Preparation of bioplastic film from gadung starch (Discoreahipida) and chitosan plasticized with glycerol

M Hasan*, D Afdal and M Nazar

Department of Chemical Education, Faculty of Teacher Training and Education, Universitas Syiah Kuala, Darussalam Banda Aceh 23111

*Corresponding author: muhammadhasan.kimia@unsyiah.ac.id

Abstract. Bioplastic film based on gadung starch (Discoreahipida) and chitosan plasticized by glycerol were prepared through solvent casting method. The aim of the study was to determine the effect of starch and chitosan composition on both mechanical properties and lyophobicity of the films. The results indicated that incorporating the chitosan in the starch matrix induced structural modification due to interaction between hydroxyl functional group and amino group of the starch and chitosan. The films produced in this research exhibit smooth surface, homogeneous and both porosity and cracks were not occurred which was evidenced by Atomic Force Microscopy (AFM) data. The findings also revealed that adding more chitosan in the starch matrix have significantly enhance tensile strength of the film while reduce the extension at break. Films with more chitosan absorbed more water compared to less chitosan film.

1. Introduction
The use of synthetic plastics as packaging materials, stationery, pipes, household appliances, and children's toys is increasing [1] due to low cost compared to metal-based materials thus waste from plastic increase significantly. Commercial plastics are not microbially decomposed in the soil. Therefore, the problem caused by plastic waste is globally very worrying. The amount of plastic waste produced annually in Indonesia is around 5.4 tons which is the 2nd higher of domestic waste production. Based on Indonesia's domestic waste data, the amount of plastic waste constitutes 14% of the total waste production in Indonesia as reported by the Indonesia Solid Waste Association. Based on data from the Jakarta Regional Environmental Management Agency (BPLHD), the waste generated in Jakarta is over 6000 tons per day and 13% of the waste is plastic waste. The problem caused plastic waste has become not only a national problem but also a global concern. Environmental researchers revealed that pollution of plastic waste in the ocean had reached 269,000 tons according to expedition data presented by researcher group who had traveled the world for six years. The synthetic plastic pollutes the environment severely due to microorganism incapability of degrading and decomposing, thus plastic decomposition takes hundreds of years to be completed [2].

Development of biodegradable plastic thus become very urgent and crucial in order to overcome the problem of plastic waste [3]. Biodegradable plastics are prepared from renewable sources or organic compounds obtained from plant parts such as cellulose [4], protein [5], and starch [6]. Starch
Starch can be obtained from carbohydrate-rich biomass like rice, corn, sago, and sweet potatoes. Starch consists of amylose and amylopectin. Amylose is a straight-chain polymer while amylopectin is a polymer with branched chains. The ratio of amylose to amylopectin in starch determines the properties of the film formed. Native starch has low thermomechanical properties [7-9]. However, various studies have been carried out to improve the properties of starch, including combination with synthetic polymers [10]. In this way, the plastic produced can improve thermomechanical properties although low in biodegradability [11]. Blending starch with various natural polymers is more promising and attracts many researchers because not only improving the thermomechanical properties of starch it also maintains the biodegradability characteristics of polymers [12].

One of the most interesting natural polymers that has been widely studied by many researchers is chitosan. The polymer is a deacetylation product of chitin and is ubiquitous and second most abundant polymer in nature after cellulose. In addition, chitosan has a good film forming capacity, excellent biocompatibility and proven as antimicrobial active compound [13]. Various publications on the addition of chitosan to the film matrix from starch have been reported such as corn [14], potatoes [15], wheat [16], cassava [17], pumpkin [18]. In this article we report the characteristics of films prepared by combining poisonous tuber starch (gadung starch) and chitosan plasticized by glycerin. Poisonous gadung is rarely used by the people of Aceh, usually consumed as additional food after cyanide removal. Based on literature search, until now there are no publications reported the plastic films made from gadung starch and chitosan.

2. Methods

2.1. Materials and Equipment
The equipment used in this research are analytical scales, magnetic stirrers, hot plates, tensile testing devices (computer type universal testing machines) and multimode Atomic Force Microscope (AFM). While The materials used in this study were chitosan, starch from gadung (gadung poisonous tuber), glycerol, ethanol, hydrochloric acid pH 5, sodium hydroxide pH 10, and acetic acid.

2.2. Experiments

2.2.1 Preparation of gadung Starch. Preparation of gadung starch was carried out by a modified procedure. Gadung was obtained from the city of Lhokseumawe, North Aceh. The tubers had been traditionally processed by the community and the poison has been removed. The gadung was mashed into starch powder with mortal, then sifted with 180 mesh sieves until the white powder of Gadung starch was obtained.

2.2.2 Film preparation. Plastic films were prepared by solvent casting method referred to Abdul Khalil [19], weighed chitosan, gadung starch and glycerol with a predetermined varied mass (Table 1). Chitosan was dissolved in 5% solution of acetic acid and was continuously stirred with a magnetic stirrer until completely dissolved, the starch was then added to the acetic acid solution and was stirred until completely dissolved. Both solutions were subsequently mixed in a beaker and 15% glycerol was added. After the sample begins to form a gel, the sample was poured into a mold and dried on a hotplate at a temperature of 75°C until all the solvents evaporate and the biodegradable plastic were obtained.
Table 1. Experimental Design

| Chitosan/Starch | Weight of chitosan (g) | Weight of starch (g) |
|-----------------|-----------------------|---------------------|
| 0:100           | 0,0                   | 2,0                 |
| 25:75           | 0,5                   | 1,5                 |
| 50:50           | 1,0                   | 1,0                 |
| 75:25           | 1,5                   | 0,5                 |
| 100:0           | 2,0                   | 0,0                 |

2.2.3 Solvent uptake test. This test referred the method performed by Hermawan, et al [20]. The film was cut to the size of 1.0 cm x 1.0 cm, weighed with an analytical balance, and put into a 50 ml beaker filled with 5 ml of the solvent, the film was then sterilized at room temperature. The film was simultaneously taken every minute, and the solvent remained on the film surface was gently wiped with a tissue, and then weighed. The absorption capacity of the solvent then was calculated using the following formula:

\[ \text{Solvent uptake} = \frac{W - W_0}{W_0} \times 100\% \]

where: \( W_0 \) = weight of initial sample while \( W \) = weight of final sample, after immersion in the solvent.

2.2.4 Tensile test. The films were cut in certain shapes (dumbbells) with a length of 4 cm, width of 4 mm and the moisture content of the samples was measured (Table 4.2). Tool parameters were kept with a tensile speed of 50 mm / minute with a maximum load of 10 kgf. Samples were clamped on a tensile test apparatus. The tool was run according to the conditions that have been determined until the sample is cut off and the above procedure was repeated for each sample 4 times the tensile test.

2.2.5 AFM Study. A multimode Atomic Force Microscope (AFM) was used to examine the porosity of the films. Mode of tapping with a constant tip oscillation, and topography of the sample were recorded. To obtain image of topographic, the amplitude ratio of the free tip in intermittent contact with the material was set to 90% (light tapping).

3. Results and Discussion

3.1 Bioplastic film
The obtained film is depicted by Figure 1. Based on visual observations, the film produced is transparent, and there is no color difference with the increase in the percentage of both starch and chitosan.
Figure 1. Transparent film bioplastic from gadung starch and chitosan.

3.2 Water solvent uptake test
Lyophobicity test was carried out by weighing the mass of bioplastics before and after dipping in various solvents. This study used four different solvents including water, ethanol, hydrochloride acid and sodium hydroxide. This procedure carried out in ten repetitions until a constant absorption data was obtained. The result of the test is displayed in Table 2.

Table 2. Water solvent uptake data

| Chitosan/Gadung Starch | Water  | Ethanol | HCl (pH = 5) | NaOH (pH = 10) |
|------------------------|--------|---------|--------------|----------------|
| 0/100                  | 21.81  | 0.03    | 28.18        | 25.20          |
| 25/75                  | 41.62  | 0.01    | 47.01        | 43.39          |
| 50/50                  | 32.63  | 0.19    | 30.72        | 39.78          |
| 75/25                  | 54.06  | 0.02    | 53.36        | 53.24          |
| 100/0                  | 65.51  | 0.01    | 54.59        | 60.13          |

Based on Table 2, the highest lyophobicity was found to be in ethanol, while the lowest film lyophobicity was showed by water. This findings revealed that the lyophobicity is influenced by the bonds of hydrogen where starch and chitosan having OH groups that bind water molecules. The presence of hydrogen bonds increases the interaction between film and solvent [21-22].

3.3 Tensile Properties
Tensile testing is very important to examine the maximum load that can be held by plastic. Ultimate strength is the maximum strength of the material that holds the maximum stress given at a constant withdrawal rate until the specimen breaks, while extension is the increase in the length of the specimen after being drawn with a certain load with a constant drawing rate. Table 3 displayed the results of bioplastic tensile test from gadung starch, chitosan, and glycerol with various ratios of chitosan and starch.

Table 3. Mechanical properties of film

| Chitosan/Starch | Tensile Strength (MPa) | Elongation (%) |
|----------------|------------------------|----------------|
| 0:100          | 61.29                  | 79.78          |
| 25:75          | 67.62                  | 69.90          |
| 50:50          | 72.94                  | 59.02          |
| 75:25          | 59.36                  | 50.74          |
| 100:0          | 118.26                 | 33.92          |
Based on table 3 it is clear that the tensile strength of film bioplastics is obtained at the chitosan content of 100%. While the optimum percentage elongation arises from the sample without chitosan. This result is in line with the publication reported by Akter [23] where the higher the content of chitosan in a polymer mixture the greater the value of the tensile strength of the film will be. This improvement was contributed by the presence of protonated amine groups in the chitosan molecular chain backbone. The cluster causes hydrogen bonds with other polymer chains such as starch. The high flexibility of film is influenced by the interaction of amylose molecules from starch and chitosan since the interaction of amylose and chitosan molecules is easier to occur than amylopectin [24].

3.4 AFM Study
AFM can be used to study the surface topology of bioplastic films. In addition to study the surface topography of solids at high resolutions, this tool can also be used to measure force versus distance curves. The resulting curves are called force curves, which provide valuable information about the specific properties of materials having pores and valleys on the surface of bioplastics films. AFM measurement of the film bioplastic is shown in figure 2/

![Figure 2](image)

**Figure 2.** Topography of film surface of chitosan/gadung starch 50/50 (a) film surface topography (b) film topography displayed the height of surface (c) force curve

4. Conclusion
Bioplastic films from gadung starch and chitosan are transparent and have a flat surface. The more gadung starch content the greater the percentage of bioplastic lyophobicity to various solvents, except for ethanol. The greater the chitosan content in the matrix, the greater the tensile strength of films in spite of decrease in the elongation of bioplastic films.

References
[1] Hasan M, Zulfadli, Nazar M, Rahmayani R F I, Fajri G, and Fansuri H 2019 *Rasayan J. Chem*, 12 1390
[2] Hasan M, lai T K, Gopakumar D A, Jawaid M, Owolabi, F A T, Mistar, E M, Alfatah T, Noriman N Z, Haafiz M K M, and Abdul Khalil H P S 2019 *J. Polym. Environ.* 27 1602
[3] Caroline M J, Oswaldo O-Y, Celina B, and Lucia F 2017 *Carbohydr. Polym.* 176 187
[4] Hasan M, Chong E W N, Jafarzadeh S, Paridah M T, Gopakumar D A, Tajaruddin H A, Thomas S, and Abdul Khalil H P S 2019 *Polymers* 11 210
[5] Suderman M, Isa M I N, and Sarbon N M 2018 *Food Biosci.* 24 111
[6] Jaiber H R L, and Carmen C T 2018 *Int. J. Biol. Macromol.* 107 371
[7] Paramanathan H P, and Thottiam V D R 2018 *Int. J. Biol. Macromol.* 120 361
[8] Saud K, Long Y, Mingyue F, Linghan M, and Ling C 2018 Food Pack. Shelf Life 18 71
[9] Karine D S C, Nathalie A L, Tania M H C, Adriano B, Florencia C-O 2018 Food Pack. Shelf Life.
[10] Clemence H-J, Juliesta R M, and Tomi J G 2019 Food Hydrocoll. 89 67
[11] Thewika W, Piyarat S, and Thawin W 2015 Food Hydrocoll. 50 54
[12] Marium S, Salman H, Tahira M, and Abid H 2019 Int. J. Biol. Macromol. 124 209
[13] Wang K, Lim, P N, Tong S Y, and Thian E S 2019 Food Pack. Shelf Life 100396
[14] Lili R, Xiaoxia Y, Jiang Z, Jin T, and Xingguang S 2017 Int. J. Bio. Macromol. 105 1636
[15] Huiming Y, Xingchi W, Ruyu B, Ziqing M, and Jin L 2019 Food Hydrocoll. 90 216
[16] Natasya Y, John A, Elisabeth G, and Stefan K 2017 Helyon3(10):e00421
[17] Yujia Z, Januana S, Teixeira, Michael M G, Marleny B A, and Saldena 2018 J. Supercrit. Fluid 137 101
[18] Hasan M, Rahmayani R F I, and Munandar 2017 IOP Conf. Series: Mat. Sci. Eng. 333 012087
[19] Abdul Khalil H P S, Yap S W, Owolabi F A T, Haafiz M K M, Fazita M R, Gopakumar D A, Hasan M, and Rizal S 2019 J. Phys. Sci 30(suppl.1) 23
[20] Hermawan, D, Lai T K, Jafarzadeh S, Gopakumar D A, Hasan M, Owolabi F A T, Sri Aprilia N A, Rizal S, and Abdul Khalil H P S 2019 Bioresources 14(2) 3389
[21] Rungsiri S, Rafael A A, and Pornchai R 2018 Ind. Crop & Prod. 122 37
[22] Kitisak J, Noppol L, Phisit S, Sochai W, and Toshiaki O 2016 Eur Polym.J. 84 292
[23] Akter N, Khan R A, Tuhin M O, Haque M E, Nurnabi M, and Islam R 2014 J. Thermoplast.. Compos. Mater. 27 933
[24] Hu X, Jia X, Zhi C, Jin Z, and Miaom M 2019 Carbohydr. Polym. 210 204