

# Morphology of Composite Membranes based on Chitosan-Pahae Natural Zeolite

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**Abstract:** Composite membranes based on Chitosan-Pahae Natural Zeolite have been fabricated by solution casting method. The composite membranes are Chitosan and Chitosan with variation of composition zeolite relative to the mass of chitosan. The composition of Pahae natural zeolite are 5%, 10%, 15%, 20% and 25%. The samples were made by two step. The first step, the zeolite rock was crushed by mortar, and then zeolite was sieved with particle size of 200 mesh. Zeolite was activated by soaking into Sulfuric acid for 2 hours, then rinsed with distilled water until the pH about 7.0. Furthermore, the zeolite was sieved and burned in furnace with temperature 100°C for 5 hours. The second step, chitosan was dissolved in the acetic acid solution and stirred by using magnetic stirrer. Furthermore, zeolite was added into the solution. The resulting solution were stirred for 24 hours and dried in atmosphere at room temperature. From FTIR spectra was confirmed the existence of chitosan with stretching and bending at absorption wavenumber of 3250 cm<sup>-1</sup>, 2877 cm<sup>-1</sup>, 1640 cm<sup>-1</sup>, 1543 cm<sup>-1</sup>, 1401 cm<sup>-1</sup> and 1014 cm<sup>-1</sup>. The morphology of surfaces were obtained by using Scanning Electron Microscope (SEM) and showed that zeolite was evenly distributed within chitosan.

## 1 INTRODUCTION

One of the polymer materials that is widely used in making a membranes is chitosan. Chitosan is natural polymers that has good characteristic such as chemical inertness, hydrophilicity, biodegradability, biocompatibility, good film formation properties and more low cost (Liu et al, 2005 and Yavuz et al, 2009). The membranes based on chitosan have received considerable attention as membrane of polymer electrolyte because the membranes have good thermal and chemical stability, low conductivity, good mechanical properties, etc. Low conductivity properties caused by the absence of hydrogen ions moving in the structure (Xiao et al, 2013). So, for increase the efficient membranes based on chitosan, various modification approaches are needed like doping, blending and cross-linking.

The modification approaches based on chitosan have been done by adding other materials such as Carbon Nanotubes (CNTs), Polyaniline/Silica

(PAni/SiO<sub>2</sub>) and Sulfonated Graphene Oxide (SGO), etc. CNTs were used to modify polymer electrolyte membranes in energy conversion devices. The addition of CNTs to chitosan matrix cause the conductivity is increased (Wang et al, 2018). Ionic cross-linked based on chitosan by using nanocomposites of PAni/SiO<sub>2</sub> show increased mechanical properties and improved the stability of oxidation (Vijayalekshmi and Dipak, 2018). Sulfonated chitosan (SCS) and SGO nanosheets are fused into a membrane of chitosan have effect on the electrochemical properties of the membrane such as the increasing of conductivity, the reducing of permeability and increasing of selectivity relative to the pure chitosan. Furthermore, the addition of SCS and SGO to chitosan leads more proton conductivity than the individual additives due to the synergistic effect of SCS and SGO (Shirdast et al, 2016).

Zeolite is alumino-silicate compound with tetrahedral bound linked by oxygen. Aluminium Atom is negative that can be neralized by cation. The

exchangeable cation affects the adsorption ability of zeolite. For example, the zeolite was used as water vapor filter to purify hydrogen gas (Susilawati et al, 2017). Besides that, Zeolite is inorganic materials that has good mechanical properties and thermal stability. It can be a great potential to modify chitosan. The presence of hydrogen bonds between chitosan and zeolite, the membranes shows the desired thermal and mechanical stability (Wang et al, 2008).

In this study, chitosan was chosen as a matrix and Pahae Natural zeolite as a filler. Pahae Natural Zeolite was used because this mineral rock is widely available in Indonesia, especially Tapanuli Utara, Sumatera Utara. This study aims to fabricate composite membranes and knowing the morphology of membranes.

## 2 EXPERIMENTAL METHOD

### 2.1 Materials

There are two main materials in this study, Chitosan and Zeolite. Chitosan medium molecular weight with a degree of deacetylation about 85% was obtained from Sigma Aldrich Chemical (Singapore) and Natural Zeolite was obtained from Tarutung, Tapanuli Utara, Sumatera Utara. Furthermore, some of chemical materials needed to fabricate composite membranes, such as acetic acid, sulfuric acid and distilled water.

### 2.2 Membranes Preparation

The pure chitosan membrane and Chitosan-Zeolite membranes were fabricated by using solution-casting method. For the first, zeolite rock was crushed by mortar and then this zeolite was sieved with particle size of 200 mesh become zeolite powder. After that, zeolite powder was activated by soaking into Sulfuric acid 6% for 2 hours using magnetic stirrer and hot plate. Then the zeolite powder was flushed with distilled water until the pH of flushing solution is reached normal pH about 7.0, which confirmed that zeolite powder was completely free of sulfuric acid. Furthermore, the zeolite powder was sieved by sieve paper and then burned in furnace with temperature 100°C for 5 hours.

The second step, 1.5 g of chitosan was dissolved in the 75 ml, 2wt% acetic acid solution. Then, this solution of chitosan and acetic acid were stirred by using magnetic stirrer and hot plate. After chitosan and acetic acid were mixed, the zeolite powder was added into this solution with variation zeolite com-

position of 5%, 10%, 15%, 20% and 25%. The resulting solution were stirred for 24 hours and then this mixtures were poured onto a glass mold and dried in atmosphere pressure at room temperature. Finally, the composite membranes were obtained. For pure chitosan membrane, the chitosan was fabricated in same way with others devoid adding of zeolite powder.

## 2.3 Characterization

### 2.3.1 Spectra of Fourier Transform Infrared (FTIR)

The spectra of Fourier Transform Infrared were measured by Agilent/Cary 630 in transmittance mode. This instrument has resolution of 16  $\text{cm}^{-1}$  and spectra of every sample was measured in the wavenumber range between 4050  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  at room temperature.

### 2.3.2 Scanning Electron Microscope (SEM)

For scan of the surface morphology of composite membranes were used by Zeiss/SEM EVO MA10 instrument with magnification 500 x. The SEM morphology was obtained to show the existence of zeolite in composite membranes.

## 3 RESULTS AND DISCUSSION

### 3.1 Spectra of Fourier Transform Infrared (FTIR)

The spectra of FTIR ensured the existence of hydrogen bonds. The hydrogen bonds occur between chitosan and Pahae Natural zeolite in composite membranes. Figure 1 showed the FTIR spectra of chitosan and composite membranes with variation of zeolite composition. The peak of absorption spectra for all of membranes at around 3250  $\text{cm}^{-1}$ . This wavenumber was confirmed to stretching of hydroxyl groups (-OH).

Aliphatic groups ( $\text{CH}_2$  and  $-\text{CH}_3$ ) could be observed about 2877  $\text{cm}^{-1}$ . The absorption peaks around 1640 and 1543  $\text{cm}^{-1}$  were confirmed to C=O stretching (the band of Amide I) and  $-\text{NH}_2$  Bending (the band of Amide II), respectively (Yuan et al, 2007). The existence of C-O Stretching of Primary alcohol was showed by absorption of wavenumber at 1401  $\text{cm}^{-1}$  and the last of absorption peak was showed at 1014  $\text{cm}^{-1}$ . It was confirmed to glycosidic  $-\text{C}-\text{O}-\text{C}-$  groups that connect between Monomer of Chitosan.

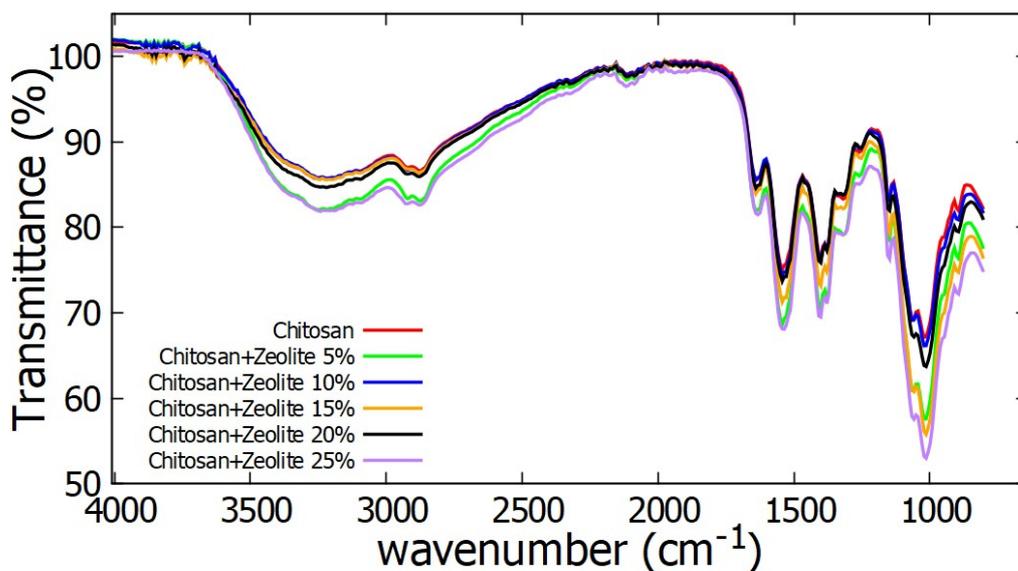


Figure 1: FTIR Spectra of Chitosan and composite membranes with variation of zeolite composition.

### 3.2 Scanning Electron Microscope (SEM)

Morphological analysis in this research was performed by using Scanning Electron Microscope (SEM) with magnification 500 x. The surface of membranes were scan by Zeiss/SEM. These surface morphology could be seen from Figure 2 (a-f). According to Figure 2, Pahae natural zeolite particles distribution were relatively homogenous in the chitosan phase because of its efficient dispersion. Figure 2 also was confirmed that the increasing of zeolite particles composition cause zeolite particles more evenly distributed in chitosan. The surface of all composite membranes were uniform and smooth without tolerable defect. Finally, the composite membranes from chitosan and zeolite was successfully fabricated with no visible zeolite aggregation existing in the membranes.

## 4 CONCLUSIONS

Composite membranes based on chitosan-zeolite with variation of zeolite composition were obtained.

The variation of zeolite composition are 5%, 10%, 15%, 20% and 25% relative to mass of chitosan. From FTIR spectra, the absorption peaks were occur at wavenumber around 3250  $\text{cm}^{-1}$ , 2877  $\text{cm}^{-1}$ , 1640  $\text{cm}^{-1}$ , 1543  $\text{cm}^{-1}$ , 1401  $\text{cm}^{-1}$  and 1014  $\text{cm}^{-1}$ . These wavenumbers were confirmed to stretching of hydroxyl groups, aliphatic groups. Amide I and II band, C-O Stretching of Primary alcohol and glycosidic -C-O-C- groups. All of this peaks related to chitosan. Furthermore, the Pahae natural zeolite could be evenly distributed in chitosan. It was confirmed by scanning electron microscope morphology. The surface of composite membranes showed that membranes were uniform and smooth without defect and aggregation.

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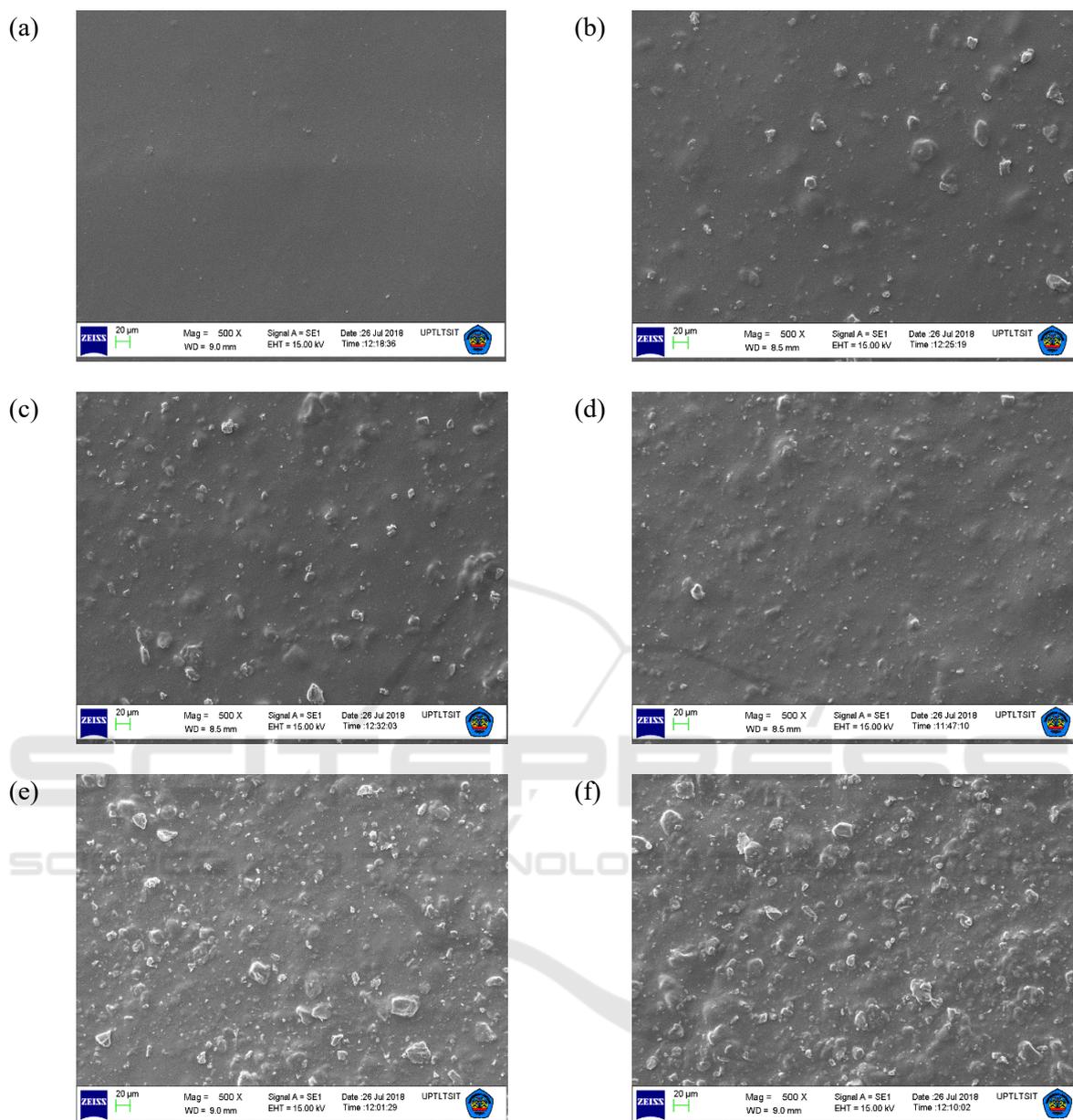


Figure 2: Morphology of composite membrane by using SEM; (a) pure Chitosan, (b) Chitosan/Zeolite 5%, (c) Chitosan/Zeolite 10%, (d) Chitosan/Zeolite 15%, (e) Chitosan/Zeolite 20% and (f) Chitosan/Zeolite 25%.

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