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Study of the Mechanical Properties of Chitosan/*Onggok* Starch (*Arenga Pinnata*) Biocomposite Films Reinforced with Cellulose from Rice Straw

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ABSTRACT

Bioplastics are biodegradable polymers derived from biomass sources, and starch is the substrate of choice for bioplastic production because of its ability to decompose into environmentally friendly compounds. Nevertheless, bioplastic films composed solely of starch demonstrate hydrophilic characteristics and are highly vulnerable to water, leading to insufficient durability. In order to enhance the mechanical integrity, this issue is resolved by blending polymers and integrating cellulose into the bioplastic structure. The objective of this study is to investigate the effects of incorporating cellulose at different percentages ranging from 3% to 20% on the mechanical capabilities, water absorption capacity, and biodegradation properties of the *onggok* chitosan-starch biocomposite. Overall, the addition of cellulose to bio-composite significantly impacts these characteristics.

Keywords: bioplastic, biodegradable, *onggok* starch, cellulose

1. INTRODUCTION

Rising human activity correlates with a corresponding rise in the quantity of waste generated. Plastic and packaging waste exerts a significant environmental impact. Plastic, known for its durability, suffers a lengthy process of natural degradation. The annual output of plastic totals around 34 million tons, with only 7 percent being recycled [1]. The majority of the remaining waste is disposed of in the environment. The efforts to recycle plastic as a solution to this problem are regarded as somewhat restricted. The process of segregating different types of polymers during recycling poses a significant difficulty, leading to a decline in the quality of recovered plastic in comparison to its initial state. Hence, it is crucial to discover alternative approaches for utilizing plastic in order to mitigate the potential environmental consequences.

Bioplastics are polymers derived from biomass sources that possess the ability to biodegrade. Biodegradable plastic, as defined, can degrade or decompose through interactions with bacteria or other organisms. Bioplastics can be divided into two distinct categories: those derived from sustainable sources, such as poly-3-hydroxybutyrate (PHB) and polyhydroxy valerate (PHV), and those that utilize additives to enhance their biodegradability. Nevertheless, the widespread manufacture of bioplastics for various applications is constrained by their elevated cost in comparison to synthetic polymers derived from fossil oil [2]. Several drawbacks are associated with certain bioplastics, such as heightened water vapor permeability, oxygen permeability, brittleness, restricted temperature resistance, reduced tensile properties, susceptibility to degradation, and limited processability [3], [4], [5].

Starch is a preferred raw material for the synthesis of bioplastics due to its capacity to readily decompose into eco-friendly compounds [6]. Furthermore, the excellence of this component is enhanced by its cost-effectiveness, plentifulness, and extensive accessibility in diverse starch-producing plants, such as sago, cassava, corn, and potato [7]. It is worth mentioning that bioplastic films manufactured exclusively from starch have hydrophilic properties and are very prone to water damage. These attributes have a detrimental effect on their mechanical and barrier properties, ultimately imposing severe limitations on their prospective uses [8], [9], [10].

Improved features of pure starch-based bioplastic films can be achieved through the incorporation of additional polymers, such as chitosan, which has hydrophobic characteristics [11][12]. Chitosan is derived from chitin, a polymer that is abundantly found in nature, particularly in the exoskeletons and cephalothoraxes of crustaceans including crabs, lobsters, and shrimp [13]. The technique of de-acetylation is used to create chitosan from chitin. Chitosan's non-toxic and cost-effective properties make it a suitable option as a co-polymer in the creation of bioplastic film. The purpose of this application is to enhance the mechanical capabilities of the film, while simultaneously decreasing the hydrophilic characteristics typically found in starch-based bioplastic films [11]. Moreover, the integration of chitosan into starch-based bioplastic films enhances their desirability for food packaging purposes, owing to chitosan's intrinsic antibacterial properties. The biodegradability and mechanical strength of lignocellulose-based natural polymers have been utilized to enhance the mechanical properties of bioplastics [14]. Furthermore, lignocellulose serves as a viable substitute for non-biodegradable synthetic fibers, offering numerous advantages for the manufacture of biomaterials. These advantages include its widespread availability, renewable nature, affordability, and competitive particular mechanical properties [15].

Typically, combining multiple polymer solutions is a technique employed to create novel materials with improved and diverse properties [16]. *Onggok* starch is a plentiful agricultural crop in Klaten. This starch has the capability to serve as a bioplastic material. Hence, the objective of this study is to merge *onggok* starch with chitosan and cellulose derived from rice straw at different levels of concentration. The mechanical characteristics, water absorption capacity, and biodegradability were evaluated as factors to be taken into account for potential uses of bioplastics in the future.

2. MATERIALS AND METHODS

The study employed a completely randomized design (CRD) to examine the impact of different cellulose masses (0.3; 0.4; 0.5; 1; 2 grams) on the dependent variable. The dependent variables include tensile strength, elongation percentage, water resistance percentage, and biodegradation percentage. The fixed variable is the ratio of *onggok* starch to chitosan, which is 1:1.

2.1 Materials

The materials used in this research include acetic acid, sodium hydroxide, hydrogen peroxide, glycerol purchased from Merck, chitosan from IPB, *onggok* palm starch obtained by a local store from Klaten.

2.2 Experimental Procedures

2.2.1 Cellulose Preparation

40 grams of rice straw powder that were able to pass through a 100 mesh filter was placed into a glass beaker. Then, 1 litre of a 3% NaOH solution (w/v) was added. The mixture was then heated at 100°C for 6 hours, and filtered after cooling. The resultant solid was subsequently rinsed multiple times until a pH level of neutrality was achieved.

The delignified fibers were introduced into a solution containing 4.0% (v/v) sodium hydroxide and 24.0% (w/v) hydrogen peroxide in a 1:1 (v/v) ratio. The addition was performed incrementally at a temperature of 50°C and for 120 minutes. The fiber-to-solution ratio is 1:40 (w/v). Subsequently, the reaction proceeded for 30 minutes. The bleached fiber is strained and rinsed with distilled water. The washing process was done repeatedly until the pH level reached 7.0, after which it was dried.

The hydrolysis of cellulose powder was carried out using 10 ml/gram of 64% (v/v) H_2SO_4 at a temperature of 45°C for 60 minutes. The hydrolysis process was terminated by employing cold distilled water with a volume eightfold that of the beginning volume. The suspension was supplemented with 2 N NaOH until reaching a pH of 7, after which it was subjected to centrifugation for 20 minutes. The suspension is subsequently dried to get cellulose.

2.2.2 Bioplastic Preparation

Bioplastics are prepared by mixing a solution of chitosan in acetic acid with *onggok* starch, cellulose, and the plasticizer glycerol. A solution was prepared by dissolving 10 grams of chitosan in 100 mL of a 2% acetic acid solution. The solution was agitated until the chitosan fully dissolved. 5 grams of *onggok* starch, 2 mL of glycerol, and cellulose in accordance with the specified mass percentages (3%, 4%, 5%, 10%, and 20% of the chitosan mass) were introduced into the chitosan solution. The resulting mixture was then agitated and heated at a temperature of 80°C for 40 minutes. The bioplastic mixture was allowed to rest briefly in order to eliminate any trapped air bubbles, after which it was carefully poured onto a 15x20 cm glass plate mold. The mold is subjected

to a temperature of 40-50°C and exposed to heat for 5 hours in an oven. The bioplastic film is extracted from the mold once it has cooled down to the ambient temperature. The results displayed represent the mean of three repetitions for each sample.

2.3 Bioplastic Characteristics Testing

2.3.1 Tensile Strength and Elongation Test

The tensile strength test was carried out using a Universal Testing Machine (UTM) Model WDW-5. Bioplastic film is cut to size according to ASTM D-412 requirements. The tensile test was carried out with a testing speed setting of 10 mm/minute and a tensile strength of 100 N and carried out at room temperature. The thickness of the bioplastic film is around 0.1 mm. Plastic elongation testing is carried out by comparing the increase in length that occurs with the length of the bioplastic film before the tensile test is carried out. Elongation is calculated by **equation 1**. The tensile and elongation test results presented are the average values of three repetitions for each sample.

$$\text{Elongation} = \frac{l - l_0}{l_0} \times 100 \qquad (1)$$

where: l = length at break; l_0 = initial length.

2.3.2 Water Absorption Test

The water absorption test is conducted to quantify the film's capacity for water absorption. The experiment was conducted using three samples of bioplastic film, each measuring 5 x 1 cm. Subsequently, the weight of each item was measured as the beginning sample weight. Subsequently, the bioplastic film sample was immersed in a beaker filled with 100 ml of distilled water for 15 minutes. Next, the sample is collected and cleaned using a tissue on the exterior surface, followed by measuring its weight. The calculation of water absorption capacity is determined by **equation (2**).

$$\text{Water Absorption Capacity} = \frac{m - m_0}{m_0} \times 100 \qquad (2)$$

where: m = mass of the sample after being soaked in water; m_0 = initial sample mass.

2.3.3 Biodegradation Test

Biodegradation testing, which assesses the plastic's capacity for decomposing, involves burying samples in the soil for a duration of 7 days. The biodegradation properties of the chitosan-sugar palm biocomposite, reinforced with cellulose, were determined by measuring the initial and final mass of the sample after burying it in the soil. The calculation was performed using equation (3).

$$\text{Biodegradation} = \frac{w_1 - w_2}{w_2} \times 100\% \qquad (3)$$

where: w_1 = initial weight; w_2 = final weight

3. RESULTS AND DISCUSSION

3.1 Tensile Strength and Elongation

Tensile strength refers to the highest level of tensile stress that a film can endure during a tension test. Typically, a film needs to have a high level of tensile strength, although this number is often modified to match the specific requirements of the film's application. **Figure 1** demonstrates the impact of cellulose content in the chitosan-starch *onggok* biocomposite film on its tensile strength capabilities. The tensile strength of the biocomposite film exhibited a substantial reduction upon increasing the cellulose content. The bioplastic film with the lowest cellulose content, specifically 3%, possesses the maximum tensile strength, reaching 106 MPa. The study found that the chitosan-starch *onggok* biocomposite film, with a ratio of 1:1, had a tensile strength of 64.47 Mpa [17]. This indicates that adding cellulose to the chitosan-starch *onggok* matrix resulted in an improvement in the film's tensile strength. The decrease in tensile strength observed in this trend is in contrast to the chitosan bioplastic that incorporates cellulose from rice straw [18]. The rise in tensile strength as cellulose content increases can be attributed to the effective dispersion of fibers within the polymer matrix and the optimization of hydrogen bonding in the bioplastic matrix. The reinforcement of cellulose by polysaccharides is affected by the chemical similarities and intermolecular hydrogen bonding between the hydroxyl groups of macromolecules [19].

Additionally, the incorporation of macro-sized cellulose into bioplastics manufactured from starch and cellulose might lead to a decrease in their tensile strength. This occurs because the presence of macro-sized cellulose creates areas of concentrated energy inside the bioplastic matrix when subjected to axial stress. Furthermore, the utilization of cellulose fibers on a larger scale may not exhibit sufficient strength due to the coagulation of the fibers within the polymer matrix [15]. Therefore, it is important to take into account the quantity of cellulose in the production of cellulose-based bioplastics. Excessive cellulose can

lead to the clumping together of cellulose granules in the polymer matrix, resulting in a decrease in mechanical strength and barrier properties due to suboptimal hydrogen bond optimization [15].

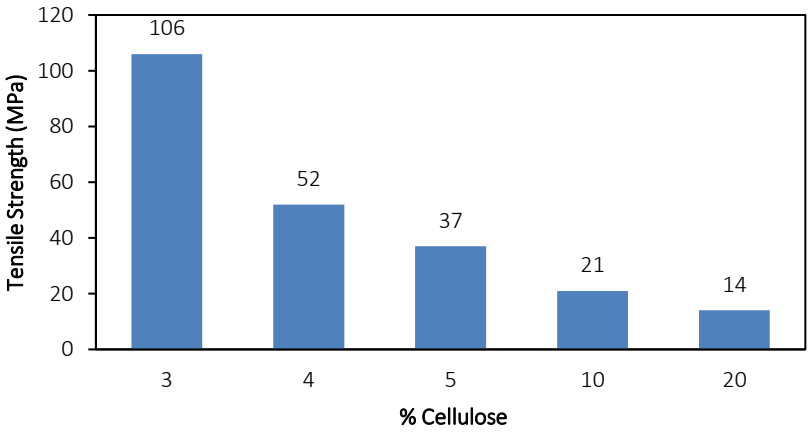

Figure 1. Tensile strength of chitosan-starch *onggok* bioplastic film as a function of % cellulose

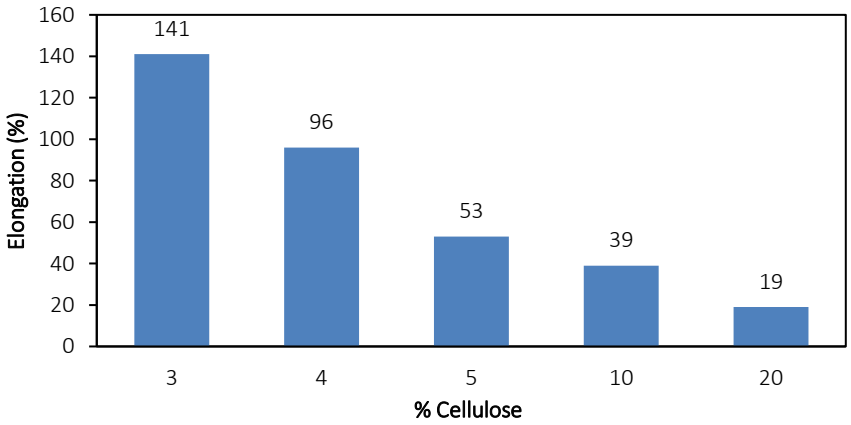

Figure 2. Elongation of chitosan-*onggok* starch bioplastic film as a function of % cellulose

The film's elongation at break is directly linked to the material's flexibility and capacity for elongation. **Figure 2** shows the changes in elongation properties of the chitosan-starch *onggok* biocomposite film as the amount of cellulose added varies. Increasing the amount of cellulose in the chitosan-pati *onggok* film causes an increase in film elongation. The film that contained an additional 3% cellulose exhibited the greatest elongation. The reduction in film elongation can be attributed to the saturation phenomenon, wherein the intermolecular interactions between chitosan-starch molecules intensify as the cellulose content increases, eventually reaching a saturation point that hinders the infiltration of glycerol molecules into the molecular chain [7].

3.2 Water Absorption Capacity

The water absorption test was carried out to determine the hydrophilic properties of the bioplastic film. **Figure 3** illustrates the water absorption capability of the biocomposite that has been produced. When the cellulose content in the film is increased from 3 to 4%, there is a little rise in the film's ability to absorb water, from 46% to 50%. However, further increasing the cellulose percentage decreases the film's water absorption capacity. The presence of water can have an impact on the mechanical characteristics of bioplastics, specifically, a high level of water absorption can lead to a decrease in structural integrity and a negative effect on strength and other mechanical qualities. Bioplastics with high water absorption capacity may experience alterations in their dimensions. This might provide a challenge in applications where maintaining dimensional stability is of utmost importance. The

biodegradability of bioplastics can be influenced by the absorption of water. Certain bioplastics are specifically engineered to undergo decomposition through the action of microbes. The rate at which this degradation occurs can be influenced by the absorption of water, either accelerating or decelerating the process.

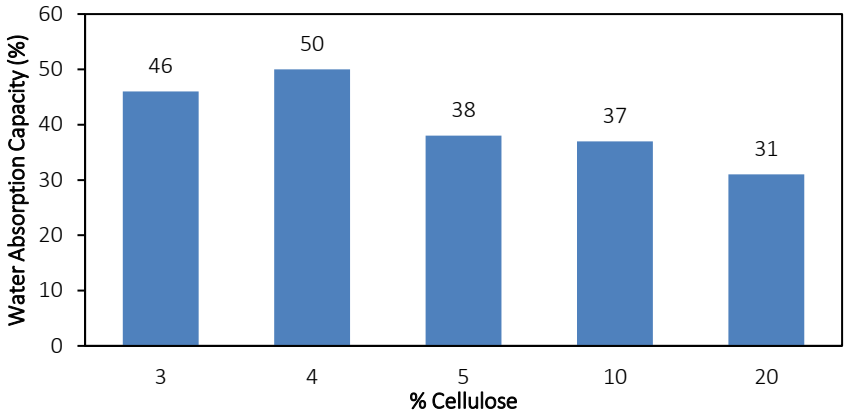

Figure 3. Water-absorbing ability of chitosan-starch *onggok* bioplastic film with variations in % cellulose

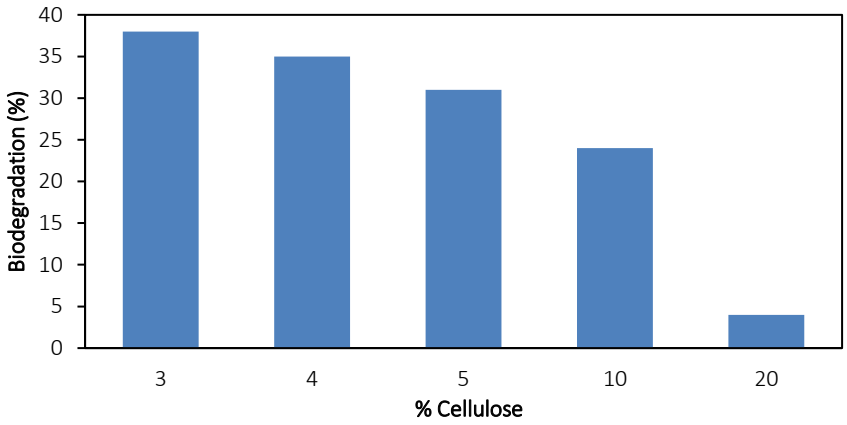

Figure 4. Percentage of biodegradation of chitosan-pati *onggok* bioplastic film with variations in % cellulose

3.3 Biodegradation

Biodegradation test are conducted to determine the rate at which microorganisms in a given environment break down bioplastics. The biodegradation properties were assessed by quantifying the reduction in mass of the film following burial in the soil for some days. **Figure 4** demonstrates the impact of cellulose content on the chitosan-*onggok* starch bioplastic. The biodegradation characteristics of the chitosan-*onggok* starch biocomposite diminish as the cellulose percentage increases. The chitosan-*onggok* starch biocomposite film with a cellulose concentration of 20% exhibited the least decrease in film mass. This outcome aligns with the findings of the water absorption test, indicating that films having a higher capacity to absorb water will undergo degradation at a faster rate.

Cellulose is insoluble in water, possesses a substantial molar mass, and is organized in the form of nanofibers. Cellulose exhibits regions with disordered structure and other regions that are highly ordered, defining it as a semi-crystalline fiber. The chosen media for biodegradation is soil due to its abundance of microorganisms, including bacteria, algae, and fungi, which facilitate the degradation process

4. CONCLUSION

Chitosan and *onggok* starch were combined with cellulose to create biocomposite films. These films were then examined for their mechanical qualities, water absorption capacity, and biodegradation properties, all of which yielded successful results. Increasing the cellulose content in the film substantially diminishes the tensile strength and elongation of the film. Similarly, the capacity to absorb water in the chitosan-starch *onggok* biocomposite film is in line with its ability to degrade in soil. As the cellulose content increases

in the film, both the water absorption capacity and the rate of degradation decrease. While this study demonstrates that the cellulose concentration has an impact on the mechanical properties of bioplastic sheets, the exact relationship between cellulose concentration and these qualities remains uncertain. Hence, additional empirical research is required to enhance and optimize the provided results.

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the author(s).

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Nur Hidayati: conceptualization, methodology, writing—review and editing, supervision;
Deni Wila Awwalian: resources, investigation, data curation;
Nabilah Miftachul Jannah: writing—original draft preparation, writing-review editing.
All authors have read and agreed to the published version of the manuscript.

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