Biodegradable plastic from cross-linked rice flour: Effect of cross-linking agent and plasticizer

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ABSTRACT

Plastics made from petroleum have long been used in packaging. However, most plastics end up in landfills and bodies of water. Moreover, plastic does not degrade for hundreds of years, creating an issue for the ecosystem. One of the solutions is to use biodegradable plastic instead of petroleum-based plastic. Numerous studies have been conducted on manufacturing biodegradable plastic from renewable resources like starch. Rice flour, which contains up to 93.3% starch, is a potential material for biodegradable plastic. The flour was modified by cross-linking with sodium trimetaphosphate (STMP) before producing biodegradable plastic. This work aimed to study the effect of the amount of STMP (1%, 2% and 3%), the type of plasticizer (glycerol and sorbitol), and the amount of the plasticizer (40%, 50% and 60%) on the properties of the plastic. The amount of STMP decreases the swelling index and increases the tensile strength, but it does not significantly affect the biodegradability of the plastic. Although the plasticizer enhances biodegradability and reduces the tensile strength, it has little effect on the swelling index. The glycerol-plasticized plastic has a higher swelling index and biodegradability but lower tensile strength than the sorbitol-plasticized plastic. Plastic with 40% sorbitol and 3% STMP has the highest tensile strength (4.3 MPa).

Keywords: Biodegradability, STMP, Swelling index, Tensile strength.

1. INTRODUCTION

Indonesia is the second-largest country after China in generating plastic waste (Jambeck et al., 2015). It was reported that the total plastic waste generated was 5.9 to 9.5 million tons per year. Only 2.9 to 3.6 million tons were collected for recycling, while the rest ended up in landfills and water bodies (World Bank, 2021). It will raise an environmental problem because it takes centuries for the plastics to decompose (Moshood et al., 2022).

Even though plastic causes environmental problems, people can barely avoid using plastic in daily activities. It is because of its low cost, good mechanical properties, hydrophobicity, and durability (Lebreton and Andrady, 2019). The primary usage of plastics is for packaging, which accounts for 42% of total production (Geyer et al., 2017). Many attempts have been made to replace petroleum-based plastics with biodegradable plastics. Biodegradable plastic is plastic that living organisms can decompose into water, carbon dioxide, and biomass (Song et al., 2009). Starch is the most widely used natural material for making biodegradable plastics for packaging applications. In addition, producing starch-based plastic is straightforward (Marichelvam et al., 2019).

Starch is a polymer of glucose consisting of two types of molecules, i.e., linear and branched polymer. The linear polymer, known as amylose, is made of glucose monomers interconnected through \( \alpha(1 \rightarrow 4) \) linkage. In the branched polymer, known as amyllopectin, the glucose units are interconnected by \( \alpha(1 \rightarrow 4) \) linkage in the linear chains and by \( \alpha(1 \rightarrow 6) \) linkage in the branch points (Seung, 2020). The amylose and amyllopectin...
contents in starch may vary, depending on the source, as presented in Table 1 (Marichelvam et al., 2019).

<table>
<thead>
<tr>
<th>Source</th>
<th>Amylose (%)</th>
<th>Amylopectin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>35.0</td>
<td>65.0</td>
</tr>
<tr>
<td>Corn</td>
<td>28.0</td>
<td>72.0</td>
</tr>
<tr>
<td>Arrowroot</td>
<td>20.5</td>
<td>79.5</td>
</tr>
<tr>
<td>Wheat</td>
<td>20.0</td>
<td>80.0</td>
</tr>
<tr>
<td>Cassava</td>
<td>18.6</td>
<td>81.4</td>
</tr>
<tr>
<td>Potato</td>
<td>17.8</td>
<td>82.2</td>
</tr>
<tr>
<td>Banana</td>
<td>17.0</td>
<td>83.0</td>
</tr>
</tbody>
</table>

Amylose positively affects the tensile strength of starch-based plastics (Ceseracciu et al., 2015). Among the sources in Table 1, rice starch has the highest amylose content. Therefore, rice starch is a potential material for biodegradable plastic. However, a biodegradable plastic made from rice starch alone and glycerol has a low tensile strength (Dias et al., 2010; Detduangchan et al., 2014; Hasan et al., 2020). Therefore, Detduangchan et al. (2014) enhanced the tensile strength of the rice starch-based biodegradable plastic using cross-linked rice starch. They used sodium tripolyphosphate (STPP) and STMP as the cross-linking agents.

The mechanical properties of rice starch-based biodegradable plastics are affected by the type of plasticizer used. For example, Shafqat et al. (2021) made biodegradable plastics from banana peel, corn, and rice starch. They used glycerol and sorbitol as the plasticizers for the plastics. They revealed that the plastics with sorbitol had higher Young's modulus and tensile strength than those with glycerol. Alonzo-Gonzalez et al. (2022) reported similar findings that Young's modulus, maximum stress, and deformation at break of the biodegradable plastics made with sorbitol were higher than that with glycerol.

Biodegradable plastic for packaging applications should have acceptable mechanical properties. The parameters commonly used to evaluate the properties of biodegradable plastic are tensile strength, elongation at break, and biodegradability. According to the National Standardization Agency of Indonesia, through standard number SNI 7818:2014, biodegradable plastic for packaging must have a tensile strength of at least 13.7 MPa and elongation at break of 400–1120% (BSN, 2014).

Rice flour may contain carbohydrates (amylose and amylopectin) up to 93.3% (Oppong et al., 2021). Many groups of researchers have reported the preparation of biodegradable plastics from rice starch (Detduangchan et al., 2014; Marichelvam et al., 2019; Dias et al., 2020; Hasan et al., 2020; Shafqat et al., 2021). However, only a few studies documented the preparation of biodegradable plastic from rice flour (Dias et al., 2010; Ratnawati et al., 2022). Therefore, this work focused on rice flour as the primary material for biodegradable plastics for packaging applications. The rice flour was cross-linked with STMP before the preparation of the biodegradable plastic. The cross-linking is intended to improve the mechanical properties of the plastics. STMP was used because it is a non-hazardous material, but the cross-linking reaction proceeds slowly (Shah et al., 2016). The reaction can be accelerated by raising the pH. At pH around 11, amylose is ionized, forming alkoxy anions. The reaction of STMP is faster with alkoxy anions than with non-ionized amylose. Therefore, the favorable pH for cross-linking starch with STMP is between 10 and 11 (Woo and Seib, 1997).

This work aimed to study the effect of the type of plasticizer (glycerol and sorbitol) and the concentration of STMP and the plasticizer on the properties of rice flour-based biodegradable plastics. The novelty of this work was the utilization of STMP-crosslinked rice flour for biodegradable plastic preparation.

2. MATERIALS AND METHODS

2.1 Materials

The rice flour was purchased from the local market. STMP (CAS Number 7785-84-4), sorbitol (CAS Number 50-70-4), glycerol (CAS Number 56-81-5), NaOH (CAS Number 1310-73-2) and HCl (CAS Number 7647-01-0) were purchased from Sigma-Aldrich, Indonesia.

2.2 Modification of Rice Flour

The cross-linking of rice flour was conducted by following the method of Detduangchan et al. (2014) with a little modification. One hundred grams of rice flour was dispersed in 250 mL of distilled water. A predetermined amount of STMP was added to the mixture. The amount of STMP was varied from 1% to 3% (g of STMP/100 g of flour). The pH of the mixture was adjusted to 10.5 using 0.05 N NaOH solution. The mixture was heated at 45°C for 2 h with constant stirring. After that, the pH of the mixture was adjusted to 5.5 to terminate the reaction by adding 0.1 N HCl solution. Next, the flour slurry was neutralized with a 0.05 N NaOH solution and washed using distilled water until neutral. The slurry was filtered using a vacuum filter, and the flour was dried in an oven at 50°C for 24 h. The dry flour was ground and sifted using a 60-mesh screen. The flour was stored in a closed container for further use.

2.3 Biodegradable Plastic Preparation

The biodegradable plastics were prepared using the solution casting method (Retnowati et al., 2015). Four grams of flour were dispersed in 100 mL of distilled water. The mixture was heated at ± 85°C for 10 min with constant stirring. The solution was cooled to 50°C. A predetermined amount of plasticizer was added to the solution. The amount of the plasticizer ranged from 40% to 60% (g of plasticizer/100 g of flour). The formulation for the plastic preparation is presented in Table 2. The mixture was stirred for 2 min, poured into an acrylic plate, and and dried at ± 50°C for 24 h in an oven. The plastics were peeled off from the mold and...
Table 2. Biodegradable plastics formulation

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Name of plasticizer</th>
<th>STMP (%)</th>
<th>Plasticizer (%)</th>
<th>Sample code</th>
<th>Name of plasticizer</th>
<th>STMP (%)</th>
<th>Plasticizer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G0</td>
<td>Glycerol</td>
<td>0</td>
<td>40</td>
<td>S0</td>
<td>Sorbitol</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>G1</td>
<td>Glycerol</td>
<td>1</td>
<td>40</td>
<td>S1</td>
<td>Sorbitol</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>G2</td>
<td>Glycerol</td>
<td>1</td>
<td>50</td>
<td>S2</td>
<td>Sorbitol</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>G3</td>
<td>Glycerol</td>
<td>1</td>
<td>60</td>
<td>S3</td>
<td>Sorbitol</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>G4</td>
<td>Glycerol</td>
<td>2</td>
<td>40</td>
<td>S4</td>
<td>Sorbitol</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>G5</td>
<td>Glycerol</td>
<td>2</td>
<td>50</td>
<td>S5</td>
<td>Sorbitol</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>G6</td>
<td>Glycerol</td>
<td>2</td>
<td>60</td>
<td>S6</td>
<td>Sorbitol</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>G7</td>
<td>Glycerol</td>
<td>3</td>
<td>40</td>
<td>S7</td>
<td>Sorbitol</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>G8</td>
<td>Glycerol</td>
<td>3</td>
<td>50</td>
<td>S8</td>
<td>Sorbitol</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>G9</td>
<td>Glycerol</td>
<td>3</td>
<td>60</td>
<td>S9</td>
<td>Sorbitol</td>
<td>3</td>
<td>60</td>
</tr>
</tbody>
</table>

kept in a closed container for further analysis.

2.4 Fourier Transform Infrared (FTIR)
The functional groups in the plastics were analyzed using an FT-IR apparatus (Perkin Elmer PC 1600, Houston, TX, USA).

2.5 Swelling Index
The swelling index of the plastics was determined following the method of Basiak et al. (2018) with a slight modification. First, the plastics were cut into 2 × 2 cm, weighed, and soaked in 20 mL of distilled water for 5 min. Then, the sample was removed from the water, wiped using a paper tissue to remove the excess water on the surface, and weighed. The measurement was conducted in triplicate. Finally, the swelling index was calculated using Equation (1).

\[
\text{Swelling index} = \frac{W_s - W_i}{W_i} \times 100\%
\]  

\(W_i\) and \(W_s\) are the weights of the samples before and after soaking, respectively.

2.6 Biodegradability
The biodegradability test was performed following the method used by Shanmathy et al. (2021) with a little modification. First, the plastics were cut into 2 × 2 cm and weighed. Then, the samples were buried in the soil inside a beaker glass. The samples were placed 5 cm from the bottom and 5 cm from the soil’s surface. After being buried for 24 days, the plastics were carefully cleaned from the dirt and weighed. The measurement was carried out in triplicate. The percentage of weight loss was calculated using Equation (2).

\[
\text{Biodegradability} = \frac{W_i - W_b}{W_i} \times 100\%
\]

\(W_i\) and \(W_b\) are the sample weights before and after 24 days of burial, respectively.

2.7 Tensile Strength
The biodegradable plastics were tested for tensile strength according to ASTM D882 using Lloyd Instruments/Ametek TA Plus Texture Analyzer.

3. RESULTS AND DISCUSSION

3.1 FTIR
The FTIR spectra of the biodegradable plastic samples (G0, S0, G8 and S8) are depicted in Fig. 1. It is seen in the figure that all samples have similar spectra with a little difference in peak intensity.

![FTIR spectra of four biodegradable plastic samples](image)

There are several weak peaks at wavenumber between 400 and 800/cm. This band is attributed to the skeletal modes of amyllose and amylopectin as the major components of rice flour (Flores-Morales et al., 2012). The peaks between 800 and 1200/cm are characteristic of the stretching C-O bond. The peaks at 1011 and 1077/cm are characteristic of the stretching anhydroglucose ring C-O (Fang et al., 2002).

The peaks at 996/cm of samples G0 and S0 (biodegradable plastic with native rice flour) are shifted to 1011/cm for samples G8 and S8 (biodegradable plastic with modified rice flour). It could be related to a new bond formed by the reaction between C-O groups in the anhydroglucose ring with STMP. The reaction is depicted in Fig. 2.
It is shown in Fig. 1 that new low-intensity band peaks emerge at 1100/cm for the samples G8 (pink line) and S8 (orange line), as indicated by a blue dashed ellipse. The band at 1100/cm is related to the symmetrical and asymmetrical stretching of the PO$_2$ group (Sechi and Marques, 2017) due to cross-linking by STMP. The following peaks observed are at 1363 and 1411/cm, which are assigned for the vibration of the bending C-H bond. The peak at 1642/cm is attributed to the bending N-H bond in the protein structure (Antunes et al., 2015), as rice flour may contain as much protein as 5.01% to 8.14% (Oppong et al., 2021). The peak at 1642/cm is also a feature of tightly bound water in the plastics (Antunes et al., 2015). The peak at 2929/cm is characteristic of stretched C-H. Finally, the strong broadband at 3276/cm is attributed to the vibration of stretching hydrogen-bonded O-H bonds in amylose, amylopectin, glycerol, and sorbitol (Fang et al., 2002).

3.2 Swelling Index

The swelling index of the plastics with glycerol and sorbitol as the plasticizing agents are depicted in Fig. 3. It is seen in the figure that the amount of plasticizer (both glycerol and sorbitol) has only a small effect on the swelling index of the plastics. As an example, the swelling index of the glycerol-plasticized plastics increases from 74.1% to 75.0% and 76.6% when the percentage of glycerol rises from 40% to 50% and 60%, respectively. Basiak et al. (2018) reported a similar result. The wheat flour-based plastic with 33% and 50% glycerol had a 39.0% and 39.2% swelling index, respectively. The modest influence of the plasticizer on the swelling index could be due to its full plasticizing effect, which is associated with a swollen matrix. Hence, the immersion of the swollen matrix with different amounts of plasticizer in water does not result in a different swelling index of the matrix (Basiak et al., 2018).
It is seen in Fig. 3 that for all plastics, the swelling index decreases as the amount of STMP increases. As an example, the swelling index of the plastic with 40% of glycerol as the plasticizing agent prepared with rice flour cross-linked with 1%, 2% and 3% of STMP was 74.1%, 67.3% and 63.3%, respectively, as shown in Fig. 3(a). A similar result was reported by Awasthi and Singhal (2015). They studied the effect of cross-linking agents (glycidyl methacrylate) on the swelling profile of poly (AM-co-AA-co-HEA) hydrogels. They found that increasing the amount of cross-linking agent from 1% to 2%, 3% and 4% caused a decrease in the swelling ratio from 24.5 to 15.2, 7.9 and 3.5, respectively. As the amount of cross-linking agent increases, more network is formed, making the plastic more rigid, and fewer water molecules can penetrate the spaces inside the network (Awasthi and Singhal, 2015).

The swelling indexes of the glycerol-plasticized plastics, as shown in Fig. 3(a), are higher than those of the sorbitol-plasticized plastics, as depicted in Fig. 3(b). A similar result was reported by Prasetyo et al. (2017). The swelling of a polymeric matrix is related to the penetration of water molecules into the matrix. Glycerol has a greater affinity to water than sorbitol (Ooi et al., 2012). Hence, glycerol-plasticized plastic attracts more water than sorbitol-plasticized plastic does.

### 3.3 Biodegradability

Fig. 4 shows the biodegradability of the plastics, which is represented by the weight loss of the plastics during the burial test for 24 days. It is depicted in the figure that the amount of STMP for the modification of the flour does not have a significant effect on biodegradability.

Fig. 4 illustrates how the weight loss of the plastics increases as the percentage of the plasticizers (both glycerol and sorbitol) increases. For example, it is seen in Fig. 4(a) that the weight loss of the plastic made from the rice flour previously modified with 1% of STMP increases from 42.0% to 43.4% and 48.7% when the amount of glycerol used is 40%, 50% and 60%, respectively. The other researchers found similar results. For example, Inayati et al. (2019) reported that after 20 days of burial, the weight loss of the rice straw-based biodegradable plastics increased from 12.0% to 12.7% and 21.3% as the amount of glycerol rose from 25 to 30 and 35%, respectively.

The decomposition of biodegradable plastic occurs through several mechanisms caused by bacteria, fungi, or other microorganisms (Tarique et al., 2021). The effect of glycerol and sorbitol on the biodegradability of the plastic could be related to the affinity of glycerol and sorbitol to water. As the amount of glycerol or sorbitol increases, the plastic may absorb more water from the environment. It will, in turn, favor biodegradation by microbial activity (Mustapha and Wan, 2022). Therefore, glycerol-plasticized plastic is more biodegradable than sorbitol-plasticized plastic because glycerol has more affinity to water than sorbitol. For example, using 40% plasticizer and 1% STMP, the weight loss of the glycerol-plasticized plastic is 42.0%, while that of the sorbitol-plasticized plastic is 34.4%, as shown in Fig. 4.

### 3.4 Tensile Strength

The effect of STMP and plasticizer on the tensile strength of the glycerol-plasticized and sorbitol-plasticized plastics is presented in Fig. 5. The tensile strength of the plastic is higher for a higher amount of STMP used. For example, as seen in Fig. 5(a), the tensile strength of the glycerol-plasticized plastic prepared using 40% of glycerol and rice flour modified with 1%, 2% and 3% of STMP are 1.3, 1.6 and 1.7 MPa, respectively. Other researchers reported similar findings. Detduangchan et al. (2014) prepared biodegradable plastics using STMP-cross-linked rice starch with sorbitol as the plasticizer. They reported that the tensile strength of the plastics prepared using rice starch cross-linked with 1%, 2% and 3% of STMP were 6.3, 7.23 and 8.23 MPa, respectively. Musa and Hameed (2021) made biodegradable plastics
using a PVA/starch blend with 5%, 8% and 10% of glutaraldehyde as the cross-linking agent. They found that the tensile strengths of the plastics with 0%, 5%, 8% and 10% of glutaraldehyde were 21.0, 26.9, 30.7 and 35.1 MPa, respectively.

![Graph](image)

**Fig. 5.** Effect of (a) glycerol and STMP and (b) sorbitol and STMP on the tensile strength of the biodegradable plastic

The effect of the cross-linking agent on the tensile strength of the plastics is related to the reinforcement effect of the cross-linking. One molecule of cross-linking agent connects two molecules of amylose or amylopectin. It is also possible that the cross-linking involves more than two molecules of amylose or amylopectin. As a result, when the plastic is subjected to tensile stress, it is not easily cracked because cross-linking provides strong adhesion among the amylose or amylopectin molecules (Musa and Hameed, 2021).

Fig. 5 shows that the tensile strength of the biodegradable plastics decreases as the amount of glycerol and sorbitol as the plasticizing agent increases. It can be seen in Fig. 5(a) that the plastics prepared using rice flour cross-linked with 1% of STMP are 1.3, 0.9 and 0.5 MPa when the amount of glycerol used is 40%, 50% and 60%, respectively. Retnowati et al. (2015) reported that the tensile strength of the biodegradable plastics made from jackfruit and durian flour with 30% glycerol was higher than that with 40% glycerol. Ratnawati et al. (2022) made biodegradable plastic from PVA/starch/lignin blend with glycerol as the plasticizer. They discovered that raising the glycerol concentration from 20% to 40% and 60% reduced the tensile strength of the plastics from 6.7 to 7.1 and 6.6 MPa, respectively.

The effect of plasticizers on the tensile strength of the plastic can be related to molecular interactions between the components. Amylose and amylopectin are two major components in rice flour. Both molecules have hydroxyl groups, which allows hydrogen bonds to form between them. Glycerol and sorbitol, which have hydroxyl groups but are considerably smaller than amylose and amylopectin, can easily penetrate between amylose and amylopectin molecules. As a result, the molecular interaction between amylose and amylopectin molecules reduces, and hence, the tensile strength of the plastic decreases (Ooi et al., 2012; Ratnawati et al., 2022).

The effect of STMP on the tensile strength of the plastic with 60% sorbitol is more pronounced. Cross-linking agents and plasticizers have a different impact on the plastics. STMP, as the cross-linking agent, forms molecular covalent bonding with amylose and amylopectin (Sechi and Marques, 2017), resulting in higher tensile strength. On the other hand, sorbitol interacts with amylose and amylopectin molecules through hydrogen bonding, increasing the plasticizing effect as water is a plasticizing agent (Cheng et al., 2006; Ratnawati et al., 2022). As a result, the interaction between amylose and amylopectin molecules loosens, resulting in a lower tensile strength.
The biodegradable plastic with the highest tensile strength (4.3 MPa) is made with 3% STMP and 40% sorbitol. However, it is still below the standard set by the Indonesian National Standard for biodegradable plastic, i.e., 13.7 MPa (BSN, 2014).

4. CONCLUSION

Biodegradable plastics have been successfully formulated using STMP-cross-linked rice flour with glycerol and sorbitol as the plasticizing agents. The amount of STMP was varied from 1% to 3% (g of STMP/100 g of flour). The plastics were prepared with glycerol and sorbitol as the plasticizing agents, with concentrations varying from 40% to 60% (g of plasticizer/100 g of flour). The amount of STMP decreases the swelling index and increases the tensile strength, but it does not significantly affect the biodegradability of the plastic. The plasticizer reduces the tensile strength and increases biodegradability but does not significantly affect the swelling index. The glycerol-plasticized plastic has a higher swelling index and biodegradability but lower tensile strength than the sorbitol-plasticized plastic. The plastic with the highest tensile strength (4.3 MPa) is prepared with 3% STMP as the cross-linking agent and 40% sorbitol as the plasticizing agent.

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