The Effects of Anti-UV on Cornhusk-LLDPE Mulching Films

M Kurniati 1,*, A Maddu 1, and I Sulyani 2

1 Division Biophysics, Department of Physics, IPB University, Bogor 16680, Indonesia
2 Department of Physics, IPB University, Bogor16680, Indonesia

*E-mail: mersikurniati@gmail.com

Abstract. The plant's wastes can be recycled as a source of natural fiber to fabricate biodegradable films. The utilization of natural waste cornhusk for the production of environmentally friendly mulch was studied. The cellulose of cornhusk can be extracted with alkali treatment so that the cellulose produced can be used as a material for mulches. The mulch film can be synthesized with a variation content of cornhusk cellulose at 5, 10, and 15%, Low Linear Density of Polyethylene (LLDPE), variations in anti-UV concentration (1, 4, and 6 %) and the addition of additives using the extrusion-calandering method. Variations in the added anti-UV concentration could affect the optical and mechanical properties of the mulch film produced. The mulches film produced has a black color, smooth and elastic surface. The mechanical properties of the film have increased. Significant tensile strength 20.75 MPa, elongation 354 % and modulus of elasticity 0.62 GPa were found in films with the addition of 4 % tinuvin concentration and 15 % cellulose content. The addition of anti-UV resulted in a shift in the peak in the UV range so that no dominant peaks appeared for T1, T4, and T6 mulches. The mulches film T4 at 5 % cellulose content absorbs maximum light at a wavelength of 300-400 nm. SEM analysis showed that the homogeneous mulch film morphology has a lump and is porous.

1. Introduction
The use of plastic mulch has become a common standard in the production of horticultural crops of high economic value, both in developed countries and in developing countries, including Indonesia. Plastics mulches are a cover material for cultivation plants to guard soil moisture [1], reduce evaporation, suppress weed growth and maintain fluctuations in soil temperature [2]. Plastics commonly used for mulch technology come from synthetic plastics such as LLDPE, which generally cause environmental problems because plastics cannot be decomposed in the environment. The development of biodegradable plastic materials is one alternative to solve this problem [1, 2].

One of the natural fibers that have not been utilized optimally and has the potential to be developed into bioplastic is cellulose of cornhusk which is still considered as waste [3]. Cellulose is a macromolecular polymer in the presence of bonds intermolecular and intramolecular hydrogen between cellulose chains [4]. The mechanical properties of cellulose due to the presence of cellulose crystal structure, make cellulose can be utilized as reinforcement in polymer composites [5].

Based on data from BPS (2017), the target of corn production is to reach 28 million tons to meet the needs of corn in Indonesia. The high amount of corn production has an impact on the amount of
waste produced. From corn yields throughout Indonesia, the weight of cornhusk is 38.38% [6]. So far, the use of cornhusk is still not optimal, where its utilization is limited to animal feed and food wrappers [5, 6]. The chemical composition of cornhusk includes 38.2% cellulose, 44.5% hemicellulose, 6.6% lignin, 2.8% ash, and 1.9% protein [4].

The development of the mulch market makes it possible to produce on a large scale and because the production process is so simple and a fair price margin is also an interest in consumer interest. LLDPE is a plastic that has a good capability to maintain heat and long wave transmission radiation compared with other plastic, but LLDPE could be degraded with UV radiation under sunshine [7]. Anti-UV is very important because the mulch plastic can control the rate of degradation due to exposure to the sun's ultraviolet rays [8]. Ongoing research has focused on the preparation, optical and mechanical properties of cornhusk-LLDPE mulch films with the effect of anti-UV and cellulose of cornhusk concentration on mulches.

2. Materials and Methods

2.1. Materials

The materials used in this study were the 5th to 10th segments of cornhusk obtained from markets in Bogor. Cornhusk obtained from markets in Bogor were sorted and cleaned. Cornhusks were then dried in an oven at 60 °C for 8 hours. After drying, the cornhusk was milled until they reached a size of 100 mesh (0.149 mm). LLDPE with the analytical grade received from Chandra Asri Petrochemical Tbk (Indonesia), The chemicals used are technical and analytical grade, obtained from Sigma-Aldrich and J.T. Baker, Indonesia.

2.2. Film preparation

An alkaline treatment was applied to cornhusk. The cornhusk was cleaned and then soaked in a concentrated 17.5% w/w sodium hydroxide (NaOH) solution. After 2 hours treated cornhusk was washed with distilled water. The pre-treated pulp was hydrolyzed by 1 M of hydrochloric acid (HCl) at 80 ± 5°C for 2 hours and then washed with distilled water repeatedly. The pulp was treated once more with the 2% w/w of NaOH solution at 80 ± 5°C for 2 hours. The alkali-treated pulp was washed several times with distilled water until the pH of the fiber suspension became neutral before being dried at room temperature.

Synthetic polymer (LLDPE) was first mixed with irganox, glycerol, oleic acid as a coupling agent in which the weight of oleic acid was 2% of the total weight of the mulch. The mulch black dye is added. The results were mixed with 100 mesh-size cellulose of cornhusks, with 1.4 and 6% anti-UV concentration. They were then extruded at T = 180 °C with a 30-rpm rotational speed. Then, 14 grams of extrusion results were put inside the film printing equipment with a 14 cm diameter, then they were put inside a calandaring machine, without pressure at 5 bars of pressure at 180 °C for 4 min. This process was continued with cooling at 40 °C with 1 bar of pressure for 12 min. After the mulches had been printed, samples were conditioned at 23 °C for 2 days.

2.3. Film characterization

2.3.1. Characterization of raw material

Cornhusk powder is characterized by its components (moisture content, crude protein, crude fat, crude fiber, ash, and carbohydrates) using a method based on SNI-01-2891-1992. Testing of fiber components such as cellulose, lignin, and hemicellulose on the pulp is carried out using the Van Soest method.

2.3.2. Mechanical properties

Mechanical testing was carried out using the Universal Testing Machine (UTM) Shimadzu AGS-10kNG with ASTM D368 standard with a speed of 5 mm/minute, with a thickness of ± 0.3 mm and 60
cm wide. The sampling process is carried out at a speed of 5 mm/min at 22.4 °C and 58 % relative humidity.

2.3.3. Optical properties

UV-Vis test aims to determine the characteristics of absorbance and the effect of anti-UV on mulch. The test was carried out with the UV-Vis Ocean Optics device with the USB4000FL series. Measurements were made from a range of 200-800 nm, where the UV range is at 200-400 nm and visible light is 400-800 nm.

2.3.4. Morphology

The mulches surface morphology was observed using Scanning Electron Microscopy (SEM) type JEOL JSM-6510 LA with an electron acceleration voltage of 15 kV and magnification 2500 times.

3. Results and Discussion

One characteristic that can be seen from cornhusk powder extracted is color. Good cellulose results have a bright color, close to white. The appearance of the final product before and after extracted can be seen in Figure 1. Figure 2 showed the product of mulches on 4 % of anti-UV and 5 % cellulose content.

![Figure 1. Corn husk powder (a) before extraction (b) after extraction](image)

![Figure 2. Product of mulch](image)
Cornhusk has a small ash content which is equal to 2.14 %. The ash content in the size of 14-50 µm can increase the tensile and impact strength of composites with the HDPE matrix [3]. The content of fat and protein content ranged respectively at 1.25 % and 5.24 %. Fat and protein can increase the modulus of elasticity. Crude fiber and carbohydrate have the highest concentration which is around 38.32 % and 43.65 %. Fiber has good mechanical properties and has often been used to make composites by mixing it with various polymers [2].

| Parameter        | Content (% w/w) |
|------------------|-----------------|
| Moisture water   | 9.40 ± 0.15     |
| Ash              | 2.14 ± 0.10     |
| Lipid            | 1.25 ± 0.21     |
| Crude fiber      | 38.32 ± 0.14    |
| Crude Protein    | 5.24 ± 0.23     |
| Carbohydrate     | 43.65 ± 0.42    |

Table 1. Proximate content of cornhusk powder 100 mesh.

Fiber content analysis was carried out on cornhusk powder before and after extraction, the comparison of the levels of cellulose, hemicellulose, and lignin from the Van Soest test of cornhusk powder before and after extraction can be seen in Table 2.

The results of Van Soest's analysis showed that there were changes in cellulose, hemicellulose and lignin levels in the treatment before and after extraction. Cellulose content after extraction was higher compared to before extraction, whereas hemicellulose and lignin levels were lower when compared to before extraction. Lower lignin levels after extraction indicate the lignin delignification process can break the lignin bond in cellulose and hemicellulose so that cellulose and hemicellulose can be released from lignin because lignin dissolves in the delignification process. Hemicellulose which is still bound to cellulose can dissolve by hydrolysis treatment using an acid solution [9].

| Parameter       | Before extraction (% wb) | After extraction (% wb) |
|-----------------|--------------------------|-------------------------|
| Cellulose       | 31.81 ± 0.23             | 40.65 ± 0.65            |
| Hemicellulose   | 38.12 ± 0.18             | 12.82 ± 0.56            |
| Lignin          | 21.12 ± 0.31             | 1.54 ± 0.32             |

Table 2. The fiber content of cornhusk powder 100 mesh

Mechanical properties can be in the form of strength, hardness, stiffness, and plasticity. Mechanical analysis carried out on biomass film produced in the form of tensile strength, percent elongation at break, and modulus of elasticity. The results of the analysis of the mechanical properties of mulches films with variations anti-UV and cellulose concentration are shown in Figure 3. Cellulose was reported to be positively related to the stress transfer and mechanical strength of the mulches. The cellulose showed significant effects on mechanical properties, especially in the aspect of strength [10]. The addition of cellulose can increase the tensile strength of mulch films in certain variations because cellulose has a long and straight polymer chain so that it can make the mulch films stronger. Judging from the chemical structure of cellulose has a strong hydrogen bond so it is difficult to join with water. However, the addition of excess cellulose can increase cellulose absorption because hydrogen bonds in cellulose tend to form intramolecular bonds, including water [11].

The tensile strength of the film showed the resistance of the mulches film when receiving the load [12]. The highest tensile strength value was found in T4 mulch (15 % of cellulose) with the addition of
4 \%\text{ anti-UV} of 20.75 MPa while the lowest tensile strength value was found in T1 (5 \% of cellulose) with the addition of 1 \% anti-UV of 4.56 MPa. Characteristics of mulch films that are easily decomposed according to SNI 7818: 2014 are a minimum of 13.7 MPa. Tensile strength test results showed an increase along with an increase in the percentage of cellulose [12]. The results of this study are also consistent with other studies on rice husk / wheat-MAPP composites that the increase in tensile strength is due to the formation of ester bonds between these natural fibers and synthetic polymers. Cellulose has more hydroxyl groups than hemicellulose and lignin and can form hydrogen bonds with other molecules [13].

Based on the picture it can be seen that the tensile strength of the film has increased until the T4 film then decreases in T6 film with the addition of 6 \% anti-UV concentration. This increase in tensile strength is influenced by the concentration of anti-UV added. The addition of anti-UV causes the formation of interactions between anti-UV and celluloses polymer chains in the form of hydrogen bonds [14]. This hydrogen bond will affect the tensile strength in the film.

![Figure 3. The tensile strength of mulches with various of cellulose and anti-UV](image)

Elongation at break is a condition where the film breaks after experiencing a long change from its initial length when experiencing stretch and is produced in percent (\%) form [12]. The elongation value of the mulches produced can be seen in Figure 4. The resulting elongation value has decreased due to the addition of the content of cellulose and anti-UV. SNI 7818:2014 standard for elongation of easily decomposed mulch films at the 400-1120 \%. Only T4 at 5 \% cellulose meets the standard, while T4 at 10 \% and 15 \% cellulose is still below SNI standards. Films with the addition of plasticizers will produce films that are not rigid because the addition of plasticizers aims to eliminate the rigidity of a material. The oleic acid and glycerol added to the film will insert in the bond between the film molecules so that it will provide enough space for the movement of cellulose and anti-UV molecules [9].

Modulus of elasticity is the value of the stiffness of a material or the resistance value of material until the deformation occurs when the material is subjected to force [9]. A material that has a high stiffness when it gets a load within its elastic limit will experience elastic deformation but only a little. Material stiffness is usually indicated by the modulus of elasticity. The greater the modulus of elasticity, the more rigid the composite material [9]. Elasticity is obtained from the comparison between tensile strength and elongation. Figure 5 shows the modulus of elasticity value of mulch with
variations in anti-UV, it can be seen that the modulus of elasticity increases until certain anti-UV concentrations (4 %) and then decrease.

Analysis of the optical properties of mulch was measured using a UV-Vis spectrophotometer in the wavelength range of 300-800 nm. Figure 6 shows that mulch with 1 % anti-UV variation absorbs UV light in the range 300-400 nm and that the light appears purple and blue at wavelengths of 400-500 nm. For mulch with the anti-UV variation of 4 % in the wavelength range of 300-400 nm absorbs UV light and at wavelengths of 400-550 nm absorb visible light, namely the colors purple, blue, and green. Whereas mulch with the anti-UV variation of 6 % absorbs UV light at wavelengths of 300-400 nm and absorbs visible light at wavelengths of 500-800 nm, namely green, yellow, orange, and red. Due to the addition of anti-UV absorbance value decreases, meaning that for the wavelength range of
500-800 nm all the light energy is reflected or some of it is passed on by the mulch. This is caused by anti-UV absorbing maximally in the 300-400 nm region and minimally in the visible region (> 400 nm). The reflected sunlight and some that are transmitted through the surface of the mulch is trapped on the surface of the ground that is covered [15]. This trapped heat will increase the surface temperature of the soil, modify the balance of groundwater, soil carbon dioxide, suppress weed growth, and increase the activity of organisms [16]. This will be useful at night because mulch is useful as a warmer that can regulate the surface temperature of the soil and plant environment at night which tends to be a lower temperature than during the day. These optical properties test results prove that the use of mulch will prevent direct radiation from the sun so that mulch has a higher reflectivity than ordinary plastic mulch [17]. Mulches that have higher cellulose that is 15 % have low heat conductivity, so that heat reaches the surface less soil than without mulch or with ordinary plastic mulch [18]. By lowering the temperature of the air and soil can reduce the loss of groundwater from the soil surface thereby reducing drought stress. Low soil temperature can reduce the rate of root respiration so that the assimilates can be donated for stockpiling food reserves more than without mulch [19].

The anti-UV material used is Tinuvin P. Tinuvin P has a maximum absorbability of ultraviolet light in the range 300-400 nanometer and is stable against light during irradiation [20]. From the data obtained by mulch, T4 has better UV absorption than T1 and T6. The peak in the UV range is only detected at a concentration of 5 % at a wavelength of 300 nm. This shows the absorption of UV radiation caused by anti-UV. In T1 and T6 mulch, there is no dominant peak, due to the influence of celluloses addition. The addition of anti-UV causes the peak to shift in the UV range so that no dominant peaks appear for mulch T1 and T6 [15].

The observation with SEM aims to determine the surface structure and homogeneity of the film mixture made. The films analyzed for surface morphology were films T4 and T6 with the highest tensile strength and T4 films. SEM analysis results can be seen in Figure 7.

The results of the analysis did not show any cracks on the surface of the film, so the T4 film was quite tight but not perfect because there were pores and lumps. Large lumps on the resulting surface morphology are visible to T6. The solid is in the form of a large lump and there is a pore between the clots. These solids are thought to be tinuvin particles that bind to cellulose and oleic acid with large
particle size. The presence of large lumps showed that tinuvin particles experienced agglomeration grouping, causing the distribution of tinuvin in the film layer not to be evenly distributed.

**Figure 7.** Surface morphology of mulches (a) 4% of anti-UV and (b) 6% of anti-UV.

### 4. Conclusion

Cornhusk cellulose can be extracted with alkali treatment so that the cellulose produced can be used as a material for mulches. Mulch films can be synthesized with a mixture of cornhusk cellulose, LLDPE, variations in anti-UV concentration and the addition of additives such as glycerol, oleic acid, and irganox. The mulch films produced have different characteristics. Variations in the added anti-UV concentration affect the physical and mechanical properties of the mulch film produced. This is following the results of the analysis of the variety carried out. The mulch film produced has a black color, smooth and elastic surface. The mechanical properties of the film have increased. Significant tensile strength, elongation, and modulus of elasticity were found in films with the addition of 4% anti UV and 15% cellulose content. The optic analysis indicates the decreasing of the absorption with addition of anti-UV and increased of cellulose content in mulch, so that at T1 and T6, all the light energy is passed or only some of the light can be absorbed the mulch in the wavelength 480 nm, while T4 absorbs maximally in the 300-400 nm region according to maximum anti UV absorption.

### Acknowledgments

The authors would like to acknowledge the DIKTI for financial support (Grant of Research and Scientific Publication with contract No.3/E1/KP.PTNBH/2019).

### References

[1] Kasirajan S and Ngouajio M 2012 *Agron. Sustain. Dev.* 32 501.
[2] Zhijian T, Yongjian Y, Hongying W, Wanlai Z, Yuanru Y and Chaoyun W 2016 *Appl. Sci.* 6 147.
[3] Martin-Closas L, Botet R and Pelacho A 2014 *Polym. Degrad. Stab.* 108 250.
[4] Yang X, Han F, Xu C, Jiang S, Huang L and Liu L 2017 *Ind. Crop. Prod.* 109 241.
[5] Shubhra Q T H, Alam A K M M and Quaiyyum M A 2011 *J. Thermoplast. Compos. Mater* 26 362.
[6] Dirgantara, M and Kurniati M 2013 Effects of Corn Husk and LLDPE Ratio on the Properties by Thermo-pressing *Proceedings The International Conference on Innovation in Polymer Science and Technology* (Yogyakarta: Inna Garuda Hotel) 77.
[7] Zhang Feng L, Ping L, Di Cai, Qiuchi C, Peiyong Q, Tianwei T and Hui C 2017 *Ind. Crop. Prod.* 95 521.
[8] Martin-Closas L, Pelacho A M, Picuno P and Rodriguez D 2018 *Acta Horticulturae* 801 275.
[9] Du C, Li H, Liu M and Zhan H 2016 *Bio. Resour.* 11 5276.
[10] Ham J M, Kluitenberg G J and Lamont W J 2013 *J. Am. Soc. Hortic. Sci.* **118** 188.
[11] Hasan M, Chong E W N, Jafarzadeh S, Partidah M T, Gopakumar D A, Tajarudin H A, Thomas S, and Khalil H P S A 2019 *Polymers* **11** 210.
[12] Bledzki A K, Mamun A A, Bonnia N N and Ahmad S 2012 *Ind. Crops Prod.* **37** 427.
[13] Nourbakhsh A, Baghiani F F and Ashori A 2011 *Ind. Crops Prod.* **33** 183.
[14] Kaijanen L, Maaret P, Suvi P, Eeva J and Satu-Pia R 2015 *Int. J. Electrochem. Sci.* **10** 2950.
[15] Vojta D, Karlsen E M and Spanget-Larsen J 2017 *Spectrochimica Acta part A: Mol. Biomol. Spectrosc.* **173** 182.
[16] Ciolacu D, Ciolacu F and Popa V I 2011 *Cellul. Chem. Technol.* **45** 13.
[17] Mbah C N, Nwite J N, Njoku C, Ibeh L M and Igwe T S 2010 *World J. Agricult. Sci.* **6** 160
[18] Kader M A, Senge M, Mojid M A and Ito K 2017 *Soil Tillage Res.* **168** 155.
[19] Miles C, DeVetter L, Ghimire S and Hayes D G 2017 *Hort. Science* **52** 10.
[20] Liu M, Huang Z and Yang Y 2010 *J. Polym. Environ.* **18** 148.