

The Modification of PVDF Membrane via Crosslinking with Chitosan and Glutaraldehyde as the Crosslinking Agent

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Received May 22, 2017; Accepted September 8, 2017

ABSTRACT

Poly(vinylidene fluoride) (PVDF) has outstanding properties such as high thermal stability, resistance to acid solvents and good mechanical strength. Due to its properties, PVDF is widely used as a membrane matrix. However, PVDF membrane is hydrophobic properties, so as for specific applications, the surface of membrane needs to be modified to become hydrophilic. This research aims to modify PVDF membrane surface with chitosan and glutaraldehyde as a crosslinker agent. The FTIR spectra showed that the modified membrane has a peak at 1655 cm^{-1} , indicating the imine group ($-N=C$)- that was formed due to the crosslink between amine group from chitosan and aldehyde group from glutaraldehyde. Results showed that the contact angle of the modified membrane decreases to 77.22° indicated that the membrane hydrophilic properties ($< 90^\circ$) were enhanced. Prior to the modification, the contact angle of the PVDF membrane was 90.24° , which shows hydrophobic properties ($> 90^\circ$). The results of porosity, ε (%) for unmodified PVDF membrane was 55.39%, while the modified PVDF membrane has a porosity of 81.99%. Similarly, by modifying the PVDF membrane, pure water flux increased from $0.9867\text{ L/m}^2\text{h}$ to $1.1253\text{ L/m}^2\text{h}$. The enhancement of porosity and pure water flux for the modified PVDF membrane was due to the improved surface hydrophilicity of PVDF membrane.

Keywords: polyvinylidene fluoride membrane; chitosan; glutaraldehyde

ABSTRAK

Polyvinylidene Fluoride (PVDF) merupakan polimer yang tahan terhadap suhu, pelarut asam dan memiliki kekuatan mekanik yang baik. Karena sifat tersebut, PVDF banyak digunakan sebagai bahan membran. Membran PVDF ini bersifat hidrofobik, sehingga untuk aplikasi tertentu perlu dilakukan modifikasi permukaannya agar bersifat hidrofilik. Penelitian ini bertujuan untuk memodifikasi permukaan membran PVDF dengan kitosan dan pengikat silang glutaraldehid (GA). Hasil spektra FTIR membran PVDF termodifikasi menunjukkan adanya puncak pada bilangan gelombang 1655 cm^{-1} yang mengindikasikan adanya gugus imina ($-N=C$)- akibat terjadinya ikat silang antara gugus amina dari kitosan dan gugus aldehid dari glutaraldehid. Uji sudut kontak pada membran PVDF termodifikasi menunjukkan sifat hidrofilik ($< 90^\circ$) dengan nilai $77,22^\circ$. Membran PVDF tanpa modifikasi memiliki sudut kontak $90,24^\circ$ yang menunjukkan sifat hidrofobik ($> 90^\circ$). Hasil uji persen porositas ε (%) dari membran tanpa modifikasi adalah 55,45% dan pada membran termodifikasi mengalami kenaikan yaitu 81,97%. Hasil serupa terjadi pada uji fluks air (pure water flux) untuk membran tanpa modifikasi adalah $0,9867\text{ L/m}^2\text{.jam}$ dan untuk membran termodifikasi menjadi $1,1253\text{ L/m}^2\text{.jam}$. Kenaikan nilai persen porositas dan fluks air pada membran termodifikasi membuktikan bahwa sifat membran PVDF telah berubah menjadi hidrofilik.

Kata Kunci: membran polyvinylidene fluoride; kitosan; glutaraldehida

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has received great attention as the membrane main material due to its

outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and hydrophobicity [1]. In general, PVDF membrane is widely applied for filtration process, i.e. ultrafiltration

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and microfiltration. Due to the hydrophobic properties of PVDF membrane, the application of PVDF membrane is limited. Therefore, PVDF membrane needs to be modified with other materials to enhance its hydrophilic properties.

Several researches to obtain hydrophilic surface have been reported. For examples, hydrophobic polystyrene surface was coated with hydrophilic chitosan [1-2], carboxymethyl chitosan was coated on poly(ether sulfone) surface [3], and polyvinyl alcohol was dip coated on the polypropylene surface [4]. The coating was conducted by immersing the hydrophobic polymer into the hydrophilic polymer at certain condition [4-5].

Chitosan is one of the materials that has hydrophilic properties, owing to have two functional groups, namely hydroxyl (OH) and amino (NH₂) group. The groups are capable to interact with other polymers by hydrogen bonds [6-7]. Due to having hydroxyl and amino groups, chitosan has been widely used in pervaporation of water-ethanol, enzyme immobilization, separation of proteins, concentration and environmental applications.

The hydrophilic properties of chitosan make it possible to be coated on the surface of hydrophobic PVDF membrane by surface modification method [2]. However, the structure of chitosan is not stable [6] for common surface modification method. In order to ensure a steady structure of Chitosan, crosslinks process is required using crosslink agents. One of the crosslink agents is glutaraldehyde [8]. This research was aimed to enhance the hydrophilic properties of PVDF membrane by modifying using chitosan crosslinked with glutaraldehyde.

EXPERIMENTAL SECTION

Materials

PVDF (Polyvinylidene Fluoride) Kynar ®740 from Arkema Inc. Philadelphia, N-methyl-2pyrrolidone (NMP), Ethylene glycol (EG), Chitosan (MW 50.000 Da, 85% deacetylation), Glutaraldehyde (GA) (Grade II, 25%), Acetic Acid 2%, Sodium hydroxide 1 M, and Ethanol were used as materials for membrane preparation in this research.

Instrumentation

The hollow fiber membranes were fabricated by dry-jet spinning technique. The samples were characterized by a variety of characterization techniques. Functional groups of hollow fiber membrane were obtained using Nicolet 5700, Thermo Electron Fourier transforms infrared (FTIR) spectrometer. The 3D atomic force microscopy (AFM) images and the

scanning electron microscopy (SEM) images were taken by NEOS N8 microscope and TM 3000, Hitachi, respectively. Contact angle values were carried out on OCA15EC Goniometer, while porosity and pure water flux values were conducted on a water permeation (Ultrafiltration) hollow fiber system.

Procedure

Preparation of hollow fiber membrane

Eighteen weight % (wt.%) PVDF pellets were first dried in an oven at 100 °C for 5 h to remove the moisture contents. Next, the pellets were added slowly into 76 wt.% NMP solution and mixed using mechanical stirrer at 600 rpm. 6 wt.% EG solution which acts as the additive was added slowly when a homogenous solution of PVDF and NMP was obtained. The dope solution was spun using the dry-jet spinning technique at the air gap of 10 cm. The hollow fiber membranes have the inner and outside diameters of 1.15/0.55 mm/mm. The hollow fiber membranes were then immersed with water at room temperature for 24 h before they were post-treated with ethanol aqueous solution (50 and 100 wt.%). Finally, the post-treated membranes were air-dried at room temperature before they were subjected to the crosslinking process.

Crosslinking hollow fiber membrane PVDF with chitosan and crosslink agent, glutaraldehyde

Preparation of chitosan and glutaraldehyde solutions. The solution was prepared by dissolving chitosan (0.1 g) in 40 mL of 2% acetic acid and was mixed by magnetic stirring to homogenous. Then, 5 mL of glutaraldehyde was added to the chitosan solution until it became homogeneous.

Membrane modification. The hollow fibers were immersed in the chitosan-glutaraldehyde solution for 30 min at room temperature and then dried for 24 h at room temperature. Later, the coated fibers were dried in the oven at 45, 50, 55 °C for 1 h at each temperature and then at 60 °C for 2 h to vaporize all solvents from the coated layer. After drying, the coated membranes were immersed in 2 mL of sodium hydroxide in 50%(v/v) of ethanol solution for 1 h. Afterwards, the coated membranes were rinsed twice with deionized (DI) water and were left to dry in an oven at 60 °C for 24 h [8].

RESULT AND DISCUSSION

FTIR Analysis

The hollow fiber was examined using FTIR to confirm the interaction between chitosan, glutaraldehyde, and PVDF based on the identification

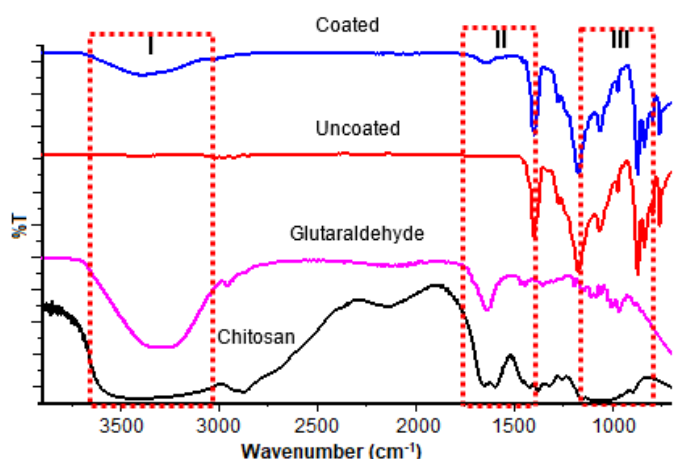


Fig 1. FTIR spectra of uncoated and coated PVDF hollow fiber membrane

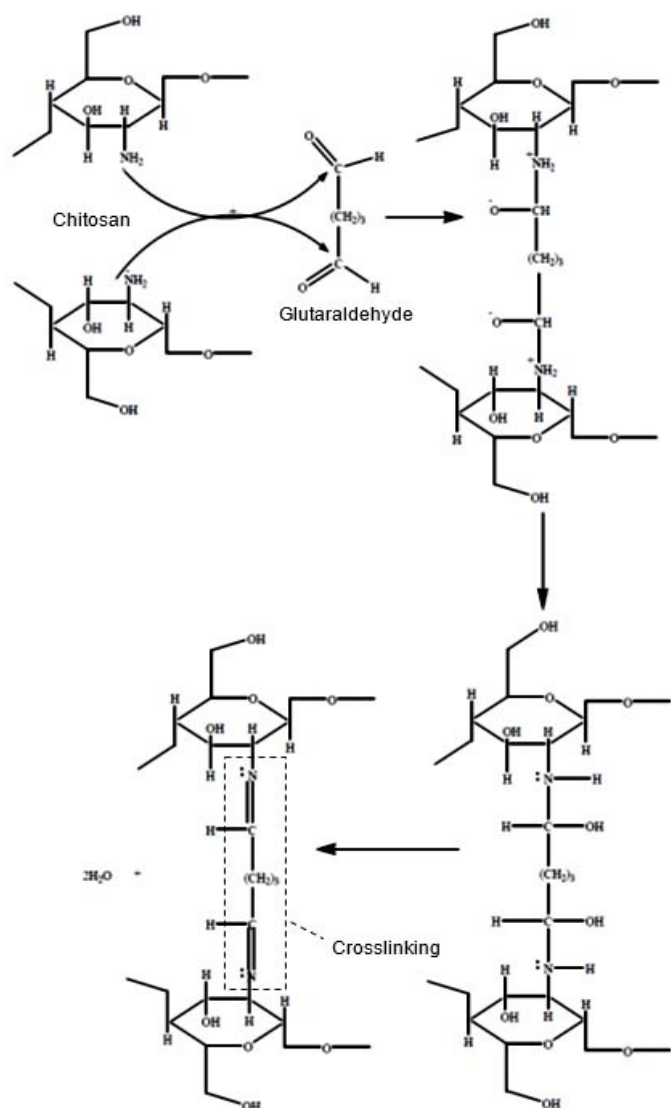


Fig 2. Crosslink of chitosan and glutaraldehyde, and interaction with PVDF

functional groups of coated and uncoated membranes. Fig. 2 illustrates the interaction between chitosan and glutaraldehyde and PVDF. From Fig. 1, at region, I, the existence of broad peaks in the region of 3200–3600 cm^{-1} [6] indicated the existence of O-H stretching of the hydroxyl group and N-H stretching of the amine group from chitosan. The existence of the hydroxyl group peak, which comes from glutaraldehyde was observed at 3270 cm^{-1} on the modified membrane. The existence of carbonyl (C=O) group at 1725 cm^{-1} and N=C at 1640 and 1655 cm^{-1} indicated the presence of glutaraldehyde and chitosan, respectively. At region II, it was indicated that the crosslink between the amino group and aldehyde group from chitosan and glutaraldehyde has occurred.

The FTIR spectrum of the coated membrane (region III) showed the disappearance of an amide group (N-H) at the bending group (1567 cm^{-1}). It was caused by the microparticle of chitosan layer, which did not cover all membrane surface as the crosslinking degree via the formation of Schiff's base linkage decreases [9]. For modified PVDF membrane, the absorbance peaks appeared at 1180 and 1400 cm^{-1} , which were assigned for C-F and C=C stretching showed the typical characteristic of PVDF [10].

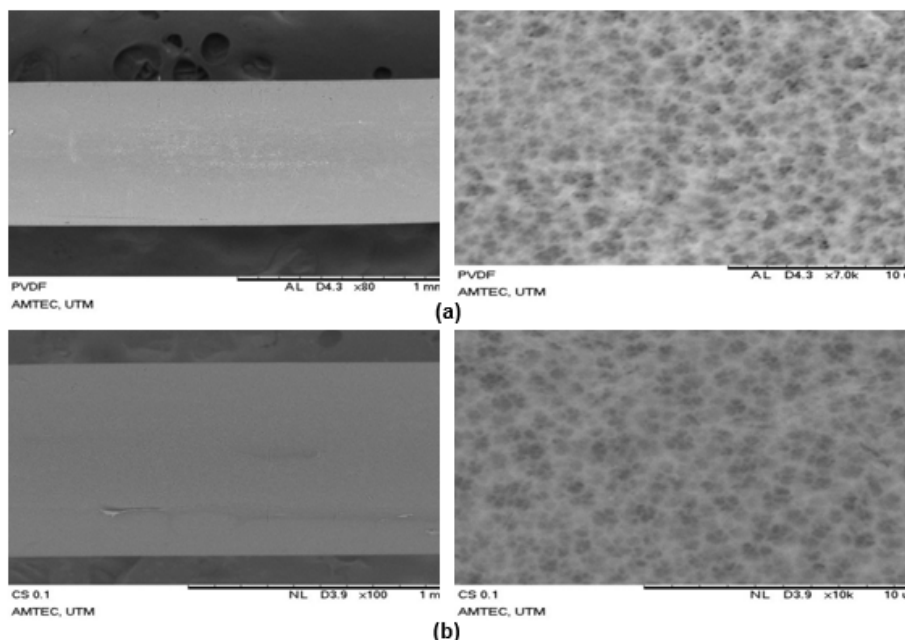
Membrane Hydrophilicity, Pure Water Flux, and Porosity

The changing of PVDF membrane properties from hydrophobic to hydrophilic due to the surface modification with chitosan and glutaraldehyde was observed based on the results of contact angle, pure water flux, and porosity. Table 1 shows the different properties of coated and uncoated membrane. The value of contact angle of coated membrane surface reduced from 90.24° to 77.22°. This proved the changing of membrane properties from hydrophobic to hydrophilic after coating with chitosan and glutaraldehyde. The hydrophobic property of membrane was characterized by contact angle at > 90° [6,8,11,13].

For coated PVDF hollow fiber membrane, the contact angle was 77.22°, showing higher wettability or hydrophilic properties (< 90 °C). The uncoated PVDF membrane properties were changed after the crosslink with glutaraldehyde taking place. However, as previously discussed in FTIR section, the microparticle from chitosan layer did not cover all membrane surface as the crosslinking degree via formation of Schiff's base linkage decreases [9]. This happened due to the high swelling degree of Chitosan [13], which made the interaction between chitosan and water much stronger [8].

Table 1. Characterization of uncoated and coated membrane

Characterization	Uncoated Membrane	Coated Membrane
Contact Angle	90.24°	77.22°
Pure Water Flux	0.84 L/m ² h	1.12 L/m ² h
Porosity	55.45%	81.97%

**Fig 3.** SEM images of (a) uncoated and (b) coated hollow fiber membrane surface

Due to the high swelling degree of chitosan, the molecule of water could diffuse through the modified membrane surface. The easier flow of water through the membrane surface increased the pure water flux of coated membrane (1.12 L/m²h) as compared to the uncoated PVDF membrane (0.84 L/m²h). Chanachai et al. [8] reported that the coating of the membrane with a hydrophilic polymer could increase the hydrophilicity of the membrane surface. Hydrophilic properties of the coated membrane increased the result of porosity, which is 81.97% compared to the unmodified membrane (55.45%) as shown in Table 1. The higher porosity of the coated membrane was due to the plentiful absorbed water through membrane pores compared to the uncoated membrane.

Morphology and Topography Analysis

The difference in the morphology and topography of uncoated and coated membrane with chitosan and glutaraldehyde were studied using SEM and AFM. The results of the surface morphology of unmodified and modified membrane were shown in Fig. 3.

From the SEM images, the uncoated membrane (Fig. 3(a)) shows the smoothest surface and white in color, because there was no chitosan and

glutaraldehyde presence. Besides, it has an asymmetric and uneven pores distribution. While for the coated membrane (Fig. 3(b)), it can be clearly seen that the membrane outer surface was all covered by chitosan and glutaraldehyde. Thermal treatment conducted did not change pores size and distribution, due to the low thermal used, 45–60 °C [15].

SEM images of the membrane cross-section were shown in Fig. 4. At the upper side, it macro voids finger-like can be clearly seen and at the bottom side, irregularity of cavity was found around the membrane due to the use of NMP as a solvent. Bottino et al. [10] reported that using NMP as a solvent for PVDF polymer will cause the formation of the irregular shape of cavity below the membrane. The addition of EG as additive and pore former into the dope solution caused the hollow fiber membrane to be porous. Kesting et al. [15] reported that the formation of irregularity cavity and macro voids finger-like was caused by the coagulation process. On the other hand, it was due to the different solubility limits of water and NMP and the weak affinity between water and NMP. As reported by Kesting et al. [15], generally the biggest macro void finger-like resulted from the rapid coagulation process.

The topography of coated and uncoated membranes using AFM is shown in Fig. 5. The 3D

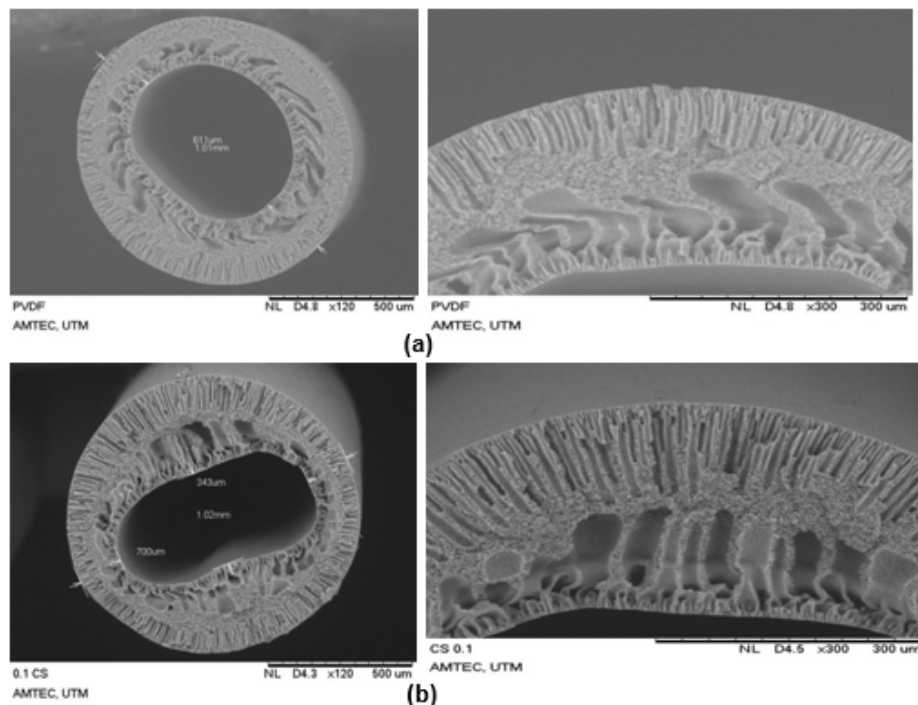


Fig 4. SEM images of cross section of (a) uncoated and (b) coated hollow fiber membrane

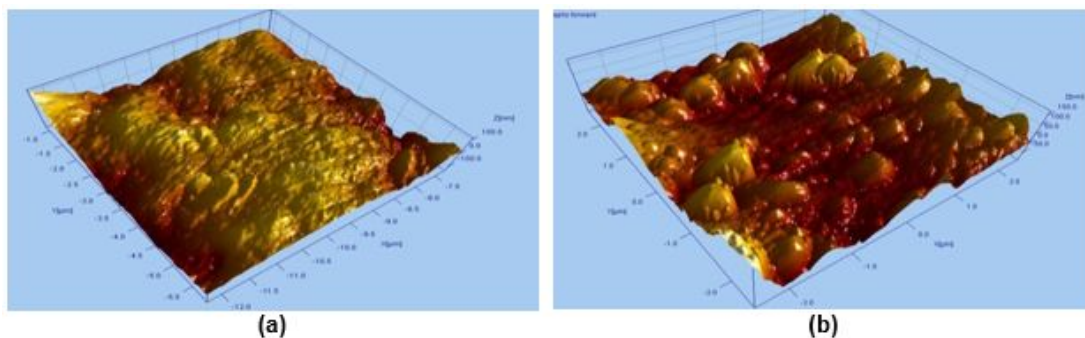


Fig 5. AFM topography (a) uncoated and (b) coated hollow fiber membrane

images showed a little surface roughness, with the mean surface roughness (S_a) and mean height distribution roughness (S_q) were 0.661 and 0.895 nm, respectively on uncoated PVDF membrane. For the coated PVDF membranes, the S_a and S_q values were 0.868 and 1.31 nm, respectively. Irregular valley and peak structures were seen on the coated PVDF hollow fiber membrane surface that caused the roughness to increase, due to the existence of crosslinking chitosan and glutaraldehyde on the PVDF membrane surface [4].

CONCLUSION

It can be concluded that by modifying with chitosan and glutaraldehyde, hydrophobic PVDF membrane was changed into hydrophilic. As a result, pure water flux and

porosity of the membranes increased due to the enhanced hydrophilicity. The surface of the modified membrane was rough due to the modification, while the uncoated membrane surface was smooth.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Indonesian Ministry of Research and Higher Education for providing BPPDN scholarship for pursuing Master Degree for Romaya Sitha Silitonga in the Department of Chemistry, Institut Teknologi Sepuluh Nopember. The authors also would like to thanks the Laboratory of Energy–Institute of Research and Community Service, ITS for supporting research facilities.

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