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Bio-Plastic Characteristics From Cassava Starch Modified In Variations The Temperature And pH Of Gelatinization.

Bambang Admadi Harsojuwono*, I Wayan Arnata, and Sri Mulyani.

Department of Agricultural Industrial Technology, Faculty of Agriculture Technology, Udayana University, Badung, Bali, 80361, Indonesia.

ABSTRACT

The purpose of this study was to investigate the effect of temperature and gelatinization pH on the characteristics of modified cassava starch bio-plastic, to determine the temperature and pH of gelatinization to produce modified cassava starch bio-plastic with the best characteristics. This research uses Factorial Random Block Design. Factor I is a gelatinization temperature consisting of 5 levels i.e. 70; 75; 80; 85 and 90^{o}C. Factor II is a gelatinization pH consisting of 4 levels of 4; 5; 6 and 7. Each treatment combination is grouped into 2 based on the time of the bio-plastics making process, so that there are 40 experimental units. The data obtained were analyzed of variant and continued with the Duncan comparison test. The observed variables include mechanical tests consisting of tensile strength, elongation at break and Modulus Young test, duration of bio-plastic degradation and surface profile and bio-plastic functional groups. The results showed that the temperature and pH of gelatinization and its interaction had a very significant effect on tensile strength, elongation at break, Modulus Young, volume swelling percentage and degradation duration of modified cassava starch. The gelatinization temperature of 75 $\pm$ 1^{o}C at pH 5 produces the best characteristics of modified cassava starch bio-plastic, i.e. tensile strength 1,657.43 MPa, elongation at break of 10.32%, Modulus Young of 16,060.37 M Pa, percent of volume swelling by 9% and duration of degradation 7.33 days. The profile of the bio-plastic surface of the longitudinal view indicates the presence of dense and regular tissue formed by modified starch polymers with relatively small airspace variations. The cross-profile bio-plastic profile shows a fiber arrangement that forms a regular network or cross linking of a modified cassava starch polymer. Modified cassava starch bio-plastics contain hydroxyl (O-H) based functional groups with hydrogen, alkanet (C-H), aldehydes (C-OH), simple aromatic compounds, carboxyl (C-O), alkenes (C = C) and hydrocarbons –(CH2) n.

Keywords: Bio-plastic, modified cassava starch, temperature and pH of gelatinization

**Corresponding author*

INTRODUCTION

Starch-based bio-plastic production has been widely developed, but the resulting bio-plastic characteristics still have weaknesses. Darni and Utami (2010) stated that the use of starch in the manufacture of bio-plastics produces waterproof bio-plastics and very low mechanical strength. To overcome this, then in making bio-plastic need to use raw materials that have been modified and optimize the factors that affect the quality. One such factor is the temperature and pH of gelatinization. Setiani et al. (2016) showed gelatinization temperature of 73.98°C on breadfruit and chitosan composite produces characteristic of plastic film with water absorption value 212.98%, tensile strength value 16,34 MPa, elongation when broken 6,00% and Modulus Young 2.72 MPa . Meanwhile, Sari (2016) using gelatinization temperature 80° C produces bio-plastic from *suweg* starch and CMC with tensile strength characteristic 18.68 MPa, extension 12.22%, thickness 0.14 mm and 8 days degradation. Bourtoom (2007) explained that cassava starch with gelatinization temperature of 95°C for 5 minutes without known pH resulted in plastic film with maximum tensile strength but increased heating temperature will decrease the percentage of elongation, permeability and water vapor solubility. In addition to temperature, gelatinization process is also influenced also by pH. According to Henrique et al (2007), gelatinization of starch occurs in the pH range of 4 - 7, further explained that if the pH used is too high, gelatinization process runs fast but rapidly retrogrades, if the pH is too low then the gelatinization process runs slowly. Rosa et al. (2004) also explains that an inaccurate pH of gelatinization under continuous heating conditions will cause a decrease in viscosity which affects the failure of the formation of post-drying plastic sheets. Meanwhile. Anonymous (2003) explains that pH influences the formation of cross linked bio-plastic starch. It is further explained that the precise pH conditions will produce starch bio-plastic with acid resistance characteristics, high temperature heating, and stirring (shearing) as well as stronger granules (not easily expandable) with high viscosity. It shows that the use of different temperature variations and gelatinization pH will produce different bio-plastic characteristics. Appropriate temperature and pH of gelatinization for modified cassava starch, unknown information. Therefore, the purpose of this research is to know the effect of temperature and gelatinization pH on the characteristics of modified cassava starch bio-plastic as well as to determine the characteristics of good bio-plastic (meets the specified standards).

MATERIALS AND METHODS

Materials

The tools used include glass beaker, spatula, water bath, teflon, automatic dryer type cabinet, SEM spectrometer (Scan Electron Microscope) and FTIR (Fourier Transform Infra Red). The study materials include modified cassava starch, aquadest, 25% acetic acid and glycerol solutions.

Experiment design

This research uses Factorial Random Block Design. Factor I is gelatinization temperature consisting of 5 levels that is 70°C, 75°C, 80°C, 85°C, and 90°C. Factor II is a gelatinized pH consisting of 4 levels i.e. 4; 5; 6 and 7. Each treatment combination is grouped into 2 based on the time of the bio-plastics making process, resulting in 40 experimental units. The data obtained were analyzed for their diversity and continued by the Duncan comparison test.

Making of modified cassava starch bio-plastic

Modified cassava starch weighing 6 g plus aquadest 92.8 g then adjusted pH according to treatment with acid vinegar and stirred for 10 minutes with a spatula in a beaker glass, after which the plasticizer added 1g glycerol. The mixture is stirred back with a spatula for 10 minutes to keep the mixture homogeneous. Next, the mixture is heated and stirred in a water bath at a temperature corresponding to the treatment to form a gel. The formed gel is then printed on a teflon with a diameter of 20 cm. After that dried in a dryer with temperature 50°C for 5 hours. The formed plastic layer is cooled at room temperature above teflon and released after 26 hours. Variables observed included mechanical tests consisting of tensile strength, elongation at break and Young Modulus test with ASTM D638 tool, bio-plastic degradation time, surface profile using scanning electron microscope (SEM) and bio-plastic functional group using FTIR spectrometer.

RESULTS AND DISCUSSION

Tensile strength, elongation at break, Young modulus, volume swelling and degradable time

Analysis of variant showed that the temperature and pH of gelatinization as well as their interactions had a very significant effect on tensile strength, elongation at break and Young Modulus, the percentage of volume swelling and degradable time of bio-plastic of modified cassava starch. The mean values of tensile strength, elongation at break and Young Modulus of modified cassava starch bio-plastics were respectively 674.70 - 1657.43 M Pa, 10.32 - 24.09% and 2800.75 - 16060.37 M Pa, 9.00 - 11.57% and 4 - 7 days as shown in Table 1. It can be seen in Table 1 that the smallest tensile strength value of 674.70 M Pa is shown by modified cassava starch bio-plastic made at gelatinization temperature of 90±1°C at pH 7 which is significantly different from the others. Meanwhile, 75±1°C gelatinization temperature at pH 5 yielded the largest tensile strength of modified cassava starch bio-plastic namely 1657.43 M Pa, which is also significantly different from the others. This value is higher than the results of Harsojuwono, et al (2017) which to made bio-plastic with the same material, which only shows the value of tensile strength 1057.40 M Pa. This result is also much higher than research result of Utomo et al. (2013) which shows the value of tensile strength 104,648 M Pa and research result of Setiani et al (2016) using gelatinization temperature 73, 98° C on composite of breadfruit starch and chitosan with value of tensile strength equal to 16,34 M Pa and Sari (2016) using 80°C gelatinization temperature yields bio-plastic from tuber starch suweg and CMC with value 18.68 M Pa. Nevertheless, this modified cassava starch bio-plastic only meets the UK PCL plastic standards that set a minimum tensile strength value of 190 M Pa but not yet meet the international plastic standard (ASTM5336) for PLA plastics from Japan which sets a minimum value of 2050 M Pa (Averous, 2009).

Table 1: Value of tensile strength, elongation at break, Young Modulus, volume swelling and degradable time of bio-plastic of modified cassava starch

Treatments	Mean of tensile strength (M Pa)	Mean of elongation at break	Mean of Young modulus (M Pa)	Mean of volume swelling (%)	Mean of degradable time (day)
Temperature 70±1°C, pH 4	997.40bc	22.95bc	4345.97bc	9.92c	7.00a
Temperature 70±1°C, pH 5	1088.40bc	19.06c	5710.39bc	9.99c	7.00a
Temperature 70±1°C, pH 6	1032.70bc	19.11c	5403.98bc	10.03b	7.33a
Temperature 70±1°C, pH 7	1090.30bc	19.42c	5614.32bc	10.29b	7.33a
Temperature 75±1°C, pH 4	1295.90b	18.63c	6955.99b	9.62c	7.33a
Temperature 75±1°C, pH 5	1657.43a	10.32d	16060.37a	9.00c	7.33a
Temperature 75±1°C, pH 6	1336.70b	18.70c	7148.13b	9.12c	7.67a
Temperature 75±1°C, pH 7	1027.40bc	18.90c	5435.98bc	9.40c	7.67a
Temperature 80±1°C, pH 4	1263.60b	16.65cd	7589.19bc	9.59c	6.33b
Temperature 80±1°C, pH 5	1285.40b	16.80cd	7651.19b	9.77c	6.33b
Temperature 80±1°C, pH 6	981.60bc	21.70bc	4523.50bc	9.97c	6.67b
Temperature 80±1°C, pH 7	841.20c	22.20bc	3789.19c	10.33b	6.67b
Temperature 85±1°C, pH 4	1021.30bc	18.93c	5395.14bc	9.67c	5.00c
Temperature 85±1°C, pH 5	1178.30b	17.56c	6710.14b	9.79c	5.33c
Temperature 85±1°C, pH 6	954.38bc	21.56bc	4426.62bc	9.89c	5.67c
Temperature 85±1°C, pH 7	773.67d	22.46bc	3444.66d	10.12b	5.67c
Temperature 90±1°C, pH 4	997.45bc	21.67bc	4602.90bc	10.25b	4.00d
Temperature 90±1°C, pH 5	1098.35bc	18.78c	5848.51bc	10.37b	4.33d
Temperature 90±1°C, pH 6	867.40c	22.32bc	3886.20c	10.47b	5.67c
Temperature 90±1°C, pH 7	674.70d	24.09a	2800.75d	11.17a	5.67c

Description: The same notation behind the mean in the same column shows no significant difference at the error rate of 5%.

Table 1 shows that the smallest mean of elongation at break value of 10.32% is produced from modified cassava starch bio-plastic made at 75±1° C gelatinization temperature at pH 5, which is significantly different from the others. The value of elongation at break is smaller than the result of Harsojuwono, et al (2017) study in the manufacture of bio-plastic using the same material which shows the value of 15.95%. Similarly, when compared to the results of research Sari (2016) using gelatinization temperature 80 ^{o} C produces bio-plastic of *suweg* tubers starch and CMC with elongation at break of 12.22%. But still bigger than research of Setiani et al (2016) in making composite of breadfruit starch and chitosan which yields value of elongation at break equal to 6.00%. The results still meet international plastic standards (ASTM5336) which specify the value of elongation at breaks of less than 500% for UK PCL plastics, although they have not met the standard for PLA plastics from Japan, but are close to the maximum elongation at breaks set by 9%.

Based on calculations of tensile strength and elongation at break, it is also known the Modulus Young value of modified cassava starch bio-plastic. The highest Modulus Young is shown by modified cassava starch bio-plastic made at gelatinization temperature of 75 ± 1^{o}C with pH 5, which is 16060.37 M Pa. This value is significantly different from that of modified cassava starch bio-plastic made at other temperatures and pH of gelatinization. These results provide greater value than the results of Harsojuwono, et al (2017) research that makes bio-plastics with the same material. The results of Harsojuwono, et al (2017) only give Young Modulus value of 6629.47 M Pa. The results are much higher than the results of research Setiani et al (2016) showed composite of starch and chitosan produces Young Modulus of 2.72 M Pa.

Table 1 shows that the temperature of gelatinization of 90±1^{o}C at pH 7 yields modified cassava starch bio-plastic with the largest percentage of volume swelling of 11.17% which is significantly different from the others. Meanwhile, other temperatures and pH of gelatinization showed a varying percentage of volume swelling. This result is slightly lower than the result of Harsojuwono, et al (2017) study using the same material and showing the percentage range of volume development of 9.91 - 11.28%. However, this value is much lower than the result of Utomo (2013) and Setiani et al (2016), each showed volume swelling value of 41.23% for bio-plastics from aloe vera mixed with chitosan and 212.98% for composite of starch breadfruit and chitosan.

Table 1 shows that the bio-plastic degradation time of modified cassava starch ranges from 4 - 7.67 days. This value is relatively lower than the results of research Sari (2016) which uses 80^{o}C gelatinization temperature that produces bio-plastic from *suweg* tuber starch and CMC with 8 days old degradation. The results also show a tendency that higher gelatinization temperatures and lower pH lead to a shorter degradation time of modified cassava starch bio-plastic. This may be due to the process of hydrolysis of starch by acid accelerated by temperature which increases the energy that accelerates the process of hydrolysis or decomposition. Rosa et al. (2004) also explains that inaccurate pH conditions of gelatinization and heated for too long will cause a decrease in viscosity that results in the failure to form plastic sheet post-drying. Meanwhile. Anonymous (2003) explains that pH influences the formation of cross linked of bio-plastic starch.

Bio-plastic surface profile of modified cassava starch

The surface profile of the modified cassava starch bio-plastic that observed by Scanning Electron Microscopy (SEM) as shown in Figure 1a while the comparator is shown in Figure 1b. Figures 1a and 1b show a longitudinal appearance of a modified cassava starch bio-plastic profile. Figure 1a shows the existence of dense and regular webs formed by modified starch polymers with relatively small air cavities variant compared to Figure 1b. Figure 1b shows an irregularity of tissue formed by a modified cassava starch polymer with a bigger air space size. This demonstrates have improved surface profile characteristics of preformed modified cassava starch bio-plastic ago.

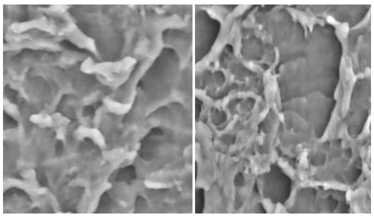


Figure 1: The longitudinal view of the surface profile of the modified cassava starch bio-plastic on magnification 3000x, (a) surface profile in the effect of gelatinization temperature and pH, (b) the surface profile of the research results Harsojuwono et al. (2016)

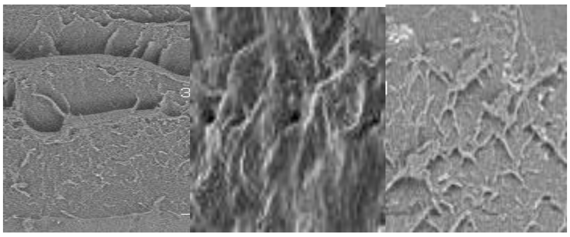
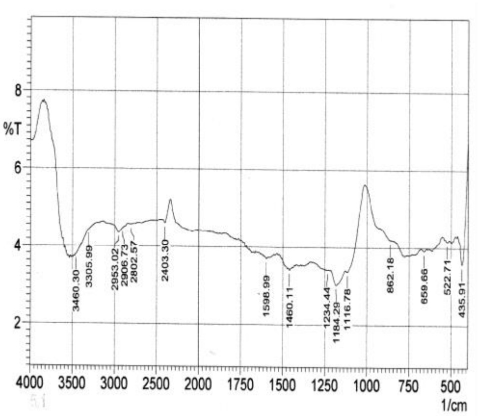


Figure 2: The transverse view of the surface profile of the modified cassava starch bio-plastic on magnification 180 x , (a) surface profile in the effect of gelatinization temperature and pH, (b) the research results of Harsojuwono, et al, (2016), (c) transverse view of edible film of starch and gelatin (Al-Hassan and Norziah, 2012)

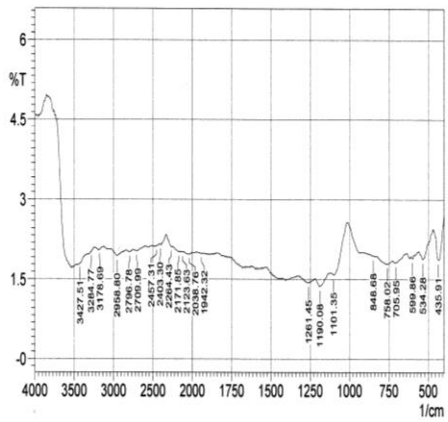
Figure 2 shows the bio-plastic profile of modified cassava starch on transverse view. Figure 2a presents profiles with the arrangement of fibers forming cross links of modified cassava starch polymers, while Figure 2b shows the existence of separate lumps but there are despite small nets. The existence of this cross link tends to increase the mechanical properties due to the stronger polymer bonds. The results of Fig. 2a are similar to the results of the study (Al-Hassan and Norziah, 2012) showing the transible edible film surfaces of starch and gelatin as in Figure 2c. Meanwhile, Anonymous (2003) explains that the pH of gelatinization affects the formation of cross linked of starch bio-plastic. It is further explained that the precise pH conditions will produce starch bio-plastic with characteristics : resistant of acid, high temperature heating, stirring (shearing) as well as stronger granules (not easily swelling) with high viscosity.

Functional groups

Modified cassava starch bio-plastic was made using the main ingredients of starch, acetic acid, perchloric acid, glycerol and other additives and glycerol as plasticizers. This will cause a change in the functional group due to the chemistry reaction that happened. The reading using FTIR spectrophotometer (Fourier Transform Infra Red) to functional group of bio-plastic , obtained wave number 3460.3; 3305.99; 2953.02; 2906,73; 2802.57,99; 1598.99; 1460.11; 1234,44; 1184.29; 1116.78; 862.18; 659.6602; 522,71; 425,91cm-1 as shown in Figure 5. Anonymous, (2012) explains that the absorption peak at 3200 - 3500 cm-1 indicates that hydroxyl (O-H) groups are attached to hydrogen. While the absorption peak at the wave number 2850- 2970 indicates the presence of alkenes (C-H), 2750 - 2850 there are aldehyde groups (C-OH). Wave numbers 1650 - 2000 cm-1 indicate the presence of simple aromatic compounds. Aromatic rings are also present at moderate to strong intensity uptake around the wave number 600-900 cm-1. Meanwhile, in the wave number 1000 - 1300 cm-1 there is a carboxyl group (C-O). According to Anonymous (2013), in absorption of wave numbers 675 - 995 cm-1 there are alkenes functional groups (C = C) and below 700 cm-1 there are other hydrocarbon compounds such as - (CH_2) n.



(a)



(b)

Figure 3: the wavelength spectrum of the modified cassava starch bio-plastic in the effect of gelatinization temperature and pH, (b) Bio-plastic wavelength spectra of modified cassava starch were resulted of research Harsojuwono, et al, (2016)

If Figure 3a is compared with Figure 3b, then the modified cassava starch bio-plastic spectrum shows the same spectral pattern only a few functional groups in Figure 3a are not clearly visible.

CONCLUSION

The conclusion that can be drawn from this research were

a) The temperature and pH of gelatinization as well as their interactions have a great influence on tensile strength, elongation at break, Young Modulus, percentage of volume swelling and degradation time of modified cassava starch bio-plastic.
b) The gelatinization temperature of 75 $\pm$ 1°C at pH 5 produces the best characteristics of modified cassava starch bio-plastic, i.e. tensile strength of 1657.43 M Pa, elongation at break of 10.32%, Young Modulus of 16,060.37 M Pa, percent volume swelling by 9% and time of degradation 7.33 days.
c) The profile of the bio-plastic surface of the longitudinal view shows the presence of dense and regular webs formed by modified starch polymers with relatively small airspace variations. The transverse profile of modified cassava starch bio-plastic shows the arrangement of fibers forming cross link of a modified cassava starch polymer.
d) Bio-plastic of modified cassava starch contains a hydroxyl (O-H), alkenes (C-H), aldehyde (C-OH), simple aromatic compounds, carboxyl (C-O), alkenes (C = C) and hydrocarbons -(CH_2)n.

REFERENCES

[1] Al-Hassan, A.A. and. Norziah, M. H. Starch-Gelatin Edible Films: Water Vapor Permeability and Mechanical Properties as Affected by Plasticizers. Journal Food Hydrocolloids. Volume 26, Issue 1. January 2012. Page 108-117.
[2] Anonymous. Tapioca Starch and Modified Starch. SCT.Co.Ltd., Bangkok. 2003.
[3] Averous, L. Biodegradable Multiphase System Based on Plasticized Starch: A Review, Journal of Macromolecular Science, United Kingdom. 2004.
[4] Darni, Y., and Utami, H. Study on Preparation and Characteristics of Mechanical Properties and Bio-Plastic Hydrophobicity of Sorgum Starch. Journal of Chemical Engineering and Environment. University Of Lampung. 2010. Vol. 7, No. 4, P.88-93.
[5] Bourtoom, T. Effect of Some Process Parameters on The Properties of Edible Film Prepared from Starch. Department of Material Product Technology, Songkhala. 2007. Http://Vishnu.Sut.Ac.Th/Iat/Food_Innovation/Up/Rice%20Starch%20film.Doc. Accessed September 2017).
[6] Harsojuwono, B. A. And Arnata, I. W. Characteristic of Bio-Plastic's Physical and Mechanical (Study on Tapioca Concentration and Composition Mixture of Plasticizer). J. Scientific Media of Food Technology. 2016. Volume 3, No. 1, Page 1-7.
[7] Harsojuwono, B.A. Arnata, I W. Arnata And Mulyani, S. Surface Profiles and Functions Group of Bio-

Plastic of Modified Cassava Starch. J. Scientific Media of Food Technology. 2016.. Vol 3, No. 2, P. 97 - 103.

[8] Harsojuwono, B.A., Arnata, I. W. and Mulyani, S. Biodegradable Plastic Characteristics of Cassava Starch Modified in Variation Temperature and Drying Time. J. Chemical And Process Engineering Research. 2017. Vol 49, 2017. Page 1 - 5.

[9] Sari, L. Influence of Stirring Temperature on Biodegradable Plastic Characteristics of Suweg (Amorphophallus Campanulatus) Bulbs with Addition of Glycerol and CMC (Carboxyl Methyl Cellulose), Digital Library UIN Kalijaga. 2016. Http://Digilib.Uin-Suka.Ac.Id/ 22356 (Accessed Oktober 2017).

[10] Setiani W, Sudiarti, T., Rahmidar, L. Preparation and Characterization of Edible Films from Poliblend Chart Bread-Chitosan. Journal of Chemical Valence: Journal of Research and Development of Chemistry, 2016. P-ISSN: 2460-6065, E-ISSN: 2548-3013.

[11] Utomo, A. W., Argo, B. D. And Hermanto, M. B. Effect of Temperature and Drying Time on Biodegradable Physicochemical Plastic Characteristics of *Aloe vera* Composites-Citosan. Journal of Bioprocesses of Tropical Commodities. 2013. Vol. 1 No. 1.