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Glycerol and Temperature Effects on Mechanical Properties of Biodegradable Plastic from Rice Four with Rice Husk Filler

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Biodegradable plastics were fabricated from rice flour by the extrusion method using glycerol and rice husk powder as the plasticizer and filler, respectively. The independent variables were temperature (100−120°C), glycerol (25−45%), and rice husk powder (0−20%). The independent variables were varied at three levels following the Box-Behnken experimental design. Three response surface models describing the effect of the independent variables on the tensile strength, elongation at break, and stiffness of the plastics were proposed. The tensile strength and the elongation at the break of the plastics were significantly affected by glycerol and rice husk, while the stiffness of the plastic was only significantly influenced by glycerol. The response optimizer was applied to estimate the optimum conditions for preparing the plastics, i.e., 100°C for temperature, 25.81% for glycerol, and 0% for rice husk. The tensile strength, elongation at break, and stiffness of the plastic estimated by the optimum conditions were 7.27 MPa, 12.45%, and 10630 N/m, respectively. The biodegradable plastics prepared with the optimum conditions had a tensile strength of 7.13 MPa, elongation at break of 13.05%, and stiffness of 10400 N/m. These values are closely similar to the predicted values.

1. Introduction

Petroleum-based polymers or plastics are extensively utilized for packaging, medical supplies, and other applications due to their superior properties, such as lightweight, durability, hydrophobicity, and formability (Dey et al., 2021). In 2019, the global plastics production reached 370 million tons where about 50% of them were used for single-use purposes, and only 15-18% were recycled. Therefore, most plastic waste ends up in landfills and numerous water bodies, especially oceans, rivers, lakes, and ponds. Because plastic requires several centuries to decompose, it will continuously accumulate and induce environmental issues (Putra et al., 2022).

From an environmental point of view, biodegradable plastic is a better alternative to petroleum-based plastics. Renewable materials such as polysaccharides are the potential raw material for biodegradable films (Retnowati et al., 2015). Being an edible and low-price material, starch is the most preferred raw material for biodegradable plastic manufacturing (Woggum et al., 2015). It comprises two natural carbohydrate polymers, which are amylose and amylopectin. Amylose is a linear polymer of anhydroglucose unit, while amylopectin is a branched polymer. Amylose contributes more to plastic strength than amylopectin (Woggum et al., 2015). Because rice flour contains 18-33% of amylose (Chaiwanichsiri et al., 2014), it can be a potential candidate for biodegradable plastic raw material. Another advantage of rice flour is its low price if it is made from brewer's rice as a by-product of rice processing (Ma'As et al., 2020). Unfortunately, biodegradable plastic derived from rice flour alone has poor mechanical properties (Hasan et al., 2020).

Blending rice flour with glycerol and rice husk can be expected to enhance plastic's mechanical properties. Glycerol acts as a plasticizer which increases plastic's processability and flexibility (Wang et al., 2018). Retnowati et al. (2015) used glycerol as much as 30-40% of the total solid weight in preparing biodegradable plastic from durian and jackfruit flours. Ratnawati et al. (2022) prepared biodegradable film from PVA, cassava starch, and lignin by adding glycerol to as much as 25-65% of the total solid weight. They found that the tensile strength of the plastics decreased, while the elongation at break increased as the amount of glycerol increased. Therefore, fillers, such as cellulose can be added to plastics as a reinforcement to improve their tensile strength.

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Commonly, an appropriate combination of plasticizer with filler can increase the mechanical properties of biodegradable plastics. The filler's ability to strengthen the composite depends on its dispersibility as well as its interaction with the matrix materials (Majeed et al., 2017). Rice husk, which is renewable, biodegradable, lightweight, and tough is a sustainable source of cellulose. Rice husk contains cellulose (32.67%), hemicellulose (31.68%), lignin (18.81%), and ash (11.88%) (Ma'ruf et al., 2017). The rice husk ash comprises silica up to 94%, which can give a higher stiffness to the plastic (Premalal et al., 2002). Premalal et al. (2002) added rice husk powder as much as 0-60% w/w to the polypropylene composite. Kargarzadeh et al. (2017) used 0-10% of rice husk powder in preparing cassava starch-based plastic.
This work applied the extrusion technique for the fabrication of biodegradable plastics. The objective of this work was to study the effect of both glycerol and rice husk percentages as well as the extrusion temperature on the mechanical properties of biodegradable plastics. The Box-Behnken experimental design was utilized to set up the necessary experiments. Finally, an optimum condition for plastic preparation with the best mechanical properties was estimated using the Response Surface Methodology (RSM).

2. Materials and method

2.1 Materials

Materials used in this work were rice flour, rice husk, glycerol, distilled water, and a reusable plastic plate. The rice flour was obtained from a local producer, PT. Budi Makmur Perkasa, while rice husk was obtained from a local rice mill. The glycerol was purchased from PT. Hepilab Sukses Bersama. The distilled water was prepared in the laboratory. The plastic plate was purchased from a local market in Semarang (Indonesia).

2.2 Composition analysis of rice flour

The proximate analysis of the rice flour was determined according to AOAC International (1990). Carbohydrate was calculated by differences. Amylose was analyzed using a spectrophotometer according to Juliano (1971). The rice husk moisture content was determined using the gravimetric method. Each measurement was conducted in duplicate.

2.3 Experimental design

The independent variables used in this work were temperature (T), glycerol (G), and rice husk (H). The independent variables were varied at three levels according to the Box-Behnken design (BBD), i.e., 100, 110, and 120°C for T, 25, 35, and 45% (g/100g of solid) for G, and 0, 10, and 20% (g/100g of rice flour) for H. The independent variables were arranged in 15 runs as tabulated in Table 1. RSM was employed to evaluate the effect of the independent variables on the tensile strength (TS), elongation at break (EB), and stiffness (ST). The response (Y), representing TS, EB, and ST, is correlated to the independent variables (X_i) according to:

$$Y = b_0 + \sum_i b_i X_i + \sum_i b_{ii} X_i^2 + \sum_i \sum_j b_{ij} X_i X_j + \varepsilon \quad (1)$$

where b_0 is the intercept of Y, b_i is the linear effect coefficient, b_{ii} is the square effect coefficient, b_{ij} is the interaction coefficient of two independent variables, and ε is a random error (Ratnawati et al., 2022). Statistical analysis was conducted using Minitab version 19 software.

2.4 Preparation of biodegradable plastic

Initially, rice husk was washed and dried under the sun for two days to dryness, ground and sieved into 60–80 mesh, and stored in a closed container for further use. The plastic was prepared by mixing 100 g of rice flour, distilled water (75% w/w of total solid), glycerol, and rice husk. The compositions of the mixture followed the experimental design presented in Table 1. The mixture was homogenized using a mixer and kept overnight in a closed container at room temperature. The mixture was extruded at 100-120°C (higher than the rice flour gelatinization temperature) to form a plastic slab. The plastic slab was then dried at 50°C using an electric oven for 24 hours and stored in a closed container for further analysis.

2.5 Characterization of biodegradable plastic and reusable plastic plate

The TS, EB, and ST of the plastics were determined using Lloyd Instruments/Ametek TA Plus Texture Analyzer. The plastic slabs were cut into 5 mm × 150 mm slices for the analysis. All the analysis was done in triplicate

3. Results and Discussion

The proximate composition (wet basis) of the rice flour was moisture 11.14 ± 0.16%, ash 0.24 ± 0.00%, crude lipid 1.59 ± 0.09%, protein 6.66 ± 0.27%, and total carbohydrate 80.37 ± 0.33%. The amylose content was 26.36

± 0.38% (wet basis) or 30.14 ± 0.39% (dry basis). The moisture content of the rice husk was 9.16 ± 0.18%. The TS, EB, and ST of the plastic plate are 10.27 MPa, 33.07%, and 4702 N/m, respectively. The mechanical properties of the biodegradable plastics are presented in Table 1.

Table 1: Experimental design and the mechanical properties of the biodegradable plastic

Run	Independent variable			Experimental value			Predicted value		
	T (°C)	G (%)	H (%)	TS (MPa)	EB (%)	ST (N/m)	TS (MPa)	EB (%)	ST (N/m)
1	100	25	10	4.62	3.11	9312	5.32	3.82	9503
2	120	25	10	5.61	6.99	6536	6.44	5.03	7763
3	100	45	10	2.73	12.93	1631	2.20	14.64	283
4	120	45	10	2.45	13.98	1193	2.05	13.01	879
5	100	35	0	3.11	27.76	2780	3.79	24.47	3341
6	120	35	0	4.03	22.05	2248	4.62	21.42	1749
7	100	35	20	2.71	9.54	1591	2.42	9.92	1969
8	120	35	20	2.95	9.51	3101	2.57	12.55	2417
9	110	25	0	9.61	6.58	11391	8.67	8.93	10487
10	110	45	0	1.77	22.25	796	2.04	23.31	1411
11	110	25	20	4.05	3.52	9848	4.08	2.20	9111
12	110	45	20	1.96	9.22	1302	3.20	6.62	2083
13	110	35	10	3.24	17.23	1866	3.11	13.69	2023
14	110	35	10	3.11	13.54	2498	3.11	13.69	2023
15	110	35	10	2.52	10.69	1887	3.11	13.69	2023

3.1 Statistical analysis

The effect of T, G, and H on the TS, EB, and ST was analyzed using the Box-Behnken Analysis of Variance (ANOVA). The mathematical models obtained for the TS, EB, and ST are as follows:

$$TS = -3.6 + 0.43T - 0.697G - 0.476H - 0.00126T^2 + 0.01022G^2 + 0.00369H^2 - 0.00318TG - 0.00170TH + 0.01438GH \quad (2)$$

$$EB = 53 - 2.39T + 5.49G - 1.73H + 0.0113T^2 - 0.0570G^2 + 0.02271H^2 - 0.0071TG + 0.0142TH - 0.0249GH \quad (3)$$

$$ST = 37145 + 618T - 3192G - 909H - 4.1T^2 + 29.94G^2 + 7.56H^2 + 5.84TG + 5.10TH + 5.12GH \quad (4)$$

The p-values of the models and all the components are presented in Table 2 along with their contribution percentages. The coefficient of determination (R^2) of the equations for TS, EB, and ST were 90.15%, 90.82%, and 95.83%, respectively. It indicated that the models could explain 90.15%, 90.82%, and 95.83% of the variations of the TS, EB, and ST, respectively, as a result of the variation of T, G, and H.
The p-values of all components of the three models along with their respective contribution percentages are listed in Table 2. The contribution percentage was calculated based on the adjusted sum of squares (Ratnawati et al., 2022). Table 2 exhibits that the p-values of TS, EB, and ST models are 0.044, 0.031, and 0.053, respectively. Based on the obtained p-values (less than 0.05), the models are statistically significant. The models are used to predict the TS, EB, and ST of 15 runs as tabulated in Table 1. The models were also used to describe the simultaneous effect of T, G, and H on the TS, EB, and ST as response surface plots as depicted in Figures 1–3.

3.2 Effect of T, G, and H on the mechanical properties of the biodegradable plastic

Table 2 demonstrates that the G gives a significant effect on the mechanical properties of biodegradable plastic. It contributes 53.18, 26.02, and 73.20% to the TS, EB, and ST, respectively. As shown in Figures 1a, 2a, and 3a, the effect of G is not linear. It can be explained by the contribution of G^2 to the TS, EB, and ST, i.e., as much as 7.31, 17.10, and 18,74%, respectively. Figures 1a and 3a also show that an increase in G leads to a reduction of both TS and ST, while Figure 2a shows that the EB of the plastic increases as G increases. A similar effect of G on TS and EB was reported by other researchers (Ratnawati et al., 2022; Retnowati et al., 2015).

Table 2: Analysis of variance for TS, EB, and ST

Source	DF	p-value			Contribution (%)		
		TS	EB	ST	TS	EB	ST
Model	9	0.044	0.038	0.006			
T	1	0.545	0.940	0.539	0.83	0.01	0.35
G	1	0.003	0.013	0.000	53.18	26.02	73.20
H	1	0.063	0.006	0.702	11.12	39.18	0.13
T^2	1	0.822	0.575	0.540	0.11	0.67	0.35
G^2	1	0.112	0.029	0.005	7.31	17.10	18.74
H^2	1	0.517	0.282	0.280	0.95	2.71	1.20
TG	1	0.560	0.711	0.375	0.76	0.29	0.77
TH	1	0.752	0.467	0.433	0.22	1.15	0.59
GH	1	0.037	0.226	0.432	15.67	3.55	0.59
Error	5				9.84	9.32	4.07
Total	14				100.00	100.00	100.00

As a small molecule, glycerol can easily fill the spaces between the amylose and amylopectin molecules. In addition, its hydroxyl groups allow more intensive interactions with both amylose and amylopectin molecules through hydrogen bonding and thus reduce the interactions between the amylose and amylopectin molecules. As a result, the mobility of the amylose and amylopectin increases, and hence the TS and ST are lower. Another effect is the enhancement of both flexibility and EB of the plastic (Ratnawati et al., 2022; Retnowati et al., 2015).

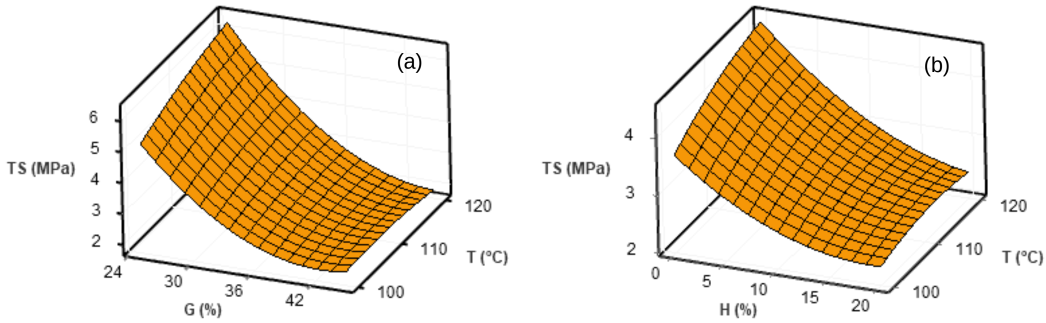

Figure 1: Effect of (a) G and T and (b) H and T on the TS of the biodegradable plastic.

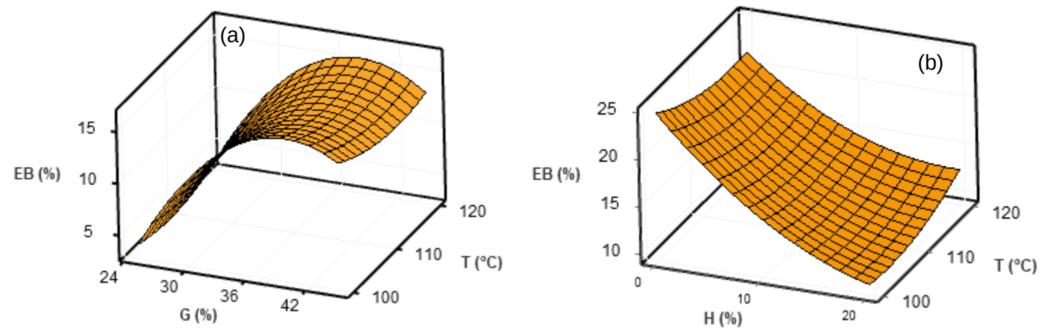

Figure 2: Effect of (a) G and T and (b) H and T on the EB of the biodegradable plastic.

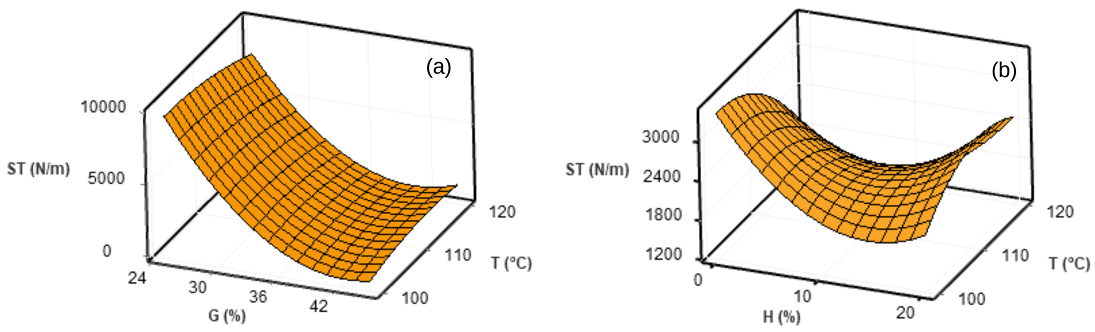

Figure 3: Effect of (a) G and T and (b) H and T on the ST of the biodegradable plastic.

Rice husk (H) provides a significant effect on the TS and EB with 11.12 and 39.18% contributions, respectively. The effect of H on the TS and EB of the biodegradable plastic is shown in Figures 1b and 2b. The TS and EB decrease with the increase of H. A similar effect of H on TS and EB was reported by other researchers (Premalal et al., 2002; Kargarzadeh et al., 2017). The negative effect of H on TS could be related to poor interfacial adhesion between the rice husk and the matrix. As the rice husk powder increases, it tends to agglomerate, which may induce mixture inhomogeneity (Premalal et al., 2002). Consequently, the discontinuity of the composite increases which leads to reducing both TS and EB. The effect of H on ST is not significant. The contribution of both H and H^2 to ST is only 0.13 and 1.20%, respectively.

Table 2 indicates that temperature (as both T and T^2) does not have any significant effect on the TS, EB, and ST of the biodegradable plastic. The objective of extrusion and heating is to mix the blend and gelatinize the rice flour. The gelatinization of rice flour with moisture content from 100 to 300% (w/w of dry flour) ranges from 65.4 to 74.4°C (Saif et al., 2003). Therefore, at the temperature of the extrusion (100–120°C), the rice flour with a moisture content of 75% (w/w of dry flour) must have been gelatinized. Furthermore, 120°C is well below the degradation temperature of starch (Zhang et al., 2002). Therefore, there is no significant difference in mechanical properties of the biodegradable plastics prepared at 100, 110, and 120°C.

3.5 Optimization

The optimum conditions for the making of biodegradable plastics were predicted using the response optimizer. The optimum conditions were 100°C for the temperature, 25.81% for the glycerol, and 0% for the rice husk. It shows that the plastic without rice husk powder is better than that with the addition of rice husk. Similar results were reported for polypropylene-based plastic (Premalal et al., 2002) and cassava starch-based plastic (Kargarzadeh et al., 2017). It indicates poor adhesion between the filler and the matrix. It could be related to the chemical composition of the rice husk. The rice husk used in this work was native without any chemical treatment. It contained cellulose and hemicellulose (hydrophilic), as well as lignin (relatively hydrophobic). The hydrophobic part might cause poor interaction between the rice husk and the matrix (Boonsuk et al., 2021). Furthermore, without any chemical treatment, the surface of the rice husk powder was relatively smooth, which also led to poor adhesion between the rice husk and the matrix (Bihst et al., 2020).

The predicted TS, EB, and ST were 7.27 MPa, 12.45%, and 10630 N/m, respectively. A validation experiment was conducted to verify the accuracy of the model equations. A biodegradable plastic was prepared using the optimum conditions. The TS, EB, and ST of the plastic were 7.13 MPa, 13.05%, and 10400 N/m, respectively. The TS and ST are below the predicted values while the EB is above the predicted value. However, they are still within a 95% confidence interval. Therefore, the models can predict the responses with 95% confidence.

The TS and EB of the biodegradable plastic are lower than those of the reusable plastic plate, while the ST is higher.

4. Conclusions

Biodegradable plastics have been successfully prepared from rice flour with glycerol as a plasticizer and rice husk powder as a filler by using an extrusion method. The independent variables in the plastic making were temperature (100–120°C), glycerol (25–45%), and rice husk (0–20%). Three models describing the effect of the input variables on the TS, EB, and ST were developed. Among all input variables, glycerol was the only variable having a significant effect on TS, EB, and ST. Rice husk powder has a significant effect on the TS and EB, while T does not have any significant effect on all the mechanical properties. The optimum conditions for preparing the plastic are 100°C, 25.81%, and 0% for the T, G, and H, respectively. The predicted TS, EB, and ST of the plastic calculated with the optimum conditions are 7.266 MPa, 12.45%, and 10630 N/m, respectively. The mechanical properties of the plastic prepared with the optimum conditions have TS of 7.13 MPa, EB of 13.05%, and ST of 10400 N/m, which are still within the 95% confidence interval of the models. The TS and EB of the biodegradable plastic are less and the ST is higher than those of the reusable plastic plate.

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