Optimization of mechanical properties of bioplastics with the addition of ZnO and glycerol plasticizer

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Abstract. Bioplastics are an alternative to conventional plastics that have been used in society. The advantage of bioplastics is that they are easily degraded in nature because they come from easily renewable materials such as starch which comes from plants. However, biodegradable plastics have shortcomings in terms of tensile strength so that additional supporting materials are needed in their manufacture. Optimization using the Response Surface Methodology (RSM) central composite design (CCD) in this study aims to obtain optimal mechanical properties (tensile strength). The independent variables used in this study include ZnO concentrations (3%, 6%, and 9%) and glycerol concentrations (2 ml, 5 ml, and 8 ml) as well as mechanical properties such as tensile strength and elongation in response. The optimum conditions were obtained at a concentration of ZnO 6.99% and glycerol 5.32 ml with a tensile strength value of 1.58456 MPa and 9.082201% elongation.

1. Introduction

Plastic is inseparable from the daily life of the Indonesian people. The use of plastic in various needs continues to increase along with the increase in population. Plastics come from materials that are quite cheap, are not prone to weathering, are light, and also have anti-rust properties [1], so they are widely used by the public. [2] Indonesia is ranked second in the world for disposing of plastic waste into the sea with a rate of 0.52 kg of waste / person / day or equivalent to 3.22 MMT / year.

Apart from being a container for groceries, the use of plastic is very widely applied by farmers, such as making plastic as a nursery or plant seeds called polybags, as well as a land cover on plantation land to avoid scrambling for food and nutritional sources needed by parent plants, weeds (weeds). It is not surprising that the largest waste generated comes from plastic waste because it is large in number and very difficult to decompose. Based on these conditions, an action is needed to overcome the problem of environmental pollution due to plastic waste that is difficult to decompose. Bioplastics are a solution to overcome the increasing presence of plastic waste.

Bioplastic is a type of plastic packaging that is environmentally friendly because it comes from organic materials so that it is easily broken down in the soil by the help of soil microorganisms. Sources of natural materials that can be used in making bioplastics come from materials containing starch, cellulose, chitin, collagen, and also fat [3]. Bioplastics which have biodegradable properties are expected to replace the presence of synthetic polymer type plastics which are very difficult to decompose.

Bioplastics with basic ingredients from nature are easily degraded by the bacteria psedomonas and bacillus which break the polymer chains into their monomers. Bioplastics which have biodegradable
properties when burned do not cause harmful chemical compounds, they can actually improve soil quality because the decomposition of microorganisms can increase nutrients in the soil. The results of plastic degradation can also be used as animal feed or as compost [4].

In this research, a bioplastic will be made from a combination of starch source materials, namely from jackfruit seed starch added with corncob starch. Both of these materials are agricultural waste that is not used. Jackfruit seeds and corn cobs are very easy to obtain in any region in Indonesia and have a low price. Usually jackfruit seeds are just thrown away after the pulp is taken. By utilizing it as a basic material for making bioplastics, it can increase the use value of the waste.

Response surface methodology (RSM) was used in this study to obtain optimal conditions from the bioplastic manufacturing process, so as to provide optimum bioplastic mechanical properties. Optimization was carried out using response surface methodology (RSM) where the experiment was designed using the central composite design (CCD) method.

2. Materials and methods
2.1. Materials
Materials used in the research include jackfruit seed starch and corncob starch, glycerol, ZnO, acetic acid, thermometer, electric stove, blender machine, and glass molds.

2.2. Methods
Optimization using central composite design (CCD) with two factors and each consists of three levels, namely the concentration of ZnO ($X_1$) consist of 3%, 6%, 9% and concentration of glycerol ($X_2$) consists of 2 ml, 5 ml, and 8 ml which is the independent variable and the mechanical properties of bioplastics include tensile strength and % elongation is the dependent variable (Y). [5] using the model of central composite design (CCD) with the design of $2^k$ factorial ($k = 2$) so that the design is $2^2$, which were obtained by the value of $\alpha (2^{k/4}) = 1,41421$ (star point), and the centre point ($n_c$) or middle value (0.0) is repeated 5 times, it will get 13 combined treatment. Data analysis was performed using software Design Expert 7.0.0.

3. Results and discussion
By using an instrument in the form of a tension test to determine the value of the mechanical properties of the bioplastic, it can be seen the tensile strength and % elongation values.

| Run | ZnO (Coded) | Glycerol (Coded) | ZnO (%) | Glycerol (ml) | Tensile Strength (MPa) | Elongation (%) |
|-----|-------------|-----------------|---------|---------------|------------------------|----------------|
| 1   | 0           | -141,421        | 6       | 0.76          | 1.761                  | 1.1353         |
| 2   | 0           | 141,421         | 6       | 9.24          | 0.017                  | 12.9923        |
| 3   | -1.4142     | 0               | 1.76    | 5             | 0.782                  | 11.8857        |
| 4   | 1.41421     | 0               | 10.24   | 5             | 2.171                  | 5.4271         |
| 5   | 1           | 1               | 3       | 8             | 0.091                  | 13.6309        |
| 6   | 1           | 1               | 9       | 2             | 2.312                  | 2.3064         |
| 7   | 1           | 1               | 9       | 8             | 0.864                  | 9.2562         |
| 8   | -1          | 1               | 3       | 2             | 1.273                  | 3.6734         |
| 9   | 0           | 0               | 6       | 5             | 1.531                  | 9.1919         |
| 10  | 0           | 0               | 6       | 5             | 1.436                  | 9.8362         |
| 11  | 0           | 0               | 6       | 5             | 1.614                  | 9.9434         |
| 12  | 0           | 0               | 6       | 5             | 1.631                  | 9.2362         |
| 13  | 0           | 0               | 6       | 5             | 1.31                   | 8.5367         |
Table 2. Summary of responses ANOVA mechanical properties of bioplastic.

| Source             | Responses | Tensile Strength | Elongation |
|--------------------|-----------|------------------|------------|
| Prediction models  | Quadratic | Quadratic        |            |
| Model              | <0.0001   | <0.0001          |            |
| A-ZnO (%)          | <0.0001   | 0.0002           |            |
| B-Glycerol (ml)    | <0.0001   | <0.0001          |            |
| AB                 | 0.1027    | 0.0728           |            |
| A²                 | 0.1173    | 0.1027           |            |
| B²                 | <0.0001   | 0.0019           |            |
| Lack of fit        | 0.6527    | 0.2138           |            |

| Std. Dev           | 0.071     | 0.71             |            |
| Mean               | 1.31      | 8.23             |            |
| C.V. %             | 5.42      | 8.66             |            |
| PRESS              | 0.11      | 18.14            |            |
| R-Squared          | 0.994     | 0.9811           |            |
| Adj R-Squared      | 0.9898    | 0.9675           |            |
| Pred R-Squared     | 0.9805    | 0.9034           |            |
| Adeq Precision     | 49.22     | 28.023           |            |

Source: Data Processing DX 7.0.0
The significant level of 0.05

3.1. Analysis response tensile strength

From the results of data processing using the program Design Expert 7.0.0 Trial Version obtained a second order polynomial equations (quadratic) brightness of tomatoes:

\[ Y = +0.40896+0.22881X_1+0.18714X_2-0.00738889X_1X_2-0.00287639X_1^2-0.035515X_2^2 \] (1)

Based on the ANOVA results listed in Table 2, the ZnO \((X_1)\), glycerol \((X_2)\), and glycerol quadratic \((X_2^2)\) variables have an influence on the tensile strength response of bioplastics. Based on the calculation of the roots of the characteristic matrix B, found that the root characteristics (eigen values of matrix) is \(\lambda_1 = -0.352\) and \(\lambda_2 = -0.034\). Eigen values obtained both negative so it can be concluded that the response surface that produced a maximum [6]. Response surface model can be seen in the following figure:
Figure 1. Response surface curve ZnO and Glycerol of the response tensile strength of bioplastic 3D graphics

Based on the response surface curves in Figure 1, it can be seen that the characteristics possessed by the stationary points in this study are in the maximum form. The increase in the amount of ZnO concentration is directly proportional to the increase in the value of the bioplastic tensile strength response. While the glycerol concentration is inversely related to the increase in the value of the response of the tensile strength of bioplastics. The higher the ZnO concentration, the greater the tensile strength value. The use of ZnO in the manufacture of bioplastics can act as a reinforcement and also a substitute for the intramolecular and intermolecular hydrogen bonds that are lost when combined with a mixture of starch and glicerol plasticizer [7].

3.2. Analysis response elongation

From the results of data processing using the program Design Expert 7.0.0 Trial Version obtained a second order polynomial equations (quadratic) brightness of tomatoes:

\[
Y = -2.10325 + 0.47403X_1 + 3.35264X_2 - 0.083547X_1X_2 - 0.056343X_1^2 - 0.14482X_2^2
\]

Based on the ANOVA results listed in Table 2, the ZnO \((X_1)\), glycerol \((X_2)\), and glycerol quadratic \((X_2^2)\) variables have an influence on the elongation response of bioplastics. Based on the calculation of the roots of the characteristic matrix B, found that the root characteristics (eigen values of matrix) is \(\lambda_1 = -1.764\) and \(\lambda_2 = -0.057\). Eigen values obtained both negative so it can be concluded that the response surface that produced a maximum. Response surface model can be seen in the following figure:
Based on the response surface curves in Figure 2, it can be seen that the characteristics possessed by a stationary point in this study are in the maximum form. The glycerol concentration is directly proportional to the % elongation value of the bioplastic produced, where in Figure 2, it can be seen that the more glycerol concentrations used, the greater the % elongation value. Meanwhile, the addition of the ZnO concentration in the manufacture of bioplastics causes a decrease in the % elongation value of the resulting bioplastics.

The higher the concentration of the glycerol plasticizer given, the distance between the ZnO reinforcing material and the starch formed will increase, causing the hydrogen bonds formed between the reinforcing material and the starch to decrease and turn into hydrogen interactions between the ZnO reinforcing material and the glycerol plasticizer [8]. This condition causes the resulting bioplastic to become more elastic as the glycerol concentration increases so that the % elongation value increases.

3.3. Response optimization of mechanical properties of bioplastic

Criterion or objective function is used to determine the optimal conditions adapted to the constraints as presented below:

| Name          | Goal       | Lower Limit | Upper Limit |
|---------------|------------|-------------|-------------|
| ZnO (%)       | is in range| 1.76        | 10.24       |
| Glycerol (ml) | is in range| 0.76        | 9.24        |
| Tensile Strength (MPa) | Maximize     | 0.017        | 2.312       |
| Elongation (%)| Maximize  | 1.1353      | 13.6309     |

Source: Data Processing DX 7.0.0

Response optimization results are presented in the form of contour plots and three-dimensional form as shown in Figure 3. Based on the contour plot and the resulting three-dimensional shapes in Figure 3, the program suggests the solution chosen is indicated the ZnO of 6.99 % and glycerol 5.32 ml with the optimal response to the tensile strength value is 1,58456 MPa and elongation 9,082201 % with a value of desirability that 0.659. The desirability value that can be achieved with a value of 0.659 indicates that the formula will produce optimal bioplastic mechanical properties and in accordance with the wishes or criteria of 65.9%.
Figure 3. Surface Curve Effect of ZnO and Glycerol to Response Mechanical Properties of Bioplastics 3D Desirability.

4. Conclusion
From the results of optimization using response surface methodology (RSM) methods central composite design (CCD) with DX 7.0.0 software obtained optimum variable ZnO is 6.99% and glycerol 5.32 ml with optimum tensile strength 1.58456 MPa, and elongation 9.082201% with a desirability value of 0.659.

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