# EFFECT OF BORE FLUID AND POST TREATMENT ON POLYETHERSULFONE ULTRAFILTRATION HOLLOW FIBER MEMBRANE

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## ABSTRACT

Polyesthersulfone (PES) hollow fiber membranes were prepared via the phase inversion process from dope solution containing PES, *n*-methylpyrrolidone (NMP), and polyvinylpyrrolidone (PVP). The effect of bore fluid flow rate (BFR) and bore fluid composition (BFC) on the morphology, permeability and separation performance of the spun UF membranes has been investigated. The influence of hypochlorite and microwave irradiation post treatment method was compared. Dry jet wet spinning process was the method chosen to fabricate the hollow fibers with an air gap of 10 cm. Water was used as external coagulant and the temperature was maintained at 14° Celsius. Solute separation experiments were conducted using polyethylene glycol. It was found that when the BFR is increased from 1.0 ml/min to 3.5 ml/min, the pure water permeation fluxes (PWP) increased from 0.14 L/ ($m^2$.h.bar) to 1.29 L/ ($m^2$.h.bar). The rejection rate of PEG decreased when BFR increased for all PEG solutions respectively. Characteristics of membranes using transport data revealed that the pore size of UF membranes increases as BFR increases. Experimental results also illustrated that PWP flux of the PES hollow fibers membranes spun with different percentage of NMP in its bore fluid slowly increases as the content increased from 20% NMP to 60% NMP but its rejection rate is decreased. The increasing solvent content in the bore fluid reduced the water activity and hence promoted the delayed demixing process during the membrane formation. Experimental results also revealed that the microwave post treatment produced membranes with better separation performance (approximately 10% higher) with smaller pore diameters in comparison to those post-treated with hypochlorite.

# ABSTRAK

Membran gentian geronggang polietersulfon (PES) disediakan daripada larutan dop yang mengandungi PES, *n* –metilpirolidon (NMP) dan polivinilpirolidon (PVP) melalui kaedah fasa balikan. Kesan kadar alir cecair rongga (BFR) dan komposisi cecair rongga (BFC) ke atas morfologi, kebolehtelapan dan prestasi pemisahan membrane ultrapenurasan (UF) yang dihasilkan telah dikaji. Perbandingan dibuat di antara pengaruh kaedah pasca rawatan lazim hipoklorit dengan kaedah baru penyinaran gelombang mikro. Ujikaji pemisahan bahan larut dijalankan dengan menggunakan polietilina glikol. Kami mendapati bahawa apabila kadar pengaliran cecair rongga bertambah dari 1 ml/min ke 3.5 ml/min, kadar penelapan air tulen (PWP) turut bertambah dari 0.14 L/ ($m^2$.h.bar) ke 1.29 L/ ($m^2$.h.bar). Kadar penolakan PEG untuk semua larutan PEG menurun apabila BFR meningkat. Sifat- sifat membran yang digambarkan dengan data pengangkutan mendedahkan bahawa saiz liang membran ultrapenurasan bertambah apabila BFR meningkat. Keputusan ujikaji turut menerangkan bahawa kadar alir air tulin (PWP) membran gentian geronggang polietersulfon yang dihasilkan pada peratusan kandungan NMP yang berbeza dalam cecair rongganya meningkat secara perlahan-lahan apabila kandungannya bertambah dari 20% NMP ke 60% NMP. Walau bagaimanapun, kadar penolakannya telah menurun. Peningkatan kandungan pelarut di dalam cecair rongga mengurangkan aktiviti air. Justeru itu menggalakkan proses nyahcampuran terlewat semasa formasi membran. Keputusan eksperimen turut menunjukkan bahawa rawatan pasca gelombang mikro menghasilkan membran dengan prestasi pemisahan yang lebih baik (lebih kurang 10% lebih tinggi) dan diameter liang yang lebih kecil berbanding dengan membran yang dirawat dengan hipoklorit.

# TABLE OF CONTENT

# CHAPTER 1

# RESEARCH BACKGROUND

## 1.1 Overview

Membrane technology is a rapidly emerging technology since the phase inversion method was first reported by Loeb and Sourirajan in the early sixties (Mulder, 1996). Many studies had been carried out for better understanding of the phenomena involved in the phase inversion process since. Nowadays hollow fiber configuration is the favorite choice for modules in membrane separation. In comparison to flat sheet membranes, hollow fiber membranes exhibit two major advantages. One of the advantages is hollow fibers have much larger ratio of membrane area to unit volume, and hence higher productivity per unit volume of membrane module. Another advantage of hollow fiber membranes is its self-supporting characteristic which enables this kind of membrane to be back- flushed for liquid separation.

Hollow fiber membranes are used in almost any kind of purification and separation industries from food, beverages, pharmaceutical, and hospitals to heavy metal industries. Its configuration is almost involved in all of the polymer membrane separations such as reverse osmosis, ultrafiltration, microfiltration and hemodialysis, and the key technology is development of proper hollow fiber membranes. In Malaysia, however, membrane technology has yet to release its full potential, due to the lack of technical knowledge and development in this technology. Most of the chemical industries in Malaysia still preferred the conventional separation units such as distillation columns and flash columns which involved the consumption of huge amount of energy and produced harmful side products. Though some began applying imported membrane technology in their industries, the membranes' popularity is still very limited as most small and medium sized industries are reluctant to use this technology due to its high installation and maintenances cost.

It has always been our hope that one day Malaysia will emerge as a developed country, which provides its residents a safe and stable living environment. Hence, the development of membrane technology in this country will be able to minimize the production of harmful waste from industries, reduce the operating cost for a variety of separation processes in industries, thus, increasing the total benefits of national's economy, and improve the quality of living environment. Therefore, it is very important for researchers in Malaysia to be equipped with appropriate skills and fundamental knowledge of this technology in order to produce locally fabricated membranes at lower price to serve the country.

## 1.2 Background of Problem

The main factors determining the membrane behavior in filtration process are the structure, chemical composition and operation conditions (Cheryan, 1986). Generally, polyethersulfone are widely used for the preparation of microfiltration and ultrafiltration membranes because of their favorable characteristics of wide temperature limits, wide pH tolerances, fairly good chlorine resistance, easy to fabricate membranes in a wide variety of configurations and modules. Wide range of pore sizes are available for both applications ranging from 10Å to 0.2 μm and good chemical resistance to aliphatic hydrocarbons, alcohols and acids (Cheryan, 1998).

Modification on the polyethersulfone membrane characteristic to improve the performance has been carried out and pure water flux from this membrane increased largely because of new hydrophilic characteristic (Dattatray and Ellen, 2002). Results concerning the preparation of polymeric membrane from polyethersulfone was presented to show the effect of coagulant temperature on water permeability characteristic of PES membrane (Spricigo *et al*.,2002).

In the preparation of polyethersulfone membranes, polymeric additives like polyvinylpyrrolidone (PVP) have been used to increase the casting solution viscosity and improve membrane performance. Several authors (Cabasso *et al*., 1976; Tweddle *et al*., 1983; Lafrenière *et al*., 1987; Miyano *et al*., 1990) have reported that by adding a second polymer, like PVP to solutions such as polyethersulfone, produces membrane with higher porosity, well- interconnected pores and improved surface properties of the membrane forming polymer.

Solvents with solubility parameters values similar to that of the membrane are found to have caused the greatest change in the membrane's flow resistance (Lencki and William, 1995). Research showed that as viscosity of the spinning solution increase, membrane thickness increases as well (Torrestiana *et al*., 1999). The study focused on the relationship between the presence of nonsolvent additives, the rheological behavior of spinning solutions and properties of the hollow fiber membrane using water , polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) as additives. Attempt was made by Marchese *et al*. (2003) to identify the fouling behavior of polyethersulfone ultrafiltration membrane made with different PVP.

The effect of dope extrusion speed (or shear rate within a spinneret) during hollow fiber membrane's spinning on its morphology, permeability and separation performance and the thermal and mechanical properties were studied. Water was used as the external coagulant and 86/ 14 NMP/ $H_2O$ as the bore fluid (Qin and Chung, 1999).

## 1.3 Problem Statement

From the literature review done, it was found that many researchers (Chaturvedi *et al*., 2001; Wang *et al*., 1993; Han and Nam, 2002) had been investigating methods to improve the performance of polyethersulfone ultrafiltration membrane using different approaches. However, little were focused on the effect of bore fluid on the performance of PES membrane in hollow fiber form. Santoso et al.(2006) investigated the effect of spinning speed on the irregularity of membrane's skin morphology. This work was done using mixture of polysulfone (PSU) and NMP as dope solution.

Qin and Chung (2004) work on exploring the effects of orientation relaxation and bore fluid chemistry on the performance of PES membrane. However, this work is done using membrane for gas separation purpose. In the later date, Zhou and Koros (2006) simulated the effect of pressure change in bore fluid on the performance of Matrimid hollow fiber membrane using Hagen- Poiseuille equation and discover that the bore pressure change affect the fluxes of highly permeable penetrants.

Ismail et al. (2006) had investigated the influence of bore fluid on PES UF hollow fiber membrane. However, these membranes were spun using wet spinning method. Work by Barth et al. (2002) has shown the effects of thermodynamic conditions on PES flat sheet membrane performance. There are also detailed results showing the effect of different parameters such as air gap height and concentration of additives in solution on membrane performance. Yet, there is no research work done on the effect of BFR and BFC on PES UF hollow fiber membrane spun using dry-jet wet spinning method.

The properties of hollow fiber membranes are known to be dependant on many factors. The parameters involved include the dope and bore fluid flow rate and composition, length of air gap, take-up speed, spinneret geometry and design, coagulant chemistries and temperature. Polymer like polyethersulfone has been receiving increasing attention from membranologists with the intention to heighten the membrane performance.

Therefore, the objective of this study is to determine the effect of bore fluid flow rate (BFR), bore fluid composition (BFC) and post-treatment method onto the performances of PES (fig. 1.1) ultrafiltration hollow fiber membranes under controlled and prefixed conditions. By gathering more information in these areas, it is hoped that this research can contribute to spinning locally fabricated hollow fiber membranes for ultrafiltration purposes, which plays an important role in local food processing industry, waste treatment technology etc.

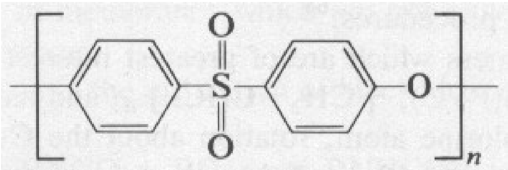

**Figure 1.1** Chemical structure of Polyethersulfone (PES)

## 1.4 Objective of the Study

This research continues the quest for practical membranes with high flux and high rejection rates. The aims of this study are as follows:

1. To synthesis, characterize and study the effect of different bore fluid flow rate (BFR) on the performance of PES UF hollow fiber membrane.
2. To study the effect of different bore fluid composition (BFC) on the performance of PES UF hollow fiber membrane.
3. To evaluate the efficiency of post treatment using traditional (Hypochlorite Method) and Microwave (MW) method for PES UF hollow fiber membrane.

## 1.5 Scope of the Study

This research consists of 3 different stages:

The initial stage of the research includes the preparation of PES UF hollow fiber membranes containing PES as polymer, *N*-methyl-2-pyrrolidone (NMP) as solvent and polyvinylpyrrolidone (PVP) as additive at different bore fluid flow rates (from 1.0 ml/min to 3.5 ml/min, with a 0.5 ml/min intervals). All experiments were conducted using cross flow ultrafiltration test. The fabricated membranes were tested for pure water permeation (PWP) and ultrafiltration experiments using polyethylene glycol (PEG) of various molecular weights (ranging from 200 to 35000 Daltons) as solutes.

The second stage of the study involved determining the optimum bore fluid flow rate for membrane separation and spinning PES UF hollow fiber membrane with the determined BFR with different BFC. These membranes were then characterized in terms of pure water permeation, solute separation and flux rates.

From these two stages, the best performing bore fluid (flow rate and composition) is identified and the effect of BFR and BFC on the membranes' performance, in terms of permeation rate and flux, is analyzed. Experiments for both stages were conducted at 4 bars, which is within the testing range for ultrafiltration tests.

The final stage of this research involved the study on the effect of microwave post treatment method on PES UF hollow fiber and the results are to be compared with the effect of traditional post treatment method. The mean pore size, molecular weight cut off and standard deviation for each membrane was characterized by solute transport data using Einstein-Stokes equation. The changes of surface and membrane morphology were also investigated using scanning electron microscope (SEM).

## 1.6 Methodology

In order to achieve the above objectives, the research methodology is outlined in the following manner:

### 1.6.1 Literature review

This was carried out to collect secondary data from library sources and seminars. This information is used to develop the framework for evaluating the solution composition to be used for the spinning of PES UF hollow fiber membrane. The technologies in spinning process to produce high selectivity membranes include modifying the surface morphology, cylindrically and quality, by varying the spinning conditions, the range of equipment to be used in characterization of membranes, testing rig and procedures for evaluating membrane performance and their availability's; general spinning constraint and problems associated when potting the membranes were all reviewed.

### 1.6.2 Spinning the hollow fiber membranes

Hollow fibers membranes are spun using spinning rig at prefixed conditions. Parameters such as temperature of coagulation baths, air gap length and dope composition that are not included in the scope of this study will be set according to information gathered during literature review.

### 1.6.3 Post Treatment

Two different types of post treatment will be done on the membranes before they were potted into modules. One is the conventional hypochlorite post treatment, while the other is the microwave irradiation post treatment. This step is meant to make comparison between these two post treatment methods and to determine the differences these methods brought upon the treated membranes.

### 1.6.4 Potting the membranes

The hollow fiber membranes will then be potted on bundles of about 30. This has to be carefully done so as not to damage the fibers as this could mean a useless separation result.

### 1.6.5 Ultrafiltration Tests

The fiber modules would then be tested on the UF unit to have its performance evaluated. The UF tests was carried out Primary UF parameters such as pure water permeation rate (PWP) and permeates rate (PR) at the specified pressure and temperature will be collected.

### 1.6.6 Solute Transport Data Analysis

The data collected from UF tests will be compiled into graphs for further analysis on MWCO and solute rejection rate. MWCO is defined as the molecular weight which is 90% rejected by the membrane (Mulder, 1996). These data is carefully calculated and plotted into meaningful graphs so that further information such as mean pore sizes, standard deviation, membrane diameter and wall thickness can be determined.

### 1.6.7 Surface Morphology Characterization

Surface morphology of the hollow fiber membranes will be investigated using scanning electron microscopy (SEM).

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