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Properties of Sago Starch-Based Biopolymers with Clay, Cellulose, Zinc Oxide and Chitosan Fillers

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Abstract. Sago (Metroxylon spp) is one of plant that contains high starch, so it has potential to be utilized as raw material for biopolymer production. This study aims to compare the properties and morphology of sago starch-based biopolymers reinforced by different filler types, including clay, cellulose, zinc oxide and chitosan. Biopolymer sample was prepared at 75 ^{o}C with ratio of water to the starch of 10 ml/gr, glycerol content of 0.1 ml/gr of the starch and filler content 6% w/w. The testing included tensile, water uptake and biodegradability properties according to ASTM D882, ASTM D570 and DIN EN ISO 846 standards, respectively. Other testing also conducted for morphology by using scanning electron microscope (SEM). The results showed that biopolymer with chitosan filler has better tensile, water uptake and biodegrability properties compared to other filler type, with tensile stregth of 11 MPa, elongation at break of 9%, water uptake of 10% and biodegrability of 40%. The SEM micrograph shows that the filler still has an agglomerated portion in the starch matrix. Increasing the biopolymer properties is still possible by improving the morphology.

Introduction

Sago (Metroxylon spp) is a type of palm plant naturally grown in swampy areas, including peat swamps, watersheds, or swamp forests. This plant is widely found in the South Pacific, Papua New Guinea, Indonesia, Malaysia and Thailand. In Indonesia, the sago plantation is more than 1 million hectares [1], with production of about 3 million tons per year [2]. Riau Province is a region that has a wide peat swamp, so it has great potential to produce sago commodity. Currently, the sago plantation in the region is about 87 thousand hectares with a production of 246 thousand tons annually [3].

Sago has long been known as one of the commodities used for food, both as a source of staple food and additionally. This is because the commodity has a high carbohydrate (starch) content, which can reach 85% [4]. Sago starch contains two important fractions, namely amylose with a linear chemical structure and amylopectin with a branched chemical structure. Tipically, the amylose content is about 27% and the amylopectin content is about 73% of the starch content. Amylose and amylopectin levels will affect the properties of starch itself. If the amylose content is high, then the starch will be dry, less adhesive and tend to seep in more water (hygroscopic). The nature of the starch is insoluble in water, but if the starch suspension is heated there will be gelatination after it reaches its gelatinizing temperature. The temperature of sago starch gelatinasi around 72-90 ^{o}C[5]. Starches mixed with suitable fillers and plasticizers can produce polymeric biocomposite materials [6], so their utilization can be expanded.

Studies related to the utilization of starch for polymer biocomposite raw materials continue to grow rapidly. One of the methods developed is the addition of filler to starch, so as to improve the mechanical properties of starch based biopolymer material [7,8,9]. The use of plasticizers can increase flexibility and can decrease the level of hardness of the material [8]. The appropriate ratio of water to starch is also one of the factors improving the mechanical properties of the biopolymer

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[10]. This paper presents the results of research on the comparison of sago starch based biopolymer properties reinforced with clay, cellulose, zinc oxide and chitosan fillers. The results of this study can be used as initial information on the development of sago starch as a raw material for the production of commercial biopolymers.

Materials and Methods

Materials. The sago as raw material was obtained from local sago plantation in Selat Panjang, Riau Province, Indonesia. As fillers were bentonite clay, microcrystalline cellulose (Flocel 101), zinc oxide (with 95% purity), chitosan (blue swimming crab type). As plasticicer was glycerol with 96% purity. All materials were purchased from local distributors.

Preparation of Sago Starch. To obtain sago starch, first sago palm cleansing of impurities and peeling out the outer shell. Then the sago is cut into pieces and mashed. As much as 1 kg of sago is soaked in 2 liters of clean water to obtain wet starch. The wet starch is then dried in the sun for drying. The dry starch is then mashed and filtered to obtain a starch of 200 mesh. The characterization test showed that the sago containing starch about 73.8%, including amylose content of 25.3% and amylopectin of 48.5%.

Preparation of Sago Starch-Based Biopolymers Compounds. A total of 10 grams of sago starch dissolved into the aquades with a volume of 100 ml. Then into the solution, glycerol was added of 0.1 ml/gr of starch, while stirring until evenly distributed. Furthermore, filler was added with ratio of 6% w/w of the starch, while continuously stirring until evenly distributed. The mixing process was carried out at 75 ^{o}C. The mixture was then poured onto a glass plate mold (size 22 cm x 22 cm x 2 mm) and dried for one day at room temperature. Furthermore the sample was prepared for its characterization.

Samples Testing. Testing of the biopolymer sample included tensile test (ASTM D882), water uptake (ASTM D570), biodegradability (DIN EN ISO 846) and scanning electron microscopy (SEM). The SEM test was performed on the fracture surface of the sample. To avoid changing the phase surface when broken, the sample was first immersed in liquid nitrogen. The sample was then coated with gold for 4 minutes with 10 mA ion current (thickness ± 300 A^{o}), using JEOL Fine Coat (Ion Sputter). The coating was performed to avoid the occurrence of electrostatic charge from the sample when tested. Testing of biodegradation was done by Soil Burial Test method. First the sample was cut with a size of 3 x 3 cm and weighed the weight (Wo). The sample was placed into a container containing the soil, then covered with soil until the sample is fully buried. After 4 weeks, the sample was taken and cleaned, then weighed (W). The percentage of biodegradation was calculated from values of Wo and W, by the formula:

$$\text{Biodegradation (\%)} = \frac{W_o - W}{W_o} 100\% \quad (1)$$

Results and Discussion

Tensile Properties. In the preparation of the biopolymer samples, the starch grains break when heated at its gelatinization temperature (75 ^{o}C). The heat causes the loose hydrogen bonds, so that the water molecules will easily get into the starch. This causes the starch to expand and eventually rupture, so that the cavities will open larger on the starch crystalline structure [11]. The presence of glycerol also helps make the cavity larger, so the filler will more easily fill the cavities and then will form a solid structures. The strength of the biopolymer depends on the type of filler used, as shown in Figure 1.

The results of this study show that biopolymer with filler chitosan has higher tensile strenght compared with other filler type, which is 11 MPa. In addition, the biopolymer with the filler also has a lower elongation at break, which is 9%. This shows that chitosan can produce more hydrogen bonds in the biopolymer, so the components in the mixture will become stronger and more difficult to break. The hydrogen bond also makes the distance between chitosan molecules with amylose and

amylopectin getting closer, so the biopolymer becomes more rigid and less elastic [12]. Similar results were also reported by other researchers [8,9].

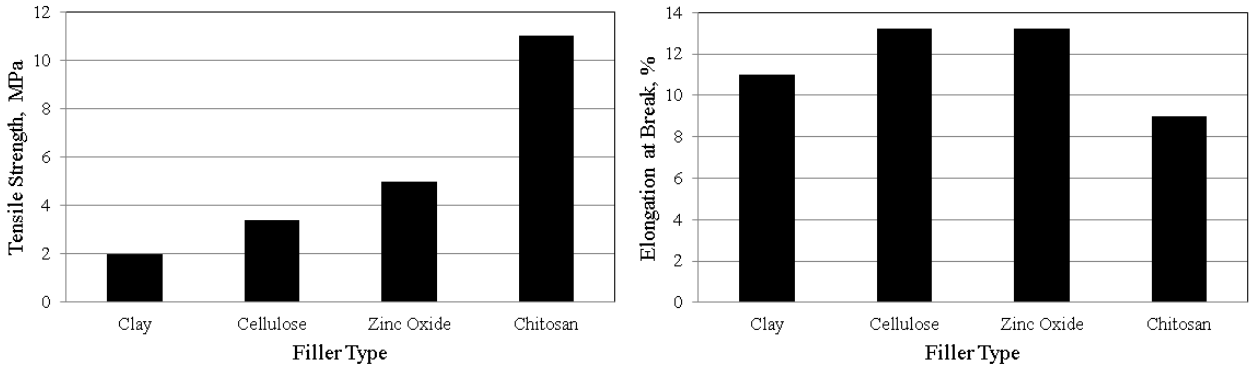

Fig. 1 Effect of Filler Type to Tensile Properties of Sago Starch-Based Biopolymer

The lowest tensile strenght properties are found in biopolymer with clay filler. This occurs because the intermolecular forces and the crystallinity of the clay are higher than the starch [13]. The forces in the clay cause it to be difficult to interact with the starch component. This causes the clay monolayer interconnected into the clay itself to form a multilayer clay-starch structure, resulting in the agglomeration of the clay component and its distribution unevenly in the starch matrix. This mechanism causes the tensile strenght properties of the biopolymer to be lower. Cellulose also has not produced biopolymer that has high tensile properties (ie 3.4 MPa), but it is estimated that this material has the potential to improve tensile biopolymer properties, especially at higher levels. This material is one type of polymer (ie fiber) that has high tensile properties. Zinc Oxide (ZnO) also showed that the material is compatible with the starch, where the tensile strenght properties of the biopolymer are also high (ie 5 MPa) at ZnO levels of 6% w/w. Biopolymer with ZnO filler can be used for biomedical applications without coating and has high radiation resistance [14]. The ZnO thin films exhibit attractive characteristics such as strong bonding, good optical quality, extreme stability of the excitron, and good piezoelectric equipment [14].

Water Uptake and Biodegradability Properties. Water uptake is defined as the level of resistance of the biopolymer to water. The smaller the water uptake, the water resistance of the biopolymer material is getting better. Biodegradability is expressed as a percentage reduction in the weight of the biopolymer material due to the activities of microorganisms. According to Wypich [15], the water component in the material structure will help the activity of microorganisms on the material. The influence of filler type on water uptake and biodegradability can be seen in Figure 2.

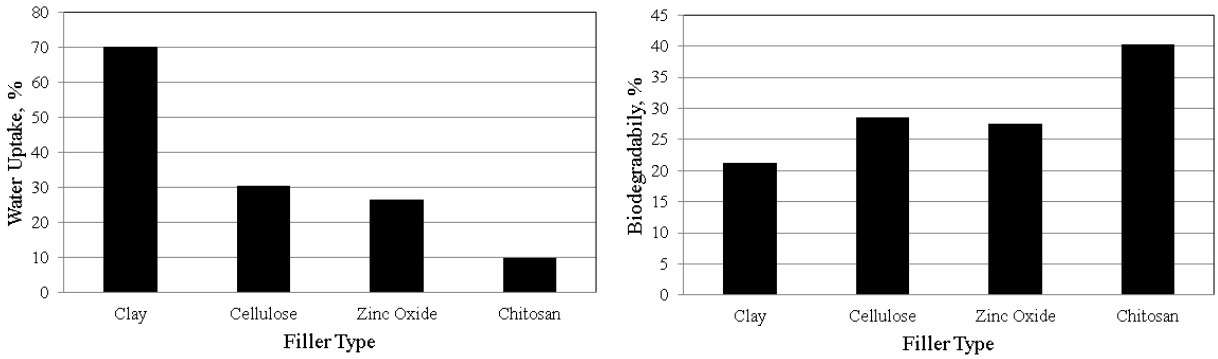

Fig. 2 Effect of Filler Type to Water Uptake and Biodegrability Properties of Sago Starch-Based Biopolymer

The results of this study show that the type of filler has a significant effect on water uptake and biodegradability. The starch material is hydrophilic. In addition, the presence of glycerol also enhances the hydrophilic nature of the biopolymer. However, chitosan filler has provided better water resistance properties in biopolymer materials compared to those using other filler types. This is because the nature of chitosan is hydrophobic and readily biodegradable [16]. The decomposition

process does not take a long time because starch, chitosan and glycerol are OH-group contributing components, so biodegradation process is easier to occur. Likewise with biopolymer with cellulose filler, although not as good as chitosan filler. The cellulosic component also helps the biopolymer become more easily decomposed by microbes [17}. However, for biopolymers with ZnO filler, the component may act as microbial activity-inhibiting agent [18], causing microorganisms to have difficulty decomposing the biopolymer, thus decreasing the biodegrability. For biopolymer that use clay as a filler component, the material is hydrophilic, so the material also contributes to increase water uptake of the biopolymer. To reduce the hydrophilic properties, it can be done by intercalating organic cations such as amino acids or alkyl ammonium to the clay component forming a hydrophobic organoclay [15]. Biodegrability of the biopolymer with clay filler is also low. This is presumably because the material also contains components that can inhibit microbial activity to decompose the biopolymer, as does ZnO.

Morphology. SEM micrographs of biopolymer samples with clay, cellulose, zinc oxide and chitosan fillers can be seen in Figure 3. The SEM micrograph of the biopolymer sample shows the presence of an agglomerated filler portion or the accumulation of some filler components in the starch matrix. The agglomeration causes the properties of the biopolymer to be less than optimal. As the agglomeration level increases, the interaction between the filler and the matrix becomes weak. In addition, the decrease in tensile properties can also be caused by the inability of the filler to support the uniform stress transfer of the matrix, so that the reinforcement mechanism by the presence of the filler does not occur well [19]. The morphology of the biopolymer which is still less optimum is thought to be caused by the relatively large filler size, so the filer is not easy to enter the cavities formed in the matrix. Another factor is that the mixing technique used has not been able to produce sufficient shear stress, so that the filler particles are not distributed well into the starch matrix.

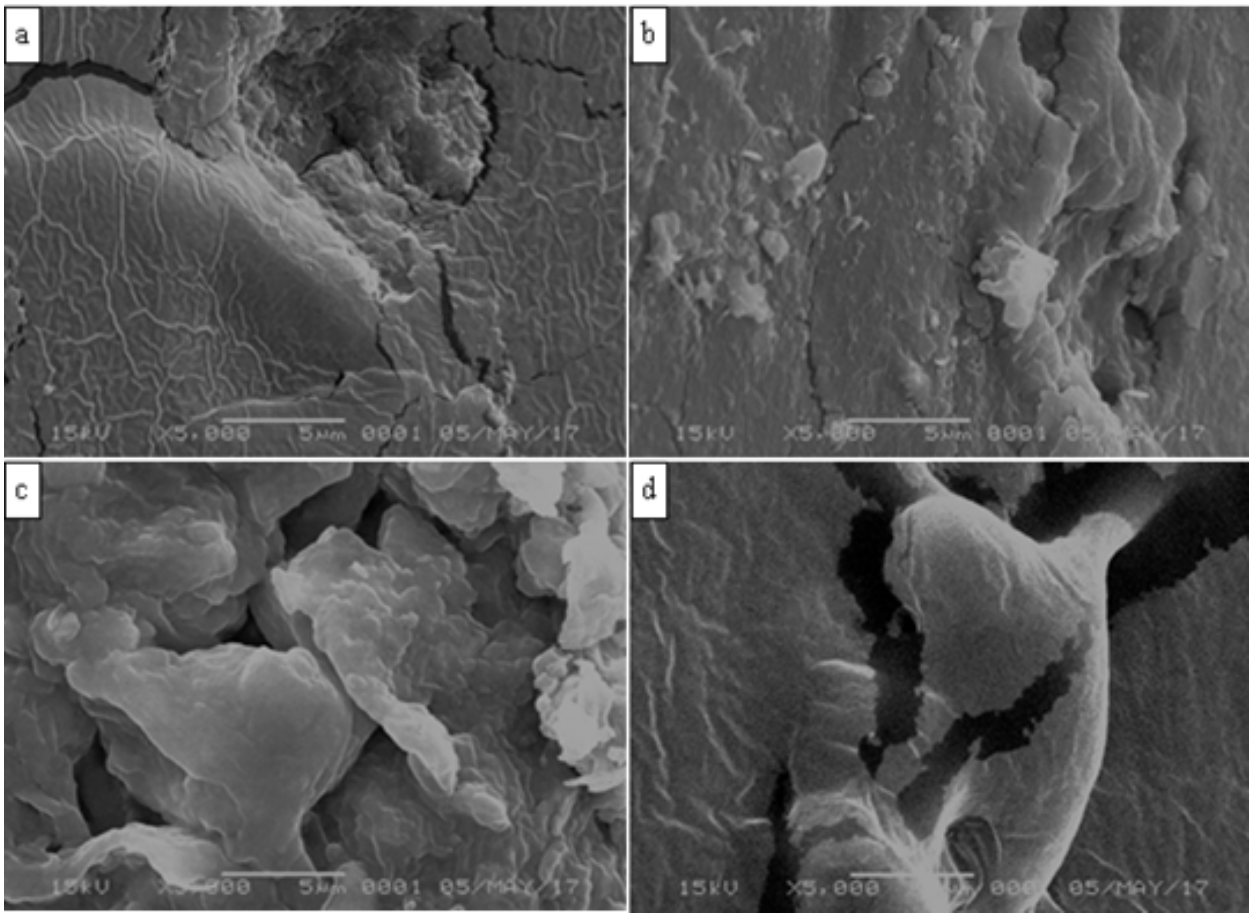

Fig. 3 Micrograph SEM of Sago Starch-Based Biopolymer with Fillers: (a) Clay; (b) Cellulose; (c) Zinc Oxide; (d) Chitosan

Summary

Typical sago used for producing of the biopolymer, containing starch about 73.8%, including amylose content of 25.3% and amylopectin of 48.5%. The results showed that biopolymer with chitosan filler has better tensile, water uptake and biodegrability properties compared to other filler type, with tensile stregth of 11 MPa, elongation at break of 9%, water uptake of 10% and biodegrability of 40% (after 4 weeks). The SEM micrograph shows that the filler still has an agglomerated portion in the starch matrix. Increasing the biopolymer properties is still possible by improving the morphology.

Acknowledgments

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