Effect of Gelatinization Temperature and Chitosan on Mechanical Properties of Bioplastics from Avocado Seed Starch (Persea americana mill) with Plasticizer Glycerol

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ABSTRACT

Bioplastics are polymers which are derived from renewable biomass resources, such as starch, cellulose and lignin for plants and casein, protein and lipid for animals. The aim of this research to obtain the effect of gelatinization temperature and chitosan on the psychochemical properties of bioplastic. Starch is the raw material for bioplastics which extracted by the avocado seeds, then characterized to determine its chemical composition. The variation composition of avocado seed starch - chitosan used 7: 3, 8: 2 and 9: 1 and temperature bioplastic solution was varied at 80, 85 and 90 °C. Bioplastics were analyzed physical and chemical properties. From the analysis, the best condition of bioplastics obtained at temperature 90 °C with comparison of mass starch - chitosan 7: 3 for tensile strength 5.096 MPa, elongation at break 14.016% and Modulus Young 36.359 MPa. From the results of FT-IR analysis indicated O-H group and N-H groups on bioplastics due to the addition of chitosan and glycerol. The results of mechanical properties were supported by Scanning Electron Microscopy (SEM) showed the bioplastic with chitosan as filler and plasticizer glycerol have the fracture surfaces were smooth and soft and a little cavity.

Keywords – avocado seed, bioplastic, chitosan, gelatinization, glycerol

I. INTRODUCTION

Plastic waste is major environment problem. Shopping plastic or plastic bag is one of the main sources of plastic waste [1]. Around 265,000,000 tons plastics produced and used every year [2]. 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 [3]. Waste of plastic bag can also stuck water canal and ditch so it becomes threat for water population when plastic bag exists in water body and can cause death to cattle if the cattle consumes it. Then, when it is filled with rain drops, plastic bag can be a place for mosquito to breed. Furthermore, plastic needs years to be decomposed [1]. One effort to minimalize the usage of plastic is by using bioplastic.

Bioplastic is renewable plastic because the compounds inside are derived from plants like starch, cellulose, and lignin and animal like casein, protein and lipid [4]. 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 [5], potato [2], banana [6] and etc. Avocado is plant that owns dark green peel, oily green pulp, and big seed that represents 10-22 % from total weight [7]. This avocado grows well in tropical country like Indonesia. Based on Badan Pusat Statistik Republik Indonesia (BPS), production of avocado in Indonesia increases from 2009 to 2013 and in 2013 production of avocado is 276,318 tons [8]. Commonly, if you consume avocado, the seed side is supposed useless so it is just thrown away. Though avocado seed also has potency as source of starch and pigment. The seed contains high starch [9]. This content of starch that becomes raw material for manufacturing bioplastic.

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. The Production of starch film needs mixture of additive materials to earn mechanical behaviour 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 [10].
II. METHODOLOGY/EXPERIMENTAL

2.1 Materials
Avocado seed is earned from the seller of Alpukat Kocok at Jalan Gaharu, North Sumatera, glycerol, shrimp chitosan, aquadest, and acetic acid glacial from Merck.

2.2 Starch Isolation
Avocado seed at amount of 100 grams were washed by clean water. Avocado seed was cut with thickness ± 2 cm, then added 100 ml water that were used to simplify the crushing process. Next, avocado seed was crumbled by using blender. Pulp of avocado seed was taken out from blender and filtered and let at free air for 30 mins to get the precipitation from the avocado seed pulp. The precipitation was separated with water, then the precipitation was added with water and deposited again for 30 mins. The precipitation now was dried in oven with temperature 70 °C for 30 mins. Earned the dried powder of starch, then sifted with sieve 100 mesh [11].

2.3 Film Preparation
Procedure of manufacturing bioplastic refers to Weiping Band method was [6]: a number of starch and chitosan mass wanted was weighed with various ratios 7 : 3, 8 : 2, and 9 : 1 in the amount of 10 grams of total dry weight of starch-chitosan. Then, being made starch solution and chitosan solution based on counted volume at beaker glass. Volume of glycerol was 0,2 ml/gram from formulation of starch-chitosan. Water bath was heated and controlled the temperature that would be used (T = 80 °C, 85 °C and 90 °C ). Beaker glass 500 ml filled with starch was put in the water bath then motor stirrer was switched on. Chitosan solution was added inside then stirred for 25 mins. After 25 mins added glycerol to the starch-chitosan solution, afterwards stirred untill homogeneous. After homogeneous occurred, water bath and stirrer was switched off. Beaker glass filled with solution was taken out from water bath, then cooled before moulded. Solution was poured as much as 50 ml into mould, then dried in the oven at T=60 °C for 24 hrs. After being dried, pulled it out and dried it to dessicator for 24 hrs. Then plastic was removed from the mould. Plastic was ready to be analyzed.

2.4 Characterization of Starch
2.4.1 Moisture Content
Procedure of analyzing water content from avocado seed starch applied standard of AOAC : porcelain dish was dried first in the oven at 105 °C for 3 hrs, then cooled in the dessicator for 30 mins and weighed untill the weight was constant. Sample was scaled approximately 3 grams in dish. Then dried in oven at temperature 100 – 105 °C for 3 hrs or untill the weight was constant. The dish filled with sample was dried in dessicator then scaled untill the weight was constant.

2.4.2 Ash Content
Procedure of analyzing water content from avocado seed starch applied standard of AOAC : Sampel was scaled as much as 5 grams to be entered into porcelain dish. Dish filled with sample was fired on flame of bunsen burner untill no haze appeared anymore. Then entered into furnace with temperature 550 °C for ± 12 hrs. Dish filled with sample was cooled in the dessicator then scaled untill the weight was constant.

2.4.3 Starch, Amylose and Amylopectin Content
Analyzing of starch, amylose and amylpectin content was observed at Laboratorium Teknologi Pangan dan Hasil Pertanian Universitas Gadjah Mada.

2.4.4 Protein and Lipid Content
Analyzing of protein and fat content was observed at Laboratorium Jasa Uji Ilmu Fakultas Teknologi Industri Pertanian Universitas Padjajaran. Method used for this analyzing of protein content by method of Kjeldhal semimicro. Method used for this analyzing of fat content by direct extraction method utilizing soxhlet equipment.

2.5 Characterization of Bioplastic
2.5.1 Mechanical Properties
Test of mechanical properties involves tensile strength, elongation at break, and Modulus Young. Product of bioplastic chosen and cut forming specimen for tensile strength test based on standard of ASTM D 638.

2.5.2 Pasting behavior and gelatinization
Anayzing of gelatinization temperature was observed at Laboratorium Jasa Uji Ilmu Fakultas Teknologi Industri Pertanian Universitas Padjajaran by using Rapid Visco Analyzer (RVA).
2.5.3 Fourier Transform Infra Red (FTIR)
Analyzing of FTIR was observed at Laboratorium Penelitian Fakultas Farmasi, Universitas Sumatera Utara.

2.5.4 Scanning Electron Microscope (SEM)
Analyzing of SEM was observed at Laboratorium Terpadu Fakultas Matematika dan Ilmu Pengetahuan, Universitas Sumatera Utara.

III. RESULT AND DISCUSSION

3.1 Characterization Avocado Seed Starch
Based on sedimentation method [11] from 100 grams of avocado seed could produce avocado seed starch as much as 24.2 grams or percentage of starch earned was 24.20 %. Figure below could be seen that avocado seed starch produced was brown. Based on experiment of Andy dkk. (2013), the emerge of brown on avocado seed starch was caused avocado seed contained phenolic dopamine compound (3,4-dihidroxy phenilalanin). This phenolic compound caused reaction of browning enzymatically which was caused by reaction between oxygen and phenolic substance with catalyst polyphenol oxidaze [12].

![Avocado Seed Starch](image1)

Figure 1 Avocado Seed Starch
Characteristics of avocado seed starch was aimed to know the percentage of each component contained in the starch produced, include starch, water, ash, fat, protein, amylose, and amylopectin content so that known the quality of starch produced. The result of avocado seed starch characteristic was provided inside the Table of 4.1 as follows.

<table>
<thead>
<tr>
<th>Components of Avocado Seed Starch</th>
<th>Percentage (%)</th>
<th>Standard of Indonesia Industry (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>67.6950</td>
<td>min 75</td>
</tr>
<tr>
<td>- Amylose</td>
<td>32.4739</td>
<td>-</td>
</tr>
<tr>
<td>- Amylopectin</td>
<td>35.3212</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>1.087</td>
<td>max 14</td>
</tr>
<tr>
<td>Ash</td>
<td>1.013</td>
<td>max1.5</td>
</tr>
<tr>
<td>Fat</td>
<td>1.860</td>
<td>-</td>
</tr>
<tr>
<td>Protein</td>
<td>10.440</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Characterization of Bioplastic
3.2.1 Tensile Strength
This graph shows effect of temperature and filler chitosan on tensile strength property of bioplastic

![Tensile Strength Graph](image2)

Figure 2 Effect of Gelatinization Temperature and Chitosan on Tensile Strength of Bioplastic
From figure above could be seen the highest tensile strength value of bioplastic at temperature 90 °C by adding chitosan 3 grams earned the magnitude 5.096 MPa, while the lowest tensile strength at temperature 90 °C by adding chitosan 1 gram earned the magnitude 2.352 MPa.

Higher the enhancement of chitosan mass could cause tensile strength value of bioplastic becomes rising. Higher the enhancement of various mass of chitosan then higher the tensile strength produced. Chitosan added in starch solution was to fill and improve the bioplastic compactness, so increase the bioplastic endure when tensile strength test was observed. Beside that, chitosan could also experience the chemical bond with starch during mixing process. The chemical bond on the material could influence the mechanical properties, depends on the number and varieties of the chemical bonds (covalent, hydrogen, and van der walls bonds) [6]. This was supported by experiment of Bourtoom (2008) about the effect of plasticizer on biodegradable film mixture characteristics from rice starch with chitosan and various of plasticizers sorbitol, glycerol, and polyethylene glycol which was stated that tensile strength value will decrease when the plasticizer concentration usage was higher then strach mixture with chitosan ratios could add the tensile strength [14].

Higher the temperature enhancement can cause tensile strength value of bioplastic becomes higher. That thing is caused by effect of higher temperature which causes the intermolecular bond on starch chains become weaker so that starch can experience the breaking of amylose long chain bond. This is supported by the experiment of Utomo, dkk. (2013) which expressed that the existing effect of higher temperature causes more bioplastic particles experience the physical changes that forms plastic becomes more homogeneous and the structure more compact, by those characteristics indeed makes the tensile strength becomes higher [15].

3.2.2 Elongation at Break

This graph shows the effect of temperature and filler chitosan on the elongation at break of bioplastic

From figure above could be seen the highest elongation at break value at temperature 80 °C by adding chitosan 1 gram was 20.312 %, while the lowest value of elongation at break at temperature 80 °C by adding chitosan 3 grams was 14.016 %.

Higher the adding of chitosan number could effect 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 [16].

By higher temperature can cause elongation at break value of bioplastic becomes sagging. That thing was caused by the effect of the higher temperature that causes intermolecular bonds of starch weaker so diminishing the internal hydrogen bond among polymer chains and increasing the molecular space. This thing is supported by experiment of Pamilia, dkk. (2014) which is stated that the enhancement of heating temperature will decline the elongation percentage of edible film [17].
3.2.3 Modulus Young

This graph shows the effect of temperature and filler chitosan on Modulus Young of bioplastic

![Graph showing effect of temperature and chitosan on Modulus Young](image)

From figure above could be seen the highest Modulus Young value at temperature 90 °C by adding chitosan 3 grams was 36.359 MPa, while the lowest Modulus Young value at temperature 80 °C by adding chitosan 1 gram was 11.484 MPa.

The higher of adding chitosan can cause the enhancement on the value of Modulus Young. The higher addition of glycerol volume can cause the declining of Modulus Young value. 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. Tensile strength and Modulus Young constantly increase by adding filler inside [18].

The higher temperature can cause the higher of Modulus Young value. This is supported by experiment of Utomo dkk. (2013) which was stated that higher temperature and drying time can influence the magnitude of plasticizer volatilization from material then the material was more arid and easy to be torn so the elastic of the material declines [15].

3.2.4 Analyze of Functional Groups

This graph shows the FTIR result among avocado seed starch, chitosan, bioplastic without/by adding filler chitosan and plasticizer glycerol

![Graph showing FTIR result](image)

From figure 5 could be earned the analyzing result of FTIR avocado seed starch which owns O-H group binded with hydrogen, C-H alkanes, C=O and C-O ethers. The existing of those groups had represented the content of avocado seed starch which is consisted of amylose and amylopectin and reducing glucose (C₆H₁₂O₆)n [19].
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 has purpose to the vibration of amino stretching 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 characteristics of chitosan [20,21].

From figure 5 got the characteristics of bioplastic without adding filler chitosan and plasticizer glycerol and bioplastic with adding chitosan and plasticizer glycerol have the same functional groups yet the behaviour of spectrum on bioplastic without adding filler chitosan and plasticizer glycerol lies under spectrum of bioplastic with adding chitosan and plasticizer glycerol. This thing is caused by adding plasticizer glycerol which enhances moisturizer content of starch solution so the starch granule could move freely. Plasticizer is additive material which can soften if it is added in the material. To increase the film flexibility, plasticizer was used because it has the ability to diminish the internal hydrogen bonds among polymer chains and increasing the molecule space [22]. One example of plasticizers was glycerol. From the result of FTIR analyze can be seen the emerge of C=O aldehyde groups on starch is caused because the occurrence of the breaking glycoside chains form C=O aldehyde groups and OH groups at the tip of amyllose or amylopectin that exists on strach [19]. Beside the existing of OH groups, the existing of other functional groups was emerged in the bioplastic like carbonyl functional groups and ester functional groups. The existing behaviour of these groups makes bioplastic easy to be composed. The existing of OH alcohol groups, C-H alkenes, span of C-H aldehyde groups, span of C=O groups, span of C-O ester groups show the structure emerged on bioplastic [6].

The peak exists on the wavelength 1593.20 cm\(^{-1}\) on bioplastic product with adding filler chitosan and plasticizer glycerol. This wavelength shows the existence NH groups which aims to vibration of amino stretching from a set of chitosan [20]. This thing shows that filler chitosan has been spread in bioplastic product. From figure 4.5 was earned the bioplastic spectrum of avocado seed starch with filler chitosan and plasticizer glycerol emerged on the bioplastic spectrum of bioplastic without adding filler chitosan and plasticizer glycerol. From the analyze result of FTIR on figure 5 can be seen that the formed of O-H groups on the wavelength 3618.46 cm\(^{-1}\). The thing shows the existing interaction among avocado seed starch, glycerol with chitosan as the compact effect by the changes of functional groups and the formation of O-H groups which is earned from the analyze result of FT-IR.

3.2.1 Analyzing Morphology of Bioplastic Surface

Characteristics of SEM (Scanning Electron Microscope) bioplastic without adding filler chitosan and plasticizer glycerol and bioplastic with adding filler chitosan and plasticizer glycerol are shown on figure 6 below.

![Figure 6 Analyzing Morphology of Bioplastic Surface](image)

Gambar 6 menunjukkan hasil analisa SEM produk bioplastik dengan penambahan pengisi kitosan dan Figure 6 shows the result of analyzing SEM on bioplastic product with adding filler chitosan and plasticizer glycerol by magnification 1000. On figure 6 can be seen that avocado seed starch has been spread well when it is mixed and formed the good unity. On the figure could be seen that the surface of bioplastic looked smooth because the existing of adding plasticizer and a little bit found space for the existing of adding chitosan as filler so when the tensile strength was observed, the product will have better capability. Need to notice that by adding more plasticizer, melting viscosity decreases which makes starch is hard to be plasticized, because the movement declines furing the process [23]. At this time, the best bioplastic product on adding filler chitosan 3 grams and plasticizer glycerol 0.2 ml/gram.
3.2.2 Pasting Behavior and Gelatinization Temperature

There are several methods to determine the nature of the starch; for example, the behavior of gelatinization is determined using Differential Scanning Calorimetric (DSC) and Rapid Visco Analyzer (RVA) [24]. In this study, the method used for gelatinisasi behavior is determined by using the Rapid Visco Analyzer (RVA) [25]. RVA analysis purposes (Rapid Visco Analyzer) is to determine the profile of starch. On gelatinization temperature profile above, we begin the first phase of the curve, the temperature is still below the starch gelatinization temperature, so low that the viscosity measured start of starch subjected to thermal treatment temperature 47 °C. Then enter a second phase, the temperature is then increased slowly until it reaches a temperature of gelatinization, which is the temperature at which the starch granules begin to swell and the viscosity increases. bioplastics with chitosan filler and plasticizer glycerol is 95.04 °C. The maximum viscosity (peak viscosity) is the point of maximum viscosity of the paste produced during the heating process. The maximum temperature at which the viscosity of the final temperature is reached is called gelatinization. At this temperature the starch granules have lost its birefringence properties and crystal granules have been no longer [26]. When most of the starch granules swell, there was a rapid increase in viscosity. In this phase, the value of peak viscosity (peak viscosity) for bioplastics with chitosan filler and plasticizer glycerol is 191 cP. The third phase, currently fixed temperature rises to 95 ° C temperature and stirring continued (holding), granules and amylose starch will break out of the granules into a liquid, which causes the viscosity decreases. At this phase viscosity values resulting from the continued stirring give viscosity values for bioplastics with chitosan filler and plasticizer glycerol amounted to 185.5 cP. At this phase of amylopectin changed into an amorphous phase, a phase in which the starch is in the transition phase between solids and liquids [27]. In the fourth phase, the mixture is then cooled, causing the association back between starch molecules (setback). Behind viscosity (setback viscosity) reflects the ability of an association or retrogradation of starch molecules in the cooling process. Avocado seed starch which has the highest viscosity behind, this suggests avocado seed starch retrogradation faster experience. This phenomenon is common because the starch granule gelatinization time does not expand to the maximum, as a result of energy to break intermolecular hydrogen bonds less. When cooling occurs, amylose can be joined quickly forming insoluble crystals [26]. The viscosity values behind for bioplastics with chitosan filler and plasticizer glycerol amounted to 128.5 cP forming gel and viscosity again increased until it reaches the final viscosity. Final viscosity grades of bioplastics with chitosan filler and plasticizer glycerol amounted to 314 cP. At this heating value derived bioplastics break down with filler and plasticizer glycerol chitosan based measurement using RVA of 5.5 cP.

IV. CONCLUSION

Based on the results of research can be concluded that the analysis of avocado seed starch obtained moisture content 1.087 %, ash content 1.007 %, starch content 67.6950 %, amylose content 32.4739 %, amylopectin content 35.3212 %, protein content 10.440 %, fat content 1.860 %, gelatinization temperature of 85.17 °C with the peak viscosity was 3847 cP and the best condition of bioplastics from starch avocado seed obtained at temperature 90 °C with comparison of starch: chitosan (w/w) = 7: 3 and plasticizer glycerol 0,2 ml/gram with tensile strength 5.096 MPa, elongation at break 14.016%, Modulus Young 36.359 MPa.
Effect of Gelatinization Temperature and Chitosan...