Effect of Hydrochloric Acid Concentration as Chitosan Solvent on Mechanical Properties of Bioplastics from Durian Seed Starch (Durio Zibethinus) with Filler Chitosan and Plasticizer Sorbitol

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Abstract The production of starch based bioplastic from durian seed as polymer matrix with addition of chitosan as filler and sorbitol as plasticizer were investigated. The aim of this research to obtain the effect of hydrochloric acid concentration as chitosan solvent on the mechanical properties of bioplastics included tensile strength, elongation at break, modulus young, functional group using FT-IR, surface morphology using SEM. Starch is the raw material for bioplastics which extracted by the durian seeds, then characterized to determine its chemical composition. The method of bioplastic production used in this research was casting method. Variation of hydrochloric acid concentration used 0.9%v, 1.0%v, 1.1%v, 1.2%v and 1.3%v. Bioplastic were analyzed physical and chemical properties. From the analysis, best condition of bioplastics obtained at hydrochloric acid concentration 0.9%v with temperature 70 °C for tensile strength 10,629 MPa, elongation at break 8,207%, and modulus young 129,514 MPa. From the results of FT-IR analysis indicated O-H group and N-H group on bioplastics due to the addition of chitosan and sorbitol. The results of mechanical properties were supported by Scanning Electron Microscopy (SEM) showed the bioplastic with chitosan as filler and plasticizer sorbitol have the fracture surfaces were a bit rough and jagged.

1. Introduction
Plastics have become an integral part of our lives. The problems of conventional plastics are taking decades to degrade in nature and produced by non-renewable sources like petroleum, coal and natural gas [1]. Renewable resources are again of importance in our modern society because of their positive effects on agriculture, the environment and the economy [2]. The energy consumption of plastic production is significantly high. The total oil consumption in the year 2008 was 87.2 Million barrels a day [3]. The known oil reserves total 1.24 trillion barrels, which at the current rate of consumption will last for approximately 41 years [4]. It is estimated that 99% of the plastic feedstock comes from petroleum. Characteristics of conventional plastics is not biodegradable. Biodegradable bioplastics break down in the environment and clearly not as persistent as conventional non-degradable plastics. Around 265,000,000 tons’ plastics produced and used every year [3]. It means that in one side, more resources produced to fulfill the increasing of plastic demand and in other sides it produces more plastic waste [5]. One effort to minimalize the usage of plastic is by using bioplastic, because bioplastic comes from raw material that is very environmentally friendly and bioplastic is degradable.
Bioplastic is renewable plastic because it contains polymers from renewable resources, like thermoplastic starch (TPS) [6], the compounds inside are derived from plants like starch, cellulose, and lignin and animal like casein, protein and lipid [7]. Native starch is the major sources of polysaccharide in plants [8]. Starch occurs as highly organized structures, known as starch granules. Starch has unique thermal properties and functionality that have permitted its wide use in food products and industrial applications [9]. Starch is used for it is easily degradable by nature to be environmentally friendly compounds. In Indonesia founded various plants yield flour (starch) like cassava [10], potato [3], durian [11] and etc. Starch can be a promising material for plastic raw material because its characteristics are universal, biodegradable, and has affordable price [12]. One plant which can be taken its starch is durian fruit seed [11]. Durian, or its scientific name, Durio Zibethinus Murr, is a seasonal fruit grown in South East Asia. Durian is normally eaten fresh [13]. Durian seed is a part of durian fruit was not consumed by the public because its taste is slimy and itchy at our tongue. Even though if we look at the nutritional content, durian seed has potential as a source of nutrition. It has protein, carbohydrate, fat, calcium and phosphorus [11].

A few earlier researches had been done to produce bioplastic. Selection of chitosan as one alternative to design environmentally friendly plastic because chitosan has biodegradable characteristic [11]. Chitosan is soluble in the organic acid / mineral dilute through protonation -NH$_2$ at position C-2 of the repeat units D-Glucosamine, which the polysaccharides are converted into cationic polyelectrolyte polymer [14]. In a concentrated mineral acid, such as HCl, chitosan dissolved at a concentration of 0.15 to 1.1%, but insoluble at a concentration of 10% [15]. The Production of starch film needs mixture of additive materials to earn mechanical behavior such as flexible, ductile, and firm. Because of that, it needs to add liquid/solid substance to improve plasticity. Process is called as plasticizing, while substance added is called as plasticizer [14]. In simple concept, plasticizer that is organic solvent with high boiling temperature is added to the resin which is hard or rigid, so that the accumulation of intermolecular forces in a long chain will decrease, consequently the flexibility, softening, and elongation of the resin will increase [16]. Polyol such as sorbitol is a plasticizer that is good enough to reduce internal hydrogen bonds thereby will increase the intermolecular distance [17].

Based on the above, the authors are interested in doing a scientific study on effect of hydrochloric acid concentration on mechanical properties of bioplastics from durian seed starch (durio zibethinus) with filler chitosan and plasticizer sorbitol. The results are expected to supply the necessary information for the Government of Indonesia in development alternative solutions for reducing conventional plastic consumption.

2. Method

2.1. Starch Extraction of Durian Seed

Starch that was used in this research of bioplastic was starch that was extracted from durian seeds. Durian seeds was obtained from merchant’s durian “Ucok Durian” located at Jalan KH Wahid Hasyim, Medan, Indonesia. Durian seeds that had been collected were then cleaned and peeled. Furthermore, durian seeds were cut, cleaned, and dried under the sun. Seeds that had been dried were blended with water at ratio 1: 5 (w/v), then those were filtered. The filtrate was precipitated for ± 12 hours and the sediment was wet starch. Wet starch was dried in an oven with temperature 45 - 50 °C for ± 24 hours to obtain the dry starch. Dry starch was refined and sieved with 100 mesh sieve. Starch durian seed was analyzed the water content, starch content, amylose content, amylpectin content, ash content, fat content, and protein content based on standard SNI-01-2891-1992, SNI-01-3194-1992, Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscope (SEM).
2.2. Manufacture Bioplastic and Testing Density, Water Absorption, Tensile Strength and Elongation at Break Bioplastic

Durian seed starch were weighed as much 20 gram and chitosan were weighed with a concentration 3% of the total volume of starch solution. Starch solution was made by dissolving starch with distilled water (H_{2}O). Chitosan solution was also prepared by dissolving chitosan which had been weighed before with distilled water (H_{2}O). Chitosan solution mixed with hydrochloric acid solution with variation concentration HCl 0,9%; 1,0%; 1,1%; 1,2%; and 1,3% w. Manufacture of bioplastic also added sorbitol as plasticizer 9 grams. Glass beaker containing starch solution was placed on a magnetic stirrer hot plate while heated. Chitosan solution was then poured into a glass beaker containing starch solution. After 20 minutes, sorbitol was added to the solution and the solution was left up until the specific heating temperature bioplastic was achieved (temperature varied, T = 70 °C, 72,5 °C, 75 °C, 77,5 °C, and 80 °C). Once the temperature was reached, the magnetic stirrer was turned off. Glass beaker containing a solution of bioplastic was cooled briefly before printing. The solution was poured into a mold bioplastic acrylic. The mold then slowly put into an oven at temperature 45 °C for 24 hours. After the bioplastic was dry, bioplastic was removed from the mold and then stored in a desiccator. Bioplastic was ready to be analyzed.

Bioplastic that was successfully created was analyzed its tensile strength based on standard procedure ASTM D638-02a 2002, elongation at break based on ASTM D792-91 1991, Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscope (SEM).

3. Result and Discussion

3.1. Characterization of Durian Seeds Starch

The yield of starch extracted from the durian seeds is 20.58%, in which the starch in the form of powder and white with the particle size of 100 mesh. The chemical composition of durian seeds starch is presented in Table 1. Durian seeds starch is quite potentially being used as bioplastics due to starch contained in the starch extracted from durian seeds is quite high, that was 76.65%, with the ratio of amylase: amylopectin 22.34: 54.32. There is a fairly large protein content in the durian seeds starch, it can induce browning reaction on bioplastics [18]. The presence of fat in the starch may form complexes with amylose thus granule surface enveloped by hydrophobic fat, it can inhibit the release of amylose from the granules during gelatinization [19]. But the fat content in the durian seeds starch is not high enough so it does not affect the gelatinization process.

| Table 1. Chemical Composition of Durian Seeds Starch |
|-----------------|---------|-----------------|
| Component       | Amount (%) | Standard Indonesia Industry (%) |
| Moisture        | 15,7     | 14              |
| Starch          | 76,6530  | 75              |
| - Amylose       | 22,3365  | -               |
| - Amylopectin   | 54,3165  | -               |
| Ash             | 0,13     | 15              |
| Fat             | 0,07     | -               |
| Protein         | 0,81     | -               |
| Carbohydrate    | 81,1     | -               |

3.2. Fourier Transform Infrared (FTIR)

The purpose of FTIR analysis is to identify the presence of hydrogen bonds that were formed in bioplastics. Figure 1 below is the FTIR analysis result of durian seeds starch, chitosan, bioplastic from durian seed starch without chitosan and HCl, and bioplastic from durian seed starch with chitosan, HCl and sorbitol.
From Figure 1 the result of FTIR bioplastics from durian seeds starch without/with chitosan and sorbitol, it can be seen that the functional groups contained in both biolastik are groups derived from their constituent components and there are no new cluster formed. From the analyzing result of FTIR could be seen that chitosan owns simetrical N-H groups, C-H alkenes, C=O, N-H bonds, C-O esters. The existing of N-H bond groups have purpose to the vibration of amino stratching from a set of chitosan [20]. The existing of C=O groups shows stretching of amide I and N-H bond groups show the stretching of amide II [21]. The existing of those groups have shown the characterictics of chitosan [20,21].

Those groups are C-H aromatic, C-O alcohol, C=C alkenes, C-H alkanes and OH hydrogen bonds which are derived from the groups of starch and chitosan. Between bioplastics without chitosan and sorbitol and bioplastics with chitosan and sorbitol, there are no existing C-N groups in starch and chitosan, this is because the C-N group are indicated derived from protein molecules undergo termination of the bond due to denaturation of proteins that occur at temperature of 55-75 °C [22]. But unlike the bioplastics without chitosan and sorbitol, there is N-H group in bioplastics with chitosan and sorbitol, this is because the N-H group derived from chitosan. There are an increase in wave numbers O-H group which are from 3340,71 cm$^{-1}$ in starch to be 3541,31 cm$^{-1}$ in bioplastics, and an increase in wave number of N-H group which are from 1589,34 cm$^{-1}$ in chitosan to be 1593,2 cm$^{-1}$ in bioplastics. Increasing the value of wavenumber O-H and N-H groups is due to the interaction of hydrogen when the component of starch and chitosan mixed on bioplastics manufacturing process, in which the hydrogen bonds consist of bonds between chains of amylose-amylose, amylose-amylopectin, chitosan-chitosan and amylose-chitosan-amylopectin.

3.3. Mechanical Properties of Bioplastic
The additional of HCl concentration as chitosan solvent greatly affect the mechanical properties of bioplastics. Testing of mechanical properties were carried out in this research were the tensile strength and elongation at break. The tensile strength is closely related with the additional of chitosan, while the elongation at break is closely related with additional of sorbitol.
3.3.1. Tensile Strength
The effect of increasing HCl concentration as chitosan solvent of bioplastic on the tensile strength of bioplastics are shown in Figure 2.

![Tensile Strength Graph](image)

Figure 2. The effect of increasing HCl concentration as chitosan solvent on the tensile strength of bioplastics

From figure 2 could be seen the highest tensile strength value of bioplastic at temperature 70 °C by adding concentration 0,9 % HCl earned the magnitude 10,629 MPa, while the lowest tensile strength at temperature 70 °C by adding concentration 1,3 % HCl earned the magnitude 2.646 MPa. Chitosan insoluble in water but soluble in the solvent acid pH below 6. Organic acids such as acetic acid and lactic acid used to dissolve the chitosan and the most commonly used as a solvent which a solution of 1% acetic acid. The solubility of chitosan in an inorganic acid is quite limited. Chitosan was dissolved in hydrochloric acid 1% but not soluble in sulfuric acid and acid phosphate [23]. So the higher the concentration of HCl, the lower solubility of chitosan. This makes the distribution of chitosan is not perfect. If the distribution of chitosan doesn’t perfect, then the plastic parts to be deprived of chitosan as a filler. But if the concentration of HCl is low, then the distribution of chitosan more perfect.

The increasing concentration of chitosan cause the value of tensile strength of bioplastics is also increasing. Chitosan that was added in the starch solution is to fill and increase the density of bioplastics formed, so that it will increase the resilience of bioplastics on the testing of tensile strength. Addition chitosan can also undergo chemical bonding interactions with starch during the mixing process. Chemical bonds in the material can affect the mechanical strength, it is depending on the amount and type of chemical bonds (covalent bonds, hydrogen and van der walls) [24]. On the addition of chitosan, there are interaction between chitosan and starch suspension which are supported by the results of FT-IR showed an increase in wave numbers O-H groups and N-H groups on bioplastics. That increase is from interaction of the amylose-amylopectin-chitosan. These hydrogen bonds increase the value of tensile strength bioplastics. The addition of sorbitol can also increase the absorption intensity of the O-H group on bioplastics. This is because the sorbitol has functional groups O-H [25]. So, that by the increasing of HCl concentration as chitosan solvent has impact on the decrease of the cohesiveness of bioplastics formed and the decrease value of tensile strength.
3.3.2. Elongation at Break
The effect of increasing HCl concentration as chitosan solvent of bioplastic on the elongation at break of bioplastics are shown in Fig. 3.

![Figure 3. The effect of increasing HCl concentration as chitosan solvent on the elongation at break of bioplastics](image)

From figure 3 could be seen the highest elongation at break value at temperature 70 °C by adding concentration 1,3 % HCl was 9,103 %, while the lowest value of elongation at break at temperature 70 °C by adding concentration 0,9 % HCl was 8,207 %. Chitosan was dissolved in hydrochloric acid 1% but not soluble in sulfuric acid and acid phosphate [23]. So, the higher the concentration of HCl, the lower solubility of chitosan. This makes the distribution of chitosan is not perfect. If the distribution of chitosan doesn’t perfect, then the plastic parts to be deprived of chitosan as a filler. But if the concentration of HCl is low, then the distribution of chitosan more perfect.

Higher the adding of chitosan number could affect the decreasing of elongation at break. This thing could be caused by the higher the compactness of intermolecular bonds in the bioplastic because the enhancement of hydrogen bond when adding chitosan, so bioplastic formed becomes stronger and more rigid. Elongation percentage inversely proportional to the addition of filler chitosan, so higher the number of filler chitosan can cause the elongation percentage will decline. This is caused by the declining of intermolecular bond distance [26].

3.3.3. Modulus Young
The effect of increasing HCl concentration as chitosan solvent of bioplastic on the modulus young of bioplastics are shown in Figure 4.

![Figure 4. The effect of increasing HCl concentration as chitosan solvent on the modulus young of bioplastics](image)
From figure 4 could be seen the highest Modulus Young value at temperature 70 °C by adding concentration 0.9 % HCl was 129,514 MPa, while the lowest Modulus Young value at temperature 70 °C by adding concentration 1.3 % HCl was 29,068 MPa. The higher of adding chitosan can cause the enhancement on the value of Modulus Young. This thing can be caused by higher the compactness of intermolecular bond in bioplastic because of hydrogen bonds when the adding of chitosan, so the formed of bioplastic becomes stronger and more rigid [27].

3.4. Scanning Electron Microscope (SEM)
The purpose of the SEM analysis was to observe the morphology of fracture surface of the bioplastics, whether all components of bioplastics has been mixed homogeneously.

![SEM micrographs of fractures](image)

**Figure 5.** SEM micrographs of fractures: (a) Bioplastics without fillers chitosan and plasticizer sorbitol; (b) Bioplastics with chitosan filler and plasticizer sorbitol

Figure 5 shows the result of analyzing SEM on bioplastic product with or without adding filler chitosan and plasticizer glycerol by magnification 5000. When we compared differences in the structure of fracture of bioplastic in Figure 5 (a) and Figure 5 (b), it can be seen that bioplastics in Figure 5 (b), bioplastics with the filler chitosan and plasticizer sorbitol has more dense and compact structure because the chitosan as a filler has been distributed homogeneously in the bioplastics that fills empty spaces in bioplastics, thus it is increasing the density of bioplastics. Need to notice that by adding more plasticizer, melting viscosity decreases which makes starch is hard to be plasticized, because the movement declines during the process [28]. Homogeneity structure of bioplastics is one indicator that can indicate improvements in the value of the mechanical strength of the bioplastics [29]. This supports the results of this research that an increase in tensile strength of bioplastics is caused by the increasing concentrations of chitosan which has been distributed homogeneously. The results of mechanical properties were supported by Scanning Electron Microscopy (SEM) showed the bioplastic with chitosan as filler and plasticizer sorbitol have the fracture surfaces were a bit rough and jagged.

4. Conclusion
Based on the results of research can be concluded that the analysis of durian seed starch obtained moisture content 15.7 %, ash content 0.13 %, starch content 76.653 %, amylose content 22.336 %,
Amylopectin content 54.316%, protein content 0.81%, fat content 0.07%, gelatinization temperature of 69.6 °C with the peak viscosity was 6115 cP and the best condition of bioplastics from starch durian seed obtained at temperature 70 °C with starch 20% and chitosan 3% w/v of starch solution, plasticizer sorbitol 9 gram, and concentration of HCl as chitosan solvent was 0.9% v with tensile strength 10,629 MPa, elongation at break 8.207%, and modulus Young 129,514 Mpa. The results of mechanical properties were supported by Scanning Electron Microscopy (SEM) showed the bioplastic with chitosan as filler and plasticizer sorbitol have the fracture surfaces were a bit rough and jagged.

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