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Optimization of Biodegradable Plastic Processed from Avocado Fruit Waste Using Hydrolysis Methods with and Without the Addition of Plasticizers and Chitosan

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Abstract. Avocado waste is currently not used optimally, only disposed of as waste that is not useful and causes environmental pollution. In avocado waste, there is a high concentration of starch, about 80.1%, consisting of 44.3% of amylose, 37.7% of amylopectin, 10.2% of water, 1.21% of crude fiber, 31.3% of starch yield, and 15 to 20% of oil. Avocado seeds and skins have the potential for the production of organic biodegradable plastic. In order to produce biodegradable plastics, three different methods are used: (1) hydrolysis in an acidic medium (2) hydrolysis followed by plasticization (3) hydrolysis and mixing of chitosan. The results showed that the combination of hydrolysis, mixing of chitosan, and plasticization was very important to obtain a material with optimal mechanical properties and biodegradability to be used as biodegradable plastic. In addition, it can reduce organic waste pollution, because all avocado waste, namely seeds and skins is used as materials for making biodegradable plastic so that nothing is wasted.

INTRODUCTION

Waste or garbage is the residual waste produced by any living being that is no longer needed. Based on Law No. 18 of 2008 on Waste Management, many innovations have emerged in the Community to transform waste into useful materials/objects that have economic value. Depending on the type of waste, a distinction is made between inorganic and organic waste. Inorganic waste is waste that consists of inorganic materials. Examples of inorganic materials include metal, plastic, glass, rubber, and cans. Plastic waste is one of the biggest problems in the world because it is overused, difficult to degrade, and has a very large total mass, which harms the environment, especially single-use plastic, which is often used for food packaging and can only be used once before being disposed of [1]. Inorganic waste is long-lasting and difficult to degrade. These wastes are not easily degraded by soil microorganisms. If inorganic wastes are disposed of carelessly, they can pollute the soil. Organic wastes are wastes that are composed of organic matter. Organic wastes are not naturally durable and decompose quickly. Usually, this type of waste comes from living things. Examples include vegetables, rotting fruit, rice scraps, leaves, and so on. Organic waste is easily decomposed by microorganisms in the soil. However, this type of waste causes unpleasant odors if not disposed of properly. Most wastes are organic wastes that decompose easily and are biodegradable. The amount of organic waste is growing every day as the population increases [2]. One of the largest sources of organic waste is the market. One of the market traders that produce the most organic waste is a trader who deals in different types of fruits. Along the way from transport to storage of the fruits, there are of course fruits that are defective or spoiled, so they are no longer used or thrown away by the traders. Avocados are fruits that are sold in large quantities in the fruit market, especially when the harvest season arrives.

The avocado is a fruit that is in great demand by the public because it not only tastes delicious but also has a high nutritional value, containing carbohydrates, protein, fat, and various vitamins and minerals such as sodium, potassium, calcium, and iron. However, avocados have a weak point: they are easily damaged or decomposed by shocks during transportation and storage. If the avocado waste generated in a week is 70 kg, the waste of avocado seeds amounts to

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19.25 kg per week. Although considered waste, avocado seeds still contain carbohydrates or starch and other important components that can make avocado seeds an alternative food source [3]. Avocado has a high starch content of 80.1% [4]. Avocado is one of the tropical plants grown in the highlands. The fruit is not only consumed directly but also processed to produce avocado oil, leaving the peel and avocado seeds as residues. These residues are rich in carbohydrates such as pectin, cellulose, hemicellulose, and starch and have the potential to produce value-added materials for the food, cosmetic, and pharmaceutical industries [5]. Avocado seeds are a site for food storage in avocado plants, and starch is the main component of food reserves in fruit seeds, so the starch content in avocado seeds is relatively high, about 80.1%, consisting of 44.3% of amylose, 37.7% of amylopectin, 10.2% of water, 1.21% of crude fiber, 31.3% of starch yield, and 15 to 20% of oil [6]. In addition, avocados are an important source of bioactive compounds due to their antioxidant activity, which makes them very attractive for the production of food packaging [7]. For this reason, avocado waste, which consists of the skin and seeds of the fruit, has the potential to produce biodegradable plastic.

Biodegradable polymers, commonly known as bioplastics, are made from materials derived from organic compounds. Bioplastics can be decomposed by the environment with the help of microorganisms and water [8]. The development of biodegradable plastics or bioplastics is widespread in Indonesia and other countries, starting from agricultural wastes such as fruit seeds, coconut shells, potato peels, wheat straw, oil palm, sugar palm, corn starch, and rice husks, which are classified as renewable sources [9]. Biodegradable plastic is a type of plastic composed almost entirely of renewable materials such as starch, vegetable oil, and microbiota, which are usually derived from renewable energy sources such as cornmeal, potatoes, tapioca, bagasse, and algae. Generally, they are fully or partially biodegradable/compostable depending on their nature [10]. Biodegradable plastics intended for biodegradation can be degraded in either anaerobic or aerobic environments, depending on the method of manufacture. There are a variety of biodegradable plastics that can be made from starch, cellulose, or other biopolymers. Some of the most common applications of biodegradable plastic are packaging materials, tableware, food packaging, and insulation [11]. Biodegradable plastics depend on the physical and chemical structure of the polymer chains, functional groups, and crystallinity. In addition, biodegradable plastics also depend on the environmental conditions to which they are exposed, such as moisture, oxygen, temperature, and pH [12]. Biodegradable plastic made from starch is the most commonly used biodegradable plastic because pure starch has the property of absorbing moisture. Starch is a polysaccharide found in plant cells and some microorganisms. The starch contained in plant cells is in the form of granules (granules) with a diameter of several micrometers. The starch granules contain a mixture of two different polysaccharides, namely amylose and amylopectin [13]. Amylose is a polysaccharide, a polymer composed of glucose as a monomer. Each monomer is linked by -1,4-glycosidic bonds. Amylose is an unbranched polymer that is a component of starch along with amylopectin. When a starch suspension is heated in water, the first granules swell until a point is reached where irreversible swelling occurs. This swelling process is called gelatinization. In addition, biodegradable plastics are defined as plastics that come from biological sources and are formed from renewable raw materials or by a variety of microbes, and therefore biodegradable plastics can reduce negative environmental impacts. In the production of biodegradable plastics from starch, other materials such as plasticizers and/or chitosan are needed to improve the mechanical properties of the resulting biodegradable plastics.

A plasticizer is an additive added to natural polymers as a plasticizer because a mixture of pure natural polymers will produce brittle and brittle properties that will increase flexibility and prevent the polymer from cracking. So the addition of plasticizers to overcome the brittle nature of plastic. Some plasticizers that are often used in the manufacture of plastics are glycerol and sorbitol. Glycerol and sorbitol are widely used as plasticizers due to their stability and non-toxicity. Glycerol and sorbitol are plasticizers to reduce brittleness and increase flexibility and film resistance, especially when stored at low temperatures. Mchugh and Krochta (1994), stated that polyols such as sorbitol and glycerol are plasticizers that function to reduce internal hydrogen bonds so that they will increase intermolecular distances. Apart from plasticizers, another material used in the manufacture of biodegradable plastics is chitosan. Chitosan is a non-toxic biodegradable polymer with a high molecular weight. Chitosan is one of the promising renewable polymeric materials for broad applications in the pharmaceutical and biomedical industries as immobilized enzymes [14]. Chitosan is a biomaterial obtained by the deacylation of chitin from shrimp shells with sodium hydroxide. Due to the environmentally friendly and non-toxic nature of chitosan, chitosan is widely used to synthesize materials that are biodegradable [15]. The use of chitosan as a filler in the process of bioplastic synthesis because chitosan can form clear, strong, and flexible thin films [16].

EXPERIMENTAL METHODS

Materials

The avocado seeds and skins used come from ripe avocados sourced from fruit juice vendors in the Situbondo District area. The seeds and fruit peels were washed by hand with tap water. They were then dried in the sun for about 2 days or 48 hours until they are completely dry. The dried avocado waste is mixed with a special powder machine. To obtain a fine powder, it is sieved with a sieve with a mesh size of 200, as shown in Fig. 1. The plasticizers used in this study were glycerol and sorbitol. The chitosan used in this study was pharmaceutical grade A (Krebs) chitosan.

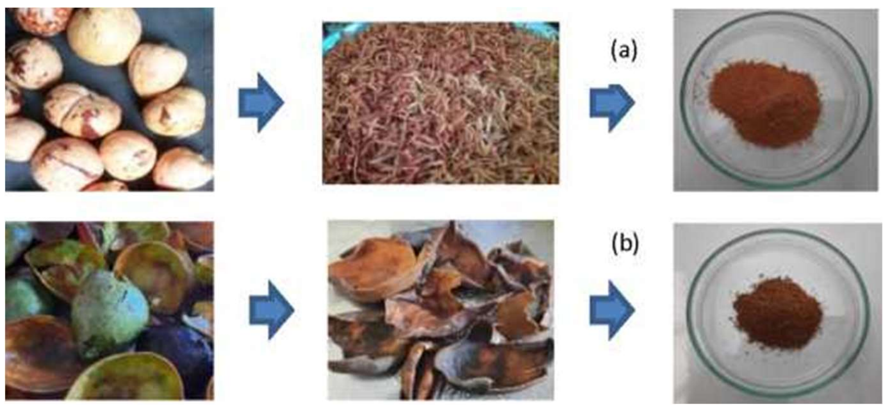

FIGURE 1. Process of making (a) seed powder and (b) avocado skin

Methods

Attempts were made to obtain biodegradable plastic from seed starch and avocado skin by mixing seed powder and fruit peel in a ratio of 50% by weight of seed and 50% by weight of avocado skin to obtain a mixed powder of avocado peels seeds (APS). To find out the effectiveness of the hydrolysis method with and without added plasticizers in producing biodegradable plastic from processed avocado waste, biodegradable plastic was produced by 3 hydrolysis methods. The following are the research methods carried out:

(1) Hydrolysis in acidic media
Five grams of seed powder, peel, and APS were dissolved in 50 ml of distilled water and 5 ml of 1 N HCl solution was added and stirred for 2 hours. Then 10% NaOH solution was added until the pH was in the range of 6.8 to 7 using a meter (pH). The mixed solution was stirred again and heated at a temperature of 65 to 85°C for ±30 minutes and printed in a Petri dish covered with aluminum foil. The samples were then placed in the sun to dry.

(2) Hydrolysis with plasticization
In the same way, 5 grams of APS powder was dissolved into 50 ml of distilled water and 5 ml of 1 N HCl solution was added and stirred for 2 hours. Then, 10% NaOH solution was added until it became a normal pH in the range of 6.8 to 7 using a pH meter. The solution of seeds, skin, and APS was added with a plasticizer of sorbitol and glycerol with a volume ratio of 1:1 and then added plasticizer with a composition of 6 ml, 8 ml, and 10 ml. The mixed solution was stirred again with heating at a temperature of 65 to 85°C for ±30 minutes and printed in a petri dish covered with aluminum foil. Next, the samples were dried in the sun to dry.

(3) Hydrolysis with the addition of chitosan
One point five (1.5) grams of chitosan powder was dissolved in 40 ml of 1 N HCl acid media and stirred for ± 30 minutes and neutralized using 10% NaOH solution. APS solution was made by dissolving APS powder into distilled water and soaking it for 12 hours and stirring again for ± 30 minutes. The two solutions are then stirred again with heating at a temperature of 65 to 85°C. until the solution boils completely for about 30 to 45 minutes. The fully mixed biodegradable plastic solution is poured into molds or Petri dishes. Next, the samples were dried in the sun to dry.

RESULTS AND DISCUSSION

Hydrolysis in acidic media

From the results of making biodegradable plastic using the hydrolysis method in acid media, the biodegradable plastic films of seeds, skins, and APS have very brittle mechanical properties, this is shown by the presence of cracks in the sample as shown in Fig. 2. This indicates a poor cohesive bond between the particles, so the sample was not analyzed further. To improve this condition, the researchers tried to increase the stirring time to 1 hour, but the result was still the same with cracks in the sample drying process so it was not analyzed further.

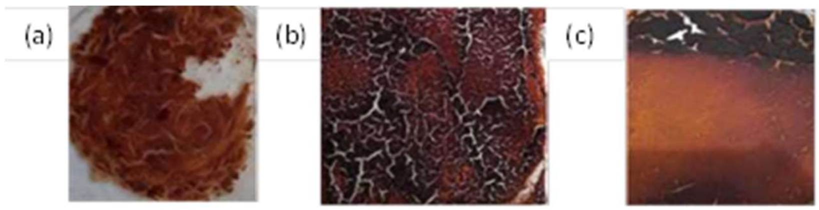

FIGURE 2. Appearance of biodegradable plastic film (a) avocado seed; (b) avocado skin; and (c) APS resulting from hydrolysis of acid media

Hydrolysis with plasticization

From the results of making biodegradable plastic using the hydrolysis method in acidic media accompanied by plasticization using a plasticizer mixture of sorbitol and glycerol with a 1:1 composition of 6, 8, and 10 ml on APS powder, it was found that the plasticizer was able to improve the properties of the resulting biodegradable plastic. This can be seen from the visual of the resulting biodegradable plastic film sample, no cracks appear as shown in Fig. 3.

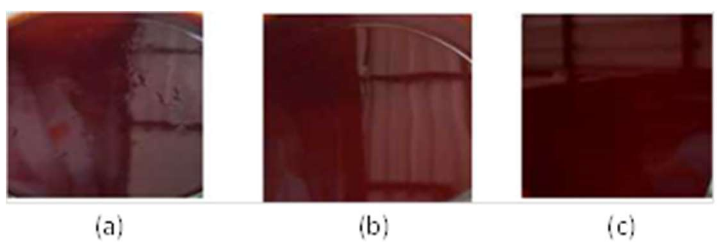

FIGURE 3. Appearance of biodegradable plastic film (a) APS06; (b) APS08; and (c) APS10 resulting from hydrolysis of acid media with plasticization

From the appearance of the biodegradable plastic samples above, it can be seen that the more the amount of plasticizer added, the samples with smoother and darker surfaces are obtained. This shows that the addition of plasticizers can improve the properties of biodegradable plastic produced in first method, it appears that the cohesion bonds between particles are stronger and the gelatinization process can occur quite optimally than before. However, the drawback of this method is that in the drying process, the sample takes a very long time to become a biodegradable plastic film as desired. This is in line with previous research [17]. This showed the addition of plasticizers could reduce the crystallinity process of biodegradable plastic samples as indicated by the XRD test results where the initial sample (without plasticizer) was amorphous (B), namely the avocado skin powder sample or polymorph (A) is avocado seed powder which is indicated by changes in the pattern of X-ray diffraction peaks, as shown in Fig. 4.

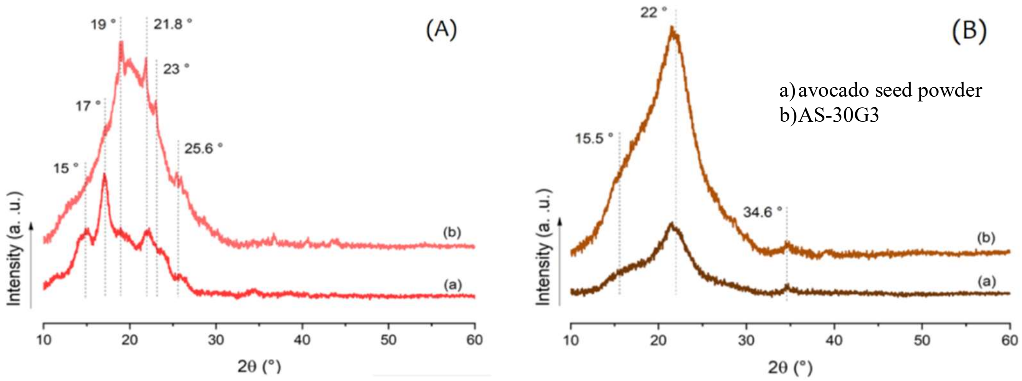

FIGURE 4. X-ray diffraction pattern on (A) the avocado skin powder sample and (B) initial sample

In Fig. 4, it can be seen that there was a decrease in the peak of XRD intensity when the sample was added with plasticizer, especially in the diffraction pattern (A), namely peaks of 15° and 17°, a significant increase in the change in the amorphous form was seen. This shows that the addition of a plasticizer or plasticizer is effective in reducing the crystallinity process of biodegradable plastic samples, this can be due to the stretching of the OH group in the polysaccharide and the symmetrical or asymmetric stretching of the CH group chain from the CH2 group due to the presence of carbohydrates (starch). The interaction of hydrogen bonds between hydrolyzed polysaccharides in avocado seeds and skin and the plasticizer can cause a shift in the relative intensity peak in the XRD pattern [17]. Therefore, an appropriate plasticizer composition is needed to obtain biodegradable plastic samples with good mechanical properties.

Hydrolysis with the addition of chitosan

From the results of making biodegradable plastic using the hydrolysis method in acid media with the addition of chitosan, the samples or biodegradable plastic films are quite good. This is indicated by the results of the biodegradable plastic film obtained from the hydrolysis process of APS powder samples with the addition of 1.5 grams of chitosan as shown in Fig. 5.

FIGURE 5. APS samples with the addition of chitosan

In Fig. 5, APS biodegradable plastic has been successfully made with a composition of 1.5 grams of chitosan. This is in line with previous research [13] which explained that the addition of chitosan was able to slow down the biodegradation process, which means that biodegradable plastic can last longer. This can be seen in Fig. 5 where the process of making biodegradable plastic with the addition of chitosan can facilitate APS starch to form plastics and is easy to print, as well as in the drying process, so it does not take a long time to dry the samples into biodegradable plastic films. Besides that. this is because chitosan is a non-toxic biodegradable polymer with a high molecular weight besides that chitosan is hydrophobic and has antimicrobial properties so it takes longer to damage and shrinks the mass. The properties of chitosan are inversely proportional to plasticizers and starch. Plasticizers tend to be hydrophilic, thus accelerating the rate of degradation. This is similar to the results of previous studies which explained that starch-chitosan-based bioplastics still have drawbacks, namely their low elasticity value. This low elasticity value can be corrected by adding plasticizers. Plasticizers reduce inter- and intra-molecular forces and increase the distance between polymer molecules [18]. For this reason, further studies are needed to obtain the right composition between avocado waste starch, chitosan composition, and also the composition of plasticizers in the manufacture of biodegradable plastic, to obtain biodegradable plastic that meets the standards for their use as organic mulch.

CONCLUSION

The result of processing avocado waste is alternative exploitation of starch compounds, especially starch from avocados. In this study, further research is needed to obtain biodegradable plastic that can be developed and can be optimized for use. The three methods that have been carried out in this study indicate the need for a combination of methods in the process of making biodegradable plastic with the right composition for the addition of plasticizers (sorbitol and glycerol) and the addition of chitosan. Both of these materials can cover the lack of properties of the raw material of avocado waste starch. As well as being able to reduce organic waste pollution.

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