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Original Research Article

DEVELOPMENT OF BIOPLASTIC BASED ON CASSAVA FLOUR AND ITS STARCH DERIVATIVES FOR FOOD PACKAGING

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Abstract: This research aimed to develop bioplastic from cassava flour and its derivatives, i.e. starch and nanoparticles. Tapioca starch was extracted from cassava flour and further processed into its nanoparticle by ethanol precipitation. All biopolymers in this study, which were cassava flour, tapioca starch, and tapioca starch nanoparticle, were used to produce bioplastics with the presence of glycerol as plastisizer. The results showed that both cassava flour and tapioca starch bioplastics were potent to be applied as sweet soy sauce and vegetable oil packagings, but not as water and chili sauce packagings. All bioplastics were transparent, similar to conventional plastic. The resulted bioplastics absorbed UV-A so that the products inside could be protected from photooxidative degradation.

Keywords: Bioplastic, cassava, glycerol, packaging, UV absorption

1. Introduction: One of the current concerns with the environment is the accumulated waste of non degradable plastics. It creates a great expectation for more ecological and economically viable alternative to minimize the environmental impact. Several materials from agricultural resources have been used to produce renewable, biodegradable, and even more edible packaging. Cassava flour is one of the most commonly used biopolymers as food packaging material because it is nontoxic, biodegradable, biocompatible, low cost, renewable and abundantly available in nature. Its major component is starch, but it may content small amount of lipid, protein, fiber and ash[1]. The starch plays important role in bioplastic forming. Today starch based bioplastic dominates 66% of the global bioplastics market.

Starch based bioplastic is made by gelatinizing starch[2]. In general, smaller starch granule needs longer time and higher temperature to undergo gelatinization process[3]. For tapioca starch, a common name for starch extracted from cassava, gelatinization temperature is quite low, only about 52-64°C[4]. To obtain a flexible starch based bioplastic, sorbitol, glycerol, and xylitol are often added as plasticizers[5]. The molecule of plasticizers can insert themselves into three-dimensional networks of biopolymers and lower

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the interaction force between the molecules of biopolymers[6].

The mechanical properties of starch based bioplastics have been published well. Its tensile strength ranged from 0.02-302 MPa, depended on the source of starch and the plasticizer added[7-11]. Therefore, to continue those previous reports, this research was focused to evaluate the potency of starch based bioplastic for liquid and semisolid food products as well as the optical properties of starch based bioplastic.

2. Materials and Methods

2.1. Materials

The materials used in this study were purchased from the local market, such as cassava flour, vegetable oil, filter cloth, plastic wrap, aluminum foil, sweet soy sauce, and chili sauce. Chemicals such as ethanol and glycerol were analytical grade (Merck®). The equipments used were drying tray, magnetic stirrer, vacuum oven, sentrifugator Sorvall Legend RT®, and spectrophotometer UV / VIS Shimadzu UV - 2450.

2.2. Tapioca starch extraction

As much as 100 grams of starch was suspended in 100 ml of distilled water and filtered by the filter cloth. The filtrate was centrifuged at 3000xg for 15 min twice and the pellet was dried in oven at 70°C until its weight was constant and the yield was determined[8].

2.3. Nanoparticles tapioca starch preparation

Tapioca starch nanoparticle was prepared by ethanol precipitation[12]. Five grams of tapioca starch was suspended in 100 ml of distilled water and heated for 60 min at 90°C so that the starch was totally gelatinized. As much as 85 ml of absolute ethanol was added dropwise constantly. Then, the gelatinized starch was cooled down to room temperature. The mixture was poured into 50 ml eppendorf tube and centrifuged for 20 min at 8888xg two times. The pellet was collected and dried in a vacuum oven for 4 hours at 50°C.

2.4. Bioplastics preparation: The bioplastics were made using cassava flour, tapioca starch, and tapioca starch nanoparticles. Those biopolymers were separately mixed with glycerol which the concentration was varied as 20, 25, and 30% (w/w) in order to obtain total weight of 10 g. The solution was poured on a drying tray with the area of 310 cm^2 and dried at 30^{o}C for 24 hours. The obtained bioplastic was kept in a closed container for further step.

2.5. Application of bioplastics as packaging for liquid and semisolid foods

The application test was conducted using sweet soy sauce, chili sauce, vegetable oil, and distilled water as the test samples[13]. Bioplastic was cut to size of 1.5 cm x 1.5 cm, weighed as the initial weight (W_1), and immersed in the test sample in the beaker. The beaker was covered with plastic wrap and incubated at room temperature for 120 ± 4 min. After the incubation time was completed, the bioplastic was cleansed and weighed again as the final weight (W_2). The percentage weight change of bioplastics was calculated as described in Equation 1. If the weight change of bioplastic after being immersed in the test food products was less than 10% (w/w), the bioplastic is considered as compatible with those test food.

$$\%\Delta W = \frac{W_2 - W_1}{W_1} \times 100\% \qquad \text{(Eq. 1)}$$

2.6. UV absorptivity and transparency of bioplastic

The bioplastics was cut to 1 cm x 3 cm to match the width and height of cuvette. Bioplastics were then attached to the side of the cuvette. After that, the “wavelength scan” method was selected from the menu of UV-VIS spectrophotometer and the absorbance was recorded from 800 nm to 200 nm [14]. The UV absorptivity of bioplastics was calculated as the maximum absorbance at a certain wavelength devided by the thickness of bioplastic (mm). The transparency was determined using Equation 2.

$$Transparancy = \frac{\log \%T}{b} \qquad \text{(Eq. 2)}$$

Where %T is transmitans at 600 nm and b is the thickness of bioplastic (mm). Conventional plastic bag from polyethylene was used as control for this step.

2.7. Statistical analysis

All experiments were repeated three times and the data were evaluated by ANOVA for the relationship between composition of bioplastics and the characteristics of bioplastics. Microsoft Excel 2007 was used in such analysis.

3. Results and Discussion

3.1. Tapioca starch and its nanoparticle

The yield of tapioca starch extraction was 88.2% (w/w), higher than that of previous research, which was 73.9-83.5% (w/w)[1]. The yield of starch extraction depended on the varieties and water content of cassava. Previous research[1] used fresh cassava root that contained more water than cassava flour used in this research. In addition, genetic variation played important role in starch physicochemical properties. From 1077 seedlings randomly selected, the amylose content in cassava roots ranged from 10 to 25%, with the amylose: amylopectin ratio between 1:3 and 1:9. Their solubility and swelling power ranged from 1-15g/100g and 40-140g/100g starch at 60°C, respectively. Fresh cassava root yielded starch ranged from 18 to 34%, with dry matter content varying from 19-47%[15].

The yield of tapioca starch nanoparticle was quite high, i.e. 75.0% (w/w). Previous study reported that waxy maize starch nanoparticles could be prepared with high yield (78%) and size about 50-90 nm diameters by 4°C hydrolysis for 6 days followed by ultrasonication [16]. Szymońska *et al.*[17] reported that cassava starch nanoparticles obtained by grinding starch-ethanol suspensions in a vibration mill had the size between 50 nm to 100 nm and their properties were qualitatively different from those of native starch granules. The iodine binding capacity of tapioca starch nanoparticle was less than that of its native starch (1.32 vs 0.91), while the aqueous solubility at room temperature and swelling power were much higher than those of native starch (0.48 vs 37.50% and 1.70 vs 12.75 g H_2O/g starch, respectively). Other report said that the size and shape of sago starch (*Metroxylon sagu*) nanoparticle produced by nanoprecipitation using ethanol depended on the synthesis parameters, such as the ratio of starch to ethanol and the use of appropriate surfactant[18]. Buthanol was also applied to produce starch nanoparticle with higher amylase content and solubility than its native starch[19]. On the other hand, the same amylose content of starch resulted in similar size and crystallinity of nanoparticles, regardless the botanic origin of starch. Also, particles tended to show square shapes with increasing native starch's amylopectin content[20].

3.2. Bioplastics from cassava flour and its derivatives

All bioplastics obtained in this research was odorless, transparent, and smooth. The addition of glycerol on bioplastic increased its flexibility, except for nanoparticle based bioplastic. The bioplastic of starch nanoparticle was brittle eventhough the concentration of glycerol was maximum so that it could not be further characterized. However there was no bubble in the starch nanoparticle based bioplastic (Figure 1). The bioplastics of cassava flour and tapioca starch were flexible enough while the ratio of biopolymer to glycerol was 3:1, but some bubble was noticed (Figure 2).

Fig. 1: Bioplastic from tapioca starch nanoparticle with ratio biopolymer : glycerol = 7:3.

From cassava flour From tapioca starch

Fig. 2: Bioplastic with ratio biopolymer : glycerol = 3:1

Possibly, starch nanopaticle was potential as nanomaterial containing products, such as laminate and composite. Atomic layer deposition has demonstrated its capability of depositing 2 or more layers of materials and thus to create nanolaminates[21]. Nanocomposites, anoclays, kaolinite, carbon nanotubes and graphene nanosheets improved mechanical strength, heat resistance, and the ability of plastic packaging against migration of gases and flavour compounds, as well as boosting shelf life[22].

Table 1 showed the weight change of cassava flour based bioplastic and tapioca starch based bioplastic after being immersed in distilled water, chili sauce, sweet soy sauce, and vegetable oil. The compatibility of starch based bioplastics depended on the biopolymer, the concentration of glycerol, and the test food products. In general, it can be said that cassava lour and tapioca starch could be used as the packaging for sweet soy sauce and vegetable oil, but they seemed not compatible with chili sauce and distilled water.

Table 1. The weight change of bioplastic (%w/w) after being immersed in test food for 2 hours

Biopolymer and its ratio with glycerol		Sweet soy sauce	Vegetable oil	Chili sauce	Distilled water
Cassava flour	7:3	9.17 ± 4.66	3.17 ± 0.94	51.67 ± 3.41	239.48 ± 2.45
	3:1	1.74 ± 1.42	2.21 ± 1.13	30.77 ± 9.05	222.88 ± 50.67
	4:1	7.05 ± 3.45	1.83 ± 1.67	90.49 ± 44.83	223.93 ± 40.70
Tapioca starch	7:3	6.86 ± 1.31	19.73 ± 4.64	60.19 ± 38.14	95.17 ± 19.44
	3:1	10.31 ± 4.09	8.52 ± 2.94	275.22 ± 24.59	71.89 ± 8.91
	4:1	16.05 ± 5.11	1.67 ± 0.63	213.41 ± 23.71	165.06 ± 38.27

The major component of cassava flour was starch, but it also contained small amount of lipid, protein, fiber and ash[1]. This study suggested that those nonstarch components influenced the compatibility of bioplastic to food products. The presence of nonstarch components hindered the permeability of sweet soy sauce, vegetable oil, and chili sauce into the bioplastics, so that the weight change of cassava flour based bioplastic was less than that of tapioca starch based bioplastic.

The presence of glycerol in bioplastics increased the weight change of both cassava flour and tapioca starch based bioplastics after being immersed in vegetable oil. It indicated that the more glycerol in bioplastic, the easier the vegetable oil penetrate the surface of bioplastic. Glycerol was hydrophilic polyol with strong affinity to water. Godbillot *et al.*[23] reported that the maximum glycerol in wheat starch based bioplastic was 20% (w/w). Above this percentage, phase separation occurs and the amount of adsorbed water increased as it bound to starch as well as to free glycerol.

Sweet soy sauce was an intermediate moisture food due to its high sucrose content. A survey reported that sweet soy sauce contained 67.8% (w/w) of sucrose[24] and that product met the criteria of Indonesian National Standard[25] which stated that the minimum sucrose in sweet soy sauce was 40% (w/w). Water content in vegetable oil was 0.085 sampai 0.214[26]. In the future, applied research to obtain biosachet or biopouch for sweet soy sauce and vegetable oil could be conducted.

The weight of all tested bioplastic in this study increased after being immersed in chili sauce and distilled water. The water activity of chili sauce is 0.96 [27] so that the water might interrupt the biopolymer network and caused the bioplastic swelled. The weight of cassava flour based bioplastics increased almost 2.4 times as much as its initial weight after being immersed in distilled water. It indicated that the biopolymer of cassava flour could imbibe significant amounts of water. Therefore, hydrogel might be another potential product that could be derivatized from cassava flour. Hydrogels are considered to be one of the most promising biomaterials used today and have many applications in medical research, especially in tissue engineering and drug delivery[28].

Most polymers were carefully measured for their UV absorption due to the fact that the absorption of UV had a significant relationship to UV degradation of the polymers. Polymer that did not absorb UV radiation was considered as not susceptible to photodegradation[29]. However, the ability of bioplastic to absorb UV was beneficial when the bioplastic was used as food packaging. The bioplastic was able to protect food products from UV radiation so that it prevented photooxidative degradation that might alter the aroma and induce free radicals formation. In further, those radical induced lipid rancidity and DNA mutations that caused various diseases such as cancer, impaired nerve function, and coronary heart disease[30].

Figure 3 showed the spectrogram of bioplastic. Both cassava flour and tapioca starch based bioplastics had similar pattern and all of them absorbed UV with the maximum absorptivity was in the wavelength from 322 nm to 345 nm. This finding indicated that the bioplastic obtained in this study absorbed UV light, especially UV-A. UV light was divided into 3 regions, namely UV-C (100-280 nm), UV-B (280-315 nm), and UV-A (315-400 nm). Polycarbonate, one of common conventional plastic which had high degrees of clarity in the visible light spectrum, had high degrees of UV absorption. Other bioplastic, namely polylactic acid, allowed full transmission of UV light, similar to polymethylathacrylate and polytetrafluosoethylene[29].

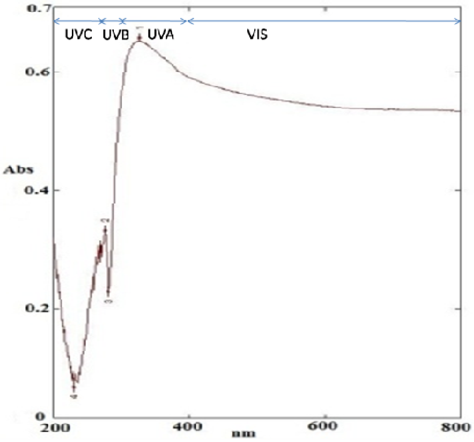

Fig. 3: Pattern of UV VIS absorptivity of bioplastic.

Figure 4 presented the UV absorptivity of bioplastic. All bioplastics obtained in this study had higher UV absorptivity than conventional plastic had. It implied that at the same thickness, bioplastic absorbed UV greater than conventional plastic did. The glycerol concentration in bioplastic also influenced the UV absorptivity of bioplastic. The higher the concentration of glycerol in bioplastic, the higher the ability of bioplastic to absorb UV light was. While the concentration of glycerol ranged from 20-30% (w/w), in which it was the common concentration reported to obtain bioplastic with good mechanical characteristics from various starch, the correlation of glycerol concentration to the UV absorptivity was linear[7-8,10,31-32]. Glycerol protected products against near-UV light and the protection was maximum in UV-A range and decreased rapidly at wavelengths above and below UV-A. A possible role of hydroxyl group in UV absorption activity was also observed in benzoate that had maximum UV absorption at 334-nm UV[33].

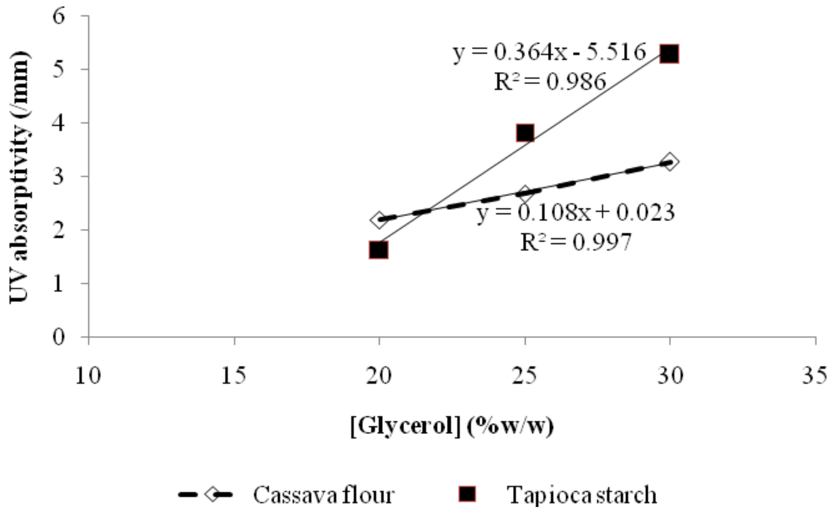

Fig. 4: UV absorptivity of bioplastic (Note: UV absorptivity of conventional plastic: 1.14/mm)

Figure 1 and Figure 2 showed that the bioplastic was transparent and to obtain the quantitative data, the transparency was determined using spectrophometer by measuring the transmitted light at visible wavelength (600 nm). The transparency of cassava flour and tapioca starch based bioplastics was comparable to that of conventional plastic (Table 2). The data also indicated that at the same thickness, transparency depended on the purity of starch and concentration of glycerol. Low levels of glycerol resulted in highly transparent bioplastic and the higher the concentration of glycerol, the more transparent the bioplastic was[34]. However, when the concentration of glycerol achieved saturation, the bioplastic lost its transparency.

Table 2. Thickness and transparency of bioplastik (mm^{-1})

Biopolymer and its ratio with glycerol		Thickness (mm)	Transparancy (/mm)
Cassava	7:3	0.14	2.67 ± 0.00^{c}
	3:1	0.08	2.80 ± 0.01^{d}
	4:1	0.20	2.15 ± 0.01^{a}
Tapioca	7:3	0.13	2.63 ± 0.04^{b}
	3:1	0.10	2.79 ± 0.00^{d}
	4:1	0.05	3.13 ± 0.0^{e}

Note: Thickness and transparency of conventional polyethylene plastic was 0.11mm and 2.90/mm, respectively.

The same letter behind the values indicated that the values are not statistically significant different ($p<0.05$).

4. Conclusion: Bioplastics from cassava flour and tapioca starch can be used as packaging for vegetable oil and sweet soy sauce. These bioplastics are transparent so that consumers can see the product inside. However, these bioplastic can absorb UV light, particularly UV-A. The addition of glycerol increases the ability of bioplastics in absorbing UV-A, so it protects the product from photooxidative degradation. Further research to develop biosachet or biopouch from cassava flour and tapioca starch for vegetable oil and sweet soy sauce is recommended. However, nanoparticles of tapioca starch are not suitable for use as biopolymer solely in the manufacture of packaging because it is too fragile, but it may be potential for other applications, such as nanolaminate and nanocomposite.

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