properties of the MW membranes. The results also indicate that LiCl interacts very strongly with DMF compared to LiBr and LiF due to its relative nucleophilicity under microwave radiation since nucleophilicity Cl^{-1}>Br^{-1} ions. This leads to the formation of LiCl –DMF complexes and hence, reduces in the solvation power of DMF for PES. The introduction of LiCl additive in the casting solution increases the membrane porosity thus produces high permeation rate membranes.

In the case of LiF the additive merely acts as a pore former at very low concentration. Increasing the concentration of LiF results in improvement of permeation rates but reduced the separation rates. The pore size obtained at 90% rejection rate are larger than membrane with LiBr and LiCl. The contact angle and water uptake measurement does not show significant changes which do not indicate change in hydrophilic properties. Overall results concluded that ultrafiltration membranes produced from series of lithium halides in terms of performance is, LiBr >LiCl >LiF.

5.2 Recommendation

This study has been examined the performance of microwave application for cost effective high performance membranes production. Further practical studies should be extensively performed to investigate and fully comprehend in a number of aspects of this work.

1) The universality of this modified microwave technique should be investigated. This microwave system can be applied for other commercial glassy polymers for membrane production such as polysulfone, cellulose and its derivatives, chitosan, polystyrene, polyethylene, polyimide, polyamide, polycarbonate, polypropylene, poly(methyl methacrylate), poly(viny1 alcohol), poly(viny1 chloride), poly(acry1ic acid), poly(ethy1ene oxide), polyacrylonitrile, poly(viny1 acetate), poly(viny1 butyral) as well as thermoplastic fluoropolymer such as polyvinylidene fluoride and poly tetrafluoro ethylene.
2) The influence of LiBr, LiCl and LiF on other polymeric materials such as CA, PSf, PAN, PA and PVDF could be investigated.

3) In this project, the feed solution used is PEG solution of various molecular weight. It would be useful to test the membranes with multicomponent separations or waste effluents from industries.
4) Hollow fibres should be strategically spun from other polymer systems.
5) Besides membrane preparation, this modified microwave system is applicable in textile and tanneries industries. It is also can be used in the petrochemical, petroleum refineries, palm oil industries, pharmaceutical, sugar industries as well as water distillation system.

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