Effect of filler and plastisizer on the mechanical properties of bioplastic cellulose from rice husk

M Jannah M, A Ahmad M, A Hayatun M, P Taba M and S Chadijah M

1 Master Program, Departement of Chemistry, Faculty of Mathematics and Natural Science, Physic Lab., Hasanuddin University, Perintis Kemerdekaan Street Km. 10 Tamalanrea, Makassar 90245, Indonesia
2 Departement of Chemistry, Faculty of Mathematics and Natural Science, Hasanuddin University, Perintis Kemerdekaan Street Km. 10 Tamalanrea, Makassar 90245, Indonesia
3 Laboratory of Research Centre and Developing of Sciences, Faculty of Natural Sciences, Hasanuddin University, Perintis Kemerdekaan Street Km. 10 Tamalanrea, Makassar 90245, Indonesia
4 Departement of Chemistry, UIN Alauddin Makassar, Makassar 92113, Indonesia

Abstract. Rice husk is a product of the rice milling process. The high cellulose contents in rice husk that supports the use of it as raw material for bioplastic. This study aims to determine the effect of supporting polymer such as chitosan to the mechanical properties of bioplastic. The stages of this research were cellulose extraction from rice husk by maceration method, optimization of NaOCl concentration as a bleaching agent and printing of bioplastics with various treatments, namely cellulose-sorbitol (CS), cellulose-chitosan (CC) and cellulose-sorbitol-chitosan (CSC). Characterization was conducted by Fourier Transform Infrared (FTIR) and Universal Testing Machine (UTM). The study showed that the optimum NaOCl concentration was 2.0% with a cellulose content of 59.2% in the form of white powder. The best bioplastic was bioplastic cellulose-sorbitol-chitosan (CSC) with the tensile strength of 0.060 Kgf/cm² and the elongation of 4.75%. The peaks appeared in the FTIR spectrum were O-H, N-H and C-O at 3450.64, 1638.41, and 1087.76 cm⁻¹, respectively. The interaction between cellulose from rice husk, filler addition, and plasticizer effected the quality of bioplastic.

1. Introduction
Plastic waste is one of the environmental problems that have not been solved optimally. Plastic waste requires a lot of time to decompose naturally so that its presence accumulates in the environment. Furthermore, the use of large quantities of synthetic plastics impacts the depletion of fossil raw materials. Synthetic plastics have replaced other materials, leading to the production to continuously increase. Therefore, new materials are needed to overcome this problem. This material is bioplastic, where its material can be obtained from natural materials. Agro-polymers based bioplastics have been largely developed. One of them is the starch-based bioplastic [1] and protein [2]. Biomass able to also
be developed as a bioplastic raw material. One of them is rice husk waste which is a side product of rice production. Rice production in Indonesia in 2018 was at 49.65 million tons of milled dry grain [3]. Production of rice husk worldwide in 2014 reached 1,482 x 10^8 tons, while it reached 14,166,400 tons in Indonesia [4]. Meanwhile, the existence of rice husk in the environment is a waste that has not been fully utilized. In addition to the high silica content in the rice husk, this biomass also has high cellulose of approximately 76% [5]. The high cellulose contents in the rice husk can be used potentially as a raw material for bioplastic. Therefore, the purpose of this study was to found the best cellulose-based bioplastic as well as their effects on the constituent polymers.

2. Materials and Method

2.1. Materials

The materials of this study were rice husks obtained from Gowa, Indonesia, CV. ChiMultiguna chitosan, 5% NaOH, 5% Na₂CO₃, 2.5% NaOCl, methanol, 10% H₂SO₄, sorbitol, 0.6 M CH₃COOH.

2.2. Instruments

The instruments of this research were glassware, grinding tools SMJIM Disk Mill FFC-23, sieves Retsch As200 Tap, ovens Genlab, Burchner ME 4C, Fourier Transform Infrared (FTIR) Thermo Scientific Nicolet iS10, Universal Testing Machines (UTM) XB-OTS- 600.

2.3. Procedure

2.3.1. Cellulose isolation of rice husk. Rice husk was dried under the sun. Dried rice husk was milled and sieved to 80 mesh size. Rice husk powder was macerated with methanol for 7 days and filtered. 300 mL of 5% NaOH and 5% Na₂CO₃ (w/v) was added into 10 g of methanol-free residue. 10% H₂SO₄ was added into the mixture to achieve a pH of 3-4. The residue was dried in an oven at 50 °C to a constant weight [5].

2.3.2. Optimization agent of bleaching. Bleaching was done by using NaOCl (0.5, 1.0, 1.5, 2.0, and 2.5%) [6]. 300 mL of NaOCl was added into the dried powder and the mixture was stirred for 5 hours at the room temperature [5]. The bleached residue was washed several times with distilled water. The neutral residue was dried in at a temperature of 50°C in the oven to a constant weight.

2.3.3. Bioplastic of cellulose-sorbitol (CS). Cellulose with variations of 0.4, 0.6, 0.8, 1.0 and 1.2 g was put in 5 different beakers, then 2 mL of sorbitol was added into each beaker. The mixture was stirred until homogeneous. The slurry was pressed on the top of the glass plate mold and flattened. The flattened mixture was dried in an oven at 60°C [7].

2.3.4. Bioplastic of cellulose-chitosan bioplastic (CC). Cellulose with variations of 0.4, 0.6, 0.8, 1.0 and 1.2 g was put in 5 different beakers, then 2.7% of chitosan solution (w/v in 0.6 M of CH₃COOH) was added into each beaker. The mixture was stirred until homogeneous. The slurry was pressed on the top of the glass plate mold and flattened. The flattened mixture was dried in an oven at 60°C [7].

2.3.5. Bioplastic of cellulose-sorbitol-chitosan bioplastic (CSC). Cellulose with variations of 0.4, 0.6, 0.8, 1.0 and 1.2 g was put in 5 different beakers, then 2.7% of chitosan solution (w/v in 0.6 M of CH₃COOH) was added into each beaker. The mixture was stirred until turned homogeneous. 2 mL of sorbitol was added into each beaker and stirred again. The slurry was pressed on the top of the glass plate mold and flattened. The flattened mixture was dried in an oven at 60°C [7].

3. Result and Discussion
3.1. Isolation of cellulose and optimization of bleaching agent concentration

The extracted cellulose formed blackish brown powders. This indicated that lignin was still bound to the cellulose. The bleaching process affects the color of the cellulose produced. In this observation, there was a significant color change along with an increase in NaOCl concentration. However, the color remained unchanged at the NaOCl concentration of 2.0%. These changes can be observed in Figure 1. The obtained cellulose in this study that formed a white powder and did not smell. Cellulose obtained was the same as the previous observation and compatible with the commercial cellulose [6].

Figure 1. Morphology of cellulose powder with variations of NaOCl concentration (a) 0% (b) 0.5% (c) 1.0 (d) 1.5% (e) 2.0% (f) 2.5% in bleaching process.

Cellulose levels have decreased with increasing concentration of NaOCl as shown in Table 1. It was because the bleaching process eliminated residual lignin and hemicellulose. Cellulose content at the 2.0% NaOCl concentration was 59.2%. The cellulose level of this study was higher compared to the previous observation which was 51.5% [8]. The high cellulose content of rice husk has the potential to be used as raw material for bioplastic.

| Concentration of NaOCl (%) | Cellulose level (%) |
|---------------------------|---------------------|
| 0.5                       | 77                  |
| 1.0                       | 67.2                |
| 1.5                       | 64                  |
| 2.0                       | 59.2                |
| 2.5                       | 59.2                |

3.2. Mechanical characteristic of bioplastic

The tensile strength and elongation of each variation of bioplastic can be observed in Figures 2 and 3. The tensile strength of CS bioplastic can only be carried out at a cellulose amount of 0.4 g cellulose because the bioplastic film of study was quite dense compared to other bioplastics. The tensile strength
value of the CS bioplastic was 0.005 Kgf/cm². The tensile strength of the CC bioplastic increased with the addition of cellulose amount. This was due to the increasing number of cellulose which formed crosslinking with chitosan, thus increasing the rigidity of bioplastic film. While the tensile strength of the CSC bioplastic has increased up to 1.0 g cellulose amount but has decreased at a cellulose amount of 1.2 g.

![Figure 2](image)

**Figure 2.** Effect of cellulose amount on bioplastic tensile strength of CS, CC, and CSC.

![Figure 3](image)

**Figure 3.** Effect of cellulose amount on bioplastic elongation of CS, CC, and CSC.

Elongation of the CS bioplastic can only be done at a cellulose amount of 0.4 g that was 0.76%. The highest elongation of the CC bioplastic was at a cellulose amount of 0.6 g. While the highest elongation of the CSC bioplastic was at a cellulose amount of 0.4 g and continues to decrease with the increase of cellulose amount.

The lowest tensile strength was found in the CS bioplastic, which was 0.005 Kgf/cm², while the highest value was found in the CC bioplastic which was 0.266 Kgf/cm². This is consistent with the
theory that chitosan acts as an amplifier in bioplastics [7]. The addition of chitosan can increase the tensile strength of bioplastic. The lowest elongation was found in the CS bioplastic which was 0.76%, while the highest value is found in the CSC bioplastic which was 9.93%. The addition of sorbitol aims to increase the flexibility and elasticity of bioplastic. The interaction among cellulose, chitosan and sorbitol can improve the mechanical properties of bioplastic. High tensile strength and elongation can occur if there are free O-H groups that can still cross with other O-H groups. The results of this study indicated that the CSC bioplastic was the best bioplastic with a tensile strength of 0.060 Kgf/cm$^2$ and elongation of 4.75%. The results obtained have fulfilled the elongation of SNI bioplastic which is <5%.

3.3. FTIR analysis

Figure 4 is a cellulose FTIR spectrum of various NaOCl concentrations. The peak that appeared around 3440-3500 cm$^{-1}$ of the O-H group. This was a hydroxyl group of cellulose constituents. The peak that appeared in the 1080-1094 cm$^{-1}$ region showed the C-O group which was a glycosidic bond between cellulose monomers. The results of FTIR cellulose analysis in this study also have similarities with previous studies [6].

![FTIR spectrum](image)

The peaks that appeared from the five samples were similar. Peak shift occurred along with an increase in NaOCl concentration. A significant difference was in the 0.5% NaOCl concentration, where there were several peaks that did not appear. Other functional groups can be observed in Table 2.
Table 2. The FTIR absorption band of cellulose on various concentrations of NaOCl in the bleaching process.

| NaOCl concentration (%) | 0.5   | 1.0   | 1.5   | 2.0   | 2.5   | Functional groups                      |
|-------------------------|-------|-------|-------|-------|-------|----------------------------------------|
| 3452.70                 | 3450.60| 3450.11| 3450.19| 3446.58| OH bending                             |
| -                       | 2921.71| 2921.46| 2920.28| 2919.44| CH bending                             |
| 1638.06                 | 1638.53| 1638.00| 1638.05| 1637.69| OH bond of water absorption            |
| 1093.11                 | 1092.68| 1093.71| 1094.53| 1087.45| CO stretching                          |
| -                       | 793.66 | 793.41 | 797.40 | 796.17 | CO stretching                          |

FTIR spectra of the CSC bioplastic can be observed in Figure 5. FTIR analysis of bioplastic showed the occurrence of hydrogen bonds between molecules of cellulose, chitosan, and sorbitol. This can be observed in the widening O-H peak from 3450.19 to 3450.64 cm\(^{-1}\). The peak that appeared in the area of 1638.41 cm\(^{-1}\) and that showed the N-H group derived from the chitosan primary amine group. The absorption band of 1087.76 cm\(^{-1}\) also revealed a C-O group which was a glycosidic bond of cellulose.

4. Conclusion
The produced cellulose from rice husk was 59.2% in the form of white powder with a concentration of bleaching agent of 2.0% NaOCl. The best obtained bioplastic was the CSC bioplastic at a cellulose concentration of 3.12% with a tensile strength of 0.060 Kgf/cm\(^2\) and an elongation of 4.75%. The peaks that appeared are O-H, N-H, and C-O in the regions of 3450.64, 1638.41, and 1087.76 cm\(^{-1}\), respectively.

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