ISSN No:-2456-2165

The Effect of Glutaraldehyde as Crosslinking Agent in the Sweet Potato Starch/Chitosan Membrane for Pervaporation Method

Anisa Witri Sofiarani, Nur Rokhati
Departement of Chemical Engineering
Faculty of Engineering, Diponegoro University
Semarang, Indonesia

Abstract:- The aim of this study was to investigate the dehydration of ethanol using the pervaporation process based on a sweet potato starch-chitosan membrane. The pervaporation process is an alternative to the energy-intensive methods of ethanol dehydration, like distillation and crystallization. To improve the properties of the composite membrane by adding a crosslinking agent of glutaraldehyde (1% v/v) and a support membrane of polyethersulfone (PES) were added. The sweet potato starch-chitosan membrane was modified with various concentrations of 100:0, 80:40, 60:40, 50:50, 40:60, 20:80, and 0:100. The characterization of the composite membrane used tests such as swelling degree, permeability, mechanical properties, and SEM to evaluate the hydrophilicity, structure, and performance. *The increase of hydrophilicity showed at the value of* swelling degree of 204.16 to 226.52%, and permeability of 861.34 to 964.26 L/m^2.hr.bar. The structure of the membrane improved by the addition of glutaraldehyde, shown in the mechanical properties and SEM results. The best composition is a ratio of 50:50 with a crosslinking agent used for dehydration of ethanol with the pervaporation process. The process used ethanol composition (95 wt.%) and was observed for an hour. The value of selectivity in the pervaporation process is 15% with an ethanol concentration of 98%.

Keywords:- *Pervaporation Process, Sweet Potato Starch-Chitosan Membrane, Glutaraldehyde, Dehydration of Ethanol.*

I. INTRODUCTION

Ethanol demand in 2017 was more than 100 billion liters and will continue to increase. Ethanol 96,5% (super fine-grade) is usually used as an ingredient in the mixture of industrial products such as paints, coatings, fuels, pharmaceuticals, cosmetics, detergents, and beverage mixes [1]. Ethanol can be produced by fermentation using evaporation and distillation, but these methods use high energy, and the purity reaches only 95% [2]. Pervaporation is an alternative method with more advantages using low energy with a vacuum process and purifying more than 96% [3]. Hydrophilic membranes provide good selectivity, high permeability, and sufficient mechanical strength while reducing energy requirements due to only allowing water to pass through the membrane, thus eliminating the need for distillation. These hydrophilic membranes can be made from either synthetic or natural polymers [4].

Composite films comprised of modified biopolymers have been designed to enhance film properties. Chitosan, a natural polysaccharide, is produced through the deacetylation of chitin found in the shells of invertebrates. It is characterized by its hydrophilic nature and ability to retain water, forming a gel when used as a raw material for films or membranes [5-6]. Incomplete deacetylation of chitin results in the formation of a hydrophobic acetyl group. In the pure chitosan membrane for the pervaporation process, less than 90% ethanol yields were obtained in the ethanol-water dehydration process [7]. Starch, which has amylose, is widely used to construct pervaporated composite membranes for dehydration [8]. Sweet potato starch, in particular, has the highest concentration of amylose among other starches, ranging from 8.50-37.40% [9]. Although starch has a low water vapor barrier property, its low mechanical strength can be improved by using a crosslinked film with glutaraldehyde as the crosslinking agent [10]. The sweet potato starch membrane produces an increased selectivity. However, the sweet potato starch film formed is quite brittle.

The previous results of [11] have shown that chitosan film's selectivity is insufficient and unsuitable for separating water from ethanol. Based on prior research, starch films with chitosan can achieve higher selectivity values. In order to improve the selectivity value of the pervaporation process, a support membrane is necessary. Polyether sulfone membrane (PES) has been used as a support membrane due to its good qualities and ability to reduce membrane fragility [12]. Therefore, this study intends to create sweet potato starch-chitosan composite membranes with glutaraldehyde as a crosslinking agent and PES as a support membrane to optimize water separation from ethanol during the pervaporation process.

II. EXPERIMENTAL

A. Composite Membrane Preparation

The materials for the composite membrane are chitosan with a molecular weight of 118.4 cps with a deacetylation degree of 80.4%, which was acquired from Surindo Biotech Cirebon, Indonesia. PT Hepilab Sukses Bersama Semarang provided glycerol, ethanol (95%), and glutaraldehyde. The Membran Research Center (MER-C) laboratory at

ISSN No:-2456-2165

Diponegoro University supplied sweet potato starch and distilled water.

The composite membrane preparation was sweet potato starch blended with distilled water until 3% w/v and 30% v/v of glycerol were included. The combination was stirred for an hour at 90ºC using a mechanical stirrer (400 rpm) to form a homogeneous gel solution and was allowed to stand for 5 minutes until it had cooled to an average temperature. The chitosan solution was added by variation ratio (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100), and the mixture was stirred for 30 min at 60ºC with a mechanical stirrer set at 400 rpm to achieve a homogenous gel solution. The solution was poured into a polyethersulfone (PES) membrane with a thickness of 0.3 mm, using a casting knife. Subsequently, the film was allowed to dry at room temperature for 24 hours, followed by immersion in a glutaraldehyde solution for 2 hours with concentrations of 0.0% and 1.0% v/v.

B. Water Permeability Analysis

The permeability of a membrane can be determined by how quickly a species can penetrate it and is expressed as the volumetric rate of fluid (permeate) passing through it [13]. A dead-end filtration cell (Amicon 8200, Millipore, USA) with a membrane area of 4.2 cm^2 was used to measure the value of permeability. Distilled water was pumped at a pressure of 0.1 bar into the membrane module, and the volume of the produced permeate was calculated by taking readings over 5 minutes and applying water flux. The permeability value can be determined by following equations (1) and (2).

$$J_w = \frac{(w_1 - w_2)/\rho_{aquadest}}{A\ x\ t} \quad (1)$$

$$P = \frac{J_w}{\Delta P} \quad (2)$$

Where inclusive of the container (W_1), the mass of the container (W_2), the density of distilled water (ρ), the membrane surface area (A), and the filtration time (t), ΔP is operating pressure. Once the water flux had been ascertained, permeability was computed utilizing equation (2).

C. Swelling Degree Analysis

The membrane sample was cut into 2 cm × 2 cm strips. The sample was immersed in distilled water for two hours and weighed accurately to determine the membrane's swelling degree. The swelling degree was then calculated using equation (3) [14].

$$SD = \frac{w_2 - w_1}{w_1} x100\% \quad (3)$$

Where W_1 is the initial weight in dry conditions and W_2 are the weight of composite membranes in wet conditions.

D. Mechanical Properties Analysis

The tensile strength, Young's modulus, and elongation at the break of the mechanical strength were assessed using the TA.XI Plus Texture Analyzer (Super Technology Instruments Co., Ltd., China) in compliance with the ASTM D882-18 protocol. The membrane 10 cm x 2 cm was tested, and the initial distance was set to 40 mm with a test speed of 60mm/min.

E. SEM Analysis

The morphology of the membrane's cross-section was studied using Scanning Electron Microscope (SEM) with a spot size of 30, a voltage of 10 kV, and a work distance of 10 mm. Its sample size was 0.5 cm x 0.5 cm, which was examined at a magnification of 250x with an SEM-EDX JEOL JSM-6510LA.

F. Pervaporation Method

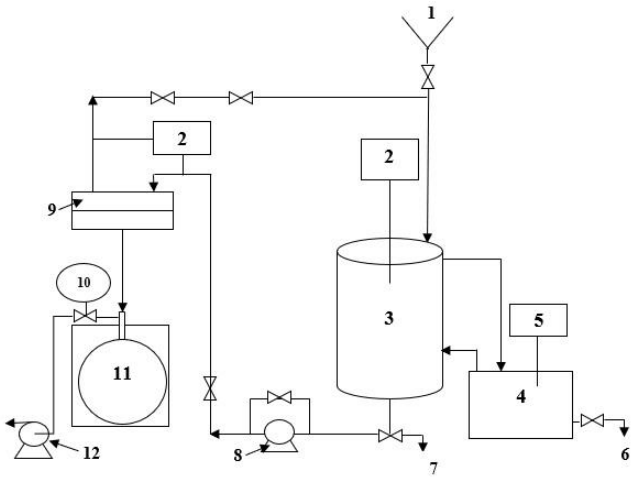

Fig 1. The pervaporation process schematic

The pervaporation process schematic was: 1) feed in (ethanol), 2) temperature indicator, 3) feed storage tank, 4) heating source, 5) temperature indicator controller, 6) retentate, 7) permeate, 8) re-calculated pump, 9) membrane cell, 10) pressure indicator, 11) cold trap, 12) vacuum pump. A pervaporation unit was used to conduct an experiment designed to separate ethanol from water. The pervaporation process involved pumping the ethanol-water mixture from the tank to the cell membrane, and the permeate was collected in a cold trap. The downstream pressure was kept below 6 cmHg, and the procedure was conducted at 30°C for one hour with an ethanol feed composition of 95 wt.%. The results showed an increase in the ethanol concentration of the retentate, and the selectivity was calculated using equation (4).

$$a = \frac{YA/YB}{XA/XB} \quad (4)$$

Where x is the weight fraction of the feed and y is the weight fraction of the permeate. Karl Fischer Titrator Mettler Toledo DL 39 analyzed the water content in ethanol solution.

III. RESULT AND DISCUSSION

A. Water Permeability Analysis

The purpose of membrane water permeability analysis is to analyze the rate of passage of a solution through a membrane as a function of time and pressure [4]. The water permeability of a sweet potato starch-chitosan composite membrane with different concentrations with and without a crosslinking agent,

and with the variation of the composite membrane composition as depicted in Table 1, was evaluated by utilizing (1) and (2).

Table 1 shows that adding chitosan affects the permeability value's decrease. A similar observed result by [15] found that adding chitosan to pure sweet potato starch decreased the permeability value from 1900 to 800. The permeability reduction is linked to chitosan's lower hydrophilicity, which is attributed to the presence of an acetyl group (degree of deacetylation 80.5%)[16].

Table 1. The effect of glutaraldehyde as crosslinking agent and values of water permeability in various ratios

Starch:Chitosan Ratio	Water Permeability (L/m^2.hr.bar)	
	Glutaraldehyde 0%	*Glutaraldehyde 1%*
100:0	1919.23	1905.44
80:20	1548.67	1027.91
60:40	1073.75	920.42
50:50	964.26	861.34
40:60	760.51	483.65
20:80	752.90	304.43
0:100	375.13	246.96

Incorporating a glutaraldehyde crosslinking agent reduced the membrane permeability value of a 50:50 sweet potato-chitosan starch membrane from 964.26 to 861.34. Glutaraldehyde reduced the membrane permeability value in line with [17], who reported that increasing the concentration of the crosslinking agent led to a decrease in permeability. This decrease can be attributed to substituting the hydroxyl group with a more hydrophilic group. The crosslinking process renders the membrane structure more dense and resistant, enhancing its water barrier capability.

B. Swelling Degree Analysis

The degree of swelling was determined by weighing the composite membrane in distilled water. The absorption of the membrane affects the swelling degree value when placed in liquid. Table 2 shows the swelling degree of the modification of sweet potato starch-chitosan composite membrane without a crosslinking agent (glutaraldehyde 0%) and with a crosslinking agent (glutaraldehyde 1.0%) as calculated by (3).

Table 2. The effect of glutaraldehyde as crosslinking agent and values of swelling degree in various ratios

Starch:Chitosan Ratio	Swelling Degree (%)	
	Glutaraldehyde 0%	*Glutaraldehyde 1%*
100:0	279.53	257.25
80:20	267.22	245.28
60:40	259.93	231.65
50:50	226.52	204.16
40:60	202.72	186.41
20:80	185.95	165.81
0:100	150.35	126.78

Among all concentrations, the 0:100 ratio on the pure chitosan membrane demonstrated the lowest swelling degree value at 126.78-150.35%. The reduction in the swelling degree value on the pure chitosan membrane was caused by the acetyl group present in the chitosan, which led to a decrease in its hydrophilicity [18]. The 50:50 ratio on the sweet potato starch-chitosan composite membrane had an average result of 200% for all various glutaraldehyde concentrations, which is consistent with the results noticed by [19]. The average outcome indicates that the combination of sweet potato starch with chitosan can augment the hydrophilicity of the membrane. The high swelling degree value found in distilled water is because the membrane is hydrophilic, causing it to swell and absorb a large amount of water [15].

The effect of glutaraldehyde in the composite membrane decreases the swelling degree value. In the ratio of 50:50, the swelling degree value decreased from 226.52%% to 204.16%. Based on research by [20] that the addition of the glutaraldehyde crosslink agent decreases the swelling degree value and improves the mechanical properties of the sweet potato starch-chitosan composite membrane. Thus, adding the crosslinking agent to the composite membrane may reduce the absorption of ethanol while still allowing it to absorb water optimally.

C. Mechanical Properties Analysis

Table 3. The values of mechanical properties

Starch:Chitosan Ratio	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
100:0 (Glut 0%)	0.09	17.59	0.93
100:0 (Glut 1%)	0.10	18.33	0.84
50:50 (Glut 0%)	0.14	21.12	0.71
50:50 (Glut 1%)	0.17	23.27	0.68
0:100 (Glut 0%)	0.18	54.37	0.58
0:100 (Glut 1%)	0.19	57.23	0.52

The mechanical properties of sweet potato starch-chitosan composite film, uncrosslinked and crosslinked, as seen in Table 3, are characterized by tensile strength, Young's modulus, and elongation at the break values [21]. Research by [22] highlighted that the highest tensile strength value was achieved in the ratio of 0:100 (pure chitosan) crosslinked with a value of 0.19 MPa. The pure chitosan membrane was thicker than the starch-chitosan composite and pure starch membrane, leading to an increase in the tensile strength value of the film. Pure chitosan crosslinked has the highest young's modulus, 47.23 MPa. This high value indicates that the resulting film is solid and resistant to external damage [23]. Nevertheless, the addition of sweet potato starch generally causes a decrease in the value of Young's modulus, demonstrating the brittleness of

ISSN No:-2456-2165

this film-forming agent [24]. The elongation at break value is inversely proportional to the tensile strength value; pure chitosan film crosslinked has the lowest value of 0.52%. The higher the chitosan concentration, the lower the break value's elongation. Sweet potato starch-chitosan film is more flexible than pure chitosan due to the addition of sweet potato starch [19].

Based on Table 3, the effect of glutaraldehyde increases tensile strength and young's modulus value and decreases elongation at break value. Glutaraldehyde acted as an intermolecular crosslinker between the starch, chitosan, and itself, thus making the film more solid and thick and increasing the values of young's modulus and tensile strength [25]. The presence of glutaraldehyde also caused a decrease in the value of elongation at break, as the crosslinked film was stiffer and less flexible than the uncrosslinked film. Despite being less flexible, the crosslinked film was more robust and more resistant to brittleness.

D. SEM Analysis

(a)

(b)

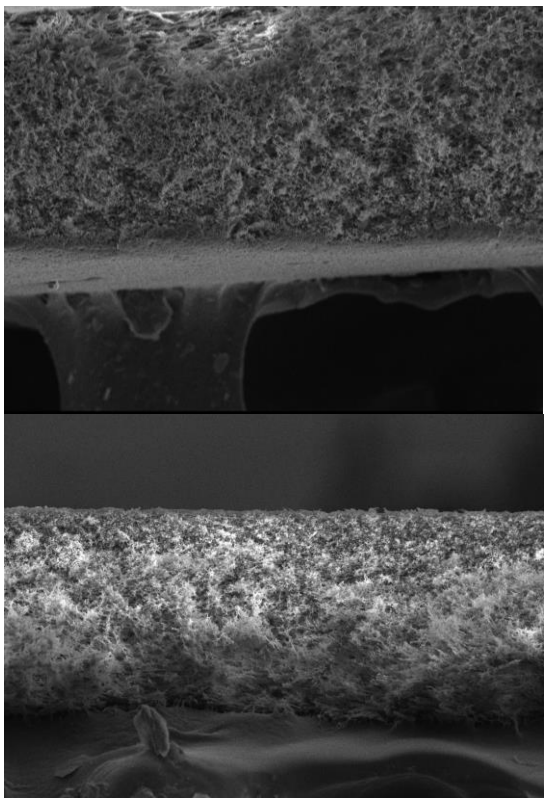

Fig 2. The effect of glutaraldehyde in SEM analysis

The morphology depicted in Figure 2(a) indicates no interaction between sweet potato starch-chitosan film and the PES membrane, leading to an impermeable barrier. The addition of a glutaraldehyde crosslinking agent, as reported by [26], can be seen in Figure 2(b), where it is observed that the bond between the sweet potato starch-chitosan film and the PES membrane has become tighter. The bond between sweet potato starch-chitosan is a result of the stabilization of the chitosan membrane by the reaction of the aldehyde group on glutaraldehyde with the amine group in chitosan, which covalently binds them together. The crosslinking agent also causes a reaction between the hydroxyl group of sweet potato starch and the aldehyde group of glutaraldehyde. This results in a network of chemical crosslinks for forming the acetal bridge structure. Moreover, the PES-supporting membrane has a sulfonate group (SO_3H^-) that produces a positive charge when it binds to the amine group in chitosan (NH_2) [27].

E. Pervaporation Method

The selectivity value of pervaporation can be improved by increasing the crosslinking of the membrane. Immersing the membrane in a crosslinking agent solution can do this. Sweet potato-chitosan membranes were tested to determine their effectiveness in ethanol-water dehydration, as shown in Figure 1. The selectivity value of the pervaporation process was calculated using (4). The amount of water absorbed by the membrane also influences its success in the pervaporation process. Good membrane characteristics are characterized by the amount of water that is taken up by the membrane [28].

Tabel 4. The selectivity values of the pervaporation process

Starch:Chitosan Ratio	**Swelling Degree (%)**	
	Glutaraldehyde 0%	***Glutaraldehyde 1%***
100:0	2.62	5.89
50:50	8.45	14.57
0:100	2.90	7.29

Table 4 shows that the sweet potato starch-chitosan ratio of 50:50 has the highest value when compared to ratios of 100:0 pure sweet potato starch and 0:100 pure chitosan due to the interaction between the starch and chitosan molecules. The hydrogen bonding between the two molecules creates physical bonding. Pure starch membranes have low selectivity values because of starch's hydrophilic properties and brittleness, adversely affecting its performance in the pervaporation process [29]. The composite membrane ratio of 50:50 with a crosslinking agent demonstrated a higher selectivity value of 15% and an ethanol concentration of 98% than the uncrosslinked membrane. According to [30] observed a selectivity value of 14%, compared to 7% without a crosslinking agent. Crosslinking agents such as aldehyde groups react with free amino groups in chitosan, forming covalent bonds and linking polymer chains. Crosslinking agent makes the membrane more stable, reducing the free volume for diffusion and absorption. In addition, the selectivity value is related to the tensile strength of the membrane, swelling degree, and contact angle.

IV. CONCLUSION

Using a composite membrane and glutaraldehyde as a crosslinking agent significantly affected the selectivity value in the pervaporation of ethanol purification. Crosslinks in the membrane increase its hydrophilicity, as indicated by the swelling degree and permeability result. This increase in hydrophilicity caused the membrane to absorb more water, as indicated by the reduction in the permeability value of 861.34 to 964.26 $L/m^2.hr.bar$ and a swelling degree from 204.16% to 226.52%. The addition of a crosslinking agent affected the mechanical properties, resulting in a solid and thick membrane.

The combination of a 50:50 sweet potato starch-chitosan membrane and the inclusion of glutaraldehyde as a crosslinking agent produces a high selectivity value of 15% and the ethanol purification of 98% in the 95% dehydration ethanol-water with pervaporation process.

ACKNOWLEDGMENT

The author would like to thank the Membran Research Center (MER-C) laboratory at Diponegoro University for providing places for this research, the tools, and the materials.

REFERENCES

[1]. Castro-Muñoz, R., Galiano, F., Fíla, V., Drioli, E., and Figoli, A. 2019. Mixed matrix membranes (MMMs) for ethanol purification through pervaporation: Current state of the art. Reviews in Chemical Engineering, 35(5), 565–590. doi: 10.1515/revce-2017-0115

[2]. Pulyalina, A. Y., Polotskaya, G. A., Veremeychik, K. Y., Goikhman, M. Y., Podeshvo, I. V., and Toikka, A. M. 2015. Ethanol purification from methanol via pervaporation using polybenzoxazinoneimide membrane. In Fuel Processing Technology (Vol. 139, pp. 178–185). Elsevier B.V. doi: 10.1016/j.fuproc.2015.07.023

[3]. Marjani, A., Mohammadi, M., Pelalak, R., and Moradi, S. 2014. Ethanol purification using polyamide-carbon nanotube composite membranes. Polymer Engineering and Science, 54(4), 961–968. doi: 10.1002/pen.23635

[4]. Rokhati, N., Istirokhatun, T., and Samsudin, A. M. 2016. Layer by Layer Composite Membranes of Alginate-Chitosan Cross-Linked by Glutaraldehyde in Pervaporation-Dehydration of Ethanol. International Journal of Renewable Energy Development, 5(2), 101–106. doi: 10.14710/ijred.5.2.101-106

[5]. Siripatrawan, U., and Vitchayakitti, W. 2016. Improving Functional Properties of Chitosan Films as Active Food Packaging by Incorporating with Propolis. Food Hydrocolloids, 61, 695–702. doi: 10.1016/j.foodhyd.2016.06.001

[6]. Mustapa, R. and Restuhadi, F. 2017. Utilization of Chitosan as the Basic Material of Making Edible Film Made from Sweet Potato Starch. 103–107.

[7]. Sumeisey, G., Umboh, S. D., and Tallei, T. E. 2019. Penyalutan Bakteri Asam Laktat Menggunakan Nanopartikel Kitosan. Pharmacon, 8(4), 843. doi: 10.35799/pha.8.2019.29361

[8]. Li, J., Chen, Z., Umar, A., Liu, Y., Shang, Y., Zhang, X., and Wang, Y. 2017. Probe into the influence of crosslinking on CO2 permeation of membranes. Scientific Reports, 7, 1–11. doi: 10.1038/srep40082

[9]. Maitra, J., and Shukla, V. K. 2014. Cross-linking in Hydrogels - A Review. American Journal of Polymer Science, 4(2), 25–31. doi: 10.5923/j.ajps.20140402.01

[10]. Wu, H., Lei, Y., Lu, J., Zhu, R., Xiao, D., Jiao, C., Xia, R., Zhang, Z., Shen, G., Liu, Y., Li, S., and Li, M. 2019. Effect of citric acid induced crosslinking on the structure and properties of potato starch/chitosan composite films. In *Food Hydrocolloids* (97). Elsevier Ltd. httpsdoi:10.1016/j.foodhyd.2019.105208

[11]. Treenate, P., and Monvisade, P. 2017. In Vitro Drug Release Profiles of PhSensitive Hydroxyethylacryl Chitosan/Sodium Alginate Hydrogels using Paracetamol as a Soluble Model Drug. International Journal of Biological Macromolecules, 99, 71–78. doi: 10.1016/j.ijbiomac.2017.02.061

[12]. Liang, J., Wang, R., and Chen, R. 2019. The impact of cross-linking mode on the physical and antimicrobial properties of a chitosan/bacterial cellulose composite. Polymers, 11(3). doi: 10.3390/polym11030491

[13]. Ahadia, L., and Kusumawati, N. 2020. Pengaruh Luas Area Cetak terhadap Permeabilitas Membran Polysulfone Effect of Casting Area on Polysulfone Membrane Permeability. *Prosiding Seminar Nasional Kimia*, 216–220.

[14]. Ren, L., Yan, X., Zhou, J., Tong, J., and Su, X. 2017. Influence of chitosan concentration on mechanical and barrier properties of corn starch/chitosan films. *International Journal of Biological Macromolecules*, *105*, 1636–1643. doi.org: 10.1016/j.ijbiomac.2017.02.008

[15]. Setiawan, D. A., Argo, B. D., and Hendrawan, Y. 2015. Pengaruh konsentrasi dan preparasi membran terhadap karakterisasi membran kitosan. *Jurnal Keteknikan Pertanian Tropis Dan Biosistem*, *3*(1), 95–99.

[16]. Martinez, A. W., Caves, J. M., Ravi, S., Li, W., and Chaikof, E. L. 2014. Effects of crosslinking on the mechanical properties, drug release and cytocompatibility of protein polymers. Acta Biomaterialia, 10(1), 26–33. doi: 10.1016/j.actbio.2013.08.029

[17]. Pinheiro, A. C., Coimbra, M. A., and Vicente, A. A. 2014. K-Carrageenan/Chitosan Nanolayered Coating as a Vehicle for Incorporation of Bioactive Compounds. 1(2), 48120.

[18]. Garavand, F., Rouhi, M., Razavi, S. H., Cacciotti, I., and Mohammadi, R. 2017. Improving the integrity of natural biopolymer films used in food packaging by crosslinking approach: A review. International Journal of Biological Macromolecules, 104, 687–707. doi: 10.1016/j.ijbiomac.2017.06.093

[19]. Gonenc, I., and Us, F. 2019. Effect of Glutaraldehyde Crosslinking on Degree of Substitution, Thermal, Structural, and Physicochemical Properties of Corn Starch. Starch/Staerke, 71(3–4). doi: 10.1002/star.201800046

[20]. Cui, Z., Wang, W., Guo, L., Liu, Z., Cai, P., Cui, Y., Wang, T., Wang, C., Zhu, M., Zhou, Y., Liu, W., Zheng, Y., Deng, G., Xu, C., and Chen, X. 2022. Haptically Quantifying Young's Modulus of Soft Materials Using a Self-Locked Stretchable Strain Sensor. Advanced Materials, 34(25), 1–8.

[21]. Ali, M., and Gherissi, A. 2017. Synthesis and characterization of the composite material PVA/Chitosan/5% sorbitol with different ratio of chitosan. International Journal of Mechanical and Mechatronics Engineering, 17(2), 15–28.

[22]. Li, P., Shen, K., Zhang, T., Ding, S., and Wang, X. 2021. High-performance polyamide composite membranes via double-interfacial polymerizations on a nanofibrous substrate for pervaporation dehydration. Separation and Purification Technology, 257, 117927.
[23]. Wang, B. 2013. High Performance Composite Membranes With A Polycarbophil Calcium Transition Layer For Pervaporation Dehydration Of Ethanol. Journal of Membrane Science, 429, 409–417. doi: 10.1016/j.memsci.2012.11.063
[24]. Hasan, M., Gopakumar, D. A., Olaiya, N. G., Zarlaida, F., Alfian, A., Aprinasari, C., Alfatah, T., Rizal, S., and Khalil, H. P. S. A. 2020. Evaluation of the thermomechanical properties and biodegradation of brown rice starch-based chitosan biodegradable composite films. International Journal of Biological Macromolecules, 156, 896–905. doi: 10.1016/j.ijbiomac.2020.04.039
[25]. Ismillayli, N., Hadi, S., Andayani, I. G. A. S., Honiar, R., Mariana, B., Sanjaya, R. K., and Hermanto, D. 2021. Synthesize of self-electrostatic interaction chitosan-carrageenan membrane and its properties. *Journal of Physics: Conference Series*, *1943*(1). doi: 10.1088/1742-6596/1943/1/012177
[26]. Sitepu, S. B. P., Harsojuwono, B. A., and Hartiati, A. 2021. Pengaruh Campuran dan Rasio Bahan Pembentuk Komposit terhadap Karakteristik Komposit Bioplastik. *Jurnal Rekayasa Dan Manajemen Agroindustri*, *9*(2), 157. doi: 10.24843/jrma.2021.v09.i02.p01
[27]. Baroudi, A., García-Payo, C., and Khayet, M. 2018. Structural, mechanical, and transport properties of electron beam-irradiated chitosan membranes at different doses. Polymers, 10(2). doi: 10.3390/polym10020117
[28]. Indriani, C., Masdar, R. P., and Razi, F. 2020. Studi Sorpsi Pemisahan Campuran Etanol-Air dengan Membran Polivinil Alkohol. 1(2), 2–6
[29]. Widodo, L.U., and Wati, S.N. 2019. Pembuatan Edible Film dari Labu Kuning dan Kitosan Dengan Gliserol Sebagai Plasticizer. Jurnal Teknologi Pangan.
[30]. Li, J., Si, X., Li, X., Wang, N., An, Q., and Ji, S. 2018. Preparation of acid-resistant PEI/SA composite membranes for the pervaporation dehydration of ethanol at low pH. Separation and Purification Technology, 192, 205–212. doi: 10.1016/j.seppur.2017.09.038