Synthesis of biodegradable plastic from corn starch and corn husk filler with addition of glycerol as plasticizer and variation of chitosan composition

R Azsarinka¹, D Saleh¹ and E Djonaedi²
¹Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia
²Department of Printing Engineering, Faculty of Printing Engineering and Publishing (FTGP), Politeknik Negeri Jakarta, Depok 16424, Indonesia

Abstract. Cellulose, contained in corn husk, is one of natural polymer that can be used as filler for bioplastics. Corn starch flour (maize) as matrix and corn husk powder in different grain size as filler is then synthesized with chitosan and glycerol. The resulting bioplastics is a thin film with muddy-brown color. Alternating the corn husk powder grain size from 150 mesh to 200 mesh modifies the physical characteristics, especially mechanical properties. The most optimal bioplastics were obtained with 200 mesh grain size of corn husk powder and 0.04 % chitosan composition with tensile strength of 286.31 N/cm², elongation of 10.19 %, Young modulus of 28.11 N/cm² and tear resistance of 705.61 mN. There are changes in molecular structure of some functional groups as compared to the elements. Bioplastics were degraded 30–35 % for 21 days in soil, started moldy after 10 days in open air and endured for one hour in temperature 100 °C.

Keywords: Cellulose, natural polymer, bioplastics, glycerol, chitosan

1. Introduction
Not every industrial and household plastics waste can be recycled. An alternative to alleviate the waste is substitution to biodegradable plastics (bioplastics). According to ASTM sub-committee D20-96, bioplastics is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae [1]. From National Standard of Indonesia (SNI), materials may be classified as bioplastics if it has tensile strength of 24.7–302 MPa and elongation of 21–220 % [2]. In this research, we investigate the production of such bioplastics using cellulose extracted from corn husk, an abundant byproduct of corn processing, which containing 36.81 % cellulose [3]. High cellulose content in plants acted as filler for bioplastics, which can strengthen the plastics by increasing the tensile strength.

Corn starch flour (maize) as matrix for bioplastics has another function as additive to strengthen the chemical bond in cellulose [4]. Plasticizer is organic solvent that decreases intermolecular force accumulation in long chain molecule [5]. Glycerol, as one kind of plasticizer, is able to attract and hold the moisture from the air [6] so it can improve the mechanical properties of the resulting bioplastics, especially elongation. Chitosan is non-toxic element, biodegradable and antimicrobial, also plays a role
in improving the mechanical properties of materials, such as stiffness and strength [7-9]. Acetic acid acted as catalyst during the synthesis process and solvent to chitosan while aquadest (purified water) is used as the solvent due to its neutral characteristic [2, 10].

2. Experimental method
The corn husk is milled and screened to obtain powder with grain size of 150 mesh and 200 mesh. Bioplastics synthesis is performed by varying the grain size and chitosan composition. Corn husk powder and corn starch flour is measured in 1:1 ratio then chitosan is added at variation of 0.02, 0.04, 0.06, 0.08, and 0.1 %wt. According to the previous research [11], the mixture is synthesized with 2.5 mL of 25 % acetic acid, 1.75 mL of glycerol and 70 mL of aquadest. The solution is then heated and stirred until it is changed color and thickened. Then, it is printed on a Teflon paper with a glass plate as supporting base and dried for two hours at 80 °C [11].

Characterization is done to determine the degradation, heat resistance [12], morphological and mechanical properties of bioplastics. Morphological properties can be known by using microscope and FTIR [13]. For mechanical properties, vertical tensometer is used to determine the tensile strength [14] while Elmendorf methods is used to determine the tear resistance [15]. The degradation test is done to determine the degradation rate at certain time. It has two different methods: the first method is performed to know the fungi resistance of bioplastics after being exposed to open air [16] and the second method is performed to know the degradation of bioplastics in the soil [17].

3. Results and discussion
The resulting bioplastics (figure 1) is a thin film with muddy-brown color which texture is smoother by the increased composition of chitosan. The difference of the two types of bioplastics is due to the ratio of corn husk powder and corn starch flour are equal, other than corn husk powder is heated as part of synthesis process so that the powder is dissolved.

Characterization results obtained from microscope (figure 2) showed that the texture of bioplastics is affected by the grain size of corn husk powder. Fifty times magnification showed that bioplastics surface with grain size of 150 mesh have a lot more cracks than grain size of 200 mesh, indicating that corn husk powder and corn starch flour did not blend perfectly [17]. Sample of bioplastics which tested at room temperature exposure for 21 days showed that it has grayish spots on the surfaces at 250x magnification, possibly caused by fungi [5, 17].

![Grain size of 200 mesh](image1)

![Grain size of 150 mesh](image2)

**Figure 1.** Sample of corn husk filler bioplastics with chitosan composition of (a) 0.02 %wt, (b) 0.04 %wt, (c) 0.06 %wt, (d) 0.08 %wt, and (e) 0.1 %wt.
Resulting bioplastics

Grain size of 200 mesh

Grain size of 150 mesh

Exposed to room temperature after 21 days

Grain size of 200 mesh

Grain size of 150 mesh

(a) (b)

Figure 2. Surface condition of bioplastics with chitosan composition of 0.02 %wt at magnification of (a) 50x and (b) 250x.

FTIR result of corn husk powder (figure 3) and corn starch flour (figure 4) showed that it has a similar spectrum and consists of ether functional groups (C–O), alcohol functional groups (O–H) and alkene functional groups (C=C) as specific functional group.

FTIR results of corn husk bioplastics with 200 mesh grain size (figure 5) and 150 mesh grain size (figure 6) showed changes in functional groups as compared to infrared spectrum of corn husk powder and corn starch flour. Changes in functional groups are caused by gelatinization process that delinked monomers in corn husk and corn starch during synthesis so that the atoms of glycerol and chitosan placed themselves between the starch–corn husk bonds [18-20].

FTIR results below (figure 7) showed shifts of wavenumber from bioplastics elements, loss of alkene (C=C) functional groups and emergence of aromatic (C–N) and amine (C–N) functional groups. Strong hydroxyl, carbonyl and ether bonds indicated that bioplastics have the capability to absorb water so the bioplastics can be degraded by microorganisms. This is because microorganism has an enzyme that can broke down the bonds [18, 19]. The difference in infrared spectrum of corn husk filler bioplastics with grain size 200 mesh and grain size 150 mesh is likely due to the type of chemical bonds between each molecule is changed.
Figure 3. Infrared spectrum of corn husk powder.

Figure 4. Infrared spectrum of corn starch flour.

Figure 5. Infrared spectrum of corn husk filler bioplastics with grain size 200 mesh and chitosan composition of 0.1 %wt.
Figure 6. Infrared spectrum of corn husk filler bioplastics with grain size 150 mesh and chitosan composition of 0.1 %wt.

Tensile test results showed that corn husk filler bioplastics with grain size of 200 mesh has higher tensile strength and Young modulus than grain size of 150 mesh while the highest elongation received by bioplastics with grain size of 150 mesh (figure 8). Based on the close observation, there are white dots all over the bioplastics, as a result of undissolved chitosan while synthesized. Tensile strength and elongation are hugely affected by grain size and dissolved chitosan. Particles with smaller size are easily inserted into the matrix and bonded with another element so the load distribution is spread evenly [21]. Delignification to the corn husk resulted in starch and glycerol lead to the difficulty to react with cellulose so hydrogen bonds have low quantities. The solubility of chitosan in bioplastics has a major effect to the tensile strength [18]. This is due to the linear chain structure of the chitosan polymer so it is able to arrange the polymer molecules and influence the number of hydrogen interactions, both intermolecular and intramolecular [22].

Referring to SNI for bioplastics standard [2], corn husk filler bioplastics do not meet these criteria. The highest tensile strength only reached 2.86 MPa, drifted with the value of SNI of 24.7–302 MPa. Similarly, according to SNI with range between 21-220 % could not be achieved due to the highest elongation only reached 10.33 % (figure 9).

The tear resistance results with the same thickness are shown in figure 10. Optimization of bioplastics tear resistance occurred at chitosan composition of 0.04 %wt. The graph also showed that the tear resistance of bioplastic with grain size of 200 mesh is bigger than the 150 mesh. It is showed that the torn samples have smoother jagged structure as well. The smoother jagged structure of the 200 mesh is due to the uniform distribution of each component. Another possibility is that the heating temperature corresponds to the synthesis process so that the corn starch gelatinization proceeded well and the chitosan dissolved completely.

The heat resistance test result showed that bioplastics sample with grain size of 200 mesh decreased slightly from its initial mass than grain size of 150 mesh (figure 11). The O–H bonds on the smaller grain size have much more quantity than the bond in larger grain size. Loss of moisture content in bioplastics is demonstrated by a curved and rigid bioplastics form that is easily fractured, as well as darker color along with higher temperatures. This is due to the reaction between hydrogen from hydrocarbon groups with oxygen to produce carbon and water vapor [23].

Table 1 shows that adding chitosan does not have a significant impact to the heat resistance of bioplastic samples. This is determined by the levels of glycerol in bioplastics. The results of bioplastic degradation test for open air degradation is shown by table 2. The bioplastic has fluctuate change
of mass in the first week, then subsequent mass reduction in the following two weeks. The increase and decrease in sample mass are due to the ability to bind or release moisture from bioplastics. Grayish spots appeared on the surface of bioplastic samples after day 10 in the 150 mesh has a lot of grayish spots on the surface than the 200 mesh. The grayish spots that appeared on the surface of bioplastics are fungi [16, 24]. Molding in bioplastics is most likely caused by cracks in the bioplastic surface. The addition of chitosan into the mixture increases the bioplastic resistance against the fungi [25].
Grain size of 200 mesh

Grain size of 150 mesh

(a) (b) (c) (d) (e)

Figure 11. Surface condition of bioplastics with chitosan composition 0.06 %wt at (a) 27 °C, (b) 100 °C, (c) 120 °C, (d) 140 °C, and (e) 160 °C.

Table 1. The heat resistance of bioplastics.

| Grain size | Chitosan composition | Initial mass (mg) | 100 °C | 120 °C | 140 °C | 160 °C | Decreasing mass (%) |
|------------|----------------------|------------------|--------|--------|--------|--------|---------------------|
| 200 mesh   | 0.02 %wt             | 118.5            | 97.9   | 91     | 85.3   | 81.2   | 31.48               |
|            | 0.04 %wt             | 88.5             | 73.5   | 67.5   | 62.3   | 59.2   | 33.11               |
|            | 0.06 %wt             | 106.4            | 88.7   | 83.2   | 77.4   | 73.5   | 30.92               |
|            | 0.08 %wt             | 93               | 76.2   | 70.7   | 65.3   | 61.9   | 33.44               |
|            | 0.10 %wt             | 71.7             | 57.6   | 52.4   | 48.5   | 46.6   | 35.01               |
|            | 0.02 %wt             | 114              | 88.4   | 81.5   | 76.4   | 72.7   | 36.23               |
|            | 0.04 %wt             | 76.7             | 62.1   | 56.3   | 52.5   | 50.3   | 34.42               |
|            | 0.06 %wt             | 122.8            | 90.8   | 84.6   | 78.4   | 74.4   | 39.41               |
|            | 0.08 %wt             | 112.4            | 91.3   | 84.7   | 77.9   | 73.7   | 34.43               |
|            | 0.10 %wt             | 100.6            | 81.7   | 76.3   | 71.2   | 67.4   | 33                  |
| 150 mesh   | 0.02 %wt             | 114              | 88.4   | 81.5   | 76.4   | 72.7   | 36.23               |
|            | 0.04 %wt             | 76.7             | 62.1   | 56.3   | 52.5   | 50.3   | 34.42               |
|            | 0.06 %wt             | 122.8            | 90.8   | 84.6   | 78.4   | 74.4   | 39.41               |
|            | 0.08 %wt             | 112.4            | 91.3   | 84.7   | 77.9   | 73.7   | 34.43               |
|            | 0.10 %wt             | 100.6            | 81.7   | 76.3   | 71.2   | 67.4   | 33                  |

Table 2. Degradation of bioplastics in open air (at room temperature).

| Grain size | Chitosan composition | Initial mass (mg) | 1st week | 2nd weeks | 3rd weeks | Degradation at 3rd weeks |
|------------|----------------------|------------------|----------|-----------|-----------|--------------------------|
| 200 mesh   | 0.02 %wt             | 92.7             | 91.2     | 83.3      | 74.4      | 19.74 %                  |
|            | 0.04 %wt             | 39.5             | 36.6     | 33.6      | 29.5      | 25.32 %                  |
|            | 0.06 %wt             | 61.5             | 66       | 56.5      | 50.4      | 18.05 %                  |
|            | 0.08 %wt             | 116.2            | 117.5    | 96.8      | 91.4      | 21.34 %                  |
|            | 0.10 %wt             | 71.9             | 68.5     | 56.1      | 43.9      | 38.92 %                  |
|            | 0.02 %wt             | 92               | 77.6     | 67.5      | 64.7      | 29.67 %                  |
|            | 0.04 %wt             | 111.3            | 103.4    | 100.2     | 87        | 21.83 %                  |
|            | 0.06 %wt             | 98.2             | 102.2    | 77.3      | 65.6      | 33.2 %                   |
|            | 0.08 %wt             | 73.3             | 68.9     | 64.7      | 55.9      | 23.74 %                  |
|            | 0.10 %wt             | 100.2            | 104.9    | 86.3      | 72.2      | 27.94 %                  |

| Grain size | Chitosan composition | Initial mass (mg) | 1st week | 2nd weeks | 3rd weeks | Degradation at 3rd weeks |
|------------|----------------------|------------------|----------|-----------|-----------|--------------------------|
| 150 mesh   | 0.02 %wt             | 92.7             | 91.2     | 83.3      | 74.4      | 19.74 %                  |
|            | 0.04 %wt             | 39.5             | 36.6     | 33.6      | 29.5      | 25.32 %                  |
|            | 0.06 %wt             | 61.5             | 66       | 56.5      | 50.4      | 18.05 %                  |
|            | 0.08 %wt             | 116.2            | 117.5    | 96.8      | 91.4      | 21.34 %                  |
|            | 0.10 %wt             | 71.9             | 68.5     | 56.1      | 43.9      | 38.92 %                  |
|            | 0.02 %wt             | 92               | 77.6     | 67.5      | 64.7      | 29.67 %                  |
|            | 0.04 %wt             | 111.3            | 103.4    | 100.2     | 87        | 21.83 %                  |
|            | 0.06 %wt             | 98.2             | 102.2    | 77.3      | 65.6      | 33.2 %                   |
|            | 0.08 %wt             | 73.3             | 68.9     | 64.7      | 55.9      | 23.74 %                  |
|            | 0.10 %wt             | 100.2            | 104.9    | 86.3      | 72.2      | 27.94 %                  |
Table 3. Degradation of bioplastics using soil burial test methods.

| Grain size | Chitosan composition | Initial mass (mg) | Final mass (mg) | Degradation at 3rd weeks |
|------------|----------------------|-------------------|----------------|--------------------------|
|            |                      | 1st week          | 2nd weeks      | 3rd weeks                |
| 200 mesh   | 0.02 %wt             | 95.5              | 52.8           | 47.5                     | 31.3                     | 67.23 %                   |
|            | 0.04 %wt             | 63.1              | 29.4           | 24                       | 22                       | 65.13 %                   |
|            | 0.06 %wt             | 112.7             | 63             | 62.2                     | 57.2                     | 49.25 %                   |
|            | 0.08 %wt             | 148.7             | 81.7           | 93.6                     | 109.2                    | 26.56 %                   |
|            | 0.10 %wt             | 98.2              | 55.1           | 62.1                     | 49.3                     | 49.8 %                    |
|            | 0.02 %wt             | 123.1             | 67.7           | 70.8                     | 44.3                     | 64.01 %                   |
|            | 0.04 %wt             | 145.9             | 85.1           | 93.6                     | 88.7                     | 39.2 %                    |
| 150 mesh   | 0.06 %wt             | 133.6             | 69.8           | 106.6                    | 59.7                     | 55.31 %                   |
|            | 0.08 %wt             | 135.8             | 65.5           | 107.8                    | 87.9                     | 35.27 %                   |
|            | 0.10 %wt             | 113.5             | 64.1           | 69.6                     | 40.8                     | 64.05 %                   |

The results of bioplastic degradation testing using soil burial test method (table 3) are not significantly influenced by chitosan composition in bioplastic degradation process while grain size generally affect the degradation [26]. In the first week, corn husk filler bioplastics with grain size of 150 mesh lost more mass than the 200 mesh grain size. However, during the second and third weeks, there is a slight change in mass. This situation is caused by the changes in temperature and moisture conditions from the environment. Uncontrolled soil water levels are also the cause of why changes in the mass of bioplastic samples are fluctuated. If the water content in the bioplastic is excessive, then the bioplastic will be degraded faster.

From table 2 and table 3, it is seen that the degradation process by soil burial test method is faster than bioplastic which is left exposed to open air. Mesh size variations have a greater impact in degradation than chitosan composition.

4. Conclusion

Based on this research, it can be concluded that bioplastics have the form of thin and muddy brown-colored sheets for all variations of grain size and chitosan composition. In average, corn husk filler bioplastics with grain size of 200 mesh has a finer texture, larger tensile strength and tear resistance, and higher endurance of heat than grain size of 150 mesh. Adding more chitosan will make the bioplastics surface texture smoother. Analysis using FTIR indicates that there are shift of wavenumbers but no sign of new functional group compared to the base materials. Bioplastics with the best characteristic is the bioplastics with grain size of 200 mesh and chitosan composition of 0.04 %wt for the reason that it has tensile strength of 286.31 N/cm², elongation of 10.19 %, Young modulus of 28.11 N/cm², and tear resistance of 705.61 mN. However, these characteristics have not met the SNI standard for bioplastics.

Acknowledgments

The author would like to thank Djonaedi Saleh and Emmidia Djonaedi for their guidance during this research; FTGP Politeknik Negeri Jakarta and FMIPA Universitas Indonesia for supporting this project by giving permission to use the labs.

References

[1] Muller R J 2005 Regulations and Methods for Testing Biodegradability of Polymers (Biopolymer Online) pp. 365-74 available at https://application.wiley-vch.de/books/biopoly/pdf_v10/vol10_19.pdf
[2] Anggarini F, Latifah and Miswadi S S 2013 *Indo. J. Chem. Sci.* 2 173-8
[3] Ningsih E R 2012 *Uji Kinerja Digester Pada Proses Pulping Kalit Jagung dengan Variabel Suhu dan Waktu Pemasakan* Diploma final project (Semarang: D3 Study Program of Chemical Engineering, Universitas Diponegoro)
[4] Ulyarti 1997 *Mempelajari Sifat-sifat Amilografi pada Amilosa, Amilopektin, dan Campurannya* Master thesis (Bogor: Faculty of Agricultural Engineering, IPB University)
[5] Marbun E S 2012 *Sintesis Bioplastik dari Pati Ubi Jalar Menggunakan Penguat Logam ZnO dan Penguat Alami Selulosa* Master thesis (Depok: Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia)
[6] Tan H W, Aziz A R A and Aroua M K 2013 *Renew. Sustain. Energy Rev.* 27 118-27
[7] Kumar M N V R 2000 *React. Funct. Polym.* 46 1-27
[8] Peelman N et al. 2013 *Trends Food Sci. Technol.* 32 128-41
[9] Murni S W, Pawignyo H, Widyawati D and Sari N 2013 *Pembuatan Edible Film dari Tepung Jagung (Zea Mays L.) dan Kitosan* (Yogyakarta: Prosiding Seminar Nasional Teknik Kimia “Kejuangan”)
[10] Hartatik Y D, Nuriyah L and Iswarin 2014 *Pengaruh Komposisi Kitosan terhadap Sifat Mekanik dan Biodegradable Bioplastik* available at https://media.neliti.com/media/publications/159022-ID-pengaruh-komposisi-kitosan-terhadap-sifa.pdf
[11] Djonaedi E and Yuniarti E 2016 Bioplastic From Corn Husk and Corn Starch With Plasticizer Variations *Proceeding of The 5th Annual South East Asian International Seminar (ASAISS Politeknik of Jakarta* 2016 pp. 1-53 available at http://asais.pn.j.ac.id/attachment/files/Proceeding%20TEC%20ASAISS%202016.pdf
[12] ASTM D5721 2002 *Standard Practice for Air-Oven Aging of Polyolefin Geomembranes* (ASTM) available at https://standards.globalspec.com/std/10388761/ASTM%20D5721
[13] Thermo Electron Corporation 2001 *Introduction to Fourier Transform Infrared Spectrometry* available at http://www.nicoletcz.cz/upload/kc/files/aplikacni-podpora/teorie/IntroductionToFTIR.pdf
[14] ASTM D882 2018 *Standard Test Method for Tensile Properties of Thin Plastic Sheet*ing (ASTM) available at https://standards.globalspec.com/std/13050669/ASTM%20D882
[15] Standar Nasional Indonesia 2009 Kertas – Cara Uji Ketahanan Sobek – Metode Elmendorf (Badan Standar Nasional) available at https://thradiokecenter.files.wordpress.com/2010/06/9089_sni-0436-2009-kertas-ketahanan-sobek.pdf
[16] ISO 1997 ISO 846:1997–Plastics: Determination of behaviour under the action of fungi and bacteria, Evaluation by visual examination or measurement of changes in mass or physical properties available at https://www.iso.org/standard/74599.html (revised) or https://id.scribd.com/document/390876490/ISO-846-pdf
[17] Ardiansyah R 2011 *Pemanfaatan Pati Umbi Garut untuk Pembuatan Plastik Biodegradable* Master thesis (Depok: Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia)
[18] Agustin Y E and Padmawijaya K S 2016 *J. Tek. Kim.* 10 40-8
[19] Septisari A, Latifah and Kusumastuti E 2014 *Indo. J. Chem. Sci.* 3 158-62
[20] Sinaga R F, Ginting G M, Ginting M H S and Hasibuan R 2014 *J. Tek. Kim. USU* 3 19-24
[21] Njoku R E, Okon A E and Ikpaki T C 2011 *Niger. J. Technol.* 30 87-93
[22] Sanjaya I G and Puspita T 2008 *Pengaruh Penambahan Khitosan dan Plasticizer Gliserol pada Karakteristik Plastik Biodegradable dari Pati Limbah Kulit Singkong* (Surabaya: Institut Teknologi Sepuluh Nopember) available at http://digilib.its.ac.id/public/ITS-Undergraduate-17047-230510060-paperpdf.pdf
[23] Bourtoom T 2008 *Songklanakarin J. Sci. Technol.* 30 149-65
[24] Jecu L, Grosu E, Raut I, Ghiurea, Constantin M, Stoica A, Stroescu M and Vasilescu G 2011
Fungal Degradation of Polymeric Materials: Morphological Aspects available at
http://www.inginerie-electrica.ro/acqu/2011/P_1_Fungal_degradation_of_polymeric_materials_Morfological_aspects.pdf
[25] Martínez-camacho A P, et al. 2010 Carbohyd. Polym. 82 305-15
[26] Emadian S M, Onay T T and Demirel B 2017 Waste Manag. 59 526-36