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**Int. Journal of Renewable Energy Development (IJRED)**

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# Layer by Layer Composite Membranes of Alginate-Chitosan Cross-linked by Glutaraldehyde in Pervaporation-Dehydration of Ethanol

Nur Rokhati<sup>a\*</sup>, Titik Istirokhatun<sup>b</sup>, and Asep Muhamad Samsudin<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Jl. Prof. Soedarto-Tembalang, Semarang 50239 Indonesia

<sup>b</sup> Department of Environmental Engineering, Faculty of Engineering, Universitas Diponegoro, Jl. Prof. Soedarto-Tembalang, Semarang 50239 Indonesia

**ABSTRACT.** Hydrophilicity of membrane causing only water can pass through membrane. Pervaporation process using organophilic membrane has been offered as alternative for ethanol dehydration. This paper investigate pervaporation based biopolymer composite membrane from alginate-chitosan using layer by layer method prepared by glutaraldehyde as crosslinking agent and polyethersulfone (PES) as supported membrane. Characterization of crosslinked of composite membrane by FTIR helped in identification of sites for interaction between layers of membrane and support layer (PES). The SEM showed a multilayer structure and a distinct interface between the chitosan layer, the sodium alginate layer and the support layer. The coating sequence of membranes had an obvious influence on the pervaporation dehydration performance of membranes. For the dehydration of 95 wt% ethanol-water mixtures, a good performance of PES-chitosan-alginate-chitosan (PES/Chi/Alg/Chi) composite membrane was found in the pervaporation dehydration of ethanol.

**Keywords:** alginate, chitosan, composite membrane, layer by layer, ethanol dehydration

**Article History:** Received April 12<sup>nd</sup>, 2016; Received in revised form June 25<sup>th</sup>, 2016; Accepted July 1<sup>st</sup>, 2016; Available online

**How to Cite This Article:** Rokhati, N., Istirokhatun, T. and Samsudin, A.M. (2016) Layer by Layer Composite Membranes of Alginate-Chitosan Crosslinked by Glutaraldehyde in Pervaporation Dehydration of Ethanol. Int. Journal of Renewable Energy Development, 5(2), 101-106. <http://dx.doi.org/10.14710/ijred.5.2.101-106>

## 1. Introduction

Pervaporation (PV) is a separation process using non-porous membrane with different concentrations as the driving force. PV has received increasing popularity in ethanol dehydration because of its ability to separate azeotrope mixture. The use of organophilic membrane, which is considered as hydrophilic, in pervaporation dehydration processes have been recommended as alternative of bioethanol purification process. The hydrophilic conditions is considered as the cause that only water can pass through the membrane (Zhang and Drioli, 1995), furthermore the energy requirement can be reduced significantly therefore distillation process is not needed anymore. The raw materials for hydrophilic membranes derived from synthetic and natural polymers.

Composite film made of various types modification of biopolymers has been synthesized to improve the

characteristics of the film (Arvanitoyannis et al., 1998; Galus et al., 2012; Kampeerappun et al., 2007; Maizura et al., 2008). Chitosan is a natural polysaccharide produced from chitin deacetylation process contained in the shells of invertebrates. Chitosan have hydroxyl and amine groups that are hydrophilic. Because its properties in a good film formation, strong adhesion in a material, biocompatible, hydrophilic, and have high mechanical strength properties (Chen et al., 2005), chitosan has good prospects for use as a raw material film or membrane. A reactive hydroxyl group and an amino functional group lead chitosan to be easily modified chemically. The nature of the cationic biopolymer chitosan can be reacted with other natural biopolymers that are anionic. However, due to incomplete chitin deacetylation process causes chitosan still contain hydrophobic acetyl group.

\*Corresponding Author: +62 85293791932  
Email: asep.musa@gmail.com

Alginate, a natural polysaccharide from seaweed extract, has a good performance as a pervaporation membrane material in dehydration processes (Shi et al., 1996). However, a very high hydrophilicity of alginate from carboxylate and hydroxyl groups leads unstable membrane product in aqueous solution during pervaporation process. This suggests that the alginic acid membrane is not strong enough to be operated in aqueous ethanol at a concentration of 50% (Mochizuki et al., 1990). Solubility in water and severe mechanical strength becomes a weakness in the possibility use of pervaporation materials regardless of very good in water rejection. Previous study successfully made sodium alginate membrane crosslinked with glutaraldehyde as a crosslinking agent and used HCl in acetone solution as a catalyst (Yeom and Lee, 1998).

In this study, alginate-chitosan composite film was prepared with layer by layer method using glutaraldehyde as crosslinking agent and polyethersulfone (PES) as supported membrane. Initial experiments have been done by filming alginate and chitosan mixing solutions, but this experiment was failed due to the very rapid formation of polyelectrolyte complexes that result in the irregular deposition which is insoluble in mixing process (Kumar et al., 2004). This is the reason to prepare alginate-chitosan composite film using layer by layer method in order to produce high mechanical strength films.

## 2. Materials and Methods

### 2.1 Materials

Chitosan (high MW, 118.4 cps) supplied from Surindo Biotech (Cirebon) with deacetylation degree of 80.4% and a viscosity of 118.4 cp. Sodium alginate obtained from Multi Kimia Raya (Semarang). Glycerol, acetic acid and glutaraldehyde were supplied from Merck.

### 2.2 Preparation of composite membrane

Sodium alginate was dissolved in 20% glycerol solution to form a homogeneous solution of 3 wt.%. Chitosan solution was prepared by dissolving 3 wt.% chitosan in dilute aqueous acetic acid solution. Alginate-chitosan-based composite membranes made with the layer by layer method. The alginate/chitosan solution was cast onto the PES membrane with of 0.3 mm thickness. The membrane was dried for 24 hours at room temperature. After drying, the chitosan/alginate solution was cast on the surface of chitosan/alginate layer. The triple top layer composite membrane were dried for 24 hours at room temperature. Cross-linking of the layers of the composite membranes was carried out by immersing them into the 90% isopropanol

solution containing 5 v. % glutaraldehyde as a crosslinking agent during the specified time period. Afterwards, the composite membranes were washed with water and dried at room temperature.

### 2.3 Membrane characterization

#### 2.3.1 FTIR Spectroscopy

Fourier Transform Infrared (FTIR), Shimadzu IR Prestige-21 was used for observation of functional groups. In this analysis, the spectrum of membranes has been compared.

#### 2.3.2 SEM Analysis

Membrane surface morphology was observed by using a scanning electron microscope (SEM), FEI Inspect S-type 50.

#### 2.3.3 Swelling Degree

The dried membranes were weighed, then immersed into water, ethanol 95 wt. %, and ethanol 99.5 wt. % for 6 hours. Membrane in the swollen state swabbed with a tissue and then weighed. Swelling degree was determined by calculating the difference between the weight of the membrane after immersion and the membrane weight before immersion, and then divided by the weight of the membrane before immersion.

#### 2.3.2 Performance of Pervaporation

Pervaporation experiments were carried out on a batch pervaporation unit. Ethanol-water mixtures in the tank were pumped to the cell membrane. The temperature was controlled using temperature controller. The downstream pressure was kept below 6 cmHg and the experiments were conducted at temperatures of 30°C in the ethanol feed composition. Feed water was diffused and evaporated toward the permeate side. Resulted permeate then condensed on the cold trap while the ethanol concentration in the retentate will increase. The selectivity is calculated as follows (Mulder, 1996):

$$\alpha_{A/B} = \left( \frac{y_A/y_B}{x_A/x_B} \right) \quad (1)$$

where:

- x is the weight fractions of the feed,
- y is the weight fractions of the permeate,

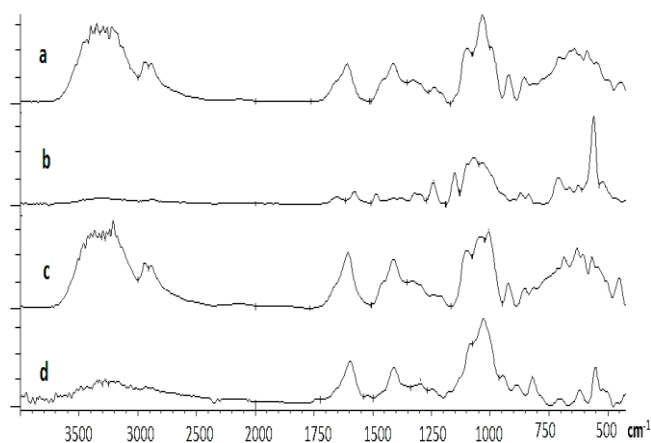
The Karl Fischer Titrator Mettler Toledo DL 39 was used to analyze water content in ethanol solution.

### 3. Result and Discussion

#### 3.1 Membrane characterization

##### 3.1.1 FTIR Spectroscopy

FTIR spectrum from composite membrane based of sodium alginate-chitosan, and PES as support layer are shown on Fig 1. The spectrum of the Alg/PES membrane (Figure 1.a) shows the spectrum of the carboxyl group at the peak wavenumber  $1608.5\text{ cm}^{-1}$ . In addition, the bands at  $1411.84\text{ cm}^{-1}$  (CO stretching),  $1326.97\text{ cm}^{-1}$ ;  $1099\text{ cm}^{-1}$ ;  $1026\text{ cm}^{-1}$  (COC stretching) and  $947\text{ cm}^{-1}$  (CO stretching) showed the saccharide structure.



**Fig. 1** FTIR spectra of (a) Alg/PES, (b) Chi/PES, (c) Alg/Chi/PES uncross linked, and (d) Alg/Chi/PES cross-linked

The spectrum of the Chi/PES membrane (Figure 1.b) shows characteristic absorption band at  $1652\text{ cm}^{-1}$  and  $1578\text{ cm}^{-1}$  which is a characteristic deformation of the amide I and amide II, respectively. The absorption band at  $1068\text{ cm}^{-1}$  (CO stretching) are characteristic of the saccharide structure (Kanti et al., 2004).

The absorption band at wavenumber  $1604\text{ cm}^{-1}$  occurred after carboxyl groups (alginate) react with amine groups (chitosan) via hydrogen bonding which shown in Fig. 1c. The peak of the spectrum at wavenumber  $1411.84\text{ cm}^{-1}$  and  $1005\text{ cm}^{-1}$  indicates the structure of saccharides. Sulfonate (S = O stretching) at wavenumber  $1024.2\text{ cm}^{-1}$  indicates the PES membrane (Stuart, 2004).

In the spectrum of PES/Chi/Alg membrane cross-linked (Figure 1.d) occurred removal in  $1604\text{ cm}^{-1}$  and  $1411.84\text{ cm}^{-1}$  were replaced with  $1595\text{ cm}^{-1}$  and  $1409.91\text{ cm}^{-1}$ , respectively. This is due to the crosslinking between the amine group and carboxyl group with the aldehyde group of glutaraldehyde.

#### 3.1.2 SEM Analysis (Membrane Morphology)

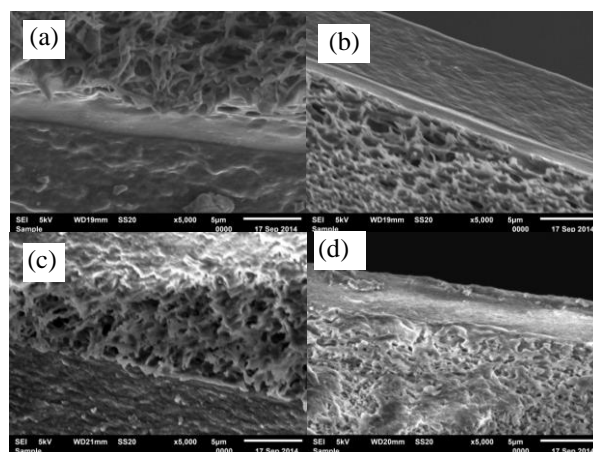
SEM is used to study the morphology of the cross-section of the composite membrane. SEM photographs of the composite membrane layer by layer of sodium alginate, chitosan, and PES as shown in Fig. 2

Figure 2 shows picture of the SEM from the cross-section of composite membrane Alg/Chi/Alg/PES uncross-linked; PES/Chi/Alg/Chi uncross-linked; PES/Alg/Chi/Alg cross-linked; and PES/Chi/Alg/Chi cross-linked. Before it was cross-linked, the inter-layer structure is clearly visible in this image. This means that after casted a layer of alginate, chitosan, and PES do not react with each other. As usual ultrafiltration membranes, PES has been known as relatively hydrophobic.

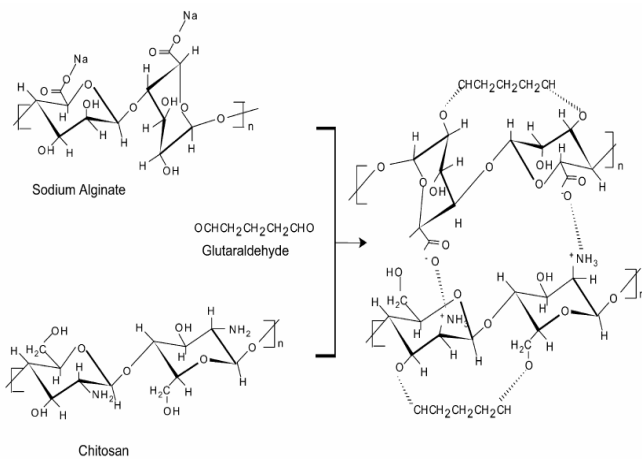
This hydrophobicity of PES contrast to the hydrophilicity of alginate / chitosan. Casting of alginate directly onto the surface of PES (Figure 2.a) resulted in swelling so that alginate film layer peeled easily from the surface of the PES. With the buffer layer films of chitosan (Figure 2b) led to casting and spreading the alginate film more easily. Chitosan forming film that is relatively good in the character and mechanical strength (Huang, 2000).

In the Alg/Chi/Alg/PES membrane has cross-linked with glutaraldehyde liquid (Figure 2.c), it appears that inter-layer structure is fused despite the alginate layer thickness is reduced. While the Chi/Alg/Chi/PES membrane cross-linked (Figure 2, d) shows that layer of chitosan, which is uniform and tight, deposited on a porous support layer.

The PES which has a sulfonate group ( $\text{SO}_3\text{H}^-$ ) with negative charge will bind quite strong due to the chitosan amine groups ( $-\text{NH}_2^+$ ) positively charged. Crosslink reaction between sodium alginate, chitosan, and glutaraldehyde are presented in Figure 3.



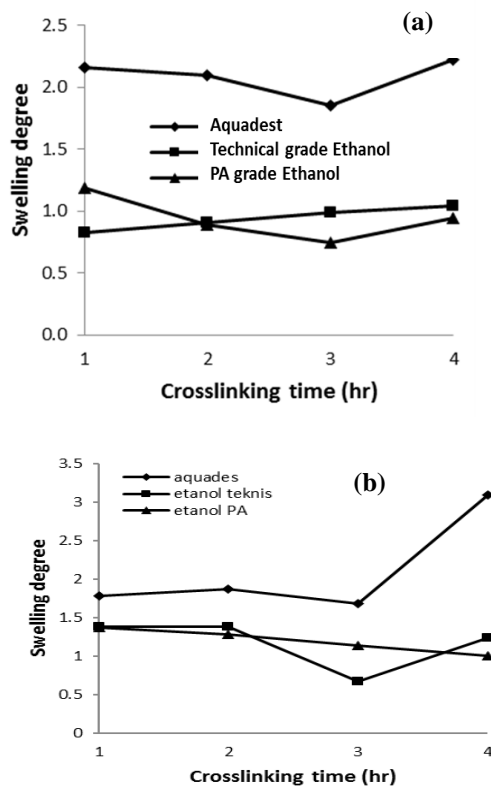
**Fig. 2** SEM pictures of the cross-section of the composite membrane; (a) PES/Alg/Chi/Alg uncross linked; (b) PES/Chi/Alg/Chi uncross linked; (c) PES/Alg/Chi/Alg cross-linked; (d) PES/Chi/Alg/Chi cross-linked



**Fig. 3** Structural representation of chitosan-sodium alginate glutaraldehyde crosslink (Kanti et al., 2004)

### 3.1.4 Swelling Degree

The swelling degree of the films depict fluid absorption behavior the performance of the pervaporation process. Membrane swelling behavior is influenced by the nature of the membrane material and membrane preparation conditions (Ghazali and Hassan, 2003).



**Fig. 4** Effect crosslinking time on swelling degree of coating sequences: (a) PES/Chi/Alg/Chi; (b) PES/Chi/Chi/Chi

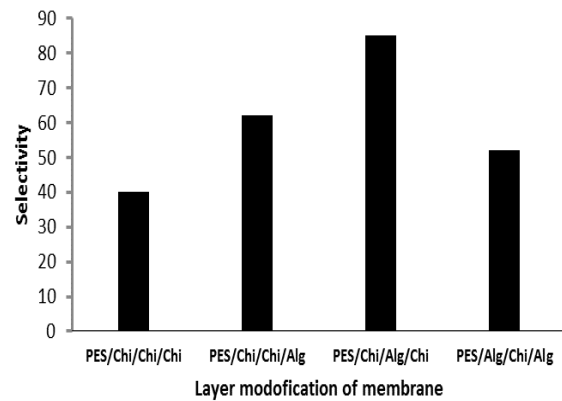
Figure 4 shows that at the beginning (crosslinking time 1-3 hours) the swelling degree of membrane decreased with increasing crosslinking time, but then increased in increments greater. Modification of the membrane through chemical crosslink yields a more dense (compact), so that the nature of the affinity and the ability to absorb liquids into decline. The swelling degree of membrane decreases with increasing degree of crosslinking since the advent of the compact structure formation which would result in reduced mobility of the polymer chains and reduce the free volume membrane (Tan and Ahmad, 2002)

Crosslinking of glutaraldehyde also cause damage to the intermolecular hydrogen bonding of the hydroxyl group and an amino group contained in the membrane so that formed free hydrophilic group which has a strong affinity to water molecules (Tan and Ahmad, 2002).

### 3.2 Pervaporation Studies

#### 3.2.1 Effect of coating sequences and crosslinking time on the separation performance

Separation performance is shown in Figure 5. The PES/Chi/Chi/Chi composite membrane possessed the lowest selectivity while the PES/Chi/Alg/Chi composite membrane possessed the highest selectivity. Chitosan has fairly good properties as a membrane material with good mechanical strength, decrease in selectivity was observed due to the contribution of hydrophobicity of chitosan film. The hydrophobic acetyl groups of chitosan caused reduction the water sorption of membrane.



**Fig. 5** Effect of coating sequences on the selectivity (Crosslinking time 1 hour)

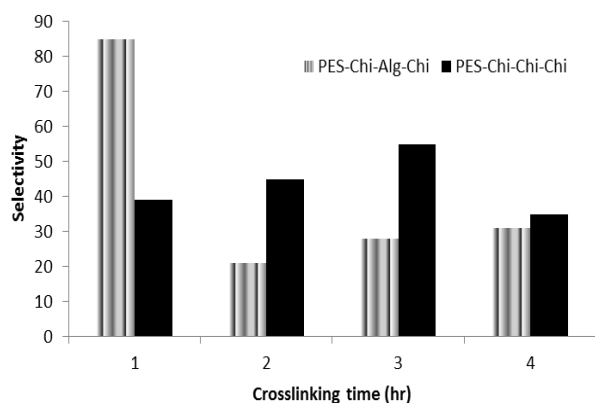
When sodium alginate as the outer layer, the more water is absorbed so increase the driving force of water diffusion through the membrane. The hydrophilicity of alginate due to its carboxylic and hydroxyl groups, results in an unstable membrane in aqueous solution during pervaporation. PES have opposite wetting properties compared to the hydrophilic alginate layer material. If the alginate was used as inner layer, the

structural stability of the composite membrane was weakened after a long pervaporation operating time, and then eventually the alginate layer became separated from the support layer. The direct casting of the alginate layer without the chitosan buffer layer can lead to a thick alginate top layer which can eventually be separated in the swollen state from the porous PES membrane

In case of the composite membrane is prepared for pervaporation dehydration, the similar hydrophilicity or chemical affinity between the support membrane and the top layer has several advantages such as improved structural stability and reduced top layer thickness resulting from the easy spreading of the top layer solution (Huang et al., 2000). If chitosan is used as inner layer and attached to the support layer PES, membrane has a small degree of swelling. The chitosan layer makes the casting and spreading of the next alginate layer much easier. Combination with the chitosan barrier can be improved because chitosan has good film forming properties and relatively good mechanical strength. The PES/Chi/Alg/Chi composite membrane has a good performance in pervaporation dehydration of ethanol.

### 3.2.2 Effect of crosslinking time on the separation performance

Crosslinking reaction can be carried out through the use of crosslinking agent having two or more groups capable of reacting with the functional groups in the polymer chain. Previous research showed that the optimum time of crosslinking reaction depend on the crosslink agent which is used.



**Fig. 6** Effect crosslinking time on selectivity of coating sequences : PES/Chi/Alg/Chi and PES/Chi/Chi/Chi

Figure 6 shows the effect of crosslinking time on the selectivity of composite membrane by glutaraldehyde crosslinked. The concentration of ethanol in feed tank was 95 wt. %. As the result that the highest selectivity for the PES/Chi/Alg/Chi composite membrane was 85 with crosslinking time at 1 hour, whereas with the PES/Chi/Chi/Chi composite membrane, the highest selectivity was 55 wt. %. with crosslink time at 3 hours.

Immediately after the dry membranes soaked in glutaraldehyde solution, the reaction of the aldehyde group in the molecule glutaraldehyde with amino groups in chitosan and carboxyl groups of alginate formed a covalently crosslinked network. An increase of the crosslinking degree lead to the compact structure formation which would result in less mobility of the polymer chains and decrease the free volume in the membrane as well (Tan and Ahmad, 2002). This could cause a decrease in the degree of swelling and increased the membrane separation factor. Glutaraldehyde is a very good agent for alginate, but increasing of the crosslink degree cause the polymer chains of chitosan become stiff and brittle.

## 4. Conclusion

Types of membranes used in pervaporation processes have different performance. Alginate-chitosan composite membrane was prepared with layer by layer method using glutaraldehyde as crosslinking agent and PES as supported membrane. Characterization of crosslinked membrane by FTIR helped in identification of sites for interaction between layers of membrane and support layer (PES). The SEM showed a multilayer structure and a distinct interface between the chitosan layer, the sodium alginate layer and the support layer (PES). The coating sequence of membranes had an obvious influence on the pervaporation dehydration performance of membranes. For the dehydration of 95 wt. % ethanol-water mixtures, the performance of multilayer membrane was found that the PES/Chi/Alg/Chi composite membrane has a good performance in pervaporation dehydration of ethanol

## 5. Acknowledgments

This research was supported by a grant from BOPTN Diponegoro University 2014.

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