**Characterization of SA-Pebax Membrane as a Potential Material for Bioethanol Dehydration**

Fadias R. A. Lakuy1, Taufik Q. Romadiansyah1, Agus W. Pratama1, Nur Lailiyah1, Triyanda Gunawan1, Nurul Widiastuti1, a)

*1Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Sukolilo,*

*Surabaya 60111, Indonesia*

*2Department of Physics, Universitas Negeri Makassar, Makassar 90223, Indonesia*

*a)Corresponding author: nurul\_widiastuti@chem.its.ac.id*

**Abstract.** Bioethanol, a kind of alcohol, is extensively utilized in diverse sectors including manufacturing, medications, and fuels. A bioethanol concentration above 90 wt% is necessary needed in these applications. Nevertheless, achieving this concentration is hindered by the azeotropic condition of the ethanol-water mixture. The sodium alginate (SA) membrane is a hydrophilic polymer that shows promise for use in the pervaporation of bioethanol dehydration. The performance of a SA membrane can be enhanced by blending it with other polymers. The combination of Pebax and SA can create ionic cross-links by connecting the acetate groups in SA with the amide groups of Pebax, which enhances the performance of the membrane. SA-Pebax membrane was successfully fabricated as a flat sheet with SA:Pebax blending ratio of 3:1 and 3:2. SA-Pebax membrane was fabricated using the EIPS phase separation method to form a non-porous solid membrane. The characterization results using Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), contact angle meter showed the effect polymer blending on the structure, morphology, and hydrophilicity properties of SA-Pebax membrane which has the potential to be applied to bioethanol dehydration by pervaporation. The surfaces blend membranes exhibited a smooth and even texture, devoid of any visible pores. Additionally, the polymer components were uniformly distributed without any phase separation. SA-Pebax membrane with 3:1 blend ratio showed the highest decrease of water contact angle value than membrane with ratio 3:2, which allowed for more efficient ethanol-water separation.

# INTRODUCTION

Producing high-concentration bioethanol is challenging due to the azeotrope. The similar molecular sizes of ethanol and water hinder efficient water removal from aqueous ethanol mixtures [1]. Membrane separation is currently the most widely used method for bioethanol purification. Pervaporation, as one of the membrane separation technologies, excels in separating azeotropic mixtures such as the water-ethanol system. This capability is based on the principle of overcoming the limitations of liquid-vapor equilibrium [2,3]. With these unique properties, pervaporation has proven to be a more efficient separation method for dehydrating organic solvents.

The performance of pervaporation membranes is significantly influenced by the choice of membrane material. For bioethanol dehydration, hydrophilic membranes are typically employed. Numerous studies have explored the application of hydrophilic polymers to enhance dehydration efficiency in ethanol-water azeotropic mixtures using pervaporation [4]. It has been identified that the selection and modification of polymer membrane types can enhance selectivity, permeability, and the strength of the membrane, ultimately leading to improved dehydration process efficiency [5]. One approach to modify polymer membranes is polymer blending (polyblend). Polyblend often exhibit superior properties compared to their pure components. The most commonly used hydrophilic polymers for ethanol dehydration membranes include sodium alginate, chitosan, and polyvinyl alcohol [6]. Under the same operating conditions and concentrations, sodium alginate membranes exhibited the highest flux and selectivity compared to PVA and chitosan membranes [7–9]. Sodium alginate is highly hydrophilic, which enhances its ability to interact with water molecules [10]. This property facilitates better permeation rates in membrane applications, particularly in processes like pervaporation where water transport is critical [11]. The sodium alginate-based polymer membrane achieved a flux of 1203 g/m².h and a separation factor of 1542 [12]. Yeom and Lee also used sodium alginate as the membrane material, resulting in a flux of 120 g/m².h and a separation factor of 3000013. Therefore, in this study, sodium alginate is chosen as the membrane material because of its beneficial properties for the intended application.

Another polymer material that can be used for polymer blending is PEBA. PEBA, or polyether-block-amide, is a copolymer that combines the flexibility and permeability of the polyether segments with the mechanical strength and thermal stability of the polyamide segments 14,15. Various types of PEBA products, known as Pebax, are available with varying molar ratios of PE to PA. Pebax 1657, with a PE/PA weight ratio of 60/40, is suitable as a blending material for sodium alginate due to its crystal-amorphous structure, which imparts thermoplastic and rubbery properties, inducing high mechanical strength and chemical resistance in the resulting blend. PEBA offers a unique combination of hydrophilic and hydrophobic properties, making it highly suitable for pervaporation membrane applications [16,17]. Therefore, in this study, sodium alginate and pebax were employed as materials for pervaporation membranes to dehydrate ethanol.

# **MATERIAL AND METHOD**

## **Material**

The materials for membrane preparation include sodium alginate (≥ 99%, Himedia), Polyether block amide (Pebax 1657), demineralized water, distilled water, hydrochloric acid (HCl) 37% (Sigma-Aldrich), isopropyl alcohol p.a. (merck), and glutaraldehyde p.a. (SAP).

## **Preparation of SA-Pebax Membranes**

The preparation of SA-Pebax membranes was conducted following the methodology by Nagar et al18. SA-Pebax membranes were prepared by dissolving 3% (w/v) sodium alginate in demineralized water. On the other hand, 3% (w/v) Pebax was dissolved in an ethanol/water mixture (80/20 v/v) at 80°C. Then, the sodium alginate and Pebax dope solutions were mixed with varying composition ratios of 3:2, and 3:1 for 30 minutes. Subsequently, the dope solution was cast onto a glass plate using a roller tube and dried at room temperature for 24 hours. The dried membranes were immersed in a mixture of isopropanol-water (90/10 v/v), 5% (w/v) glutaraldehyde (GA), and 1% (w/v) HCl for 30 minutes for cross-linking. After that, the membranes were rinsed with demineralized water and dried through an evaporation process at room temperature for 24 hours.

## **Characterization of SA-Pebax Membranes**

Characterization of the SA-Pebax material was carried out using several techniques, including FTIR, contact angle analysis, and SEM. FTIR analysis was performed with the Fourier Transform Infrared (FTIR) Thermo Scientific Nicolet iS10 to identify the functional groups present in the material. The sample was prepared by mixing the material and KBr in a 1:10 ratio, then pressed into a pellet and scanned within the range of 4000 cm⁻¹ to 400 cm⁻¹ to obtain the spectrum. Contact angle analysis was conducted using a contact angle meter to assess the hydrophilicity of the membrane by measuring the contact angle of a water droplet placed on the membrane surface. SEM analysis was performed with the Scanning Electron Microscope (SEM) Hitachi FlexSEM 1000 to examine the surface morphology of the membrane. The sample was coated with Au and Cu tips, then scanned at specific magnifications.

# **RESULT AND DISCUSSION**

## **Results of FTIR Characterization on Membrane**

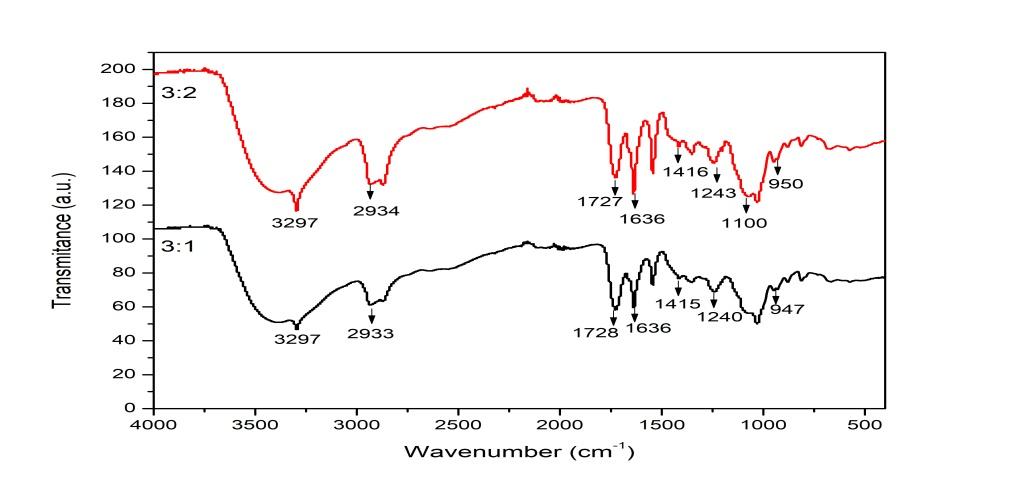


Figure 1. FTIR spectrum of SA-Pebax membranes with ratios of 3:2 and 3:1**.**

The FTIR spectrum provides valuable insights into the structure and composition of the sodium alginate-Pebax membrane blend. As shown in Figure 1, several significant characteristic peaks are observed. The significant peak at 3297 cm⁻¹ corresponds to the –OH groups, which are typical for sodium alginate due to its carboxyl (-COOH) and hydroxyl (-OH) functionalities [19]. The peaks at 2934 cm⁻¹ (for the 3:2 ratio) and 2933 cm⁻¹ (for the 3:1 ratio) indicate C-H stretching vibrations, which are attributed to the polyether amide structure of Pebax. Moreover, The peak at 1732 cm⁻¹ is associated with the –O–C=O groups present in the polyamide block20. A shift in the asymmetric stretching peak of sodium alginate’s (COO⁻) groups is observed from 1640 cm⁻¹ to 1636 cm⁻¹. Furthermore, the peak at 1416 cm⁻¹ corresponds to the asymmetric stretching of carboxylate salt groups. The characteristic features of Pebax are also evident at 1100 cm⁻¹, representing -C-O vibrations. Additional peaks at 1243 cm⁻¹ and 1240 cm⁻¹ highlight the -C-O- stretching vibrations commonly found in ether or alcohol groups, which align with the chemical composition of the polymers. Additional peaks found in spectra occurred between1245 cm-1and 1239 cm⁻¹. The peaks at 950 cm⁻¹ and 947 cm⁻¹ indicate the presence of C-O bonds [21].

## Result of SEM Characterization on Membrane

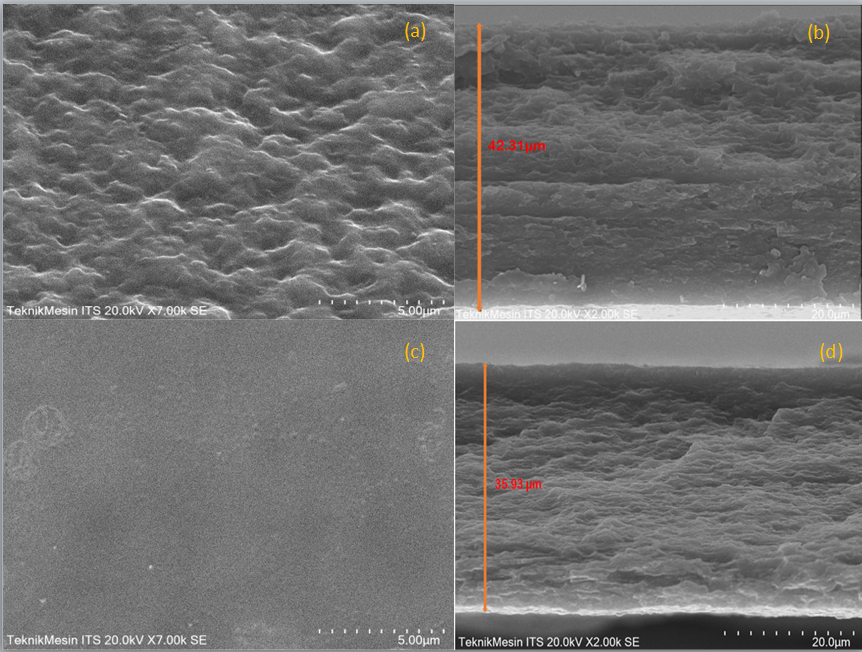


Figure 2. SEM Results of SA-Pebax Blending (a) Surface of ratio 3:2, (b) Cross

section of ratio 3:2, (c) Surface of ratio 3:1, (d) Cross section of ratio 3:1.

The SEM images display the surface and cross-sectional structures of the SA-Pebax membranes for the 3:2 and 3:1 ratios. For the 3:2 ratio, as shown in Figure 1(a), the membrane surface exhibits a rough morphology. The thickness of this membrane was measured to be approximately 42.31 µm, as illustrated in Figure 1(b). For the 3:1 ratio, as depicted in Figure 1(c), the membrane surface appears smoother and more homogeneous compared to the 3:2 ratio. The thickness of this membrane was recorded at approximately 36.93 µm, which is slightly thinner than the membrane with a 3:2 ratio, as shown in Figure 1(d). The reduction in Pebax content allows sodium alginate to dominate the structure while ensuring more uniform interactions within the matrix.

## Contact angel

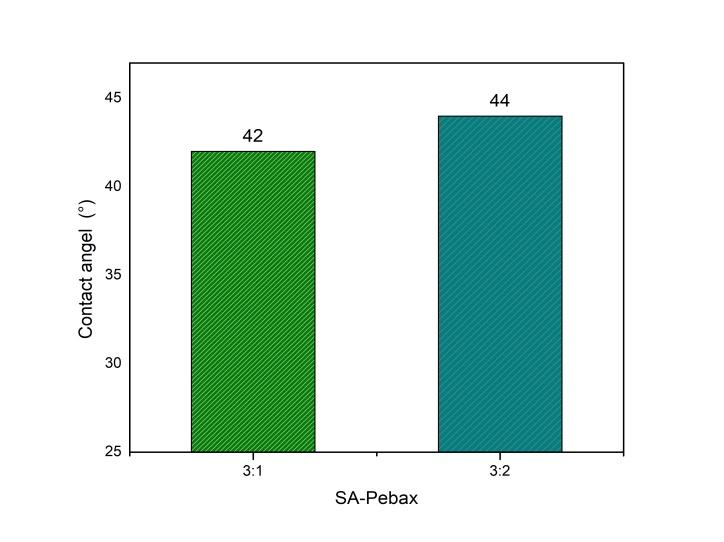


Figure 3. Contact Angle of SA-Pebax Membranes with Ratios of 3:2 and 3:1

Figure 3 shows the contact angle of the Sodium Alginate (SA) and Pebax membrane mixtures with ratios of 3:1 and 3:2. In this figure, it can be observed that the SA mixture with a 3:1 ratio has a contact angle of 42 degrees, while the mixture with a 3:2 ratio has a contact angle of 44 degrees. The increase in Pebax proportion in the mixture leads to a slight increase in the contact angle, indicating that the surface becomes slightly more hydrophobic. High water absorption reduces membrane strength, while low absorption makes proton conduction difficult. The increase in contact angle at the 3:2 ratio may be due to the dominance of Pebax's hydrophobic properties, which can maintain its tensile strength, while the rigid yet interactive amide blocks balance the hydrophilicity of the mixture [18]. As the amount of Sodium Alginate (SA) in the membrane increases, the membrane becomes more hydrophilic, which may enhance the efficiency of the ethanol-water separation process.

# **CONCLUSION**

The membrane was successfully fabricated with 3:2 and 3:1 ratios of SA and Pebax. Different blend ratios affect the morphology and hydrophilicity of the membrane. The 3:1 ratio shows better hydrophilic properties compared to the 3:2 ratio indicating its potential for use in the bioethanol dehydration pervaporation process.

# Acknowledgments

The authors thank the Indonesia Endowment Fund for Education (LPDP) from the Ministry of Finance of the Republic of Indonesia for scholarship and supporting this research.

# REFERENCE

1 M. Ehsan, H. Razzaq, S. Razzaque, A. Bibi, and A. Yaqub, “Recent advances in sodium alginate‐based membranes for dehydration of aqueous ethanol through pervaporation,” J. Polym. Sci. **60**(16), 2435–2453 (2022).

2 K.-R. Lee, M.-J. Liu, and J.-Y. Lai, “Pervaporation separation of aqueous alcohol solution through asymmetric polycarbonate membrane,” Sep. Sci. Technol. **29**(1), 119–134 (1994).

3 K.M. Song, and W.H. Hong, “Dehydration of ethanol and isopropanol using tubular type cellulose acetate membrane with ceramic support in pervaporation process,” J. Memb. Sci. **123**(1), 27–33 (1997).

4 M.S. Jyothi, K.R. Reddy, K. Soontarapa, S. Naveen, A. V Raghu, R. V Kulkarni, D.P. Suhas, N.P. Shetti, M.N. Nadagouda, and T.M. Aminabhavi, “Membranes for dehydration of alcohols via pervaporation,” J. Environ. Manage. **242**, 415–429 (2019).

5 W. Kujawski, “Application of pervaporation and vapor permeation in environmental protection,” Polish J. Environ. Stud. **9**(1), 13–26 (2000).

6 A. Listyarini, A.A. Cahyaningtyas, E. Yuanita, and G. Supeni, “Preparasi Dan Karakterisasi Polimer Blend Poli Butilen Suksinat (Pbs)/Poli Etilen Tereftalat (Pet),” J. Kim. Dan Kemasan **35**(2), 97–104 (2013).

7 X.H. Zhang, Q.L. Liu, Y. Xiong, A.M. Zhu, Y. Chen, and Q.G. Zhang, “Pervaporation dehydration of ethyl acetate/ethanol/water azeotrope using chitosan/poly (vinyl pyrrolidone) blend membranes,” J. Memb. Sci. **327**(1–2), 274–280 (2009).

8 C.-K. Yeom, and K.-H. Lee, “Pervaporation separation of water-acetic acid mixtures through poly (vinyl alcohol) membranes crosslinked with glutaraldehyde,” J. Memb. Sci. **109**(2), 257–265 (1996).

9 L. Liang, and E. Ruckenstein, “Polyvinyl alcohol-polyacrylamide interpenetrating polymer network membranes and their pervaporation characteristics for ethanol-water mixtures,” J. Memb. Sci. **106**(1–2), 167–182 (1995).

10 M. Ehsan, H. Razzaq, S. Razzaque, A. Bibi, and A. Yaqub, “Recent advances in sodium alginate-based membranes for dehydration of aqueous ethanol through pervaporation,” J. Polym. Sci. **60**(16), 2435–2453 (2022).

11 M. Dmitrenko, V. Liamin, A. Kuzminova, A. Mazur, E. Lahderanta, S. Ermakov, and A. Penkova, “Novel Mixed Matrix Sodium Alginate–Fullerenol Membranes: Development, Characterization, and Study in Pervaporation Dehydration of Isopropanol,” Polym. 2020, Vol. 12, Page 864 **12**(4), 864 (2020).

12 J. Li, X. Si, X. Li, N. Wang, Q. An, and S. Ji, “Preparation of acid-resistant PEI/SA composite membranes for the pervaporation dehydration of ethanol at low pH,” Sep. Purif. Technol. **192**, 205–212 (2018).

13 C.K. Yeom, and K. Lee, “Characterization of sodium alginate and poly (vinyl alcohol) blend membranes in pervaporation separation,” J. Appl. Polym. Sci. **67**(5), 949–959 (1998).

14 L.J. Fang, J.H. Chen, J.M. Wang, W.W. Lin, X.G. Lin, Q.J. Lin, and Y. He, “Hydrophobic two-dimensional MoS2 nanosheets embedded in a polyether copolymer block amide (PEBA) membrane for recovering pyridine from a dilute solution,” ACS Omega **6**(4), 2675–2685 (2021).

15 S.E. Brady, “Photochemically Degradable Polymers; Synthesis of Polymers with Metal–Metal Bonds Along the Backbone Using Click Chemistry,” (2012).

16 P. Cai, J. Li, N. Zhang, D. Song, N. Wang, and Q.-F. An, “Liquid-liquid interface induced high-flux PEBA pervaporation membrane for ethanol recovery,” J. Memb. Sci. **668**, 121254 (2023).

17 T. Jose, S.C. George, and S. Thomas, “Polymer nanocomposite membranes for pervaporation: an introduction,” in *Polym. Nanocomposite Membr. Pervaporation*, (Elsevier, 2020), pp. 1–16.

18 H. Nagar, C. Sumana, V.V.B. Rao, and S. Sridhar, “Performance evaluation of sodium alginate–Pebax polyion complex membranes for application in direct methanol fuel cells,” J. Appl. Polym. Sci. **134**(7), (2017).

19 M.I. Diana, P.C. Selvin, S. Selvasekarapandian, and M.V. Krishna, “Investigations on Na-ion conducting electrolyte based on sodium alginate biopolymer for all-solid-state sodium-ion batteries,” J. Solid State Electrochem. **25**(7), 2009–2020 (2021).

20 P. Bernardo, and G. Clarizia, “Enhancing Gas Permeation Properties of Pebax® 1657 Membranes via Polysorbate Nonionic Surfactants Doping, Polymers. 12 (2020) 253,” (n.d.).

21 B. Smitha, S. Sridhar, and A.A. Khan, “Chitosan–poly (vinyl pyrrolidone) blends as membranes for direct methanol fuel cell applications,” J. Power Sources **159**(2), 846–854 (2006).