THE EFFECT OF CURING TEMPERATURE ON THE PERFORMANCE OF THIN FILM COMPOSITE MEMBRANE

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Abstract. The effect of curing temperature on the performance of thin film composite membranes was studied using two different kinds of polymeric membrane supports, i.e. cellulose acetate and polysulfone. Aqueous phase solution was prepared by dissolving m-phenyldiamine, tetrabutylammonium bromide, sodium hydroxide and hydroquinone based on the composition in distilled water. Organic phase was prepared by dissolving trimesoyl chloride in n-hexane. Polymerization occurred in the organic phase by interfacial reaction of m-phenyldiamine with the presence of trimesoyl chloride to form polyesteramides. Curing temperatures ranging from 40° to 100° C were used in the air-circulated oven during the interfacial reaction process. The performances of the thin film composite membranes in terms of salt rejection and permeation rate were evaluated using the permeation cell. The results showed that cellulose acetate thin film composite membrane cured at 60°C gives the best rejection rate of 76% whilst polysulfone thin film composite membrane cured at 80°C gives the highest rejection rate of 80%.

Keywords: Thin film composite membrane, aqueous phase, organic phase, curing temperature

Abstrak. Kesan suhu rawatan pada prestasi membran komposit dikaji menggunakan dua jenis membran penyokong polimer iaitu selulosa asetat dan polisulfona. Larutan fasa akuas disediakan dengan melarutkan m-fenildiamina, tetrabutilammonium bromida, natrium hidroksida dan hidroquinon berdasarkan komposisi di dalam air suling. Larutan fasa organik disediakan dengan melarutkan trimesil klorida dalam n-heksana. Membran komposit disediakan dengan menggunakan kaedah pempolimeran antara muka. Pempolimeran berlaku dalam fasa organik melalui tindak balas antara muka antara m-fenildiamina, hidrokuinon dan trimesil klorida untuk menghasilkan rangkaian poliesteramida. Suhu rawatan di dalam julat 40°C hingga 100°C digunakan dalam oven semasa proses tindakbalas antara muka. Penilaian prestasi membran komposit terhadap kadar penyingkiran garam dan fluks dilakukan menggunakan sel penelapan ringkas. Hasil uji kaji menunjukkan membran komposit selulosa asetat dengan suhu rawatan 60°C menunjukkan kadar penyingkiran terbaik sebanyak 76% manakala membran komposit polisulfona dengan suhu rawatan 80°C memberikan kadar penyingkiran yang terbaik sebanyak 80%.

Kata kunci: Membran lapisan komposit, fasa organik, fasa akuas, suhu rawatan

1.0 INTRODUCTION

Two membrane structures are commercially available for reverse osmosis today which are asymmetric and thin-film composite. Asymmetric membranes can be

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made by casting a polymer-containing dope into a homogeneous layer by a single-step phase inversion method. The result is a dense surface skin on a porous sub-layer. The skin and the sub-layer have the same chemical composition. Thin-film composite (TFC) membranes, on the other hand, are made from a two-step procedures. First, a thick, porous support layer is created, and second, an ultra-thin barrier layer is coated on top of the support layer. Unlike asymmetric membranes, the skin and the sublayer usually have different chemical compositions [1].

The development of asymmetric membranes dates back to the early 1960s when Loeb and Sourirajan [2], working with a cellulose acetate (CA) membrane at University of California in Los Angeles (UCLA), noticed that the membrane had a rough and a smooth side. They found that when the rough side faced the feed, the rejection was low, but when the smooth side faced the feed, the rejection was high. This anisotropic property of the membrane led to the term "asymmetric" membrane. Recently, the asymmetric membranes are commercially available in the form of cellulose acetate, cellulose diacetate and triacetate grades or in blends of these grades. The asymmetric cellulose acetate membranes are resistant to chlorine in the feed up to 1 mgl^{-1}, but are subjected to hydrolysis at high pH. Blends of cellulose acetate and triacetate provide superior performance and higher rejection. Although asymmetric cellulose acetate technology predates other membrane types and remains relatively inexpensive to purchase and install, thin film composite membranes largely displace today's use of cellulose acetate.

The concept of composite reverse osmosis membranes is attributed to Francis [3], who was working under Office of Saline Water (U.S. Department of Interior) in 1964. The first composite membrane was prepared by float-casting an ultra-thin film of polymer on a water surface and then laminating it onto the Loeb and Sourirajan asymmetric cellulose acetate membrane microporous support layer [1].

The major advantage of thin-film composite (TFC) membranes is that each layer can be optimized independently. The support layer can be optimized for maximum strength and compression resistance and the ultra-thin barrier layer can be optimized for the desired solvent flux and solute rejection. Thus, TFC membranes generally can have higher salt rejection than asymmetric membranes. The TFC membranes can endure wider feed pH ranges, less susceptibility to microbiological attack, and better hydraulic stability than asymmetric membranes. However, they offer poor resistant to strong oxidant such as chlorine, resulting in chain deformation and depolymerization of the polymer [4, 5].

Until today, much research has been carried out to improve TFC membrane performance and most of these works have centered on either changing the structure of membrane monomer or coating conditions. The permeation properties of TFC membrane depend upon the material properties as well as the structural properties of the polymer forming the active layer. Cross-linked aromatic polyamide composite RO membranes showed high RO performance [6]. These membranes have higher

rupture strengths, higher salt rejections and comparatively higher water flux because of their fully aromatic network structure [7]. A more extensive study of model compound chlorine sensitivity was reported by Lowell *et al.*[8]. Their study found that ester linkages were generally chlorine resistant and Jayarani and Kulkarni confirmed this [9] when they developed composite membrane with the incorporation of ester linkages. The membrane named as composite poly(ester)amides showed higher chlorine tolerance compared to commercial composite polyamide membrane.

Various coating conditions have been carried out which led to the optimization of TFC membranes development and these included varying of concentration of reactants, reaction time, curing temperature and curing time [10]. The reaction time required for the formation of TFC membrane was found to fluctuate over a relatively wide range of 1 to 60 seconds [11]. Salt rejection and water flux of membrane did not change with reaction time longer than 1 minute [12].

The resultant composite membrane must be cured to remove any remaining solvent and reactants, and firmly affix the thin film membrane on the surface of the porous support. Curing time must be sufficient so as not to affect the desired characteristic of the TFC membrane and the porous backing support material. Excessive heat or curing time may affect the pore size of the backing material, thus resulting in a decrease of the desired flux rate of the membrane. Rao *et al.* [10] has observed that curing temperature influenced TFC membrane performance and found that as curing temperature increased, the rejection rate of dissolved salt increased.

Most of the research works done previously had studied the effect of curing temperature on the performances of TFC membranes with polysulfone as the porous support but using various other compositions of cross-linked material. Thus, this study investigates the possibility of using cellulose acetate as a micro porous support for the TFC membranes using new combination of cross-linked mixtures of acyl chlorides and polyamines, and compares its performance with polysulfone TFC membranes. The exact curing temperature is important for attaining the desired stability of thin composite membrane. This stability is important to give high pure water permeability, high product rate and high rejection rate. The mathematical model of membrane transport by Kimura-Sourirajan [13] was applied to evaluate the experimental results to predict pure water permeability constant (A), solute transport parameter ($DAM/k\delta$) and mass transfer coefficient (k). Values of A and $DAM/k\delta$ are useful in specifying a membrane. Additionally, k value is required to make use of basic transport equations to predict the membrane performance.

2.0 EXPERIMENTAL

2.1 Materials

Cellulose acetate (CA-398-3, Aldrich, USA) with an acetyl content of 39.8% and polysulfone (UDEL P-1700, USA) were used to prepare the support membrane.

Acetone (Merck, Germany) and formamide (BHD Laboratory Supplies, England) were used as a solvent for cellulose acetate and ethyl ether (BHD Laboratory Supplies, England) was used for pretreatment of cellulose acetate support membrane. Polyvinylpyrrolidone (Fluka, Switzerland) and n-methylpyrrolidone (Merck, Germany) were used as solvents for polysulfone. All chemicals were of analytical grade.

Polyesteramide was formed by interfacial reaction polymerisation between aqueous phase and organic phase. The aqueous phase was composed of 1,3-phenyldiamine (Fluka, Switzerland), hydroquinone (Fluka, Switzerland), tetrabutylammonium bromide (Fluka, Switzerland) and sodium hydroxide (Merck, Germany). For the organic phase, trimesoyl chloride (Merck, Germany) was dissolved in hexane.

2.2   Development of Microporous Support Membrane

Cellulose acetate casting solution was prepared by dissolving 25% cellulose acetate in 45% acetone and 30% formamide solvent [14]. Then, cellulose acetate support membrane was prepared by casting the cellulose acetate solution onto a clean glass plate using a casting knife with a thickness of 200 μm. Acetone was allowed to evaporate for 3 to 4 minutes in a cold box where the temperature was maintained between 0 to 10°C. Next, the membrane was immersed in an ice cold distilled water bath at 2 to 3°C together with the glass plate [15].

The polysulfone casting solution was prepared by dissolving 15% polysulfone and 18% polyvinylpyrrolidone in 67% n-methylpyrrolidone. The resultant polymer solution was poured onto a clean glass plate at room temperature and was casted on a glass plate using the casting knife. The transparent cast film of 200 μm thickness was converted to an opaque white layer through precipitation of the polysulfone. The thin film was detached from the surface of the glass after two minutes of immersion.

2.3   Pretreatment of Cellulose Acetate Microporous Support Membrane

The membranes were immersed in a water bath at room temperature and gradually heated from ambient temperature to 90°C in about 20 to 30 minutes. Next, the membranes were cooled drastically to below 60°C and allowed to undergo solvent exchange. The solvent exchange process is carried out so as to prevent film from collapsing during testing [14].

2.4   Fabrication of Thin Composite Membrane

The aqueous phase solution was prepared by dissolving 2.5% m-phenyldiamine (MPDA) and tetrabutylammonium bromide (TBAB) in the presence of sodium

hydroxide (NaOH) and hydroquinone (HQ) in distilled water [9]. Organic phase solution was prepared by dissolving trimesoyl chloride in n-hexane. The support membrane, both CA and Psf were taped to a glass plate and dipped in an aqueous solution for three minutes. Next, the membrane was allowed to dry at ambient temperature for about 10 minutes. Then, it was dipped into the hexane solution containing 0.15% trimesoyl chloride for 80 seconds, which resulted in the lamination of an ultra thin film of polyamide over the porous support surface. The resulting thin composite membrane was then subsequently cured in an air-circulation oven at temperatures ranging from 40 to 100°C and cured for about 5 minutes to attain the desired stability [10].

2.5   Membrane Performance Evaluation

The flat sheets composite membranes were evaluated for permeate flux and salt rejection using a permeation cell. Testing was done with NaCl solution of 1000 ppm concentration at a pressure of 20 bars. A circular membrane sample with a diameter of 2.2 cm was placed in the test cell. The effective membrane area was around 3.8 cm^2. The membrane was initially flushed using distilled water through the membrane. The salt solution was fed into the test cell. Nitrogen gas was used to provide pressure as the driving force to transport the salt solution through the membrane. The data for salt separation, pure water permeation rate (*PWP*) and product rate (*PR*) were collected to identify membrane performance. *PWP* and *PR* refer to pure water permeability and product rate for a given area at specified operating pressure respectively. Salt separation, R, is given as follows:

$$R = 1 - C_p/C_f \tag{1}$$

where C_f and C_p represent concentration in the feed and permeate, respectively.
The overall porosity of the membrane was measured by calculating the value of PWP constant A, which is defined as:

$$A = (PWP)/(M_W \times S \times P \times 3600) \tag{2}$$

Water flux, N_B, through membrane pores is given by:

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{3}$$

Solute flux, N_A, through membrane pores is given by:

$$N_A = (D_{AM}/k\delta)(c_2 X_{A2} - c_3 X_{A3}) \tag{4}$$

and since $X_{A3} = N_A/N_A + N_B$ and $N_B = N_A(1-X_{A3}/X_{A3})$

$$N_B = (D_{AM}/k\delta)(1 - X_{A3}/X_{A3})(c_2 X_{A2} - c_3 X_{A3}) \tag{5}$$

Using the film theory where $k = D_{AB}/1$[11], the water flux is expressed as follows:

$$N_B = c_1 k(1 - X_{A3}) \, ln \, [X_{A2} - X_{A3}/X_{A1} - X_{A3}) \tag{6}$$

2.6 Analytical Techniques

A standardized digital conductivity meter of type Hanna Instruments Model H18633 was used to measure the salt concentration in the feed and permeate to determine the membranes' rejection performance.

3.0 RESULTS AND DISCUSSION

The performances of the thin composite membranes at various curing temperatures are shown in Table 1. In order to ensure reproducibility of results, three membrane samples were tested for each temperature and the average values are tabulated in Table 1.

Table 1   Experimental data, PWP, PR and percentage salt separation at various curing temperature

Curing temp.($^\circ$C)		Cellulose acetate			Polysulfone		
		PWR ($l/m^2.hr$)	PR ($l/m^2.hr$)	% R	PWR ($l/m^2.hr$)	PR ($l/m^2.hr$)	% R
40	3.75	0.58	72.15	73.84	68.67	77.94	
60	2.28	0.21	76.00	71.87	66.42	78.51	
80	3.53	0.46	73.14	71.03	65.66	80.00	
100	3.47	0.35	73.78	75.41	70.19	76.36	

The results shown in Table 1 are clearly illustrated in Figures 1 and 2. It is interesting to observe that increasing curing temperature increases the flux rate and salt rejection but only to a certain limit. Figure 1 shows the rejection rate (R) of TFC membranes with cellulose acetate and polysulfone as the porous support. For cellulose acetate based membrane, the optimum curing temperature was found to be 60°C. Curing at temperatures above 60°C will not increase the performance of the membrane. These results can be explained in terms of the stability of the active layer when heated at specific curing temperature inside the air circulated oven. The stability of the thin active layer for cellulose acetate increased when curing temperature was increased up to 60°C. With increasing temperature, the polyesteramide cross-linked membrane that was laminated on top of the microporous support surface became more stable and this resulted in a higher cross-linking density of the active layer. During the treatment process, the pore sizes of the asymmetric membrane expanded and dried, and the support membrane rearranged its molecular structure to give consistent pore sizes [16, 17]. Thus, the polyesteramide that was between the impregnated pore size of asymmetric membrane and the top surface became denser, resulting in a very stable permanent thin layer [18]. However, the change in the asymmetric membrane molecules structure has its limit. Increasing curing temperature beyond 60°C caused a drastic physical change to occur. The composite membrane

became wrinkled and very brittle [19] and the polyesteramide cross-linked membrane broke up. This explains why the salt rejection rate decreased when the curing temperature was increased to 100°C.

The polyesteramide cross-linked membrane laminated on top of the polysulfone membrane surface made one heterogeneous layer. Figure 1 illustrates the rejection rate of the thin film composite membrane using polysulfone as the porous support. The rejection rate increased with the increase in curing temperature up to 80°C. This curing temperature was sufficient to provide the desired membrane with stable active layer. Increasing the curing temperature beyond this point will not improve the membrane's performance, as can be observed from the decline in the rejection rate. It seems a curing temperature of 80°C is sufficient to provide the desired membrane with a stable active layer. Unlike cellulose acetate, polysulfone can withstand higher curing temperature and thus can be cured over a slightly wider temperature range. However, curing over 80°C is not beneficial as it may damage the average molecular structure. When the support membrane is unstable, it will affect the stability of the active layer and reduce the rejection performance.
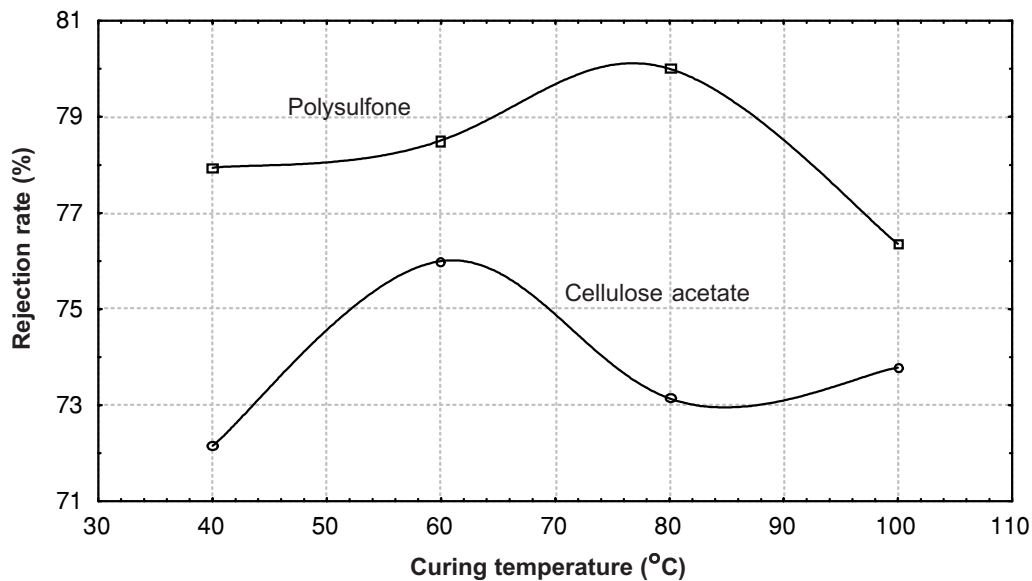

Figure 1 Rejection rate versus curing temperature

The product rate (*PR*) and pure water permeation rate (*PWP*) for both cellulose acetate and polysulfone are shown in Figure 2. The product rates for both CA and Psf are lower than the pure water permeation rate. As curing temperature increased, both product rate and pure water permeation rate decreased for the cellulose acetate TFC membranes. However, this trend is not observed for polysulfone TFC membranes.
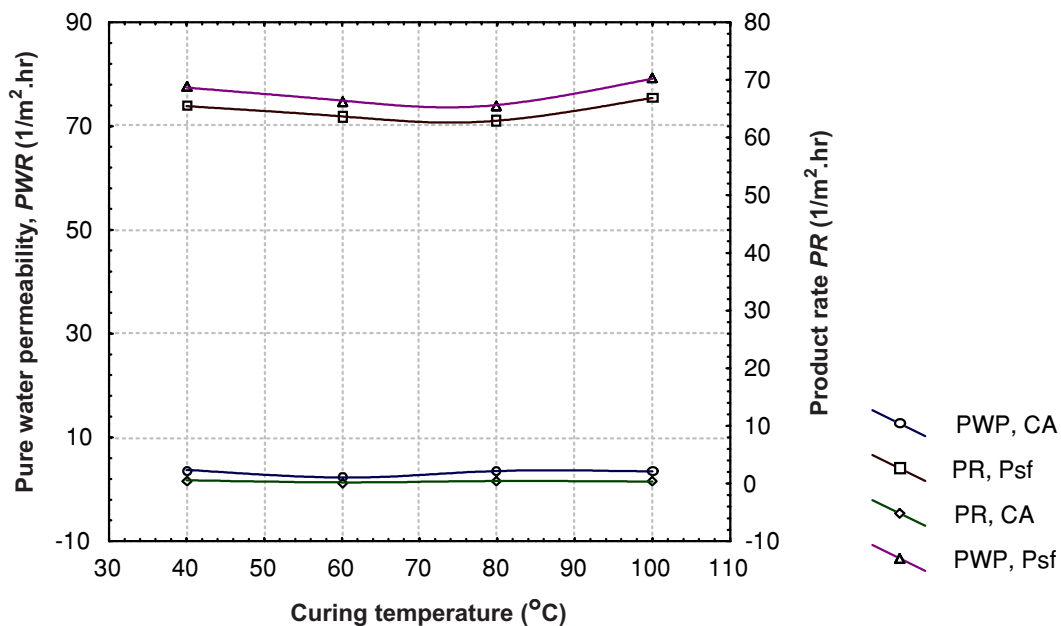
Figure 2 Product rate (*PR*) and pure water permeation flux rate (*PWP*) versus curing temperature

Cellulose acetate asymmetric membrane has two different layers consisting of asymmetric skin layer and sub-layer. The dense skinned asymmetric layer is responsible for the high salt rejection rate, while the sub-layer is recognized as the porous layer. When the curing temperature increased, the overall structure of the membrane changed. The heat treatment made the membrane structure more stable with consistent pore size in each layer of the asymmetric membrane. Applying another layer such as polyesteramide increased the thickness of the membrane. In many cases, active layer was designed to be as thin as possible. The increase in the thickness of the active layer for the CA membranes resulted in very low *PR* and *PWP* rates. When high pressure is applied during the separation process, the salt is highly rejected [20] but the water permeation received high movement resistance due to the increase of skin layer's thickness [16-18], resulting in the low flux.

Compared to cellulose acetate, the *PR* and *PWP* rates for poysulfone are remarkably better with almost 30 fold increase as can be observed from Figure 2. This is probably due the thinner active layer compared to CA. However, like cellulose acetate, it exhibits decrease in flux rate with an increase in curing temperature until 80°C. The increase in curing temperature affects the overall membrane morphology. The heat treatment reduced the pore sizes and a number of open pores on the supporting layer are also reduced, resulting in increase flux resistant [21]. However, the flux rate increases as the curing temperature reaches beyond 80°C for polysulfone. This result may explain why the membrane structure is degraded at high temperature

and at the same time lost its ability to retain salt rejection. Thus the perfect curing temperature for polysulfone is 80°C as its rejection rate is the highest at 80% with a product rate of 65.66 l/m^2.hr.

The set of reverse osmosis data in Figure 1 when analysed through basic transport Equations (2) to (6) yield local data on pure water permeability constant (A), solute transport parameter ($D_{AM}/k\delta$) and mass transfer coefficient (k) which are applicable for a particular membrane and the solute at local operating conditions are as shown in Table 2.

Figures 3, 4, and 5 show the values of A, $D_{AM}/k\delta$ and k of cellulose acetate and polysulfone at different curing temperatures. The characteristics of the membrane

Table 2 Pure water permeability constant (A), solute transport parameters ($D_{AM}/K\delta$) and mass transfer coefficient (k)

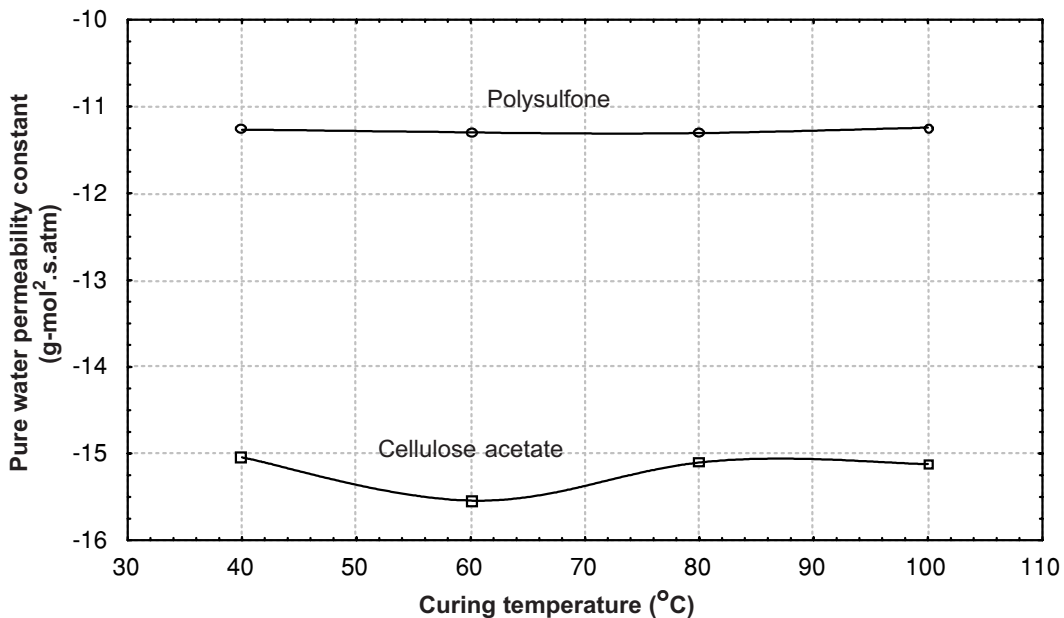| Curing temperature (°C)		40	60	80	100
Cellulose acetate	$A \times 10^7$ (g-mol/cm^2.s.atm)	2.93	1.78	2.76	2.71
	$(D_{AM}/K\delta) \times 10^7$ (cm/s)	2.07	0.62	1.54	1.14
	$k \times 10^5$ (cm/s)	0.48	0.17	0.77	0.29
Polysulfone	$A \times 10^5$ (g-mol/cm^2.s.atm)	1.28	1.24	1.23	1.31
	$(D_{AM}/K\delta) \times 10^4$ (cm/s)	5.21	4.53	4.29	5.78
	$k \times 10^2$ (cm/s)	5.16	1.60	2.57	4.36

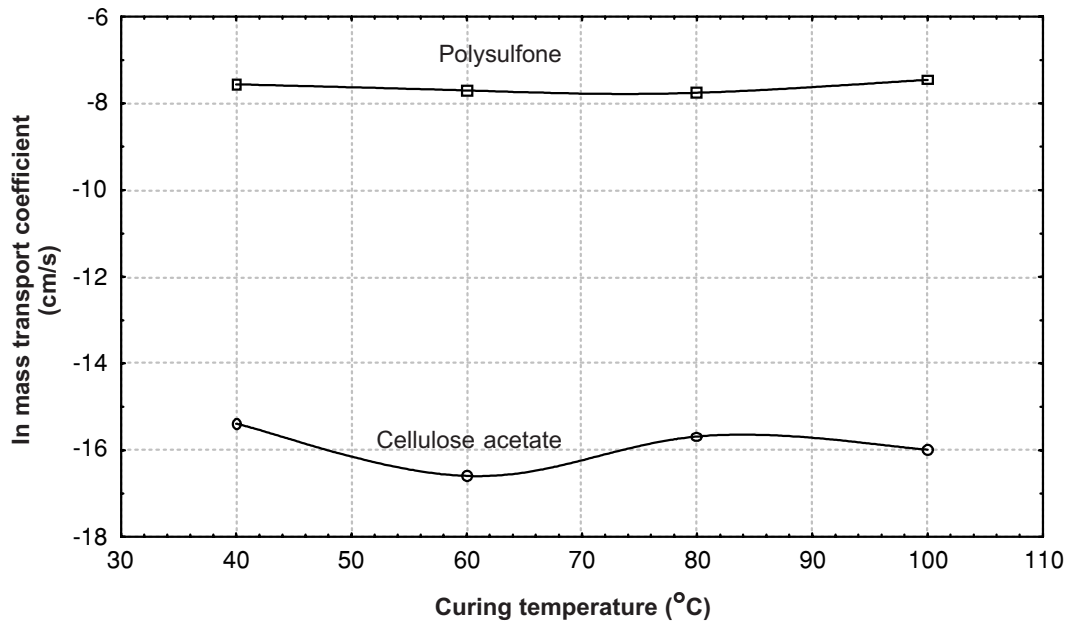**Figure 3** ln pure water permeability constant versus curing temperature

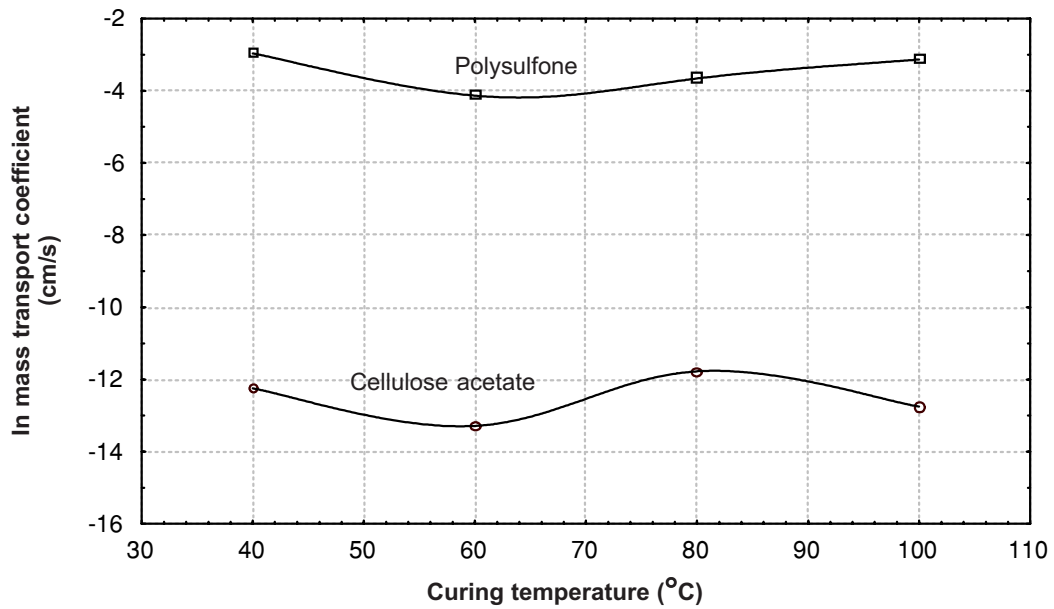**Figure 4**   ln solute transport parameter versus curing temperature

Figure 5   ln mass transfer coefficient versus curing temperature

are explained by quantities, A and $D_{AM}/k\delta$ [20, 21]. The value of pure water permeability constant, A, is a measure of the overall porosity of the membrane in terms of the permeation rate of pure water. Based on Figure 3, it can be seen that high values of A illustrates that the porosity of polysulfone TFC membrane is better compared to those of cellulose acetate based membrane, resulting in excellent flux rate as high as 65.66 l/m^2.hr. The polysulfone membrane that consists of polyvinylpyrrolidone as additive in the casting solution produces porous wall membrane [22]. The addition of n-methylpyrrolidone as a pore enlarging agent solvent contributes to the high permeability membrane [23, 24].

The quantity $(D_{AM}/k\delta)$, solute transfer parameter is the function of the chemical nature of the solute, that of the membrane material and the average pore size on the membrane surface which reflects both the equilibrium and kinetics effects governing reverse osmosis transport. Under otherwise identical operating conditions, the value of $(D_{AM}/k\delta)$ for any solute indicates solute transport through the membrane and hence solute separation in reverse osmosis. The higher values of $D_{AM}/k\delta$ that is analogous to a mass transfer coefficient for solute transport corresponds to an increase in the average pore size on the membrane surface. A difference in the overall value of $D_{AM}/k\delta$ for polysulfone TFC and cellulose acetate TFC indicates different surface morphology for both of these membranes [20].

The value of $D_{AM}/k\delta$ decreased with an increase in curing temperature because of an abrupt change in surface morphology of the membrane [20]. The membranes cured at different temperatures give different level of solute separation.

4.0   CONCLUSION

Curing temperature has a great influence on TFC membrane performance. Low curing temperatures resulted in unstable thin barrier layer lamination, while too high temperatures damaged the polyesteramide barrier layer and undesired physical change occurred on the thin composite membrane. Cellulose acetate is not a suitable porous support for thin composite membrane. The asymmetric cellulose acetate membrane containing an additive such as acetone produced closed pore and dense membrane structure that contributed to the very low flux rate. Laminating an active layer on top of the membrane surface made the skin layer thicker and increased the membrane resistance. It is suitable to add non-solvent additive such methanol [20] to the cellulose acetate polymer formulation rather than applying an active layer on top of the membrane surface to increase the flux performance of cellulose acetate. Polysulfone membrane is a very suitable porous support for thin composite membranes. The results showed that the value of the water permeability constant (A) and solute transport parameter $(D_{AM}/k\delta)$ influenced the membrane surface morphology coordinate with the curing temperature. The higher values of the water permeability constant (A) and solute transport parameter $(D_{AM}/k\delta)$ for the polysufone TFC membranes indicated better membrane performance. The polysulfone TFC

membrane exhibited highest rejection rates of 80% with flux of $65.66 \text{l/m}^2\text{hr}$ at 80°C curing temperature compared to the cellulose acetate TFC membranes.

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NOTATIONS

R	salt separation (%)
C_{A3}	concentration of sodium chloride in the permeate (kg/m^3)
C_{A1}	concentration of sodium chloride in the feed (kg/m^3)
A	pure water permeability constant (g-mol H_2O/cm^2.s.atm.)
PWP	pure water permeability through effective area of membrane surface (l/hr.m^2)
M_W	molecular weight of water (kg/kmol)
S	effective membrane area (cm^2)
P	operating pressure (Pa)
N_B	solvent water flux through membrane (g-mol/cm^2.s)
N_A	solute flux through membrane (g-mol/cm^2.s)
X_{A1}, X_{A2}, X_{A3}	mole fraction of feed solution, concentration boundary solution and product solution respectively
c_1, c_2, c_3	molar density of feed solution, concentration boundary solution and product solution respectively (g-mol/cm^3)
π	osmotic pressure of solution (atm)
$(D_{AM}/k\delta)$	solute transport parameter of sodium chloride (cm/s)
k	mass transfer coefficient on the high pressure side of membrane (cm/s)

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