Modelling and Optimization of Alginate-Chitosan Concentration towards Tensile Strength Pervaporation Membrane based Polyethersulfone-Biopolymer by Using Response Surface Methodology

Yusuf Hendrawan¹¹, Nadiya Fisriana Putri⁸², La Choviya Hawa⁹³, Muchnuria Rachmawati*⁴, Bambang Dwi Argo⁴⁵

¹¹Department of Agricultural Engineering, University of Brawijaya, Jl. Veteran, Malang, 65145, Indonesia
E-mail: ¹¹yusuf_h@ub.ac.id

Abstract— Some outstanding features in the use of pervaporation technology are light, low maintenance, low energy consumption, and eco-friendly. The optimization of membrane mechanical properties is vital to determine the strength of the membrane against the force which comes from outside and is unfortunately destructive, one of which is tensile strength. The purpose of this research is to find out the best combination of alginate and chitosan concentration, which produces polyether sulfone-biopolymer based pervaporation membrane with optimal tensile strength. Several membrane compositions have been prepared and varied in a way to obtain optimal membranes. The modeling and optimization method, which was applied by the researcher is the Response Surface Methodology (RSM). In the Central Composite Design (CCD) design, the low level included for both factors is 2% concentration, and the high level is 4% concentration, with a total of 13 experimental designs. The result of the suggested model is a quadratic model. While on the optimization result, the optimum solution result is from a combination of 3.25% alginate and 2.91% chitosan concentration, which yield tensile strength value of 0.24 kgf/cm² with a desirability value of 0.84. The validation results are withdrawn from the three test samples resulted in an average tensile strength of 0.25 kgf/cm² where this value differed 1.2% from the predicted results. The validation results are considered acceptable because the value is still within the acceptable error threshold or below 5%.

Keywords— optimization; pervaporation membrane; response surface methodology; tensile strength.

I. INTRODUCTION

Researchers continue to develop bioethanol for biofuels due to the abundant biomass availability as a raw material [1]. Before it can be used, the process of separating and purifying bioethanol are essential steps that must be passed because bioethanol as biofuel must have a purity of at least 99.5%. The widely used technology at this stage is conventional distillation [2]. Pervaporation (PV) is a separation process using membranes with different pressure from the driving force. The ability of pervaporation to separate azeotropic mixture is considered simple without the addition of chemicals [3]. Alginate is a hydrophilic ionic polymer, water-soluble and unstable in aqueous solutions. As a membrane, the alginate film coating is considered fragile and may decrease the flux if used continuously. Afterward, the chitosan membrane has a high permeability because of its ability to bind water and pass ethanol, despite some disadvantages. Similar to alginates, chitosan membranes are highly hydrophilic and can lose stability in aqueous or acidic solution with a pH of 4, and have low mechanical strength [6], [7]. Polyanionic alginate and chitosan are polycationic; if they are dissolved under the right conditions, they can interact with each other through the amino group chitosan [8]–[10]. Membrane technology can act as a unit of separation operations on different types of substrates with different end products. Membrane technology plays a role in the process of gas separation because of several advantages offered, including the use of lighter tools, lower maintenance, low energy consumption, and low cost. Membranes made of polymers and copolymers in the form of flat film or hollow fiber are widely used for gas separation [4], [5]. Polyethersulfone (PES) is selected as membrane support because it has high mechanical strength, chemical
and thermal selectivity, and excellent film formation [14]–[16]. The use of chitosan and alginate as a non-porous layer is based on its hydrophilic properties, good film adhesion capability, strong adhesion to support, biocompatibility, and its chemically modifiable nature due to amino-group chemicals in chitosan and amine groups in reactive alginates. Characterization of mechanical properties is essential to determine the strength of the membrane against the force which comes from outside, which is destructive to the membrane (tensile strength). Tensile strength is the maximum force that can be retained by the film during measurement. Tensile strength is influenced by plastic material added in the film making process.

Meanwhile, the elongation percentage during breaking is a change in the maximum length of the film before disconnection [17], [18]. Modeling is needed to explain the relationship between input and output, and optimization is needed to get expected results that are the right combination of inputs to produce the optimal output [19]–[21]. Optimization needs to be done to get the value of alginate and chitosan concentration to produce the optimum tensile strength. Optimization with conventional methods takes a long time and is expensive [22]. In using conventional methods in a one-time experiment, only one variable is varied so that one variable with another is not known clearly. Each variable is assumed to be independent with each other; therefore, a lot of gradual testing is considered important, and there were many variables involved in the study. The optimization process normally takes a long time at a high cost [23]. Many researchers have conducted membrane optimization studies by using response surface methodology (RSM) [24]–[28].

Therefore, the optimization procedure can be conducted easily by applying RSM (a model for studying the factors that affect the response simultaneously without many experiments). The optimization technique with RSM was performed to get the best solution from a combination of variables such as alginate with chitosan concentration. In this research, PES polymers were used as the main raw material for pervaporation membrane makers with mixed alginate and chitosan coatings. Several membrane compositions have been prepared to obtain optimum membrane surfaces. The use of an optimization method with RSM is used to obtain an optimal concentration of alginate and chitosan so that the membrane has optimal tensile strength value. The purpose of this research is to model and optimize the concentration of alginate and chitosan on the tensile strength of the PES-alginate-chitosan membrane.

II. MATERIALS AND METHODS

This research was conducted in the Laboratory of Food and Agricultural Products Processing Technology, Department of Agricultural Engineering, Faculty of Agricultural Technology, Universitas Brawijaya, Indonesia. The tools used in this study are as follows: 1) Magnetic stirrer (Daihan Lab Tech): as a magnetic stirrer during mixing and homogenizing materials; 3) Digital Scales (Mettler PM460, The Netherlands): as a material mass gauge; 4) Glass plate: as a plate for casting; 5) Oven (MMM Medecenter / Ecocell 55): to dry the membrane; and 6) Universal Testing Machine (Immada / ZP-200N): to test the tensile strength. The materials used in this study are as follows: 1) Polyethersulfone (PES): as the main material of the membrane where the PES membrane will be supporting. PES used is a 3-mm white clear granule obtained from goodfellow.com, United Kingdom; 2) Alginate: as a feedstock in which the alginate used is white powder sodium alginate; 3) Chitosan: as the raw material of the porous membrane. Chitosan used is a yellowish-white powder; 4) Glacial acetic acid: as a chitosan solvent, where this acetic acid has a concentration of 100%; and 5) N-Methyl-Pyrrolidone (NMP): as a solvent for making PES membrane. The NMP used has a concentration of 99.5%.

A. The Making of Porous Membranes

The making of porous membranes used PES as the main ingredient dissolved with NMP. The concentration used was 13% with 15 grams PES dissolved with 100 ml NMP. The solution was homogenized with a magnetic stirrer for 3-4 hours or until homogeneous at room temperature. After reaching a homogeneous condition, the solution was printed on a 9 x 13 cm glass plate. The molded solution was kept at room temperature for 24 hours for the coagulation process. After the solution was left untreated, a solid membrane would form. The next process was continued by washing the membrane with distilled water to remove the remaining NMP. A porous membrane had the potential to separate molecules of similar size to each other. Separation occurs through differences in solubility and diffusivity. This membrane was used for pervaporation and gas separation. The non-porous membrane was less than 0.1 μm in size.

B. The Making of Selective Porous Membrane

Selective porous membranes are made from a mixture of alginate and chitosan. The composition of the alginate solution consists of 1 gram of alginate dissolved in 100 ml of distilled water. Subsequent alginate solution could stay overnight to remove the froth in the solution. Meanwhile, for chitosan solution consists of 1 gram of chitosan dissolved with 98 ml of distilled water and 2 ml glacial acetic acid. Alginate and chitosan solutions are then mixed and are printed on a glass plate containing the PES membrane. The membrane can be said to be porous if it is 0.1-10 μm in size and is commonly used for microfiltration and ultrafiltration. The tested membranes are 27 pieces where each membrane is printed on a glass plate (90 mm x 120 mm). The membrane tensile strength measurement is carried out by clamping the membrane on both sides and is drawn to break with a certain tensile strength.

For the optimization process, the surface response method is used with a Central Composite Design (CCD) design with two factors. The two factors are alginate and chitosan concentration presented by percent. Each concentration used was 2% as low level and 4% as the highest level, presented in Table 1. The choice of low concentration was 2%, and the high concentration was 4% because in the previous study the best membrane was membrane having alginate and chitosan concentration respectively of 3% so that 3 is taken as the middle value where the low value is the middle value -1 and the high value is the middle value +1. At this stage, the highest value in the preliminary study is incorporated into the Design
Expert 10.0 software. A research treatment based on a combination of CCD design is then performed. The result of the tensile strength test of the membrane was inserted into the response table resulting in the optimal value. RSM analyzed the best response model and generate the optimal point of the response.

<table>
<thead>
<tr>
<th>Name of concentration</th>
<th>Unit</th>
<th>Low</th>
<th>High</th>
<th>+alpha</th>
<th>-alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Alginate concentration</td>
<td>%</td>
<td>2</td>
<td>4</td>
<td>1.586</td>
<td>4.414</td>
</tr>
<tr>
<td>B Chitosan concentration</td>
<td>%</td>
<td>2</td>
<td>4</td>
<td>1.586</td>
<td>4.414</td>
</tr>
</tbody>
</table>

C. Results of Strong Tensile Membrane Testing Optimization

Characterization of mechanical properties needs to be done to determine the strength of the membrane against forces that come from outside, which can damage the membrane. The closer the membrane structure, meaning that the distance between the molecules in the membrane is tighter, having a strong tensile strength. The tensile strength of the membrane can be seen from the value of Load defined as the strong value of strained membranes at breaking conditions and Stroke defined as the strain strength at the time of breaking condition possessed by the membrane [29]. When testing the tensile strength of the membrane, elongation occurs, and strength at break appears, where the formula is can be seen in equation 1 [30]:

\[
\sigma = \frac{\frac{F(N)}{A(m^2)}}{e}\]

where the pull force (N), is influenced by the cross-sectional area (m²) affecting the Stress N / m² [31].

\[
e = \frac{\Delta L}{L_0} \times 100\%
\]

The elongation calculations are shown in equation 2. E is elongation or Strain is formulated by an increase in length that occurs (dL) compared to the initial length (Lo). In tensile strength testing, the membrane is clamped and is connected to a computer-style sensor; the PES-Alginate-Chitosan Membrane tested has a dimension of 80 mm and a width of 40 mm. The tensile force has a direction from bottom to top; the membrane layer is clamped with a clamping system on both sides of the width in opposite directions.

III. RESULTS AND DISCUSSION

Optimized membranes have dimensions of 120 mm long, 90 mm wide, and 3 mm thick. The use of the RSM method in this research is to find out the optimum point on the tensile strength of the PES-alginate-chitosan membrane with two factors: alginate and chitosan concentration. Data on the research results are presented in Table 2. The result of tensile strength shows that the lowest value of tensile strength is in column 8 with a concentration of alginate and chitosan are 3% and 4.414%, respectively, which yields 0.0094 kgf/cm². Then the highest tensile strength is on the 10th column with the concentration of alginate and chitosan of 3%, which produces a tensile strength of 0.2875. In a study with alginate and chitosan concentrations of 3%, each of column 9 to 13 yields tensile strengths ranging from 0.2094-0.2875 kgf/cm². This occurs because the same concentration of alginate and chitosan is 3%; thus, it produces similar tensile strength value. The details of the research results with RSM are presented in Table 2 below.

RSM analysis with CCD has several statistical models to analyze the research data. The model offered is linear model with the equation of \( Y = \beta 0 + \beta 1X 1 + \beta 2X 2 \), two factor interaction model (2FI) with equation of \( Y = \beta 0 + \beta 1X 1 + \beta 2X 2 + \beta 3X 1X 2 \), quadratic model with equation model of \( Y = \beta 0 + \beta 1X 1 + \beta 2X 2 + \beta 3X 1X 2 + \beta 4X 1^2 + \beta 5X 1X 2 \), and the cubic shape model. The model has selected that best suits the optimum response based on the Sequential Model of Sum of Squares, Lack of Fit Tests, and Model Summary Statistics. The sequential model sum of square suggests a quadratic model.

Meanwhile, the Cubic model is a model which is not recommended with Aliased descriptions. The selection of the appropriate Sequential Model Sum of Squares statistic model has a p-value less than alpha (p < 5%), which has the sense the model has an error of less than 5%. The P-value on quadratic vs 2FI of 0.0183 is less than 0.05 or 5%. It can be said that the quadratic model is the best and is recommended. The second model selection is the Lack of Fit Tests or inaccuracy testing. The model is considered to be a statistically insignificant model. The model's inaccuracy is acceptable if the P-value is greater than 5% (P > 5%). Based on the results, the best P-value suggested is 0.0253, where the quadratic model owns this value. According to the literature, the good P-value should be above 0.05, but since most of the P-value is 0.0253 and no other option is better, the quadratic model can be suggested as the best one. According to Myers [32], the program still chooses the quadratic model as the recommended model because the cubic model is declared aliased or is not recommended by the program. The cubic model is also less supportive of
The next model is the Summary Statistics Model, where the determination of the model used is based on the standard of deviation and the maximum R² value [33]. The parameters seen are the lowest deviation standard, the highest R-square, the highest Adjusted R-square, the highest Predicted R-square and the lowest PRESS [32]. The suggested model of RSM of a quadratic model having a standard deviation value of 0.065, which is considered as the smallest. The quadratic R-square value is 0.7278, a value that is greater than the linear R-square and 2FI. The value of R-square quadratic model of 0.7278 shows the two factors, which are alginate and chitosan concentration influencing the diversity of response by 72.78%.

Meanwhile, the rest of 27.22% is influenced by other factors such as the drying process and alginate and chitosan grade. The adjusted R-square value serves as R² generalization in the population due to the population estimation element in it. The quadratic model has an Adjusted R-square value of 0.5334, the highest value. The next is the PRESS value used to indicate the prediction of the squared sum error of the model of 0.19 in the quadratic model, which is not the lowest value when compared to the linear model of 0.18 and the 2FI model of 0.17. In the Predicted R-square, the value of the quadratic model is 0.7563, which is larger than the linear and 2FI models, but is not larger than the value of the cubic model. Since the value of the standard deviation of the lowest quadratic model is compared to other models, then the R-square value is also high although it is still not higher than the R-square value of the cubic model, then the Adjusted R-square value of the quadratic model shows the maximum value, then the quadratic model is the model suggested by RSM. This is by research conducted by Razali [34], which states that the cubic model is aliased or is not recommended to be used.

Thus, the quadratic model is the most appropriate model for determining the tensile strength response of the PES-biopolymer membrane. Based on all model selection analysis from three models, which are the Sequential Model of Sum of Square, Lack of Fit Tests, and Model Summary Statistics. It explains the relationship between chitosan and alginate concentration to the tensile strength of PES-alginate-chitosan membrane; the quadratic model is the proper one because it shows consistent results. Meanwhile, the cubic model, which at some points has a better value than the value in the quadratic model is not recommended by RSM because the cubic model is not suitable for the design model with two factors.

The quadratic model, as a suggested model, is then analyzed by using Analysis of Variance (ANOVA) to find out the relationship between several variables, which are alginate and chitosan concentration. The results of ANOVA shows that the model has significant value on the results of the study in describing the results of the research. Based on the results of ANOVA, it is known that the model is not significant because the value of F shows the number of 3.74 and P-value of 0.0572 which means that there is an opportunity of 5.72% F value to have noise. This significance occurs because the value of alginate concentration has a P-value of 0.2239 where this value is greater than 5%, the P-value of chitosan concentration is also 0.9073 where this value is more than 5%. The Lack of Fit row or P-value inaccuracy is 0.0253 or 2.53%, indicating that the value is significant. This shows that the quadratic model is the most appropriate model suggested by RSM. From the analysis done by RSM the polynomial equation is obtained which consists of order model two in the form of coded and actual, RSM equation for optimization of the tensile strength of membrane in coded factors is shown in equation 3:

\[
Y = 0.24 + (0.030\times x_1)-(0.00275\times x_2) - (0.045\times x_1^2)-(0.071\times x_2^2) - (0.072\times x_1 x_2)
\]

where Y is the tensile strength response, \(x_1\) is the concentration of alginate (coded), \(x_2\) is the chitosan concentration (coded).

While the equation in actual factors is shown in equation 4:

\[
Y(\text{tensile strength}) = -1.53462 + (0.59127\times x_1) + (0.56284\times x_2) - (0.045325\times x_1x_2) - (0.070804\times x_1^2) - (0.071604\times x_2^2)
\]

where \(Y(\text{tensile strength})\) is the tensile strength response (kgf/cm²), \(x_1\) is the actual concentration of alginate (%), \(x_2\) is the actual chitosan concentration (%).

The predicted value of tensile strength compared with the actual results is presented in Table 3. The accuracy of the model is known from the comparison of actual research value with the model prediction value presented in Fig. 1. The model's accuracy is known from the comparison of the actual value to the predicted value of the model. The actual value is scattered around the line. Some values are close to the line and away from the line. Figure 1 has a standard deviation value of 0.065 and an R² value of 0.7278. This shows if the value of R² is closer to the value of 1, then the better the value of R² of 0.7278, showing that the results are quite good although there are still many actual values which are far enough from the prediction value.

<table>
<thead>
<tr>
<th>TABLE III</th>
<th>DATA OF RESEARCH RESULT AND TENSILE STRENGTH PREDICTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std</td>
<td>(% Alginat Concentration)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>1.585</td>
</tr>
<tr>
<td>6</td>
<td>4.414</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>
This study employs two variables, which are alginate and chitosan concentration used for the PES-biopolymer membrane tensile strength response. The membrane tensile strength graph obtained from RSM is presented in Fig. 2 and 3. Figure 2 is a plot of a two-dimensional contour plot which is a cross-section of the three-dimensional curve. Contour plots are used to analyze inter-factor effects on responses [32]. The contour plot shows that the concentration of alginate and chitosan significantly influences the tensile strength of the PES-biopolymer membrane. The outer line on the graph shows the lowest response value, and the more inward trend shows, the higher the response value. While Fig. 3 is a three-dimensional graphic image depicting the parabolic form where optimization obtained shows maximum results, interpreted by the effect of interaction between alginate and chitosan concentration, which is quadratic to the tensile membrane pull response of PES-biopolymer. The higher the tensile strength of the PES-biopolymer membrane, the membrane shows a better result where the tensile membrane of the PES-biopolymer pull response has maximized optimization with a mountain-shaped chart.

![Fig. 1. Comparison of actual and prediction value from membrane tensile strength of PES-Biopolymer](image)

![Fig. 2. Contour graphic of tensile strength response](image)

Optimization in this research aims to determine the best treatment value to produce the optimum response value. The response optimization criteria are adjusted to the constraints in Table 4.

In the preliminary study which has been done, the best treatment obtained is the concentration of alginate of 3% and chitosan concentration of 3%. Therefore, the middle level is 3%; the lower limit is 2%, and the upper limit is 4%. Alginate and chitosan concentration have an in-range objective, where the objective is to find out the right combination based on the alginate concentration level and the given chitosan concentration of 2, 3, and 4%. Therefore, it cannot be determined if the combination of alginate and chitosan concentration should be higher or lower. The tensile strength response of the desired PES-biopolymer membrane is higher or maximize. Thereafter, an optimal solution is presented in Table 5.

![Fig. 3. Graphic of tensile strength in 3D](image)

### TABLE IV
**The constraint for response optimization**

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Goal</th>
<th>Lower limits</th>
<th>Upper limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate Concentration</td>
<td>In range</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Chitosan Concentration</td>
<td>In range</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Maximize</td>
<td>0.0094</td>
<td>0.2875</td>
</tr>
</tbody>
</table>

The optimum point with the best response obtained is the combination of alginate concentration of 3.247% and the chitosan concentration of 2.909% which yields a tensile strength of 0.242 kgf/cm². The resulting desirability value is 0.836 in which according to Laluce [35]. The value of desirability value is 1 is indicated a perfect response, and if the desirability value is 0 then the response should be discarded. Therefore, it can be said that the selected response with the desirability value of 0.836 is considered quite good.

From Fig. 4 and 5, blue areas are indicating unwanted areas having low desirability values. The graph of desirability presented by Fig. 5 shows that the desirability value is in the orange area indicating that the red area is getting better. The value of the resulting desirability is 0.836 which means that this research has a level of accuracy of 83.6%.

![Table V_optimal solution based on RSM](image)
Thus, it can be stated that the coating of chitosan alginate affects the increasing membrane tensile strength.

### Table VI: Result of Predicted Validation and Actual Model RSM

<table>
<thead>
<tr>
<th>Variable</th>
<th>Optimum Value of RSM</th>
<th>Tensile Strength (kgf/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate Concentration (%)</td>
<td>3.247</td>
<td>0.242</td>
</tr>
<tr>
<td>Chitosan Concentration (%)</td>
<td>2.909</td>
<td>0.245</td>
</tr>
</tbody>
</table>

The previous research on the morphology and performance of the chitosan membrane found that 1% of the chitosan membrane with a larger pore size may cause membrane structure to become brittle. Tensile strength at break increases alongside with chitosan concentration. Chitosan membrane with 4% and 5% concentration has big tensile strength. This happens because the tight structure causes the distance between molecules in the membrane becoming tighter, which creates a large tensile strength. While in this optimization research, the membrane is made from alginate and chitosan mixture with a maximum concentration of 4.414%. However, it also does not yield maximum tensile strength due to the properties of alginate and chitosan that are complementary (unless the mixture between alginate and chitosan must be balanced). Research was conducted by Habiba [36]. The effect of chitosan concentration results that if more chitosan is added then the value of compressive strength or tensile tends to increase, indicating that chitosan as mixing biopolymer tends to increase the value of compressive tensile strength on certain formulations. It is because chitosan can form a hydrogen bond between chains, so the membrane becomes denser. The study was conducted by Amri [37] about alginate membrane as membrane hemodialysis found that a higher concentration of alginate solution causes higher membrane strength. This research result also presents that heavier membrane raises tensile strength. From previous research [10], [38], [39], it can be seen that a higher concentration of alginate and chitosan concentration produced a large tensile strength. Therefore, the research conducted and the referred research is valid. This study used alginate concentration of 3.247% and chitosan concentration of 2.909% producing a predictive tensile strength value of 0.242 kgf/cm² and an actual value of 0.245 kgf/cm².

### IV. Conclusion

The research result shows a model that explains the relationship between chitosan and alginate concentration and tensile strength of the PES-alginate-chitosan membrane. Based on the analysis of the three models, which are Sequential Model Sum of Square, Lack of Fit Tests, and Model Summary Statistics, the best model suggested is the quadratic model as it shows consistent results. The result of optimization of the tensile strength of PES-biopolymer pervaporous membrane with Response Surface Methodology (RSM) shows the optimum value of 3.247% for alginate and 2.909% concentration for chitosan with an optimum tensile strength response value of 0.242 kgf/cm². From the validation which is conducted with an experimental method, the researcher obtains the value of tensile strength of 0.245 kgf/cm².
kgf/cm² where the results are 1.2% different from the predicted RSM.

REFERENCES


