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EFFECT OF TEMPERATURE AND pH OF MODIFICATION PROCESS ON THE PHYSICAL-MECHANICAL PROPERTIES OF MODIFIED CASSAVA STARCH

PENGARUH SUHU DAN pH PROSES MODIFIKASI TERHADAP SIFAT MEKANIK-FISIK PATI SINGKONG TERMODIFIKASI

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ABSTRACT

The use of cassava starch for excipient in the manufacturing of the tablet has some problems, especially on physical-mechanical properties. The purpose of this study was to determine the effect of various temperature and pH in the process of modification on the physical-mechanical properties of modified cassava starch. Modifications were performed by suspending cassava starch into a solution of 3 % (w/v) PVP K30. The effect of various temperatures was observed at temperatures of 25; 45 and 65 °C, while the effect of various pH was observed at pH of 4.0; 7.0 and 12.0. The results showed that the temperature and pH did not affect the physical-mechanical properties of the modified cassava starch. Modification of cassava starch at pH and temperature of 7.0 and 45 °C was produced modified cassava starch with the most excellent solubility, while the best swelling power were formed by the modification process at pH and temperature of 7.0 and 25 °C. Overall, the most excellent compression properties of modified cassava starch resulted from the modification process at pH 12.

Keywords: cassava starch, compression properties, modification, pH, temperature,

ABSTRAK

Penggunaan pati singkong untuk bahan tambahan pada pembuatan tablet mempunyai permasalahan sifat mekanik-fisik. Tujuan dari penelitian ini adalah untuk mengetahui pengaruh perbedaan suhu dan pH pada proses modifikasi terhadap sifat mekanik-fisik pati singkong termodifikasi yang dihasilkan. Modifikasi dilakukan dengan mensuspensikan pati singkong dalam larutan PVP K3 0,3 %. Pengaruh suhu diamati pada perlakuan suhu 25; 45 dan 65 °C sedangkan pengaruh pH diamati pada perlakuan pH 4,0; 7,0 dan 12,0. Hasil penelitian menunjukkan bahwa suhu dan pH tidak mempengaruhi sifat mekanik-fisik pati singkong termodifikasi. Modifikasi pati singkong pada pH 7,0 dan suhu 45 °C menghasilkan pati singkong termodifikasi dengan kelarutan paling baik, sedangkan daya mengembang paling besar dihasilkan proses modifikasi pada pH 7,0 dan suhu 25 °C. Sifat kompresi paling baik dari pati singkong termodifikasi dihasilkan dari proses modifikasi pada pH 12.

Kata kunci: modifikasi, pati singkong, pengaruh suhu-pH, sifat kompresi.

INTRODUCTION

Cassava starch is a type of starches that are currently studied for pharmaceutical excipient. It is commercially important as the raw material for excipient of the pharmaceutical industry because cassava starch is relatively inexpensive, and has many remarkable characteristics, including great paste viscosity, great paste clarity and great freeze-thaw stability (Shanavas, Usha, & Moorthy, 2014). Cassava starch used for excipient in the manufacturing of a tablet such as a binder, filler and disintegrant. However, application of cassava starch for excipient of tablet has some limitations (Adejumo,

Aderibigbe, & Layokun, 2011; Mohammed, Isah, & Apeji, 2011; Lawal, Odeniyi, & Itiola, 2015). Cassava starch has low mechanical strength so tablets that use cassava starch as filler are fragile. In addition, cassava starch has low flow properties so it did not use to make tablet by direct compression (Wicaksono, Witono, Herlina, & Nuri, 2010). In short, the uses of cassava starch for tablet excipient encounter many problems.

Starches must be modified to enhance their functional properties as required in pharmaceutical excipient (Muzikova & Eimerova, 2011). Modifications of starch are performed by some methods. Chemical modifications of starch are made through the incorporation of specific functional groups on starch molecules which affect the physical-chemical properties of starch (Chiu & Solarek, 2009). These modifications are limited due to issues concerning customers and environment. The physical modifications are generally more preferred as these do not involve any chemical treatment that can be harmful to human. The physical modifications are primarily intended to change the granules structure, water solubility and crystallinity of the starch (Neelam, Vijay, & Lalit, 2012).

Modification of starch by physical modification is made by combining of starch particles with other pharmaceutical ingredients (Wicaksono, et al., 2010). Materials that often combined with starch include chitosan, microcrystalline cellulose, polyvinylpyrrolidone (PVP), lactose, mannitol, and calcium carbonate (Awasthi et al., 2010). Modification of cassava starch with chitosan produce modified cassava starch with better flow properties (Wicaksono et al., 2010). Cassava starch that combined with microcrystalline cellulose by co-drying improves its compression properties (Wicaksono & Shifa, 2008). Overall, cassava starch achieves new excipients with better characteristics by modifications.

The difference of temperature and acid concentrations affect the modification of starch. The modification of pinhao starch with lactic acid at different concentrations causes the hydrolysis of amylose and amylopectin of pinhao starch and it increases the starch resistance against the gelatinisation (Cordoba, Bet, & Schnitzler, 2015). While, the different heating treatments influence the resistant starch content of potato starch (Chou, Wu, Nurtama, & Lin, 2010). Although many properties of cassava starch have been studied, relatively few experiments have been reported the effect of temperature and pH on the modification of cassava starch. Therefore, the current research was conducted to investigate the effect of temperature and pH of the modification process on the physical-mechanical properties of modified cassava starch.

MATERIALS AND METHODS

Materials

Cassava starch (Amprotab®) and polyvinylpyrrolidone K30 (Deladon K30®) were purchased from PT Brataco Chemika (Surabaya, Indonesia). The chemicals were analytical grade, including sodium acetate trihydrate, acetic acid, potassium chloride, sodium hydroxide, disodium hydrogen phosphate and hydrochloric acid were purchased from Merck KGaA (Darmstadt, Germany).

Apparatus

The main equipments were hot plate-stirrer (Cimarec™ - Thermo Scientific), sentifuges, tray dryer (Memmert Universal Oven U), hydraulic press (Perkin-Elmer), pH-meter (Schott Lab 860), tap density tester (TAP-2S Logan), hardnes tester (HT 100 - Erweka), flowability tester, and scanning electron microscope (SEM) (Tabletop TM3000 - Hitachi).

Methods

Modification Process of the Cassava Starch

A 100 grams cassava starch of each formula were weighed into a beaker; added buffer solution with concentration 10 % (w/v), then heated with stirring at 500 rpm for 30 minutes. The next stage was added PVP K30 at a concentration of 3 % (w/v), and stirred at 300 rpm for 15 minutes. The suspension of cassava starch - PVP K30 was allowed settling and then sediment of cassava starch - PVP K30 separated from the supernatant. The cassava starch - PVP K30 dried by tray dryer at 60 °C for 30 minutes, then sieved with a 18 mesh sieves. The modified cassava starch dried again with fluid bed dryer (Enderscott®) at 45 °C for 15 minutes. The results were stored until further evaluation. **Table 1** shows the formula of modification process

Scanning Electron Microscopy

The modified cassava starch were mounted on a SEM specimen stub with adhesive tape and subjected to gold sputter coating to render them electrically conductive. Scanning electron micrographs were taken by a Hitachi Tabletop TM3000. The accelerating voltage and magnification was used respectively 5 KV and 100 times.

Flow Properties

The flow properties of modified cassava starch were determined by fixed-base cone method using flowability tester. In brief, the angle of repose was determined by measuring the angle of powder on a spatula lifted from a powder bed. The angle of repose was used to determine the flow properties of the sample.

Bulk Density, Tap Density and Carr Index

The bulk and tap density were measured by tap density tester (TAP-2S Logan). The samples with a certain weight were included in a 250-mL measuring cylinder and recorded the volume. Then the measuring cylinder was tapped mechanically by tap density tester at least 1500 times up to a constant volume and recorded the final volume of the sample. Bulk density was calculated as weight divided by the initial volume of the sample, while the tap density was calculated as weight divided by the sample volume after tapping. The Carr Index was calculated by equation ((tap density - bulk density)/tap density) x100 (Akhgari, Sadeghi, & Dabbagh, 2014).

Solubility and Swelling Power

The 0.1 g sample was suspended in distilled water at concentration 10 % (w/v) using centrifuge 50-mL tube, then heated on water bath at 60 °C. The tube was shaken every 10 minutes for 30 minutes then centrifuged at 2,000 rpm for 10 minutes. Supernatant was collected and dried to determine solubility, while the sludge was weighed to determine the swelling power of starch. Solubility and swelling power were calculated by equation % solubility = (weight of soluble starch/weight of sample) x 100 and swelling power = wight of sludge/weight of sample (Akpa & Dagde, 2012; Kusumayanti, Handayani, & Santosa, 2015).

Table 1. The formula of modification process of cassava starch

Material	Formula								
	I	II	III	IV	V	VI	VII	VIII	IX
Cassava starch (% w/v)	10	10	10	10	10	10	10	10	10
PVP K30 (% w/v)	3	3	3	3	3	3	3	3	3
Temperature (°C)	25	25	25	45	45	45	65	65	65
pH of buffer solution	4.0	7.0	12.0	4.0	7.0	12.0	4.0	7.0	12.0

Compression Properties

A 350 mg sample of modified cassava starch was directly compressed using 8 mm flat-faced punches in a hydraulic press under pressure 1, 2, 3 and 4 ton. The hardness of matrix of modified cassava starch was measured by hardness tester.

RESULTS AND DISCUSSION

Granules of Modified Cassava Starch

Granules of modified cassava starch were resulted of sifting with a sieve size of 18 meshes. The sizes of granules were suitable for pharmaceutical excipient of direct compression tablet. **Figure 1** displays the SEM microscopic of modified cassava starch. The particles of cassava starch had a round shape with a range of diameter about 3-12 μm (Adejumo et. al., 2011). The granules of modified cassava starch were an irregular shape with smooth surface and range of diameter 0.2-0.5 mm. Treatment of temperature and pH did not affect the shape and size of granules of modified cassava starch.

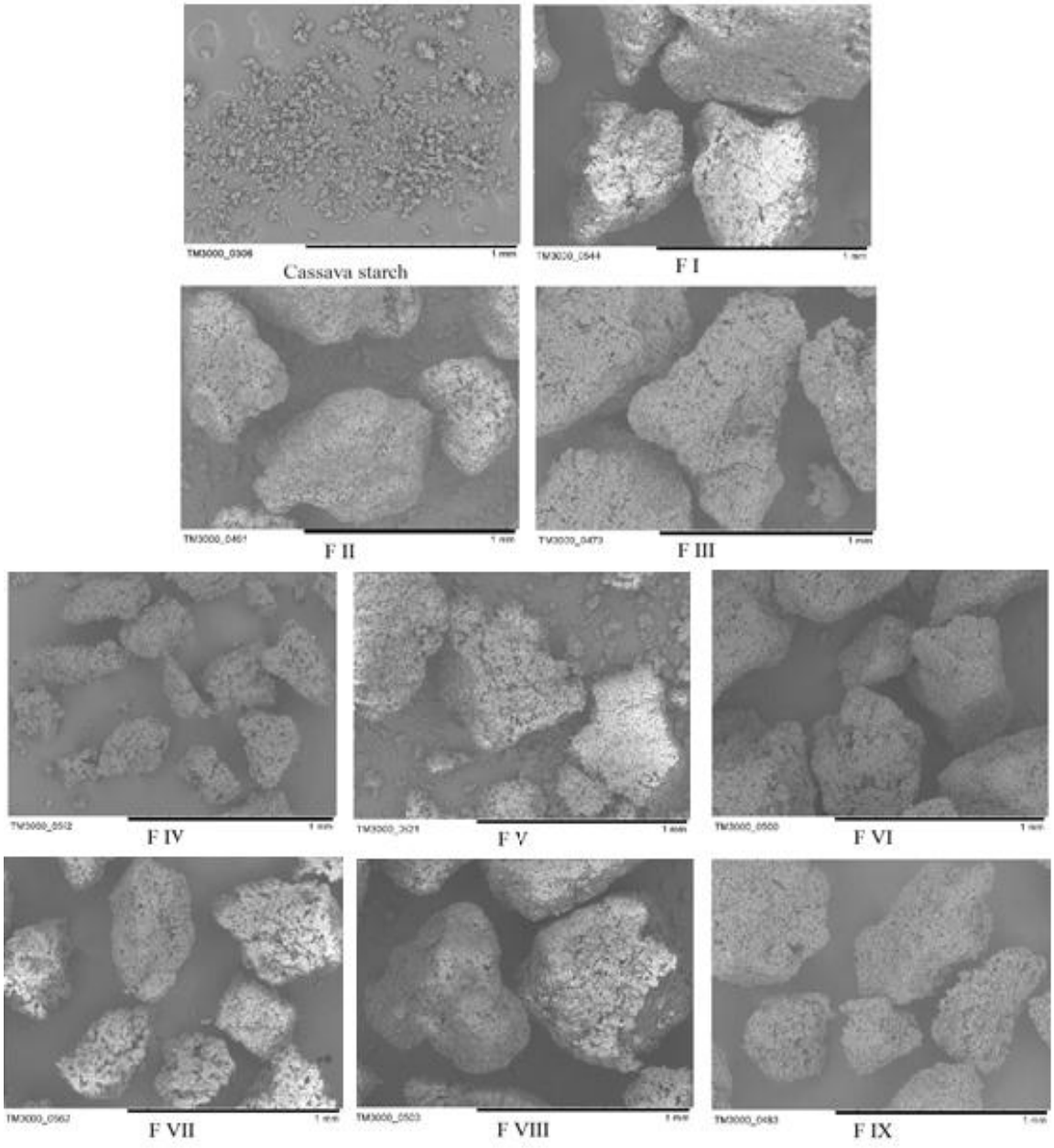

Figure 1. Micrographs of modified cassava starch (magnification 100x)

Table 2. The angle of repose and the flow properties of modified cassava starch

Formula	h (cm)	d (cm)	Tangen (h/d)*	Angle of repose (º)**
I	3.05	5.5	0.55	29
II	3.05	5.5	0.55	29
III	3.15	5.5	0.57	30
IV	2.90	6.0	0.48	26
V	3.10	5.5	0.56	30
VI	3.10	5.5	0.56	30
VII	2.90	6.0	0.48	26
VIII	2.90	6.0	0.48	26
IX	3.10	5.5	0.56	30

*h = high d = diameter

** Angle of repose < 50º = satisfactory flow properties (Staniforth, 2002)

Flow Properties

Table 2 shows the angle of repose and the flow properties of modified cassava starch. The powder of pharmaceutical excipient with the angle of repose < 50º has satisfactory flow properties (Staniforth, 2002). The modification processes were carried out at pH 4.0 produce the best flow properties of modified cassava starch with the angle of repose 26° as well as a modification at temperature 65 °C. Overall, modifications of cassava starch were produced modified cassava starch with good flow properties.

Bulk Density, Tap Density and Carr Index

Table 3 shows bulk density, tap density and Carr index of modified cassava starch. The modified cassava starches were low bulk density and low tap density indicated that the granules had nonporous and free-flowing (Chitedze, Monjerezi, Saka, & Steenkamp, 2012. The differences in pH and temperature treatment did not affect the bulk density and tap density of modified cassava starch. Modifications of cassava starch were produced modified cassava starch with Carr index < 15. The results indicated that granules of modified cassava starch had excellent (free-flowing) flow properties (Staniforth, 2002).

Solubility and Swelling Power

The solubility of the starch depends on sources of starch, swelling power and presence of other materials (Adejumo et al., 2011).

Table 3. bulk density, tap density and Carr index of modified cassava starch

Formula	Bulk density (g/mL)	Tap density (g/mL)	Carr index*
I	0.46	0.53	13.21
II	0.44	0.55	20.00
III	0.48	0.55	12.73
IV	0.46	0.52	11.54
V	0.46	0.52	11.54
VI	0.46	0.53	13.21
VII	0.48	0.55	12.73
VIII	0.48	0.55	12.73
IX	0.46	0.53	13.21

*****Carr index: 5-15 = Flowability of granules is excellent/free-flowing granules
18-21 = Flowability of granules is fair (Staniforth, 2002)

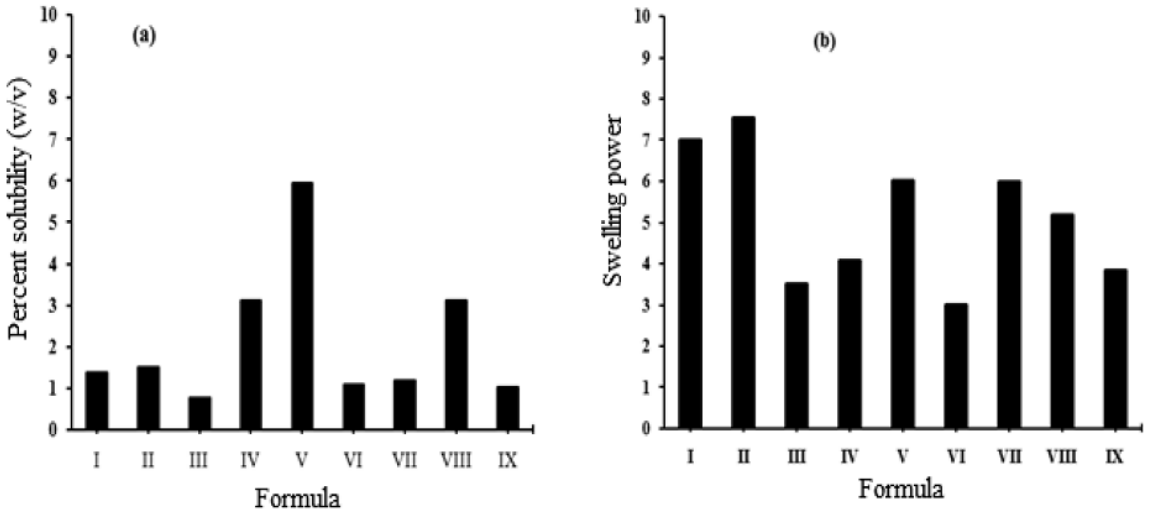

Figure 2. (a) The solubility and (b) the swelling power of modified cassava starch

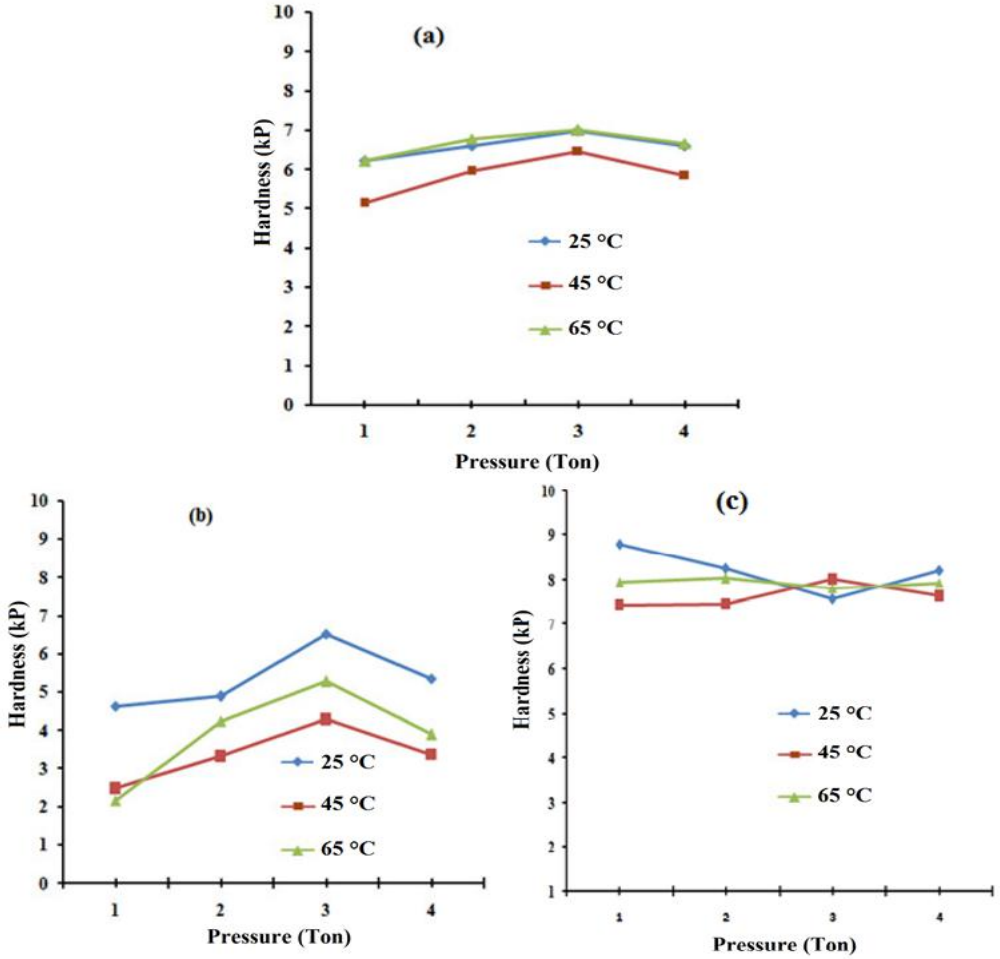

Figure 3. The temperature and pH effect of modifications process to the compression properties of modified cassava starch at (a) pH 4.0 (b) pH 7.0 and (c) pH 12.0.

The processes that led to decomposition of starch improve the solubility of starch; while treatments that improve the crystalline structure of starch decrease the solubility of starch (Nuwamanya, Baguma, Wembabazi, & Rubaihayo, 2011).

Figure 2 displays the solubility and swelling power of modified cassava starch. Percent solubility of modified

cassava starch was about 1-7% (w/v). The differences in pH and temperature of process modifications appear to affect the solubility of modified cassava starch. The best solubility of modified cassava starch was produced by modification at pH and temperature of 7.0 and 45 °C. Swelling power of modified cassava starch was ranging between 3-7 times. The modification process at pH and temperature of 7.0 and 25 °C was produced modified cassava starch with the highest swelling power. It is possible that at pH and temperature of 7.0 and 25 °C, respectively, the oxidative processes are Overall, the modification at pH 12.0 produce the hardest matrix of modified cassava starch (>7 kP), indicating that it is the best condition to modify the cassava starch for pharmaceutical excipient of the tablet.

CONCLUSION

Temperature and pH of modification process of cassava starch do not affect physical and mechanical properties of modified cassava starch. All formula of experiment produces modified cassava starch with round shape and good flow properties. Modification of cassava starch at pH and temperature of 7.0 and 45 °C produce modified cassava starch with the best solubility, while modified cassava starch with the highest swelling power produced by modification at pH and temperature of 7.0 and 25 °C. Temperature and pH of modification process affect compression properties of modified cassava starch. Modification at pH 12.0 produces modified cassava starch with the best compression properties.

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lowest (Takizawa, Silva, Konkel, & Demiate, 2004).

Compression Properties

Figure 3. displays the temperature and pH effect of modifications process to the compression properties of modified cassava starch. Modifications of cassava starch at pH 4.0 were produced modified cassava starch with comparable compression properties at temperature 25 °C and 65 °C; while modification at pH and temperature of 7.0 and 25 °C was produced modified cassava starch with the most excellent of compression properties.

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