Biodegradable Mulch Based on Cellulose of Cornhusk with Addition Anti UV-Tinuvin

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Abstract. Plastics generally cause global-scale problems because they cannot be degraded into the environment and causing a build-up of plastic waste. Biodegradable plastic material can be an alternative to solve the problem because of its nature which is easily naturally degraded by microorganisms. One of the natural wastes that can be utilized to become fillers in plastic mulch so it is more easily degraded is cornhusk because its utilization is still limited and cornhusk has high cellulose content. In this study, the extraction of cellulose was carried out on cornhusk to obtain cellulose by the alkaline method. There was a decrease in hemicellulose and lignin levels, which indicated that the extraction process was quite successful. Then in the process of making biodegradable mulch films, Tinuvin P was added as an anti-UV agent and oleic acid was carried out as plasticizer and with several variations. The results show that the addition of anti-UV agent P and addition of oleic acid reduces the mechanical properties of biodegradable mulch and can control the rate of degradation of the biodegradable mulch film.

1. Introduction
The use of mulch in Indonesia has been widely applied to a variety of vegetable crops and is very well used in areas that have a tropical climate. Mulch can help prevent water loss in the dry season and prevent water accumulation during the rainy season, suppress weed growth, improve soil structure, increase soil capacity to retain water and keep soil's temperature stable. Moreover, mulch can prevent sunlight from reaching the ground so that it can reduce soil evaporation [1]. Mulch is divided into two types based on its ingredients, which are organic mulch and inorganic mulch. Organic mulch can be in the form of crop waste such as hay and leaf litter. Whereas, inorganic mulch comes from synthetic materials, such as plastic mulch. Even though plastic mulch is very effective in controlling evaporation of groundwater and can control heat loss at night, therefore plastics cause global-scale problems because they cannot be decomposed in the environment that causing accumulation of plastic waste [2]. According to the problem, it is necessary to develop biodegradable plastic material as an alternative to solve the problem because it is naturally degraded by microorganisms to create environment conservation.

One of the natural fiber that has not been used optimally and has the potential to be developed for biodegradable plastic material was cornhusk and still considered as waste. Based on Badan Pusat
Statistik, corn production in 2017 was 28 million per year [3]. Meanwhile, the waste of corn was 50\% of the amount of corn and cornhusk waste was 10\%[4]. It indicates that the waste of cornhusk reached 1.6 million per year. In 2017, Yang et al found that cellulose from cornhusk was about 38\%[5]. The research found the alternative to develop biodegradable plastic material is by using cellulose from cornhusk. Cellulose is the main component of tough cell walls from green plants, and it is what makes plant leaves, stems, and branches so strong. The function of cellulose is to increase the mechanical properties of biodegradable plastic. In this research, Tinuvin P was added as an anti-UV agent for protecting biodegradable mulch from sunlight to avoid damage. This study aimed to determine the effect of oleic acid variations and the addition of Anti-UV to physical and mechanical properties and biodegradability of biodegradable mulch.

2. Materials and Methods

2.1. Materials

Cornhusk, NaOH, HCl, Distilled water, Tinuvin P, oleic acid, glycerol, acetone, chitosan, and soil.

2.2. Methods

2.2.1. Extraction of Cellulose.

The materials used in this study were 3rd to 10th segment of cornhusk obtained from markets in Bogor, they were sorted and cleaned. Cornhusk was then dried in the oven at 60°C. After that, the cornhusk was ground until they reached a size of 100 mesh. 10 grams of cornhusk powder was immersed in a NaOH solution with a concentration of 17.5\% w / w for 2 hours. The ratio of powder to NaOH solution was 1:20. Cornhusk that has been soaked in NaOH was then washed using distilled water until it became neutral. The neutral slurry was then hydrolyzed with 1M HCl at 80 ° C and distributed with a rotational speed of 400 rpm for 2 hours using magnetic stirrers, then washed again using distilled water until the pH of the solution until it became neutral. The comparison of cornhusk powder with an HCl solution was 1:10. The hydrolyzed slurry that has been neutralized was immersed again using a NaOH solution with a concentration of 2\% w / w at 80 ° C for 2 hours and a stirrer with a rotational speed of 400 rpm for 2 hours using a magnetic stirrer. The comparison of cornhusk powder with 2\% NaOH solution is 1:10. Then, the slurry was washed several times using distilled water until it became neutral. Some of the extracted pulp is dried in an oven at 105 ° C for 2 hours. Dry extraction results will be tested on Van Soes [6].

2.2.2. Production of Biodegradable Mulch Film.

The process of making biodegradable mulch film was done by mixing all ingredients, such as corn cellulose, chitosan 3\%, glycerol 3\%, plasticizer oleic acid, and anti-UV agent. Samples were divided into 2 groups, first, groups without the addition of anti-UV agents and groups with the addition of anti-UV agent, from each of those groups there were variations in the addition of oleic acid 0\%, 2\%, 4\%, 6\% and 8\% as the plasticizer. The process of making films that used was the solution casting method. The number of samples was 12. The sample group without an anti-UV agent was given the initials A and the sample group with the addition of anti-UV agent was given the initial T. Index number on the initial sample was based on the amount of oleic acid contained. The characterization used in this study were the crude fiber test (Proximate and Van Soest Analysis), film thickness, tensile strength, SEM, and Biodegradation Test.

3. Results and Discussion

3.1. Extraction of Cellulose

The abundant utilization of corn husk waste, one of which was by extracting the cellulose content in it. The method used was the alkali method or acid-base addition. The aim was to eliminate lignin and hemicellulose so that pure cellulose was obtained. Fiber analysis was carried out before and after cellulose extraction using the proximate test and the van Soest test. Proximate testing was carried out to provide the ingredients of corn husk. The results of the proximate analysis shown in Table 1. Table
shows that the crude fiber content of corn husk is more dominant, which is 23.43%. This shows that corn husk can be extracted to produce cellulose.

| Parameters   | Data (%w/w) |
|--------------|-------------|
| Water        | 10.73       |
| Ash          | 2.22        |
| Crude Fiber  | 23.43       |

Meanwhile, the van Soest test aims to see changes in the levels of crude fiber like cellulose, hemicellulose, and lignin in corn husk before and after the extraction process. Corn husk powder before extraction had a cellulose content of 31.81%, hemicellulose 38.12%, and lignin 25.12%. Agricultural waste which is usually used as raw material for cellulose extraction has an average cellulose content above 30% and lignin content below 20%[7]. The level of cellulose corn husk powder after extraction decreased from 31.81% to 25.11%. Hemicellulose and lignin also decreased after being treated with NaOH and acid hydrolysis. Decreasing levels of cellulose are assumed to be caused by the effects of distillation by distilled water and the screening process, cellulose was converted into sugar washed away during the rinsing and filtering process. Also, due to the presence of cellulose which dissolves or disappears when the process of NaOH soaking and delignification using HCl and also many environmental factors that can affect the cellulose extraction process such as impurity[8]. Lignin levels were reduced from 25.12% to 12.28%, indicating that the delignification process using HCl was good enough to eliminate lignin, although it was not significant. While the decrease of hemicellulose levels from 38.12% to 11.81%. Based on the results obtained, it can be said that NaOH treatment (17.5% and 2%) and acid hydrolysis are good enough to reduce lignin and hemicellulose. Cellulose levels decreased after extraction however, with a decrease in lignin and hemicellulose it can be said that the extraction process was quite successful.

3.2. The Thickness of Biodegradable mulch
The physical properties that were analyzed were filmed thickness carried out following SNI 19-4059-1996: plastic bags for plant nurseries by taking data at five different points and then take an average thickness. In this study a sample measuring 3 cm × 3 cm was measured using a screw micrometer thickness (accuracy of 0.001 mm). The difference in film thickness is influenced by the composition of the constituent material[9]. The results of film thickness measurements can be seen in Table 2.
Table 2. Physical and Mechanical Properties of Biodegradable Mulch Film

| Biodegradable Mulch Film | Mass (gram) | Thickness (mm) | Tensile Strength (MPa) |
|--------------------------|-------------|----------------|------------------------|
| A1                       | 0.04        | 0.10           | 10.72                  |
| A2                       | 0.06        | 0.13           | 5.60                   |
| A3                       | 0.07        | 0.13           | 3.64                   |
| A4                       | 0.08        | 0.17           | 2.83                   |
| A5                       | 0.09        | 0.17           | 3.59                   |
| A6                       | 0.11        | 0.21           | 1.89                   |
| T1                       | 2.08        | 0.07           | 6.02                   |
| T2                       | 1.90        | 0.07           | 5.25                   |
| T3                       | 2.08        | 0.08           | 4.26                   |
| T4                       | 2.1         | 0.07           | 1.03                   |
| T5                       | 2.07        | 0.07           | 1.6                    |
| T6                       | 2.1         | 0.13           | 0.04                   |

The thickness of the entire biodegradable mulch film approaches the thickness of commercial mulch which is 0.03 mm - 0.10 mm. Increasing thickness occurs with increasing oleic acid content in the biodegradable mulch, both in samples with the anti-UV agent and without an anti-UV agent. That happened because there was an increase in the total amount of solids in the solution which caused the matrix making polymers more and more. The thickness was also influenced by the viscosity and constituent polymer content[10].

3.3. Tensile Strength

The mechanical test carried out was a tensile test used Universal Testing Machine (UTM) with the brand Shimadzu type AGS-10kNG ASTM D638 with a tensile speed of 0 to 5 mm / minute. One of the parameters that will be discussed in this paper is the tensile strength which can be seen in Table 2 and Figure 2. The tensile strength value of the film shows the resistance of the biodegradable mulch film when it receives a load.

![Figure 2. The Tensile Strength of Biodegradable Mulches](image)

In both groups of samples, with and without the addition of anti-UV agents, samples A1 and T1 had the highest tensile strength values among the values in each of their groups, namely 10.72 and 6.02 MPa, respectively. This is due to the formation of hydrogen bonds between cellulose and chitosan functional groups[11]. The addition of oleic acid which is a saturated fat into the chitosan matrix causes an increase in molecular free volume and polymer molecular mobility so that the bonding of
the polymer chains is relaxed[11]. The bonding of the polymer chains which is stretched caused the film density and the tensile strength decreased. However, when compared as a whole, the group with the addition of an anti-UV agent had a smaller tensile strength value than the group without an anti-UV agent. The tensile strength of the biodegradable mulch decreases with the addition of anti-UV agent additives as UV stabilizers. This is due to the additive anti-UV agent’s function as a filler of the polymer molecular chain so no bonding occurred between additive molecules and the polymer molecules. The greater the concentration of the additive, the smaller the number of polymer molecules, consequently the mechanical properties also decrease[12]. The tensile strength value of biodegradable mulch film had not fulfilled the characteristics of biodegradable plastic according to SNI 7818: 2014 where the tensile strength value should be 13.7 MPa. This was because all the ingredients of the biodegradable mulch film are natural in the absence of synthetic materials.

3.4. Morphology Analysis

Morphology analysis using Scanning Electron Microscopy (SEM) can determine the homogeneity of the film, cracks, and surface smoothness of microscopic mixing[5]. Biodegradable mulch films analyzed for morphology were A1 with the best tensile strength values and A6 with the lowest tensile strength values in the group without the addition of anti-UV agent. T1 with the best tensile strength values and T6 with the lowest strong values in addition to the anti-UV agent group. The results of SEM analysis in groups without and with the addition of tin can be seen in Figures 3 and 4, respectively.

The SEM results in Figure 3 show the surface of (a) sample A1 with a magnification of 100 times that looks fibrous, uneven, and still has scratches or cavities. SEM results of sample A1 with a
magnification of 2500 times strengthen the presence of pores in the sample, besides, it appears that there is a buildup of uneven layers caused by a cavity. This occurred because the solution did not mix homogeneously perfectly. The solution did not mix homogeneously can be caused by the process of mixing the material using only a magnetic stirrer. These SEM results are supported by physical properties on the surface of A1 films which still rough when it was touched. Figures 3 (c) and (d) show the surface morphology of the A6 sample which looks flatter and has no pores. This shows that oleic acid was able to mix well with cellulose and chitosan so that the mixture of ingredients is homogeneous. This can be seen in the physical properties of sample A6 which feels smoother when touched.

![SEM images](image)

**Figure 4** Morphology of Biodegradable Mulch Films (a) T1 with 100x magnification (b) T1 with 2500x magnification (c) T6 with 100x magnification (d) T6 with 2500x magnification

Figure 4 shows the results of SEM in the sample group with the addition of the anti-UV agent. Based on the test, there was a significant difference between the samples T1 and T6. Figure 4 (a) shows the morphological structure of the biodegradable mulch film sample at 100x magnification having a surface that looks uneven, there are still fine fibers and small lumps. If the film sample is enlarged 1000x (Figure 4 (b)) the surface of the film is slightly smoother but still has small lumps that are more clearly visible. The results of the analysis did not address the presence of cracks in the film so the film was denser but not perfect because there were still small lumps. This is following the characteristics of the film which has a tensile strength value of the second spread of 6.02 MPa and when viewed directly the surface of the T1 biodegradable much film is smoother than T6. As a comparison, the T6 biodegradable mulch film sample was chosen because it has the smallest tensile strength value of 0.04 MPa. Figure 4 (c) shows the morphological structure of the biodegradable mulch film with a magnification of 100x, showing that clumps on the surface of the film. When
enlarged with a magnification of 1000x Figure 4 (d) these large lumps seem increasingly clear. The solid is thought to be an anti-UV agent which is not mixed well with other material components. This solid makes the biodegradable mulch film more rigid so that the tensile strength value produced by the biodegradable mulch film is very small. The presence of these large lumps shows that anti-UV agent particles undergo agglomeration grouping, causing uneven distribution of the anti-UV agent. The cause of the anti-UV agent is not mixed well is thought to be due to the nature of the anti-UV agent which is only soluble in organic solvents, while the solution of the material contains more water, causing anti-UV agent which is slightly soluble in water cannot bind completely.

3.5. Biodegradation

Biodegradable films were decomposed by the enzymatic action of microorganisms such as bacteria, fungi, and algae in a bioactive environment[13]. Biodegradability tests on biodegradable mulch films were carried out by the Soil Burial Test method. Soil Burial Test is a biodegradability testing method by controlling soil microorganisms as an aid to the degradation process by planting samples in the soil. Degradation refers to physical changes due to chemical bonds breaking so the molecular weight decreases and chain shortening[14]. Planting of biodegradable mulch film samples is carried out by being buried in the soil with a depth of approximately 15 cm from the ground surface, previously biodegradable mulch film samples have been calculated for mass, as initial mass (W0). The soil for the testing process is placed in plastic to facilitate analysis. The testing process is carried out for 4 weeks by taking mass data samples of biodegradable mulch films every week (Wf). Initial and final mass used to calculate the percent of mass loss during the planting process. Percent of mass loss in the biodegradable mulch film was shown in Figure 5.

![Figure 5](image)

**Figure 5.** Mass loss of biodegradable mulch for 4 weeks

A1 was degraded most rapidly than the other samples and was degraded 100% at 2 weeks. A1 can be degraded most quickly because it has pores or cavities as seen in SEM results. The presence of pores and cavities causes water to more easily enter the layer and damage the inside of the film. Sample A6 was not degrading rapidly because it had a flat, smooth surface morphology and had small and very small pores so that water or microorganisms can only destroy film from the surface. Samples A2 to A6 are more difficult to degrade because of the hydrophobic nature of oleic acid. This property will inhibit the absorption of water by the film. While in the sample group with the addition of anti-UV agent, degradation occurred more slowly so that the percentage of mass loss on the biodegradable mulch film decreased. This is because the anti-UV agent is a benzotriazole derivative that can dissolve...
in only organic solvents but is slightly soluble in water and not decomposed by concentrated acids and bases. The nature of the anti-UV agent which is difficult to dissolve in water is what caused the film sample to degrade longer. However, the T6 film sample increased because of its morphological structure which contained a large pore as seen in the SEM test results. This causes the film sample to be more fragile and easily degraded. Pores in the film also make it easier to move and absorb water so that the film degraded faster.

4. Conclusion
One of the uses of cornhusk waste is by extracting cellulose content as a basis for making biodegradable mulch. The results of extraction using the alkali method, although the results have not been maximal it has been able to significantly reduce lignin levels. Biomulsa film with a composition of a mixture of cellulose, glycerol, oleic acid, chitosan, and anti-UV anti-UV agent. Variations in cellulose acid affect the mechanical properties (tensile strength) of biomulsa films, as well as the addition of anti-UV agent additives as UV stabilizers. Variation of oleic acid and the addition of anti-UV agents influence the rate of degradation of the biomulsa film. According to the degradability test with the method of soil burial test, bio much film can decompose by soil microorganisms but has not been completely degraded within 4 weeks.

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