Modeling and Optimization of Tensile Strength of Arrowroot Bioplastic Using Response Surface Method

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Abstract. Biodegradable plastic or bioplastics made from starch or plants is one way to reduce plastic waste that is not environmentally friendly. Optimization of mechanical characteristics in bioplastics needs to be done, one of which are tensile strength and elongation. The purpose of this study is to find the best glycerol and chitosan compositions that produce the most optimal tensile strength and elongation of Arrowroot (Maranta arundinacea L) bioplastic. The modeling and optimization method uses response surface method (RSM) with a central composite design (CCD). In the CCD, the glycerol composition was 2.4%, 3.9%, and 5.3% (1.5 g, 2.5 g, and 3.5 g of a solution of 62.5 mL, 64.5 mL, and 66.5 mL, respectively), while the composition of chitosan was 1.6%, 3.1%, and 4.5% (1 g, 2 g, and 3 g of a total solution of 62.5 mL, 64.5 mL, and 66.5 mL, respectively) with a total of 13 experimental designs on the CCD. The model results suggested by RSM-CCD are quadratic models. In the optimization results, the optimal solution is the addition of 2.554 g of glycerol and the addition of 2.068 g of chitosan which produces tensile strength of 96.219 MPa and elongation of 11.78% with a desirability value of 0.902. Validation results using three repetitions produce an average tensile strength of 95.82±0.65 MPa and elongation of 11.46±0.52. Under these condition, the error rate value both of responses are still below 5%, so that the model optimization can be accepted. The duration of bioplastic degradation (more than 75%) produced from the optimum value is 12 days.

Keywords: Arrowroot, Bioplastic, Response Surface Method, Tensile Strength

1. Introduction
Plastics are inexpensive, numerous, and versatile polymer materials, which have been developed for packaging since the 1950s [1]. Plastic has some advantages that it is transparent, not easily broken, and not corrosive, but difficult to decompose so that this becomes a problem of garbage that keeps piling up and exceeds capacity [2]. One way to improve conventional plastic waste is to develop biodegradable plastic materials [3]. Biodegradable plastic or bioplastic is an environmentally friendly plastic that can be made from vegetation containing starch e.g. cassava, corn flour, and tubers [4; 5]. Arrowroot (Maranta arundinacea L) is one of the plants that are not yet utilized for the main material in bioplastics production.

Arrowroot belongs to the corm of tubers which is commonly used for starch extraction because of its very high starch content [6]. Research on the use of Arrowroot starch for bioplastics is still not much developed because it has several weaknesses i.e. less resistant to water and mechanical properties are still brittle because starch contains more amylopectin [7]. Amylopectin properties which
are more amorphous cause a lot of empty space so that the mass density between chains in starch is not too large so the water resistance is low. The addition of chitosan can increase the density of bioplastic mass and cause the amount of water absorbed to be less [8]. Chitosan is hydrophobic so it can form edible films and bioplastics well. The greater the percentage of chitosan, the tensile strength value will be stronger and harder to break [9]. Glycerol plasticizer is one of the basic materials in bioplastics production [10]. The addition of glycerol serves to reduce the fragile nature of bioplastics. The use of glycerol can also increase flexibility by decreasing intermolecular forces in the bioplastic polymer chain [11]. Therefore, the manufacture of Arrowroot-based bioplastics with variations in the addition of glycerol and chitosan need to be observed and optimized to obtain optimal tensile strength.

Tensile strength analysis is needed to determine the strength of bioplastics against forces originating from outside. Tensile strength is the maximum force that can be held by bioplastics which is affected by the addition of plastic material [12]. Appropriate optimization techniques are needed to improve the efficiency and effectiveness of product development [13-16]. Many researchers have conducted bioplastic optimization studies using response surface method (RSM) [17-19]. RSM is one of the statistical and mathematical modeling methods for building empirical models. This method can be used to predict, observe, and optimize a response (output) that is influenced by several independent variables (inputs) [20]. The purpose of this study is to model and optimize the addition of glycerol and chitosan to Arrowroot-based bioplastic tensile strength using RSM.

2. Methods

2.1 Plant material and equipments

The materials used in this study are Arrowroot starch as the main material in bioplastics; distilled water as a solvent; glycerol as a plasticizer; and chitosan as an additional material. While the equipments used in this study are ovens (MMM Medcenter ecocell 55) for drying bioplastic materials; 100 mesh sieve to separate the rough Arrowroot starch; analytical balance (Mettler PM460) to weigh the mass of material; glass plates for bioplastic molding; and tension testing (IMADA HV-110) as a tensile strength test equipment.

2.2 Bioplastic production procedures

Arrowroot of 3.5 kg which has been cleaned, then cut into small pieces for the refinement process using a blender. Arrowroot materials are blended until soft, then Arrowroot that have been mashed are squeezed using a filter cloth to separate the starch extract from the pulp. The extracted starch is then deposited in a container for one day. The water contained in a container that has been separated from the starch deposit is then discarded. The Arrowroot starch sediment was then dried using an oven at 105ºC for 12 hours. The dried starch is then sieved using a 100-mesh sieve to obtain finer particle size.

Bioplastics are made from Arrowroot starch with a mixture of distilled water as a solvent, glycerol as a plasticizer, and chitosan as an additive. Arrowroot starch of 10 g is dissolved with distilled water 50 mL. The Arrowroot starch solution is stirred for 5 minutes so that it is mixed evenly. Glycerol is weighed of 2.4%, 3.9%, and 5.3% (1.5 g, 2.5 g, and 3.5 g), then chitosan is also weighed of 1.6%, 3.1%, and 4.5% (1 g, 2 g, and 3 g) of a total solution 62.5 mL, 64.5 mL, and 66.5 mL, respectively. The weighed glycerol and chitosan are then mixed into the Arrowroot starch solution that has been dissolved with distilled water. The Arrowroot starch solution that has been mixed with glycerol and chitosan is stirred and heated on a hotplate at a temperature of 60 ºC for the gelatinization process. Arrowroot starch that has been clotted, then molded on a glass plate that has been oiled so that bioplastics are not sticky. Bioplastics that have been molded, then dried in an oven at 40 ºC for 4 hours. The tested bioplastics are molded on glass plates of 150 × 150 mm sized. Response measurement of bioplastic tensile strength and elongation is done using a tension testing equipment by clamping bioplastics on both sides and pulled until it breaks.

2.3 Modelling and Optimization using Response Surface Method
The RSM optimization process uses a central composite design (CCD) because it uses two factors i.e. the concentration of the glycerol addition and the chitosan addition. The concentration of glycerol and chitosan addition used is presented in Table 1. The choice of concentration was based on preliminary research with the best combination of glycerol concentration 2.5 g and chitosan 2 g. The best concentration is taken as the middle value.

Table 1. Central composite design

| Name           | Unit | Low | High | -alpha | +alpha |
|----------------|------|-----|------|--------|--------|
| A glycerol addition | g    | 1   | 3.5  | 1.08   | 3.91   |
| B chitosan addition | g    | 1   | 3    | 0.58   | 3.41   |

Measurement on mechanical characteristics or tensile strength and elongation needs to be done to determine the strength of Arrowroot-based bioplastics. The more glycerol is added, the greater the tensile strength until the optimum point then decreases because the plastic produced is more fragile, as well as the more chitosan added, the greater the tensile strength until the optimum point then decreases because the plastic produced is brittle. Bioplastic tensile strength can be seen from the tension at the time of breaking and the strength of the strain at the time of breaking up [21]. Measurement of bioplastic tensile strength using a universal testing machine. The tool can be used to measure the value of the tensile strength, elongation, and modulus of young.

2.4 Validation of model
The validation process of the model formed is used to test the accuracy of the model. Validation was done by comparing the results of optimal variables (glycerol and chitosan added) based on predicted value from RSM and actual or experimental study results.

3. Results and Discussion

3.1 Modelling and Optimization
The observation data can be seen in Table 2. The highest tensile strength results are shown in column 11 with the addition of 2.5 g glycerol and 2 g chitosan which produces a tensile strength value of 99.893 MPa. The lowest tensile strength value is shown in column 7 with the addition of 2.5 g glycerol and 0.59 g chitosan which produces a tensile strength value of 33.101 MPa. RSM analysis with CCD has several models to analyze the results of observation in order to get the most optimal response. Some statistical models offered include linear models, two-factor interaction models (2FI), quadratic models, and cubic models. Each of the four models was analyzed based on the sum of the squares of the Sequential Model Sum of Squares, Lack of Fit Test, and Statistical Summary Model. Mathematical models that are considered suitable are those that have a p-value of "prob> f" less than 5%.

Table 2. Tensile strength result using RSM-CCD

| Std | X_1  | X_2  | Glycerol (g) | Chitosan (g) | Tensile Strength (MPa) | Elongation (%) |
|-----|------|------|--------------|--------------|------------------------|---------------|
| 1   | -1.000 | -1.000 | 1.50         | 1.00         | 59.223                 | 6.382         |
| 2   | 1.000  | -1.000 | 3.50         | 1.00         | 65.871                 | 5.319         |
| 3   | -1.000 | 1.000  | 1.50         | 3.00         | 57.400                 | 6.185         |
| 4   | 1.000  | 1.000  | 3.50         | 3.00         | 70.324                 | 8.602         |
| 5   | -1.414 | 0.000  | 1.08         | 2.00         | 43.845                 | 4.276         |
| 6   | 1.414  | 0.000  | 3.91         | 2.00         | 42.377                 | 4.210         |
| 7   | 0.000  | -1.414 | 2.50         | 0.58         | 33.101                 | 3.125         |
| 8   | 0.000  | 1.414  | 2.50         | 3.41         | 47.604                 | 4.772         |
| 9   | 0.000  | 0.000  | 2.50         | 2.00         | 96.596                 | 11.956        |
| 10  | 0.000  | 0.000  | 2.50         | 2.00         | 98.187                 | 12.903        |
| 11  | 0.000  | 0.000  | 2.50         | 2.00         | 99.893                 | 13.186        |
Model selection based on Sequential Sum of Squares suggested that the recommended model is quadratic model, while the model that is not recommended is the cubic model. The next model selection is the Lack of Fit Test. This test is conducted to determine the incompatibility between the model with second order. Models that are considered appropriate are models that are not real. The best p-value is in the quadratic model. The p value generated from the processing of the program shows that the p value is less than 5% so that in theory all models are not significant to the response of bioplastic tensile strength and elongation, but the model that is considered in accordance with the design of two variables. The model will be considered appropriate if the p value is above the level of probability used, so the program still chooses the quadratic model as the recommended model [22].

The next model is the Summary Statistics Model, where this model is chosen based on the standard deviation value and the R² value. The parameters used to choose the right model are the lowest standard deviation, the highest R-square, the highest Adjusted R-Square, the highest Predicted R-Square and the lowest PRESS value. The recommended RSM model based on Summary Statistics Model is a quadratic model. Based on the entire analysis of the three models i.e. the Sum of Square Sequential Model, Lack of Fit Test, and Model Summary Statistics to explain the relationship between the addition of glycerol and chitosan to the bioplastic tensile strength and elongation are the quadratic model. This model was chosen because it is the most consistent compared to other models.

The modeling results obtained from RSM are polynomial equations in the form of coded variables as describe in Table 4. Model accuracy can be calculated from the comparison of actual and predicted values. Based on ANOVA analysis, the addition of glycerol and chitosan have a significant effect on the response of bioplastic tensile strength which is marked by the outer lines on the graph, which shows the higher response value. The optimal response value is indicated by the peak point on the contour of the graph. The graph of the effect of the glycerol and chitosan addition to the tensile strength and elongation responses are presented in Figure 1. Figure 1 shows the contour plot of the response so that it can be seen the influence of quadratic variables on the response of tensile strength of bioplastics. The outermost line is green indicating the lowest response value and inward indicates the response value is higher. If the glycerol and chitosan addition increase again, the response decreases.

### Table 3. Constraint to optimize response

| Criteria         | Goal     | Lower limits | Upper limits |
|------------------|----------|--------------|--------------|
| Glycerol addition| In range | 1.5          | 3.5          |
| Chitosan addition| In range | 1            | 3            |
| Tensile strength | Maximize | 33.101       | 99.8993      |
| Elongation       | Maximize | 3.125        | 13.186       |

Optimization is done to optimize the value of bioplastic tensile strength based on variables in the presence of several constraints. The optimization criteria are adjusted to the constraints as in Table 3. In Table 3, the glycerol and chitosan addition have an objective “in range”, while the desired response of the bioplastic tensile strength and elongation are “maximize”.

Based on the results obtained, the optimum point of tensile strength of bioplastic is obtained when using a combination of glycerol addition of 2.554 g and chitosan addition of 2.068 g. The optimum point of tensile strength and elongation of bioplastics are 96.22 MPa and 11.78%, respectively. The desirability value generated is 0.902, which means that this study has a level of accuracy of 90.2%. The desirability value is used to determine the outcome of the solution. The desirability value 1 indicates that there is a perfect response, whereas if the desirability value 0 indicates that the response must be discarded [23].
3.2 Validation of model

Validation is carried out on adding glycerol 2.554 g and chitosan 2.068 g with the desirability value. This result is then repeated three times and the results are not too far from the repetition. The tensile strength results of 95.82±0.65 MPa, while the calculation based on the model predictions was 96.22 MPa. The elongation result of 11.46±0.52%, while the model predictions was 11.78%. The difference in the value of the bioplastic tensile strength and elongation responses between the predicted results and experimental value were 0.42% and 2.69%, respectively. Because the deviation value is less than 5%, the model that has been obtained by RSM can be accepted and considered valid.

| Responses          | Model equations                        | Predicted value | Actual value (experimental) | Error rate value |
|--------------------|----------------------------------------|-----------------|----------------------------|-----------------|
| Tensile strength   | Y = 96.06 + 2.19 X₁ + 2.89 X₂ + 1.57 X₁X₂ - 21.11 X₁² - 22.49 X₂² | 96.22           | 95.82±0.65                 | 0.42%           |
| (MPa)              |                                        |                 |                            |                 |
| Elongation (%)     | Y = 11.74 + 0.16 X₁ + 0.68 X₂ + 0.87 X₁X₂ - 3.12 X₁² - 3.27 X₂² | 11.78           | 11.46±0.52                 | 2.69%           |

3.3 Biodegradation testing of bioplastic

Bioplastics made based on optimal glycerol and chitosan values in this study were also tested for their biodegradation properties using EM4 (Effective Microorganism). The results of the bioplastic biodegradation through visual observation and weighing the sample mass can be seen in Figure 2. Bioplastics will be degraded by bacteria during 12 days marked by a decrease in bioplastic mass and bioplastic tearing. As for several factors that influence bioplastic degradation, namely the type of microbes, humidity, additional reinforcement and the type of soil used. The duration of biodegradation produced from this study was within 12 days to be able to decompose more than 75%. These
degradation ability is in accordance with the standards used by PCL plastics from the UK and Japanese PLA plastics [24].

Figure 2. Weighing the mass of bioplastic and visual observation bioplastic in EM4 solution during 12 days.

4. Conclusion
In this study the glycerol and chitosan addition variables are modeled against the tensile strength and elongation of Arrowroot-based bioplastic using response surface method (RSM). The model suggested by RSM is quadratic. The optimization results of tensile strength and elongation of bioplastics using RSM produce the optimum value at glycerol addition of 2.554 g and chitosan addition of 2.067 g with the results of the tensile strength and elongation responses of 96.22 MPa and 11.78%, respectively. Validation that has been done produces an average tensile strength value of 95.82±0.65 MPa and an elongation value of 11.46±0.52%. This validation value has a difference with the predicted results which has an error rate of tensile strength and elongation responses are 0.42% and 2.69%, respectively, so the results of this study can be declared valid (error <5%). The duration of bioplastic degradation (more than 75%) produced from the optimum value is 12 days.

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