PERFORMANCE OF CHITOSAN MEMBRANES CROSSLINKED WITH GLUTARALDEHYDE IN PERVAPORATION SEPARATION

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Received 1 June 2002, Accepted 10 August 2002

ABSTRACT

Chitosan membranes crosslinked with glutaraldehyde (GA) were prepared through a solution method, where the dry homogeneous chitosan membranes were immersed into the reaction solutions containing 1.25×10^{-3} wt. % of glutaraldehyde (GA). The extent of the crosslinking was controlled by varying the crosslinking time from 1 to 5 minutes. The prepared crosslinked membranes were used for pervaporation dehydration of isopropanol-water mixtures. The influence of feed composition on the separation characteristics has been investigated. The 2-minute-crosslinked-membrane yields the highest water concentrations in the permeate with moderate flux at 50 wt. % of isopropanol in the feed solution. The overall pervaporation results for the homogeneous and crosslinked membranes are compared in term of pervaporation separation index (PSI). The crosslinked membranes showed higher pervaporation separation index (PSI) than that of uncrosslinked membranes especially for isopropanol in feed solution below 78 wt. %.

Key words : *Chitosan; Crosslinked; Glutaraldehyde; Solution method; Pervaporation separation index*

1. INTRODUCTION

Pervaporation is a membrane separation process where a liquid mixture is directly brought into contact with a semipermeable membrane and the permeate is removed as a vapour by creating vacuum or employing a carrier gas on the permeate side.

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Pervaporation differs from other processes in that the membrane constitutes a barrier between a liquid in the feed phase and the permeate in the vapour phase. [1] Pervaporation can be effectively used in the separation of azeotropic, close-boiling point, and heat sensitive mixtures. [2] Basically, pervaporation processes can be utilized for different types of separation such as (i) extraction of water from organic liquids, (ii) extraction of volatile organic substances from aqueous streams and (iii) extraction of organic components from mixtures of organic liquids. [3] Among numerous applications of pervaporation technique, the dehydration of ethanol is the earliest and best developed practical process. [4]

Although the pervaporation process was suggested early in the 1950s, there was no great progress in fundamental research and application studies for this separation technique until the end of the 1970s. [5] Since then, many research papers have been published. However, only in 1982-83, Gesellschaft für Trenntechnik (GFT) Co., Germany, developed the first commercial pervaporation membrane by the use of poly(vinyl alcohol)-polyacrylonitrile composite membrane for the dehydration of alcohol solutions. [6]

Depending on the membrane material used in the pervaporation of organic-water mixtures, the application may be directed towards the preferential permeation of water or towards the preferential permeation of the organic substance. [7] Since water molecules is smaller than that of organic molecules, the diffusion of water molecules through a dense membrane is faster than that of organic molecules. Therefore, hydrophilic membranes, which exhibit affinity to water, are used to remove water from the mixture of organic liquid. On the other hand, for the removal of organic compounds from their dilute aqueous solutions, a more convenient separation is extracting the organic compounds from the bulk solutions. Thus, organophilic membranes, which preferentially permeate to organic substances, are more suitable to use in this case.

Chitosan is one of the promising membrane materials and has been widely studied. [8] It is derived from chitin which being the second most abundant natural polymer found in nature. Chitosan is a non-toxic, highly hydrophilic and film-forming ability. These advantages have made chitosan as membrane making material. With its free amine groups, the structure of chitosan can be modified easily in order to improve its properties. There is a growing interest in the introduction of crosslinked structures into polymer membranes in order to improve the pervaporation separation properties of the membrane for aqueous solutions. [9] Chitosan is swellable in water and should be crosslinked by several crosslinking mechanisms for pervaporation. Crosslinking often occurs via chemical reaction, the chains being connected together by covalent bonding. Glutaraldehyde is the most commonly used crosslinking agent, which can form a Schiff's base for chitosan. [10] A compound formed by a condensation reaction between an aromatic amine and an aldehyde or ketone is call Schiff's base.

Uragami *et al.* [11] studied the chemically crosslinked membranes of chitosan with glutaraldehyde at various glutaraldehyde contents. Lee [12] investigated the pervaporation

performance to separate water from aqueous ethanol solution on four types of chemically modified chitosan through complex formation, carboxylation, sulfonation and phosphorylation. Among the modified chitosan membranes, phosphorylated membranes showed the best performance to separate water from aqueous ethanol. Yeom and Lee [13] reported on the solution method for crosslinking of membrane, where the dry poly(vinyl alcohol) membranes were immersed for a certain period of time into a glutaraldehyde reaction solution.

Mohd. Nawawi and Huang [14] studied the chemical crosslinking of the homogeneous chitosan membranes with 1,6-hexamethylene diisocyanate. They found that the 24 hours crosslinked homogeneous membrane increased the separation factor but decreased the permeation flux for pervaporation of 95 wt. % of isopropanol in feed solution. Chen *et al.* [15] studied the crosslinked of chitosan/silk fibroin blended membrane by adding an appropriate amount of glutaraldehyde into the casting solution. The results showed that the membranes with silk fibroin content not more than 40 wt. %. were water selective with improved pervaporation properties compared to the pure chitosan membrane for both uncrosslinked and crosslinked.

The performance of the membrane used to separate a given binary A-B is characterized by the main experimental parameters. The first parameter is the total permeation flux J, the amount of liquid that is transported through the membrane per unit area and per unit of time. Second, the separation factor α, which can define as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} \tag{1}$$

where y_A and y_B are the weight fractions of components A and B in the permeate and x_A and x_B are the weight fractions of the components A and B in the feed. Component A is the more preferentially permeating component in the A/B mixture.

From the practical point of view, the membrane must have a high permeation flux together with large separation factor. Nevertheless, in the actual pervaporation process there is normally a trade-off between the separation factor and permeation flux where a high separation factor is accompanied by low flux and vice versa. Thus, a new formula called pervaporation separation index (PSI) has been used for measurement of the separation ability of a membrane. It can be defined as the product of a separation factor (α) and permeation flux (J) [16]:

$$PSI = J\,(\alpha - 1) \tag{2}$$

when $\alpha = 1$, no separation occurs; a PSI of zero means either zero flux or zero separation.

The purpose of this study is to prepare the chitosan based membranes from domestic shrimp shells waste. This is something different from the previous work where most

of the researchers like to use the commercial chitosan flakes from Japan. The obtained homogeneous chitosan membranes were crosslinked with glutaraldehyde via solution method at various crosslinking times. The membranes with optimal reaction time were further characterized through pervaporation separation of isopropanol-water mixtures with effect of feed concentrations.

2. MATERIALS

Chitosan prepared from domestic shrimp shells, which were collected from the hawkers. Glutaraldehyde 25 wt. % slolution in water was purchased from Aldrich Chemical Company. Reagent grade sodium hydroxide was purchased from All Chem, ethanol and isopropanol from J. T. Baker. Deionized distilled water was used in this study.

3. EXPERIMENTAL

3.1 Preparation of Chitin from Shrimp Shells

The dried shells were cut into pieces with an average size of 2-6 mm. The shells were treated with 2-3 molar of sodium hydroxide (NaOH) aqueous solution to remove the protein content. The treatments were carried out at 80-90°C for 2 hours. Furthermore, they were treated in 2 M hydrochloric acid (HCl) aqueous solution at room temperature for 24 hours to remove the calcium from the shells. Then the shells were washed with distilled water. The sequence for preparation of the chitin is shown in Figure 1.

3.2 Preparation of Chitosan from Chitin

The chitin were further treated with 50 wt. % of NaOH aqueous solution at temperature of 90 - 110°C for 3 hours in order to remove the acetyl group (CH_3CO) from the chitin. The flakes obtained by the alkaline treatment were then washed with distilled water, dried under the sun for three hours and further dried up at room temperature. The products obtained are chitosan which were partly deacetylated. The sequence for preparation chitosan from chitin is shown in Figure 2.

3.3 Preparation of Homogeneous Chitosan Membranes

A preweighed quantity of chitosan were first dissolved in 10 wt. % aqueous acetic acid solution at room temperature and stirred them for 24 hours to produce a casting solution consisting of 2 wt. % chitosan. The chitosan aqueous solution was filtered to remove any impurities and undissolved particles to produce a clear homogeneous casting solution by using a vacuum pump. The solution is allowed to settle down for about 3-4 hours and the resulting casting solutions were cast onto a petri dish, allowing the casting solution to evaporate at room temperature for 48 hours. The formed membranes were treated in 3 wt. % NaOH solution containing 47 wt. % ethanol, and 50 wt. % of distilled water for 24 hours at room temperature. The membranes were then washed thoroughly

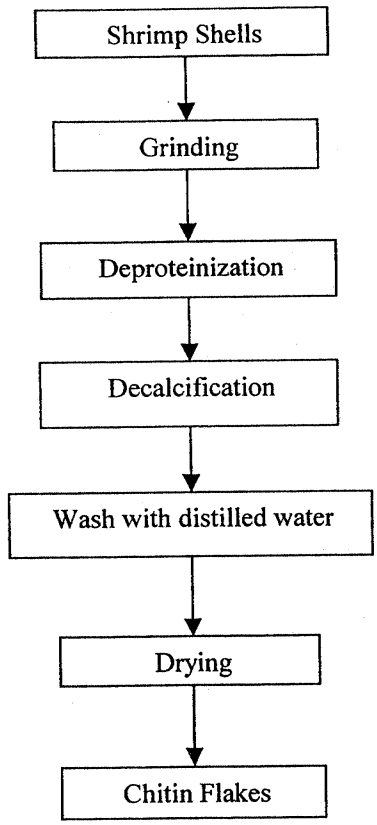

Figure 1 : *Procedure of preparing chitin from shrimp shells.*

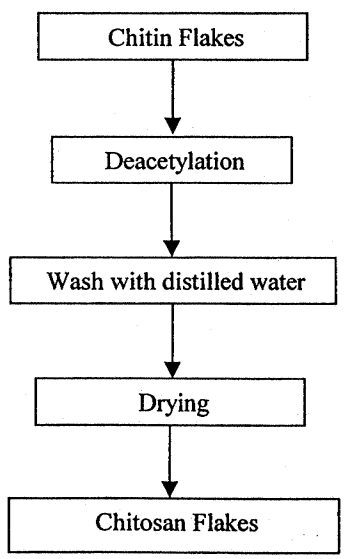

Figure 2 : *Procedure of preparing chitosan from chitin.*

with distilled water to remove excess NaOH before being peeled off from the plate and dried at room temperature. The thickness of the membranes was controlled by weighing the amount of chitosan solutions inside the petri dish. The thickness of the obtained membranes was about 25 μm. The sequence for preparation of homogeneous chitosan membranes is summarized in Figure 3.

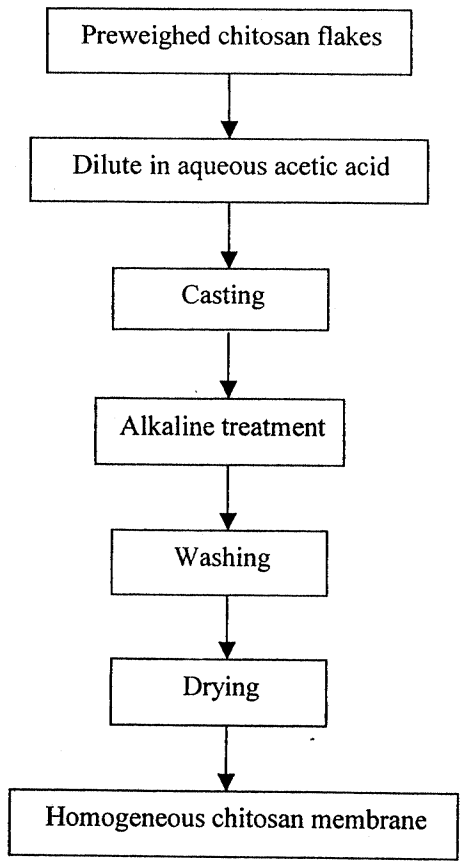

Figure 3 : *Procedure of preparing homogeneous chitosan membranes.*

3.4 Preparation of Crosslinked Membranes

A preweighed quantity of chitosan were first dissolved in 10 wt. % aqueous acetic acid solution to produce a casting solution consisting of 2 wt. % of chitosan. The resulting optical clear chitosan solution was cast onto petri dishes and dried at room temperature. The obtained chitosan membranes were further modified to produce crosslinked membranes. The glutaraldehyde solution was dilute in deionized distilled water to produce a crosslinking agent containing 1.25×10^{-3} wt. % of glutaraldehyde. The solution technique was used to prepare the crosslinked membranes. For the crosslinking reaction, each dry chitosan membrane was immersed into the prepared crosslinking agent at

various crosslinking times from 1 to 5 minutes. The crosslinked membranes were washed with the deionized distilled water to remove excess glutaraldehyde and then dried at room temperature. The sequence for preparation of the crosslinked membrane is shown in Figure 4.

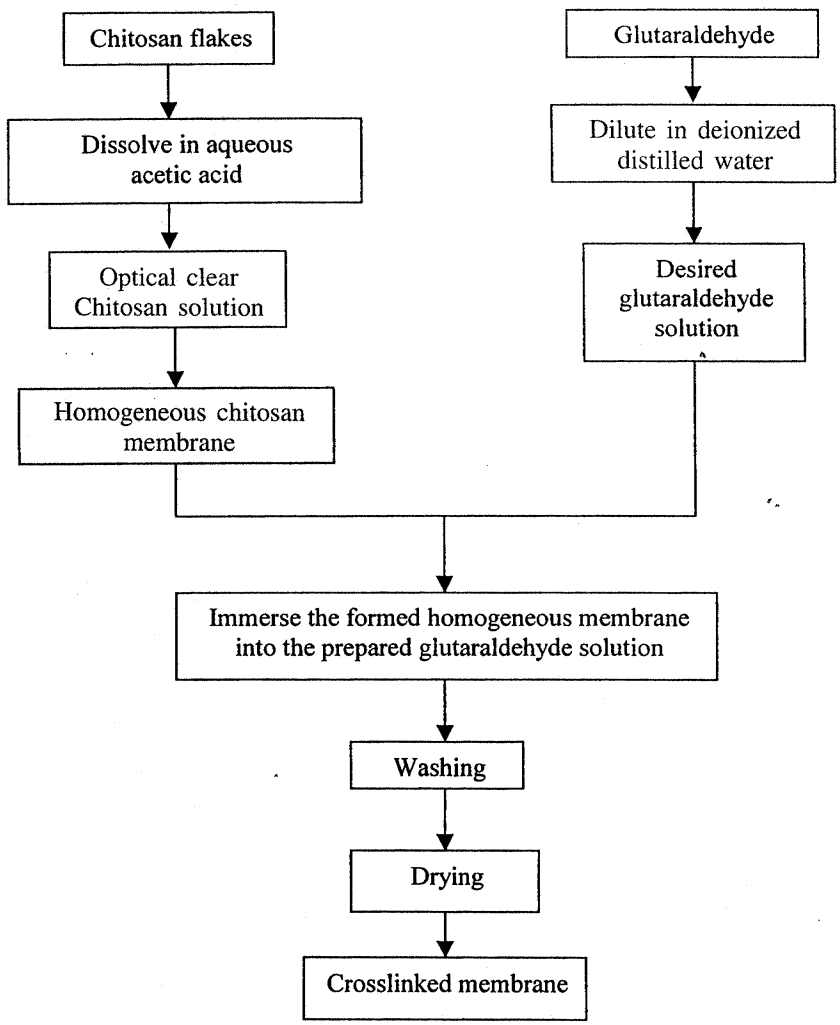

Figure 4 : *Procedure of preparing crosslinked membranes.*

3.5 Experimental Test Rig

The pervaporation test rig is shown in Figure 5. The main component of the pervaporation test rig is the membrane cell. The flat sheet membrane cell is fabricated from 316 stainless steel. The membrane cell consists of two portions namely, top and bottom. The top portion was equipped with two opening which are the inlet and outlet of the feed mixtures. Two porous stainless steel plate coated with teflon with the pores size

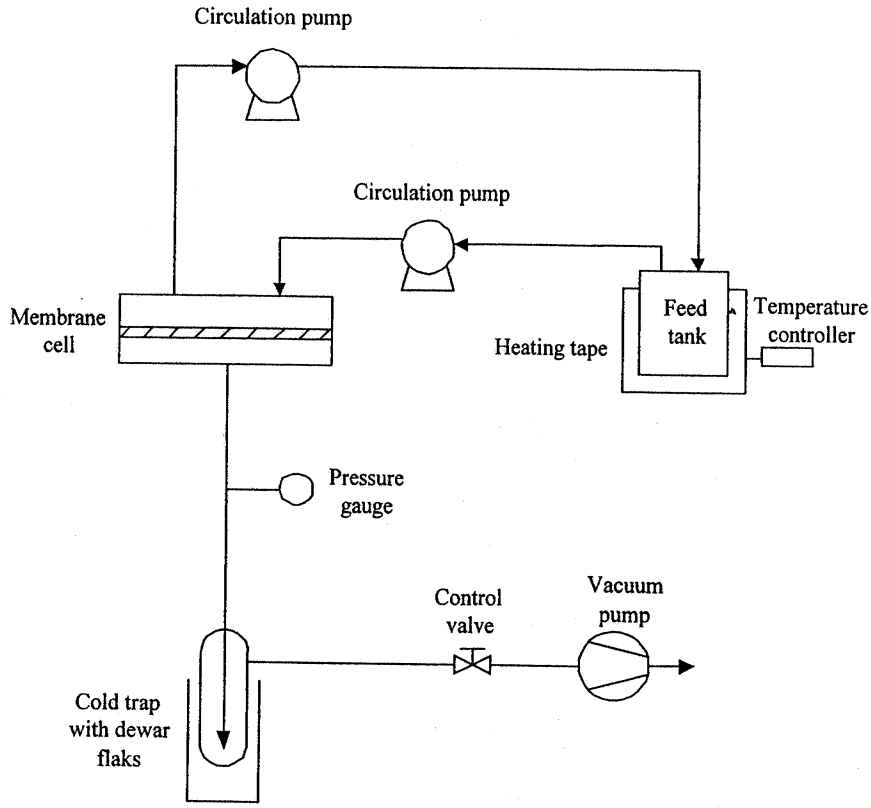

Figure 5 : *Schematic diagram of the experimental rig for pervaporation precess.*

of 30 μm, thickness of 1 mm and diameter of 90 mm were used to support the membrane. The two portions of the cell were clamped and tightly sealed using rubber O-ring. The effective area of the membrane cell was 52.81 cm^2. The permeate vapour left the cell through the bottom side opening which is kept under vacuum by the vacuum pump to supply the necessary driving force for pervaporation. The feed mixture was stirred using Bibby stirer and circulated from the feed tank to the permeation cell using Masterflex pristaltic pumps. The Cole-Parmer digital temperature controller was used to control the temperature of the feed mixtures. Furthermore, Swagelok control valve was used to control the downstream pressure. The permeate vapour was condensed in a cold trap by using liquid nitrogen. The condensed permeate was warmed up to ambient temperature and weighed to determine its flux. The compositions of the permeate were determined by using the Karl Fischer titration unit.

4. RESULTS AND DISCUSSION

Figure 6 shows the effect of crosslinking time on the total permeation flux and its separation factor of the crosslinked chitosan with glutaraldehyde membranes. The concentration of isopropanol in the feed tank was 50 wt. %. The extent of crosslinking

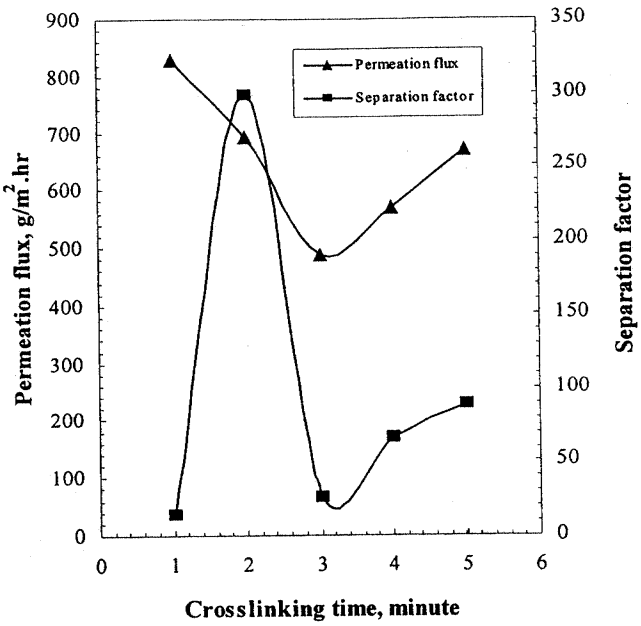

Figure 6 : *The total permeation flux and separation factor for the crosslinked membranes versus crosslinking time. Feed isopropanol 50 wt. %. Permeate pressure 5 mmHg, operating temperature 30°C.*

in the present study was controlled by the exposing time of the membrane in the reaction solution. The exposing time in the present study varies from 1 to 5 minutes. All of the crosslinked membranes showed the highest separation factor at 50 wt. % of isopropanol in feed solution. Thus, this particular concentration was chosen at the initial stages to select the best membrane in term of the trade-off between the permeation flux and separation factor.

In principle, the degree of swelling of the crosslinked membrane would decrease with an increase of the degree of crosslinking because of the compact structure formation [17] which would result in less mobility of the polymer chains [9] and decrease the free volume in the membrane as well. [10] This might cause a decrease in the permeation flux and an increase in the separation factor of the crosslinked membranes. The crosslinking technique used in the present study was a solution method, where the dry homogeneous chitosan membranes were immersed in the glutaraldehyde solution for a certain period of time. Immediately after the dry membranes were immersed into the glutaraldehyde solution, two processes occurred. Firstly, dissolution and dispersion of the glutaraldehyde into the dry chitosan membranes occur and secondly, the reaction of the two aldehyde groups in the glutaraldehyde molecule with the two amino groups in the chitosan to form a covalently crosslinked network. This indicated that only a partial dissolution occurred at the 1st minute of reaction time while a complete dissolution occurs at the 2nd minute of reaction time. Further exposure of the membrane in the

crosslinking agent would degrade the membrane performance. These could be the reasons why the permeation flux decreased from 1st to 3rd minute of the reaction. While, the separation factor increased from 1st to 2nd thereafter decreased to a minimum at 3rd minute.

According to Uragami *et al.* [11] the chitosan membrane has many intermolecular hydrogen bonds between the hydroxyl groups and amino groups. A few of these hydrogen bonds in crosslinked membranes are broken by glutaraldehyde and free hydrophilic groups such as hydroxyl and amino groups are formed. These hydrophilic groups have a strong affinity to water molecules. So the increased in both the permeation flux and separation factor in the 4th and 5th minutes of the crosslinking time were actually attributed by these free hydrophilic groups. The performance of the 2-minute-crosslinked-membrane showed the highest separation factor with moderate flux. Therefore the 2-minute-crosslinked-membrane was selected for further characterisation through pervaporation dehydration of isopropanol/water mixture with the effect of feed concentrations.

Figure 7 shows the separation factor of the homogeneous membrane and 2-minute-crosslinked-membrane versus weight percent of isopropanol in feed solution. The results show that for the weight percent of isopropanol in feed solution up to nearly 78

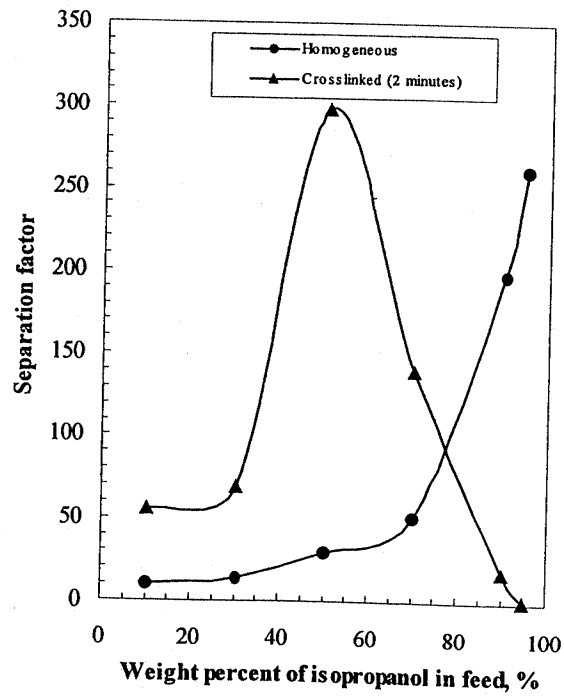

Figure 7 : *The separation factor of the homogeneous membrane and 2-minute-crosslinked-membrane versus weight percent of isopropanol in feed. Permeate pressure 5 mmHg, operating gemperature 30°C.*

wt. %, the 2-minute-crosslinked-membrane has higher separation factor than that of homogeneous chitosan membrane. With further increase of isopropanol in feed solution beyond 78 wt. %, the separation factor for 2-minute-crosslinked-membrane was lower compared to homogeneous membrane. The chitosan membrane crosslinked with glutaraldehyde exhibited higher separation factor than that of homogeneous chitosan membrane for feed isopropanol below 78 wt. %. Since, chitosan is the hydrophilic polymer so when the isopropanol content in the feed increase, the amount of liquid absorbed in the membrane would decrease. Furthermore, according to Yeom and Lee [18], usually, when a membrane is crosslinked, a membrane mobility, as well as its liquid solubility is decreased. So, when the isopropanol content in the feed solution increase beyond 78 wt. %, it won't be a significant swollen of the crosslinked membrane. Thus, the separation factor of the crosslinked membrane could not be expected to be good in high isopropanol which beyond 78 wt. % in the feed solution. Yeom and Lee [17] also reported the decreased in separation factor in high content of ethanol in feed solution for the sodium alginate membrane crosslinked with glutaraldehyde.

Figure 8 shows the total permeation flux of the homogeneous and 2-minute-crosslinked-membrane versus weight percent of isopropanol in feed solution. It was evident that the crosslinked membrane exhibited higher permeation flux regardless of the feed concentration to that of homogeneous membranes at the same pervaporation conditions. Normally the crosslinking reactions would lead to a decrease in flux due

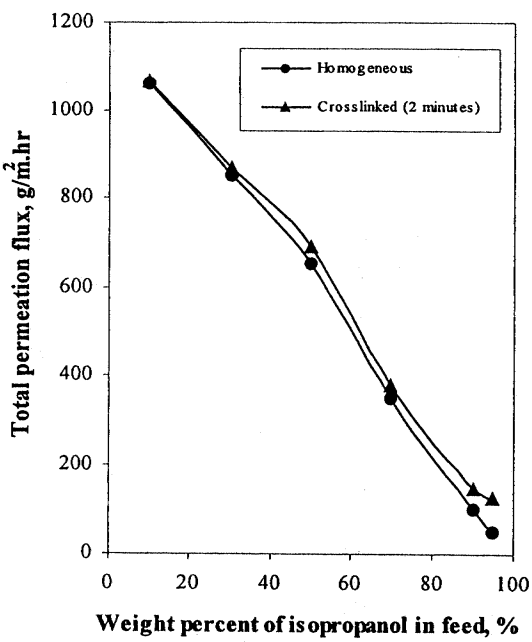

Figure 8 : *The total permeation flux of homogeneous membrane and 2-minute-crosslinked-membrane versus weight percent of isopropanol in feed. Permeate pressure 5 mmHg, operating temperature 30°C.*

to more compact structure formation. However, the present study showed that the crosslinked membranes gave better flux than that of homogeneous chitosan membranes. Uragami *et al.* [11] also obtained the same trend of results on the permeation and separation of aqueous ethanol solutions through homogeneous chitosan membranes and chitosan crosslinked with glutaraldehyde membranes. These abnormal results may be due to the relaxational process as proposed by Yeom *et al.* [19] on the qualitative model for the relaxational behaviour of glassy membrane in pervaporation.

Although there were different mechanisms have been proposed in the literature [20] to explain of the crosslinking reaction between chitosan and glutaraldehyde. However, Tual *et al.* [21] reported that the crosslinking reaction principally form a Schiff's base formation for those crosslinking times which were less or equal to 5 hours. Due to the low crosslinking times in the present study, the chemical reaction would follows Schiff's base formation and the chemical reaction is believed to be similar to the type as reported by Uragami *et. al* [11]. The structure for chitosan crosslinked with glutaraldehyde is shown in Figure 9. Depending on the extent of the crosslinking reaction, for the D-glucosamine unit in the chitosan molecule, there are:

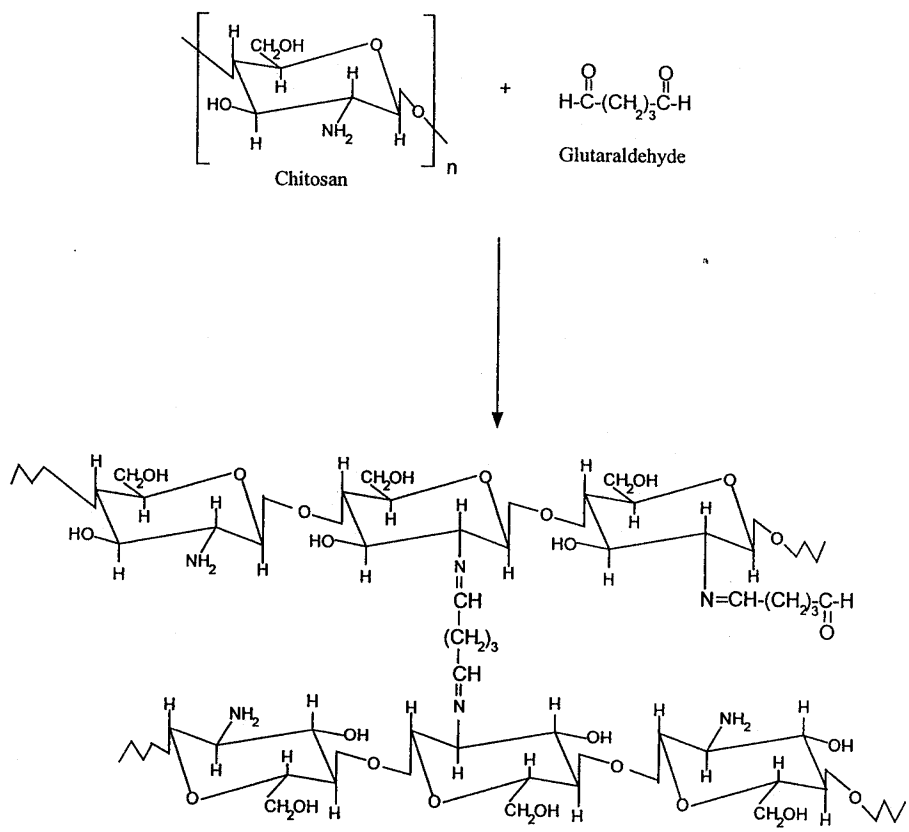

Figure 9 : *Reaction of chitosan with glutaradehyde (Uragami et al., 1994)*

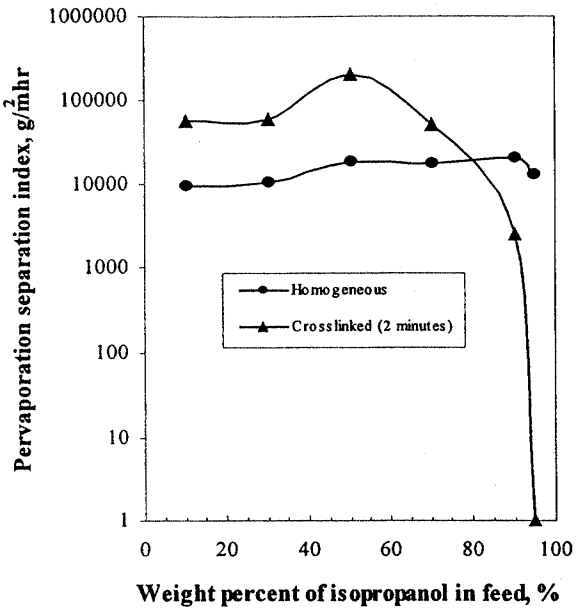

Figure 10 : *The pervaporation separation index (PSI) of the homogeneous membrane and 2-minute-crosslinked-membrane versus weight percent of isopropanol in feed. Permeate pressure 5 mmHg, operating temperature 30°C.*

(i) a crosslinked structure between two aldehyde groups in the glutaraldehyde molecule and two amino groups in the chitosan molecule,
(ii) a pendant structure due to the reaction of one aldehyde group in the glutaraldehyde molecule with one amino group in the chitosan molecule,
(iii) unreacted structure in the chitosan membrane.

Figure 10 shows the pervaporation separation index (PSI) versus weight percent of isopropanol in the feed for both homogeneous membrane and 2-minute-crosslinked-membrane. At isopropanol content up to nearly 78 wt. % in feed solution, the PSI for crosslinked membrane was higher than the homogeneous membrane. However, beyond 78 wt. % of isopropanol in the feed solution a reverse trend was observed. This implies that if the PSI were the determining factor, the 2-minute-crosslinked-membrane would be useful for the separation of dilute aqueous isopropanol solutions, while homogeneous chitosan membrane would be more effective for the pervaporation dehydration of aqueous isopropanol near its azeotropic concentration.

5. CONCLUSIONS

The chitosan membranes were successfully prepared from domestic shrimp shells and crosslinked with glutaraldehyde via a solution method. The membranes were investigated

for the pervaporation dehydration of isopropanol-water systems. The effects of the crosslinking time and feed concentration on the pervaporation performances were studied. The crosslinking time of 2 minutes showed the highest separation factor with a moderate permeation flux. In terms of the PSI, the 2-minute-crosslinked-membrane exhibited an advantage over the homogeneous chitosan membrane when the isopropanol concentraion in the feed solutions was less than 78 wt. %.

ACKNOWLEDGEMENTS

The financial support provided to this research by the Ministry of Science, Technology and Environment of Malaysia through IRPA project is gratefully acknowledged.

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