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Modeling of spinning process for efficient production of hollow fiber membranes used in wastewater treatment

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Abstract

Countries generally experience continuous growth in population, living standards and industrial development. These have resulted in an increase in water consumption. Any harmful discharge into the water supply system needs to be treated. Membrane separation technology is an effective technology for wastewater or water treatment. This study attempts to model the spinning process used for fabricating the hollow fiber membrane using the design of experiment methodology. Spinning factors investigated are the dope extrusion rate, air gap length, coagulation bath temperature, bore fluid ratio and post-treatment time whilst the response investigated is rejection. Among the common significant process factors identified are bore fluid ratio, dope extrusion rate, coagulation bath temperature and air gap length. Several 2-factor interactions are also significant. The regression model obtained can be subsequently used for determining the optimum spinning conditions. This study will ultimately enable the membrane fabricators to produce high-performance membranes that contribute towards the availability of a sustainable water supply system.

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Keywords: Spinning process; Wastewater treatment; Rejection; Design of experiments methodology; Membrane separation

1. Introduction

Water is central in each field related to the community because human activities are supported by the use of water. This shows the significance of its availability. Nevertheless, freshwater scarcity is a great issue which is captivating rising attention from many sectors. Freshwater scarcity is caused by the failure of the supply to satisfy the ever-increasing requirement. It is compelled by a number of changes; in the way that the growing population causes an increase in food, energy and water demands. Thus, increasing population numbers, intensive agricultural practices, urbanization and economic development will definitely continue to make water scarcity a worldwide concern for years to come.

As an important resource for life, sustainable development and good-condition ecosystems, water has been a very important agenda on the community's research and technological evolution programmes. Hence, membrane filtration technologies structure a promising avenue of study and innovation to give very good solutions for sufficient supply of water to fulfill human, environmental and industrial demands.

In the last thirty years, membrane filtration was not economically realistic, however with the advanced technological revolutions of new substances, procedures and targets, membrane technologies have been recognized as a very successful and commercially attractive choice for separation and purification systems [1]. Membrane technologies have been a better option because of the fact that these methods are the most economical separation technique since they possess low capital investment as well as low energy consumption and operating cost. They are also environmental friendly and yield superior product quality. With these benefits and rapid developments, membrane separation methods have turned around from a mere laboratory instrument to a world of commerce. In the current state of the art, many researchers are involved in developing, exploring and expanding high performance membranes. Generally, the membrane performance can be clarified in terms of rejection, R which is a measure of the relative

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permeation rates of dissimilar elements through the membrane. Thus, membrane with the highest *R* is necessary. The challenge of this study is to maximize the productivity of the membrane by enhancing the separation productivity. The production of good asymmetric membranes involves many important factors that must be controlled properly and the spinning conditions play an important role on the membrane performance and this aspect has received great attention from membranologist in developing ultrafiltration hollow fiber membranes [2,3,4].

Modeling approaches for the prediction of *R* can be divided into three classes which are experimental models, analytical models and Artificial Intelligence (AI)-based models. Currently, statistical regression based models have become the chosen method and these are employed by most researchers to create a model for the spinning process. The potential of statistical regression technique as a better modeling technique for *R* prediction was stated by Ravikumar et al. where the regression model presented a high accuracy rate for predicting *R* in the spinning process [5]. Khayet et al. claimed that the statistical regression model helps to produce slightly more precise *R* prediction values compared to the conventional model [6]. Since the statistical regression method is good in handling the spinning modeling problem, this paper aims to show how a regression model for the prediction of *R* can be developed based on systematic design of experiment (DOE) method. This study focuses on a more comprehensive set of operating conditions similar to those in membrane filtration plants. The experiments were operated using a hollow fiber membrane module under a constant flux mode with periodic backwashing. Synthetic water (cutting oil wastewater), simulating the characteristics of surface water, was used as feed water to minimize the impact of water quality variations. The collected spinning parameters and experimental outcomes were employed as a training database for the regression model.

The results of the proposed model can be used to give a good prediction of the spinning process during membrane fabrication. Furthermore, it helps to provide an efficient spinning process which makes the fabrication of membranes to become more effective and productive, requiring low capital investment, energy consumption and operating cost. Indirectly, this research will help manufacturers to produce high-performance membranes which can contribute to provide fresh water resources and good-quality treated water in regions around the world.

Nomenclature

DER	dope extrusion rate
AGL	air gap length
CBT	coagulation bath temperature
BFR	bore fluid ratio
PT	post-treatment time
R	rejection
PES	polyethersulfone

2. Spinning process

2.1. Overview of spinning process

Nowadays, the development of asymmetric hollow fiber membranes has gained more interest. The fabrication of an asymmetric hollow fiber membrane with a superior performance is a crucial aspect. There are several factors controlling the membrane performance. According to Rahimpour et al., the membrane performance is quite complicated due to the uncertain relationship between membrane performance and several factors [7]. However, one of the important factors which strongly affects the membrane performance is the spinning condition and there are various parameters involved in the spinning process [2,8]. Dry/wet spinning process is a quite complex process because it involves many process parameters which influence both the membrane structures and properties [9].

Most of the spinning condition parameters studied such as polymer concentration, solubility parameter and coagulation rate are dependent on the temperature factor. Spinning temperature is an important variable which determines the overall membrane performance. During membrane preparation, a number of steps are carried out either simultaneously or in succession and regulating the temperature at each step is essential. These is because temperature influences the viscosity of spinning solutions, thermodynamic interaction parameters among polymer, solvent and non-solvent, and the diffusion rate of polymer solution and non-solvent coagulant. Thus, one of the important spinning parameter is coagulation bath temperature (CBT) [10]. Besides this, the impacts of rheological states on the permeation properties for hollow fiber membranes have been widely explored in order to produce high quality membranes with good performance. The basic studies have emphasized on the effect of the dope extrusion rate (DER) within the spinneret since the dope rheology is one of the significant factor in the process of hollow fiber membrane formation [11,12]. During the hollow fiber spinning process, when the polymer solution is passed through a spinneret with a tube fixed in an orifice, DER will be produced within the thin annular. Thus, the DER possibly affects the outer skin fabrication of membranes and the structure of final membranes [13]. Air gap length (AGL) is the distance from the end of the spinneret to the water surface in the coagulation bath. According to Kim et al., the variation in the AGL affects the time when the being-spun HF membrane is entering the water. It causes the reshaping of the structure of the hollow fiber membranes and furthermore affects its performance [9]. It is evident that the bore fluid ratio (BFR) plays an important role in fabricating good hollow fiber membranes. It controls not only the open lumen formation but also affects the membrane structure and separation performance [14]. Besides, post-treatment (PT) process is done for solvent exchange process to clean off any solvent residue. This is because the drying water-wet membranes will cause significant changes in the pore structure. Wang et al. discussed the two experimental techniques used in PT. First, the wet fibers were submerged in an alcohol for 5 min at room temperature before the fibers were dried under ambient condition. In the second technique, the fibers after submerged in the alcohol for 5min were moved to an n-pentane mixture for 2 min before drying at ambient condition. The gas separation characteristics for hollow fiber membranes improved only slightly after the PT [15].

There are so many factors to control in the spinning process to produce high performance membranes and numerous efforts have been carried out to study and understand the spinning process [16,17]. Based on this review, the common spinning parameters varied in membrane fabrication. The importance of the DER, AGL, CBT, BFR and PT has been well recognized to affect the membrane performance especially *R* since many researchers have explored the effects of this five parameters in their study. As a conclusion, DER, AGL, CBT, BFR and PT were selected as spinning parameters to be controlled in this study.

2.2 Membrane characterization

To characterize the resulting membrane and its performance, the most significant characteristic is obviously the membrane productivity, which is separation (rejection of various feed components). In liquid separation for ultrafiltration process, generally the membrane selectivity for a given solute is indicated by the percentage of *R*. Fundamentally, there are two interpretations of *R*. First is the observed *R* or also called apparent *R* and second is the actual *R* and sometimes known as true *R*. The straightforward step to show the solute *R* attribute of hollow fiber membranes is through observed/apparent *R* defined as:

$$\text{Rejection, } R = \left[\frac{C_f - C_p}{C_f}\right] \times 100\% = \left[1 - \frac{C_p}{C_f}\right] \times 100\% \quad (1)$$

where C_p and C_f stand for the solute concentration of permeate phase and feed phase respectively. Generally, the *R* of the solute relies on the size and shape (linear or spherical, flexible or rigid) arrangement of the solute relative to the pore size of the membrane. It can also be affected by chemical features of the solution as well as the interaction between the membrane and solute such as adsorption. Solute *R* normally decreases with the increasing temperature; even so, *R* can remain virtually constant over a broad temperature range for some membranes and solutes [18].

By looking at previous studies, it is found that the application of regression as a rejection prediction model in polyethersulfone (PES) ultrafiltration hollow fiber membrane fabrication involving DER, AGL, CBT, BFR and PT parameters is still not given consideration by researchers. This study is interested in observing the effect of these spinning conditions in influencing the *R* result.

3. Experimental procedure

3.1. Materials and hollow fiber membranes spinning

The PES ultrafiltration hollow fiber membranes are fabricated in spinning equipment using the dry/wet phase inversion technique. They are produced using a dope solution comprising 15.25% PES concentration, 66.43% 1-methyl-2-pyrrolidone (NMP), 14.3% polyethylene glycol (PEG) and 4.02% water with a spinneret (spinneret dimensions: o.d. $1100\mu m$ and i.d. $550\mu m$).

3.2. Characterization of asymmetric hollow fiber membranes

In preparation of the modules, the hollow fiber membranes were subsequently potted into bundles consisting of 120 fibers of approximately 22 cm as shown in Fig. 1. This size of the bundles was chosen because the surface area would provide a representative average performance of a particular fiber spinning condition. In order to characterize a ultrafiltration hollow fiber membrane, the standard technique is to measure its performance in terms of *R*. The experiments were conducted in a cross flow filtration set-up. Since the outer surface of the fiber was the selective layer, the feed was pumped into the shell side of the module and the permeate came out from the lumen of the fiber. For each batch of hollow fibers, a total of 20 bundles of fibers were potted for testing 20 different spinning condition combinations. In this way, a test exhibiting the importance of the replication error in comparison to the model dependent error can be implemented.

A test rig was developed to test the hollow fiber modules. This test cell comprised a Hydra Cell pump, feed holding tank and the ultrafiltration hollow fiber module. A flow control valve was required to regulate the flow and a needle valve was adequate for this case study. The feed solution was supplied to the hollow fiber module by the pump, while the permeate (product) solution was discharged from the permeate (product) outlet which was open to the atmosphere.

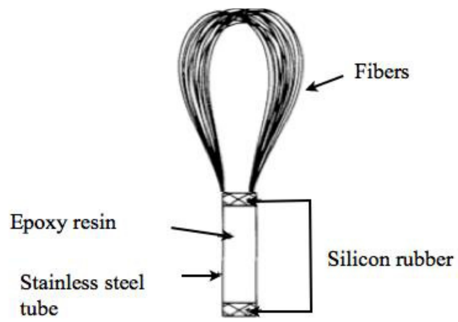

Fig. 1. Schematic diagram of hollow fiber module.

3.3. Experimental design

An experimental task was done to get the experimental data to examine the spinning conditions that contribute to the *R* performance of ultrafiltration hollow fiber membranes. Following this, a mathematical model for *R* was developed to describe the relationship between the independent spinning process variables (spinning conditions) and dependent variable (*R*) in the spinning process. The DOE method integrated with the regression technique was used in developing the *R* model.

Table 1. Setting of spinning condition values for real spinning process

Independent variables	Units	Level in coded form		
		-1	0	+1
Dope extrusion rate, (A)	$cm^3\ min^{-1}$	2	4	6
Air gap length, (B)	*cm*	0	1	2
Coagulation bath temperature, (C)	^oC	18	24	30
Bore fluid ratio (D) NMP/H_2O	%	0:100	35:65	70:30
Post-treatment time (Immerse in MeOH), (E)	hr	2	4	6

In this experiment, there were five controlled variables investigated including DER, AGL, CBT, BFR and PT. Two levels of each factor were selected for the experiment, and the units and notations are given in Table 1. These spinning conditions were chosen based on typical operating conditions of the system recommended for this operation and available literature. Center points experiment has two important roles in order to check the reproducibility and stability of results. First, it allows the experimenter to obtain an estimate of the experimental error. Second, if the sample mean is used to estimate the effect of a factor in the experiment, then center points permit the experimenter to obtain a more precise estimate of the effect. In this study, the order of the experiment has been generated randomly because Analysis of Variance (ANOVA) requires that the observations or errors be independently distributed random variables. The runs were conducted in a randomized manner to guard against systematic bias. By properly randomizing the experiment, the effects of extraneous factors or confounding variables that may be present were averaged out. A confidence level of 95% $(\alpha = 0.05)$ was used throughout the analyses of the experimental results and Fisher's F-test verified the statistical significance of the model. To handle the experiment, 20 samples of data were collected based on a half fractional factorial experiment with design resolution V as well as 4 replications of center points. A total of 20 experiments were performed as illustrated in Table 2. Design Expert 6.0.5 software has been utilized for analyzing the data.

4. Results and discussion

The outcome of the experiment (which is *R*) is presented in Table 2. A normal probability plot of the effects of parameters on *R* is displayed in Fig. 2. The method used to discover the true influence that the parameters have on *R* performance, was the graphical approach. A fitting line is drawn through the effects that are close to zero, in this aspect, if the factors are not important, the points should be found close to the line. From Fig. 2, the main effects consist of dope extrusion rate, DER (A), air gap length, AGL (B), coagulation bath temperature, CBT (C) and bore fluid ratio, BFR (D) as well as several 2-factor interactions.

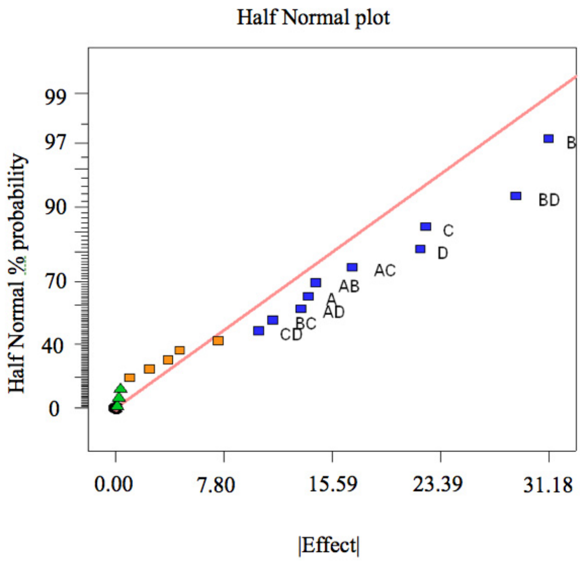

Fig. 2. Half normal probability plot of main effects for *R*.

Table 2. Experimental results for spinning experiments

		Setting values of spinning conditions					Response
Std. order	Run order	A	B	C	D	E	*R* (%)
1	8	2	0	18	0:100	6	34.7613
2	1	6	0	18	0:100	2	62.4005
3	10	2	2	18	0:100	2	41.5923
4	13	6	2	18	0:100	6	97.6651
5	7	2	0	30	0:100	2	99.9542
6	5	6	0	30	0:100	6	100.0000
7	20	2	2	30	0:100	6	71.0008
8	18	6	2	30	0:100	2	96.1881
9	2	2	0	18	70:30	2	8.9831
10	12	6	0	18	70:30	6	21.9967
11	15	2	2	18	70:30	6	65.9328
12	11	6	2	18	70:30	2	92.9976
13	16	2	0	30	70:30	6	52.8556
14	14	6	0	30	70:30	2	10.0765
15	6	2	2	30	70:30	2	85.1145
16	17	6	2	30	70:30	6	90.0005

17	9	4	1	24	35:65	4	55.0015
18	3	4	1	24	35:65	4	46.5146
19	4	4	1	24	35:65	4	47.7658
20	19	4	1	24	35:65	4	46.4241

Table 3. ANOVA table for response *R*

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	15563.95	10	1556.40	28.36	< 0.0001	sig.
A	771.87	1	771.87	14.06	0.0056	
B	3889.51	1	3889.51	70.87	< 0.0001	
C	1999.45	1	1999.45	36.43	0.0003	
D	1927.32	1	1927.32	35.12	0.0004	
AB	830.76	1	830.76	15.14	0.0046	
AC	1163.67	1	1163.67	21.20	0.0017	
AD	712.35	1	712.35	12.98	0.0070	
BC	513.35	1	513.35	9.35	0.0156	
BD	3329.38	1	3329.38	60.66	< 0.0001	
CD	426.29	1	426.29	7.77	0.0237	
Curvature	773.12	1	773.12	14.09	0.0056	sig.
Residual	439.06	8	54.88			
Lack of Fit	388.73	5	77.75	4.63	0.1185	not sig.
Pure Error	50.33	3	16.78			
Cor Total	16776.13	19				

Table 4. Model summary statistics for *R*

Std. Dev.	7.41	R-Squared	0.9726
Mean	61.36	Adj R-Squared	0.9383
C.V.	12.07	Pred R-Squared	0.7574
PRESS	4070.09	Adeq Precision	15.576

Table 3 shows the ANOVA table for *R*. The significance of the model is revealed according to the F-value of 28.36. There is only a 0.01% chance that a model's F-Value this large could occur due to noise. If the values of "Prob > F" are smaller than 0.05, the model terms will be significant; thus, A, B, C, D and interactions of AB, AC, AD, BC, BD and CD are considered as significant. The "Curvature F-value" of 14.09 implies that the curvature (as measured according to the difference between the average of the center points and the average of the factorial points) is significant in the design space. The curvature test became significant for *R*; it means that we have to use augment experiments to obtain second order model for this performance. The "Lack of Fit F-value" of 4.63 reveals that the lack of fit, related to the pure error, is not significant. There is a 11.85% chance that this "Lack of Fit F-value" could occur due to noise. Since we want to fit the model, Non-significant lack of fit is good.

The summary in Table 4 exhibits how well our model fits (or does not fit) the observed data. The R-squared value for the relationship between the set of independent variables and the *R* is 0.9726, which would be characterized as strong. It expresses the proportion of variance in *R* that is "explained" by the set of independent variables (DER, AGL, CBT, BFR and PT). For our data, this means that approximately 97.26% of the variance in *R* can be accounted for the set of independent variables.

Fig. 3 displays the normal plot of residuals for the model. The normal probability plot shows that the residuals are normally distributed along the normal probability line. It means that the error distribution is approximately normal for all series of data, which implies that the model is adequate. Fig. 4 exhibits the studentized residuals versus predicted values in which all data are shown to be in the range, and no abnormal trend exists

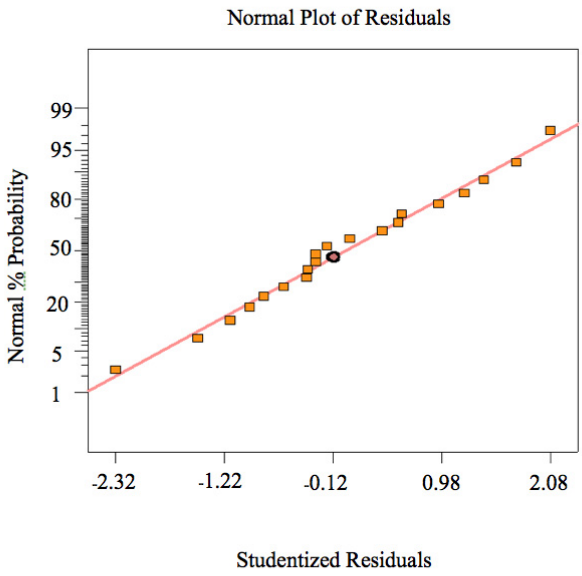

Fig. 3. Normal plot of residuals.

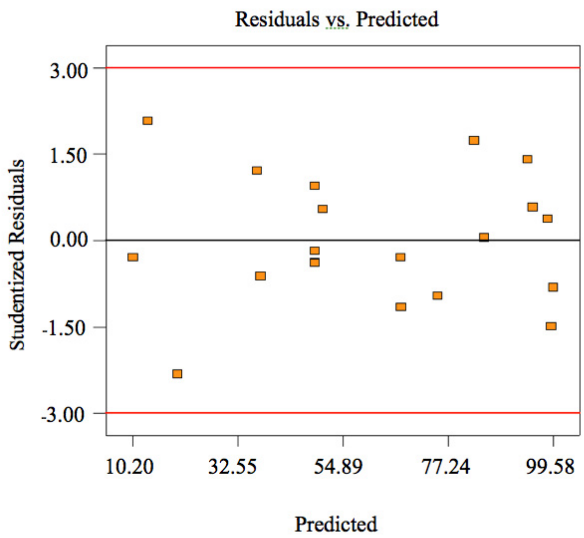

Fig. 4. Residuals versus predicted plot

The next result discussed is the development of our regression model. The final empirical equation R model in terms of actual factors which is obtained directly from the Design Expert software can be written as follows:

$$\begin{aligned}&\text{Rejection, } R = -94.79015 + 20.26251*\text{DER} + \\ &9.41201*\text{AGL} + 6.51018*\text{CBT} + 0.24546* \\ &\text{BFR} + 3.60286*\text{DER}*\text{AGL} - 0.71068*\text{DER} \\ &*\text{CBT} - 0.095321*\text{DER}*\text{BFR} - 0.94405*\text{AGL}*\text{CBT} \\ &+ 0.41215*\text{AGL}*\text{BFR} - 0.024579*\text{CBT}*\text{BFR}\end{aligned} \quad (2)$$

5. Conclusions

In this research, the effects of spinning parameters including dope extrusion rate, air gap length, coagulation bath temperature, bore fluid ratio and post-treatment time on rejection performance of PES ultrafiltration hollow fiber membranes were studied.

A half fractional factorial experiment was conducted and the experimental outputs displayed very clearly that dope extrusion rate, air gap length, coagulation bath temperature and bore fluid ratio and interaction of dope extrusion rate with air gap length, dope extrusion rate with coagulation bath temperature, dope extrusion rate with bore fluid rate, air gap length with coagulation bath temperature, air gap length with bore fluid ratio and coagulation bath temperature with bore fluid rate have a significant effect on the rejection performance of hollow fiber membranes. In addition, the best-fit regression model has been generated.

This study has proven the usefulness of the DOE method to develop a rejection prediction model. This model will be further verified by conducting the confirmatory tests. The empirical model can be subsequently utilized for predicting the optimum spinning conditions. Thus, enabling membrane fabrication to produce high-performance membranes that contribute towards the availability of a sustainable water supply system.

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References

[1] Wiesner MR, Chellam S. The promis. Environment science & technology/news. American Chemical Society 1999;33:360-366.

[2] Qin JJ, Chung TS, Cao C, Vora RH. Effect of temperature on intrinsic permeation properties of 6FDA-Durene/1,3-phenylenediamine (mPDA) compolyimide and fabrication of its hollow fiber membranes for CO_2/CH_4 separation. J Membr Sci 2005;250:95-103.

[3] Khayet M, Feng CY, Khulbe KC, Matsuura T. Preparation and characterization of polyvinylidene fluoride hollow fiber membranes for ultrafiltration. Polymer 2002;43:3879-3890.

[4] Khayet M. The effect of air gap length on internal and external morphology of hollow fiber membranes. Chem Eng Sci 2003;58:3091-3104.

[5] Ravikumar K, Pakshirajan K, Swaminathan T, Balu K. Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent. J Chem Eng 2005;105:131-138.

[6] Khayet M, Cojocaru C, Garcia-Payo C. Application of response surface methodology and experimental design in direct contact membrane distillation. Ind Eng Chem Res 2007;46:5673-5685.

[7] Rahimpour A, Madaeni SS, Mansourpanah Y. The effect of anionic, non-ionic and cationic surfactants ion morphology and performance of polyethersulfone ultrafiltration membranes for milk concentration. J Membr Sci 2007;296:110-121.

[8] Setiawan L, Wang R, Li K, Fane AG. Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer. J Membr Sci 2011;369:196-205.

[9] Kim JH, Park YI, Jegal J, Lee KH. The effects of spinning conditions on the structure formation and the dimension of the hollow fiber membranes and their relationship with the permeability in dry-wet spinning technology. J App Poly Sci 1995;57:1637-1644.

[10] Chung TS, Kafchinski ER. The effects of spinning conditions on asymmetric 6FDA/6FDAM polyimide hollow fibers for air separation. J App Poly Sci 1997;65:1555–1569.

[11] Qin J, Chung TS. Effect of dope flow rate on the morphology separation performance, thermal and mechanical properties of ultrafiltration hollow fibre membranes. J Membr Sci 1999;157:35-51.

[12] Chung TS, Qin JJ, Gu J. Effects of shear rate within the spinneret on morphology, separation performance and mechanical properties of ultrafiltration polyethersulfone hollow fiber membranes. Chem Eng Sci 2000;55:1077-1091.

[13] Qin JJ, Wang R, Chung TS. Investigation of shear rate stress effect within a spinneret on flux, separation and thermomechanical properties of hollow fiber ultrafiltration membranes. J Membr Sci 2000;175:197-213.

[14] Pesek SC, Koros, WJ. Aqueous quenched asymmetric polysulfon hollow fibers prepared by dry/wet phase separation. J Membr Sci 1994;88:1-19.

[15] Wang D, Li K, Teo WK. Highly permeable polyethersulfone hollow fiber gas separation membranes using water as non-solvent additive. J Membr Sci 2000;176:147-158.

[16] Agrawal AK, Bhalla R. Advances in the production of poly(lactic acid) fibers: A review, J Macromolecule Sci Poly Rev 2003;43:479–503.

[17] de Rovere A, Grady BP, Shambaugh RL. The influence of processing parameters on the properties of melt-spun polypropylene hollow fibers. J App Poly Sci 2002;83:1759–1772.

[18] Winston Ho WS, Sirkar KK. Part I and Part II in membrane handbook. New York: Van Nonstrand Reinhoid 1992;1-25.