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Utilization of Avocado Seeds as Bioplastic Films Filler Chitosan and Ethylene Glycol Plasticizer

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The purpose of this study is to determine the effect of ethylene glycol plasticizer on bioplastic characteristics including density, tensile strength, elongation at break, modulus of elasticity, scanning electron microscope, rapid visco analysis and functional groups. The bioplastic film was made from avocado starch filler chitosan using casting method of dissolving chitosan and starch solution with certain variations into hotplate magnetic stirrer and variation of ethylene glycol 5, 10, 15, 20 and 25 % w. Bioplastic characteristics were obtained by bioplastic density 203 g/cm^3, tensile strength 30.213 MPa, elongation at break 5.370 %, modulus of elasticity 2031.326 MPa, temperature of bioplastic gelatinization 91.55 °C.

Keywords: Avocado seeds, Bioplastic films, Chitosan, Ethylene glycol.

INTRODUCTION

The use of packaging plastics each year has increased [1], potentially producing waste that is difficult to biodegradable [2], so needed environmentally friendly plastic material (bioplastic). The research of bioplastic film usually using cellulose, protein and starch materials [3,4]. The study on starch-based bioplastic film is growing rapidly because starch is easy to obtaining and processing [5]. Research on starch-based bioplastic film has been done, including using sweet potato, rice, potato and sago [6-9]. Starch-based bioplastic films such as starch from cassava, rice and potatoes should be avoided because they interfere with food security [10], for it needs to be studied starch from unuseful grains. Study on starch-based bioplastic film from seed waste has been done such as using durian seed, jackfruit seed and others, Generally durian seed starch and jackfruit seeds have high amylose content that can be used as bioplastic materials [5,11]. Lubis *et al.* [11] reported that bioplastic from jackfruit seed has high tensile strength with 70.22 % starch and 16.39 % amylose.

This work using avocado starch because it is content starch 73.62 % and amylopectin 73.55 % so that avocado seed has potential to be plastic film material. Manufacturing this plastic film using casting method, heating the mixture of starch-filler solution at temperature approaching gelatinization [12], starch-based bioplastics have been weaknesses among others are hydrophilic, less hydrophobic and low mechanical properties, so it is necessary to additing microcrystalline cellulose fillers, chitosan (0.37-1.45 %) and corn fibers [13-15]. Manufacturing bioplastic film of starch and filler solution is rigid at heating time and hard at cooling time, so needed to additing plasticizer before drying solution. The purpose of additing the plasticizer to improve the elastic of bioplastics properties, Plasticizer is added, usually group of polyols such as glycerol and sorbitol [5,16]. The aim of this research is to know the effect of ethylene glycol plasticizer on bioplastic characteristics including density, tensile strength, elongation at break, modulus of elasticity, scanning electron microscope (SEM), rapid visco analysis (RVA) and functional groups.

EXPERIMENTAL

Avocado seeds are obtained from ice sales pokat shake Binjai, North of Sumatera Province. The avocado seeds are extracted to be starch and made a particle size of 100 mesh [11]. All chemicals such as acetic acid, chitosan, ethylene glycol and formic acid are obtained from UD. Rudang Jaya Medan, North of Sumatera.

Manufacture bioplastic: The starch and chitosan mass were weighed at a ratio of 7:3 [17]. Heat a mixture of starch solution (starch: aquades = 1:20) and chitosan solution (chitosan/acetic acid 1 % v 3: 130 w/v) in 500 mL beaker glass using hot plate magnetic stirrer at varied temperature (70, 80 and 90 °C) [12]. After 20 min added sorbitol to homogeneous solution. The bioplastic solution is poured into 20 cm^3 × 20 cm^3 × 0.3 cm^3 acrylic plate molded by oven at 45 °C for 24 h. After drying into the desiccator for 24 h.

Characterization of bioplastic

Density: Analyzing of bioplastic density was observed based on standard of ASTM D 792-91 1991 in the Physical Chemistry Laboratorium University of Sumatera Utara.

FTIR: Analyzing of FTIR was observed at Research Laboratory, Faculty of Pharmacy, University of Sumatera Utara by using instrument IR Prestige-21 Fourier Transform Infrared Spectrophotometer with Serial Number A21004602022 LP, Power 220-240 V 50/60 Hz produced by Shimadzu Corporation.

Mechanical properties: Bioplastic samples were made into specimens analyzed by tensile strength (ASTM D638-02a 2002), elongation at break (ASTM D792-91 1991) and elastic modulus using autograph-shimadzu servo control computer system universal testing machine model AI-7000 M Capacity 2000 kg, Power 1Φ 220 V 50 HZ.

Analysis of gelatinization profile: The gelatinization temperature was observed at Laboratorium Jasa Uji Ilmu Fakultas Teknologi Industri Pertanian Universitas Padjajaran by using rapid visco-analyzer (RVA).

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR): Characteristics of Fourier transform infrared (FTIR) chitosan, bioplastic without/with chitosan filler and ethylene glycol plasticizer to identify functional groups are presented in Fig. 1.

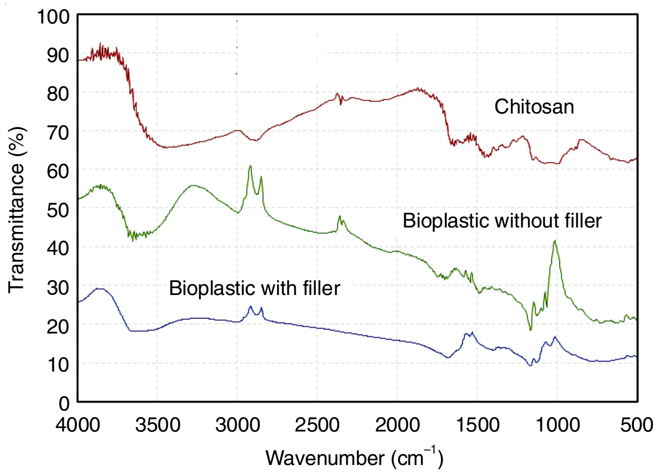

Fig. 1. Fourier transform infrared of chitosan, bioplastic without/with filler chitosan and ethylene glycol

Fourier transform infrared analysis showed chitosan filler had N-H group, wavenumber 1589.34 cm^{-1}, C-H alkana group with wavenumber 894.97 cm^{-1} and 999.13 cm^{-1}. The wavenumbers 1076.28 cm^{-1} and 1149.57 cm^{-1} represent the alcohol, ether, carboxylic acid and C-O ester groups. Wavenumber 1315.45 cm^{-1} and C-N amine-bonding group. The absorption peak at wavenumber 1651.07 cm^{-1} indicates the presence of C=O anhydride bonding group, at wavenumber 2881.65 cm^{-1} indicates the presence of C-H alkanes. The wavenumber 3437.15 cm^{-1} indicates the presence of an O-H group. Chitosan shows the presence of OH, NH_2, C=O amide and CH_3 groups.

Fig. 1 also showed the bioplastics without chitosan filler wavenumber 725.23 and 775.38 cm^{-1} showing the presence of C-H groups, wavenumbers 1122.57 and 1172.72 cm^{-1} which are due to the presence of alcohols, ethers, carboxylic acids, C-O esters. The wavenumber 1489.05 and 1593.20 cm^{-1} show the aromatic group C=C. The wavenumbers 2877.79 and 2993.352 cm^{-1} show the C-H alkane groups. The wavenumber 3557.45 cm^{-1} shows the hydrogen bonding group O-H. The groups seen in the bioplastic without chitosan are exactly the same as the constituent groups of avocado starch.

It also showed bioplastic with chitosan filler and plasticizer of the absorption peak at 3622.32 cm^{-1} wavenumber is the presence of O-H group of alcohols. Wavenumbers 2877.79 and 2997.38 cm^{-1} are clusters of C-H alkanes and C-H aldehydes. The wavenumber 783.10 and 721.38 cm^{-1} indicating the presence of C-H alkenes. The wavenumbers 1126.43 and 1172.72 cm^{-1} indicate the presence of alcohols, ethers, carboxylic acids and C-O esters, respectively. The absorption peak at wavenumber 1404.18 cm^{-1} showed an aromatic group C=C. The wavenumber 1550.77 cm^{-1} shows the primary and secondary groups of N-H amines. The wavenumber 1681.93 cm^{-1} show the presence of C=C alkenes. The wavenumber 1550.77 cm^{-1} indicates the presence of NH_3 group [16].

Density of bioplastic: The effect of variation chitosan filler and ethylene glycol plasticizer on bioplastic film density is presented in Fig. 2.

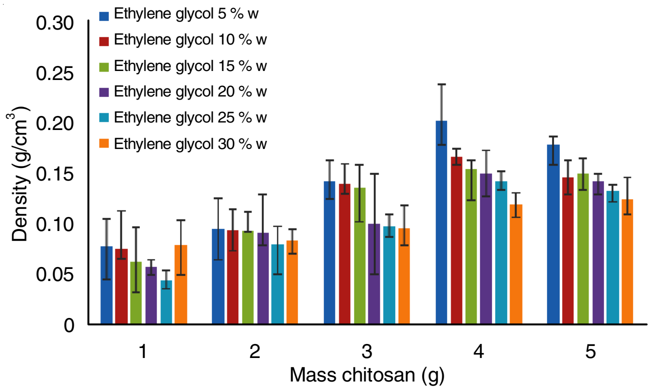

Fig. 2. Effect of variation chitosan filler and ethylene glycol plasticizer on bioplastic density

Fig. 2 showed the fluctuation of bioplastic film density on the addition of chitosan filler and ethylene glycol plasticizer, the increased density from addition 2 g until 4 g of chitosan and decreased at 5 g. The highest bioplastic film density was 0.203 g/cm^3 at 4 g chitosan and plasticizer ethylene glycol 5 % w. Increasing density of bioplastic film caused by dispersed chitosan solution in starch solution so that the bioplastic film structure is getting closer. The density will increase accompanied with the filler percentage in the composite [18]. The solubility of 5 g chitosan in the formic acid solvent decreasing film density and the film solution start saturate so that the bioplastic structure becomes porous. The addition of ethylene glycol plasticizer generally reduces the density of the bioplastic film. The decrease in film density is caused the formation of hydrogen bonds on the polymer chain, so that the polymer chain structure is more porous. Ethylene glycol decreases the internal forces between the polymer chains, thereby decreasing the level of bioplastic rigidness [19].

Tensile strength: The effect of chitosan variation and ethylene glycol plasticizer on the tensile strength properties of bioplastic film is presented by Fig. 3.

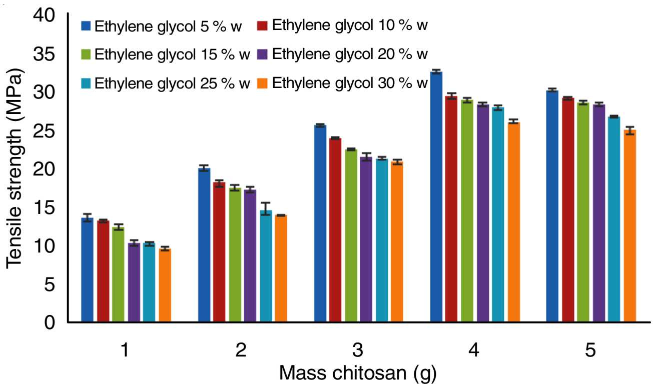

Fig. 3. Effect of chitosan filler variation and ethylene glycol plasticizer on the properties of biolastic tensile strength

Fig. 3 showed increasing chitosan filler effected on tensile strength. The additing of chitosan filler from 1 to 4 g increased the tensile strength, but the addition of 5 g chitosan make value decreased. Highest tensile strength 30.213 MPa on 4 g of chitosan and plasticizer ethylene glycol 5 %w. The increasing of tensile strength is caused to the solution of chitosan dispersed with starch solution to form a closer bioplastic film structure. The tight structures affected the density value. Density is higher then tensile strength increases. FTIR analysis showed addition of O-H and N-H groups from chitosan so that increasing the strength of intermolecular bonds and tensile strength, but the addition of 5 g of chitosan decreasing tensile strength, because the solubility of chitosan in the formic acid solvent is decreasing. The film solution start saturate, the chitosan filler is not completely dissolved in the formic acid solvent so that bioplastic structure porous resulting in decreasing density.

The effect of addition ethylene glycol plasticizer causes decreasing bioplastic tensile strength. The smallest tensile strength of 9.579 MPa on 1 g of chitosan and plasticizer ethylene glycol 1 % w. The decreasing of tensile strength is supported by Bourtoom [20], effect plasticizer on the biodegradable film mixture properties of rice starch with chitosan and variation of sorbitol, glycerol and polyethylene glycol plasticizer. The value of tensile strength will decrease as the use of plasticizer concentration then chitosan difference can increasing tensile strength.

Elongation at break: The effect of chitosan variation and ethylene glycol plasticizer on the elongation at break bioplastic properties is shown in Fig. 4.

Fig. 4 showed fluctuative elongation at break. Elongation at break down from chitosan mass 1 to 5 g. The elongation at break the highest bioplastic is 5.370 % on chitosan 1 g and plasticizer ethylene glycol 25 %w. Chitosan solution with starch solution form a tight bioplastic structure thereby increasing the density and tensile strength, otherwise decreasing the elongation at break. The tensile strength is inversely proportional to the elongation at break. The addition of ethylene glycol, causing increasing elongation at break of bioplastic, This statement is supported by the study of Zhang *et al.* [8]. Zhang *et al.* [8] reported the characteristics of film-based thermoplastic potato flour with addition of plasticizer increasing the value of elongation at break. Plasticizer is an additive that is added to making the material more elastic. Plasticizer is used because it has the ability to reduce the internal hydrogen bond between the polymer chains as well as increasing the molecular space [8].

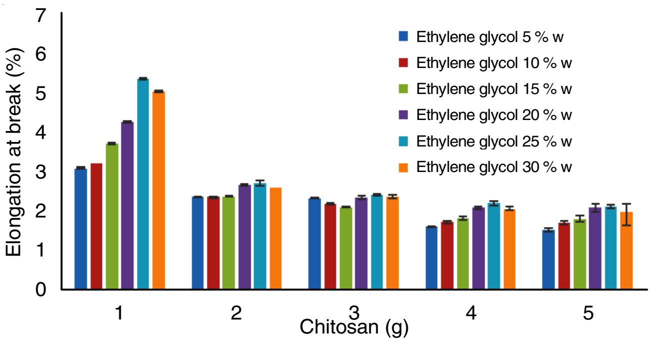

Fig. 4. Effect of chitosan variations and ethylene glycol plasticizer on elongation at break biolastic properties

Modulus of elasticity: The effect of chitosan variation and ethylene glycol plasticizer on modulus of elasticity bioplastic is shown in Fig. 5.

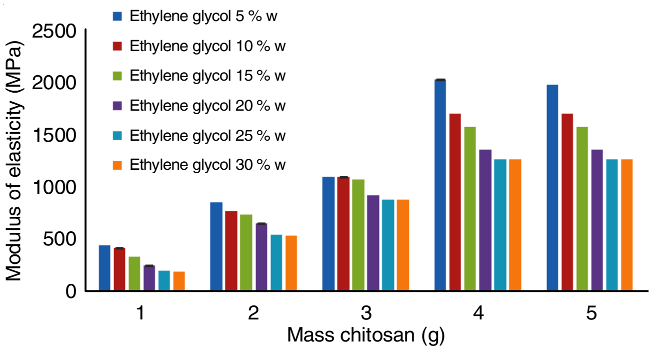

Fig. 5. Effect of variation chitosan filler and ethylene glycol plasticizer on modulus of elasticity bioplastic

Fig. 5 showed an increasing at chitosan from 1 to 4 g causing an increasing in modulus of elasticity, when the addition on 5 g chitosan modulus of elasticity decreasing. The highest modulus of elasticity bioplastic was 2031.326 MPa at 4 g chitosan and 5 % ethylene glycol plasticizer. The addition of chitosan increasing modulus of elasticity, this causes bioplastic density to increase and forming of hydrogen bonds, so the bioplastic are strong and rigid. Plasticizer is used because it has the ability to reduce the internal hydrogen bond between the polymer chains as well as increasing the molecular space. The higher the using plasticizer reduces the level of bioplastic rigidness.

Rapid visco analyzer (RVA): The purpose of rapid visco analyzer (RVA) determine the profile of bioplastic gelatinations. This characterization is related to the measurement of starch viscosity with a certain concentration during heating and stirring (Fig. 6).

Rapid visco analyser measured pasting temperature, peak viscosity, viscosity hold, final viscosity, viscosity breakdown and setback viscosity. The gelatinating process is a state of heating the starch at certain temperature with excess amount

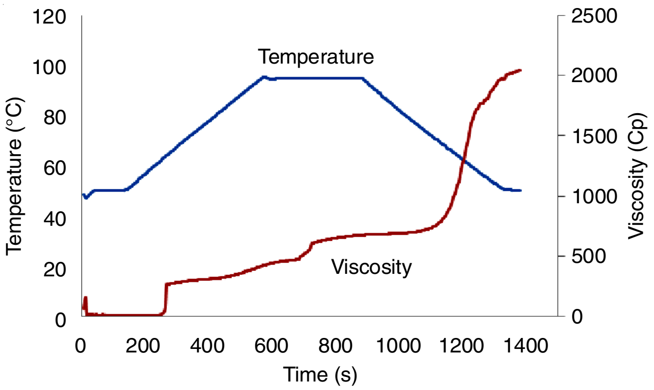

Fig. 6. Profile of bioplastic gelatinization with addition of chitosan and ethylene glycol

of water to allow the starch to be an increase in swelling power. When the viscosity start increase called pasting temperature. The optimum viscosity or peak viscosity (PV) is a parameter that shows the ability of starch granules to bound water and retain swelling during heating. During the sample holding period it is still affected by the mechanical stress-strain properties that may cause further disruption of starch granules. Viscosity during the holding period is called hold viscosity. When the sample is periodically cooled, the viscosity increases to final viscosity which is related to the process of retrogradation of the amylose molecule. Breakdown viscosity is the difference between peak viscosity and hold viscosity is stability of the paste to warming. Setback I is the difference between hold viscosity and final viscosity, indicating the ability of the starch paste to be retrograde is the process of re-forming the starch matrix at gelatinization. The Setback viscosity implies degrees of retrodegradation [21]. Fig. 6 showed the gelatinization temperature profile, gelatinization begins in the first phase of the curve, the temperature is below the starch gelatinization, so the viscosity is measured low, starch starts to be subjected to thermal treatment at 48 °C. The second phase, temperature is increased slowly until reaches the temperature of gelatinization. The temperature of gelatinization is the temperature at which starch granules begin to swell and the viscosity increases. Fig. 6 showed the temperature of chitosan filler gelatinization with ethylene glycol plasticizer of 91.55 °C. The peak viscosity phase, the highest viscosity value of the bioplastic peak is 680 cP.

Third phase, the stirring (holding) continuously until the temperature is 95 °C and the starch granules will break, Amylose out of the granule to be liquid causing the viscosity is decrease. This phase the viscosity value is 551 cP, Amylopectin change to amorphous phase, the phase in which starch is in the transition phase between solids and liquids. The fourth phase, the cooled mixture causes the re-association between starch molecules (setback). Setback or change of viscosity during cooling, obtained from the difference between the final viscosity and the viscosity after heating. The higher of the setback value, so the tendency to form gel (increase viscosity) during cooling is getting higher too. The high of setback value indicates for retrodegradation. The setback is a measure of recrystallization gelatinated starch during cooling. The bioplastic reverse viscosity value is 430 cP so that gel is formed and the viscosity is increased until it reaches the final viscosity. The viscosity value of bioplastic is 892 cP.

Scanning electron microscope: Scanning electron microscope (SEM) of bioplastics is shown by Fig. 7. In Fig. 7(a) bioplastic looks has unsmooth and flat surface, caused poor interaction between filler and starch. The filler has not yet filled the entire matrix space of avocado starch. Fig. 7(b) showed a rough and coarse bioplastic fracture surface, the bioplastic fracture have an uneven and void morphology caused to the attraction experienced by bioplastics during tensile strength testing. The tensile forces cause bioplastic bonding to be disturbed because of distantly space or uneven surface.

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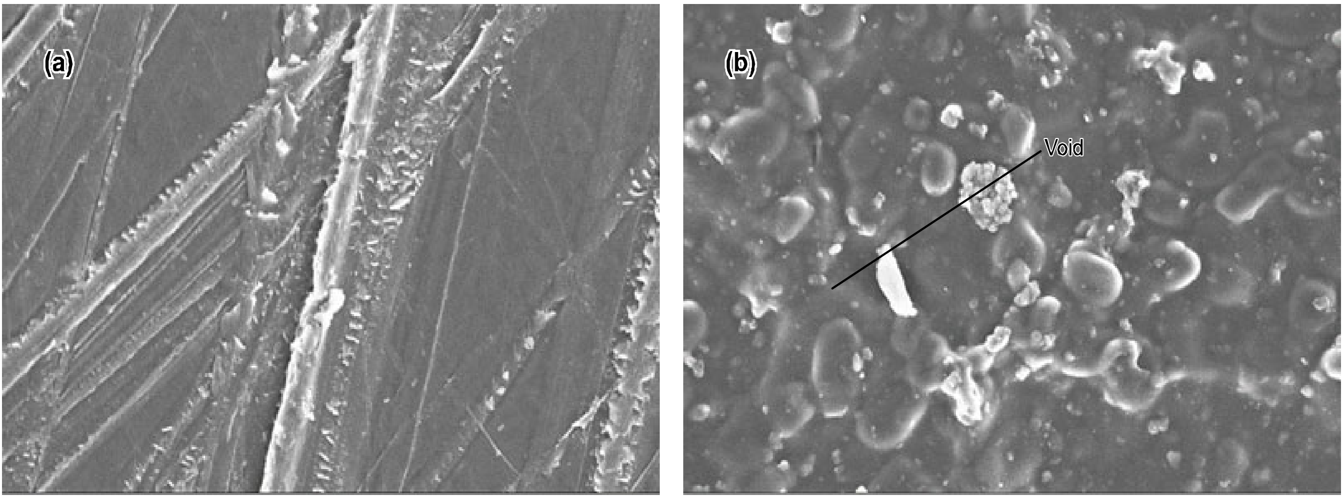

Fig. 7. Scanning electron microscope analysis fracture of bioplastic product (a) Bioplastic with 4 g chitosan addition and 25 % ethylene glycol plasticizer before tensile strength test with 1000x enlargement and (b) Bioplastic with 4 g chitosan addition and ethylene glycol 25 % plasticizer after tensile test with 1000x enlargement

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