Pasting Properties of MOCAF (Modified Cassava Flour) Using Rapid Visco Analyzer with Variations of pH Solution

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ABSTRACT

Starch is a glucose polysaccharide which includes amylose and amylopectin. Natural starch in its utilization has several weaknesses so that modified starch begins to develop, one of which is MOCAF. MOCAF is a modified cassava flour by fermentation using lactic acid bacteria (BAL). The weakness of natural starch is become thicky when the food processing at high temperature and acidic conditions. MOCAF is expected to be able to provide solutions for food processing at high temperatures and acidic conditions. This research was conducted to determine the gelatinization profile of MOCAF during processing at several pH levels. Physical properties of the MOCAF firstly were analyzed including water, starch, amylose, and amylopectin content. After that, the MOCAF gelatinization profile was measured using a Rapid Visco Analyzer (RVA), with observation parameters namely peak viscosity (PV), minimum viscosity (MV), breakdown (BD), final viscosity (FV), setback (SB), pasting temperature (PT), and peak time (Ptime). The results showed that the acidic conditions affected the gelatinization profile of the starch. In the sample which was mixed with citrate buffer solution pH 3 showed the highest peak viscosity (4206.4 cP) and breakdown (3047.6 cP), while the lowest minimum viscosity (1158.6 cP), final viscosity (1604.0 cP), setback (445.2 cP), pasting temperature (74.28°C), and peak time (4.31 minutes). Thus, the low-pH processed MOCAF has the lowest viscosity stability and retrogradability.

Keywords: Acid, modified starch, pasting properties

INTRODUCTION

Starch in everyday life is widely used not only on a household scale but also on an industrial scale. Starch has an important role not only in the food industry but also in nonfood industries such as the paper, glue, textile, and so on (Koswara, 2009). In the world of trade, starch is known to be of two types, namely natural starch and modified starch. One example of natural starch that is widely used, especially in the food industry, is cassava starch or commonly known as tapioca. The function of tapioca in the food industry is diverse, namely as a thickening agent, filler, and binder such as in the production process of baby food, ice cream, meat processing, sauces, and others including the pharmaceutical industry (Putri, 2015).

The use of natural starch such as tapioca raises several weakness, namely: when natural starch is cooked natural starch takes a long time so it requires high energy, has sticky characteristics, and is not resistant to acid treatment. This causes starch to have limitations in its application. According to (Koswara, 2009), the industry requires starch to have stable characteristics both to high and low temperature treatments, good resistance to mechanical treatment, and its thickening power to withstand acidic conditions and high temperatures. Therefore, several studies have emerged that have developed modified starch to improve the characteristics of natural starch.

MOCAF (Modified Cassava Flour) is a form of starch product development by modifying cassava cells by fermentation using lactid acid bacteria (BAL). MOCAF has different characteristics from ordinary cassava flour, including: increased viscosity, gelation ability, rehydration power, WHC (water holding capacity), and ease of dissolving. Today, there are various kinds of products that can be produced with MOCAF both as raw materials and as substitute materials such as in noodle products, bakery, cookies, and semi-wet food.

The use of MOCAF is expected not only as a substitute material but also as a filler, one example of which can be applied to sauce products. According to (Koswara, 2009), the sauce-making process is carried out under acidic conditions (pH 3.8 - 4.4) and quite high temperatures (80-100°C). These conditions will affect the characteristics of gelatinization (gelatinization profile) which can be known from the amylograph curve. The content of amylose and amylopectin has an important role in determining the gelatinization profile of starch. Amylose and amylopectin levels in sorghum flour affect the peak viscosity and gelatinization temperature of the starch (Budijanto and Yuliyanti, 2012).

Gelatinization of starch is a condition where the granules experience swelling and at a certain point are unable to return to their original condition. The gelatinization temperature is the temperature at which the starch granules break. According to BeMiller (2007), the gelatinization temperature of starch is influenced by the type of starch, the method of measurement, the ratio between starch and water, pH, the presence or absence of swelling by salt, the concentration of salt, and the concentration of solutes such as The characteristics of starch sucrose. gelatinization are divided into various types, tapioca has the characteristics of type A gelatinization, which has a high peak viscosity value and is followed by rapid dilution during the heating process (Syamsir et al., 2012). This is because the hydrogen bonds linking amylose and amylopectin in natural starch are prone to breaking during the starch gelatinization process.

Thus, tapioca is considered to have poor resistance when used in high temperature processing and under acidic conditions. Therefore, this study was conducted conducted to determine the gelatinization profile of MOCAF during processing at several pH levels.

MATERIALS AND METHODS Tools and Materials

The tools used in this research are analytical equipment such as Techmaster's Rapid Visco Analyzer (RVA), Horiba's pH meter, Precisa analytical balance, Troac brand of thermometer, pyrex brand of glassware, pipettes and pyrex stirrer. The material used in this research is MOCAF obtained from Mr. Te Jember, citrate buffer solution, and aquades.

Methods

The first MOCAF used was measured for its chemical content including water content, starch content, amylose content and amylopectin content. This research was conducted to observe the gelatinization profile of MOCAF starch using a Rapid Visco Analyzer using acid solvents with different acidity levels. The solvent used was citrate buffer solution with the following variations in pH: 3, 4, 5, 6, and 7. The measurement of gelatinization profile in each sample was carried out three times. This research consists of several stages of activities, namely: preparation of tools and materials; analysis of moisture, starch, and amylopectin amylose content; preparation of citrate buffer solution; starch gelatinization profile measurement; and data analysis.

Preparation of Citrate Buffer Solution

The citrate buffer solution was prepared using 0.1 M citric acid solution and 0.1 M Na-citrate solution as shown in Figure 1. The first step was that x mL of citric acid solution was added with y mL of Na-citrate. After that, the dilution was carried out to a predetermined pH of 100 mL. Then, the pH of each solution was measured (Sudarmadji dan Haryono, 1997).

Chemical Content Analysis

The sample to be used was measured water content using the gravimetric method, starch content using the Nelson-Somogyi method, and analysis of amylose content using the spectrophotometric method.

Gelatinization Profile Measurement

Gelatinization profile measurements were carried out using a Rapid Visco Analyzer (RVA) using the AACC 61-02.01 method. 3 grams of MOCAF dissolved in 25 mL of solvent (aquades or buffer solution), 12% water content (Imanningsih, 2012), and a stirring speed of 160 rpm (An, 2005) which is shown in Figure 2. The solvent used is divided into two, namely the control solvent and the citrate buffer solution as follows:

- K: control solvent (aquades) A: citrate buffer solution pH 7 B: citrate buffer solution pH 6 C: citrate buffer solution pH 5 D: citrate buffer solution pH 4
- E: citrate buffer solution pH 3

The RVA temperature measurement was in the range of 50-95°C for 13 minutes with a gradual increase in temperature as shown in Figure 3. The method used to measure the gelatinization profile of MOCAF on RVA is by using the flour method. Each method has different temperature, time, and rotational speed settings depending on the type of sample to be tested. Details of the settings used to measure the gelatinization profile of MOCAF using the flour method are shown in Figure 4.

The RVA heating and cooling viscometer provides information on the pasting properties, including: peak viscosity (PV), minimum viscosity (MV), final viscosity (FV), breakdown (BD), setback (SB), pasting temperature (PT), and peak time (Ptime) (Shafie et al., 2016).

Data Analysis

The data obtained will be analyzed using a descriptive method by calculating the average data and standard deviation. Presentation of data in the form of tables and figures to facilitate the discussion of the data.

RESULTS AND DISCUSSION Chemical Content of MOCAF

The chemical content of MOCAF including moisture content, starch content, as well as amylose and amylopectin content are shown in Table 1. Information on this chemical content is needed to determine its effect on the gelatinization profile of the tested MOCAF.

In Table 1 it is known that the water content of MOCAF is 12.15% which is still in accordance with Indonesian National Standar (SNI No. 7622 of 2011) concerning MOCAF with a maximum limit of 13% water content. MOCAF starch content of 83.63% lower than tapioca starch content of 85.92% (Putri, 2015). Tapioca starch content was higher than MOCAF because tapioca starch content almost covered all dry matter, while MOCAF components other than starch were still in significant amounts. Starches are composed mainly of two polysaccharides, amylose and amylopectin, that organized in complex structure called granules (Castanha et al., 2021).

The amylose and amylopectin levels on the tested MOCAF were 16.22% and 83.78%, respectively. Amylose and amylopectin levels in flour will affect the process of starch gelatinization. Measurement of amylose content was carried out using a spectrophotometric method with the principle of staining using iodine. Amylose is a polymer part with -(1,4) bonds of glucose units in each chain there are 500-2000 D-glucose bonds, forming straight chains which are generally said to be linear from starch. The characteristic of amylose in solution is that it has a tendency to form very long and flexible coils that always move in circles. The structure that underlies the interaction of iodamylose forms a blue color (An, 2005).

Amylopectin is a branched-chain polymer with α -(1,4)-glycosidic bonds and α -(1,6)-glycosidic bonds at the branching sites. Each branch consists of 25-30 Dglucose units (An, 2005). According to (Koswara, 2009), amylopectin usually contains 1000 or more units of glucose molecules for each chain. The molecular weight of glucose amylopectin for each chain varies depending on the source. Amylopectin in tubers contains a small amount of phosphate ester bonded to the 6th carbon atom of the glucose ring (Putri, 2015). The structure of starch including amylose and amylopectin is shown in Figure 5.

Gelatinization Profile of MOCAF

Gelatinization process occurs when propitious conditions are present, as sufficient amount of water and temperature higher than the gelatinization temperature of the given starch. In those conditions, the intermolecular bonds that maintain the crystalline structure of the granules are weakened, and the water in the vicinity can penetrate the formerly rigid granular structure (Castanha et al., 2021). At this conditions, the starch granule swells and loses its birefringence (Xie et al., 2006). MOCAF gelatinization profile measured using RVA with various solvents under different acidity conditions is shown in Table 2 which includes: peak viscosity (PV), minimum viscosity (MV), final viscosity (FV), breakdown (BD), setback (SB), pasting temperature (PT), and peak time (Ptime). According to (Imanningsih, 2012), in measurements using RVA there are four phases that can be identified on the resulting amylographic curve.

In the first phase, the temperature is lower than the gelatinization temperature of starch so that the measured viscosity value is low. In the second phase, there was an increase in viscosity along with increasing temperature until it reached the gelatinization temperature of starch. The increase in viscosity indicates that the starch granules are swelling. The peak viscosity of the product is called the peak viscosity (PV). The third phase, occurs when there is an increase in temperature and stirring, the starch granules will break and amylose will come out of the granules which results in a decrease in viscosity. The lowest viscosity of this phase is known as minimum viscosity (MV). The last phase, is a decrease in temperature causing a re-association between starch molecules (setback) so that the gel is formed again and the viscosity increases again so that it reaches the final viscosity which is usually called final viscosity (FV).



Measurement of the gelatinization profile using RVA will produce an amylographic curve that shows several parameters of viscosity values in the sample during the heating and stirring process as shown in Figure 6. In addition. the amylographic curve generated from measurements using RVA has unique characteristics. In the RVA amylography curve, the x-axis represents time (minutes) and the y-axis indicates viscosity (cP). In principle, during the measurement the liquid is heated and stirred. Viscosity value is measured from the resistance of the liquid to the rotating blades (Putri, 2015).

In Table 2 it can be seen that pH can affect the value of starch viscosity during the heating and cooling process. The lower the pH, the higher the peak viscosity, and the lower the minimum viscosity, breakdown, final viscosity, setback, peak time, and pasting temperature. This is due to acid hydrolysis which can break the glycosidic bonds of starch.

The pasting curve of the starh solutions mixture at pH 7 and 3 show that starch solutions had a lower peak viscosity, final viscosity, setback viscosity, pasting time, peak time, and a higher breakdown viscosity in acidic conditions than in a neutral environment (Zhang et al., 2017). Given that acid hydrolysis destroys glycocidic binds in molecule (Choi et al., 2016), the complete pasting of starch molecules in acidic conditions requires less energy anf therefore it is gelatinized faster and at lower temperatures (Zhang et al., 2017).

MOCAF amylograph curves resulting from measurements using RVA with two types of solvents, namely distilled water and buffer solutions with different pH are shown in Figure 7.

Peak Viscosity (PV)

Peak viscosity was the highest viscosity achieved during heating at 95°C.

The variation of peak viscosity is often associated with the swelling power of starch and the rate disruption of the starch granule (Shafie et al., 2016). MOCAF samples mixed with citrate buffer solution pH 3 had the highest peak viscosity value, and MOCAF samples mixed with citrate buffer solution pH 7 had the lowest peak viscosity values. The results of previous studies showed that the peak viscosity of arrowroot starch modified with 10% propylene oxide was higher at pH 3.5 than at pH 6.5 (Rahaju et al., 2013). In addition, Maulani amylopectin levels are responsible for the granule development process (Putri, 2015). MOCAF has a lower amylose content than cassava flour, this is because during the fermentation process it opens the amylopectin structure of starch resulting in an increase in amylose content which plays a role in the formation of a stable gel (Loebis and Meutia, 2012).

Minimum Viscosity (MV)

Minimum viscosity or hold viscosity was the lowest viscosity achieved during heating at 95°C. MOCAF samples mixed with citrate buffer solution pH 3 had the highest minimum viscosity value. It was reflecting different susceptibility of starch breakdown upon shearing and heating (Shafie et al., 2016). Starch granule became susceptible to shear disintegration when swelles, especially in starches with lower amylose content (Kaur et al., 2007).

Final Viscosity (FV)

Final viscosity measured the ability of the starch to form viscous paste after cooking and cooling. Final viscosity was the paste viscosity upon cooling at 50°C. At this stage, the starch granules experienced restructuring of starch molecules and retrograded (Shafie et al., 2016). The highest final viscosity value is in the sample MOCAF pH 7. This is because if the starch suspension at a certain pH and heated at a certain temperature will cause the starch to be hydrolyzed into dextrin so that starch with low viscosity is produced. (Koswara, 2009).

Breakdown (BD)

Breakdown shows viscosity stability against the heating process (Faridah D.N, Fardiaz D, Andarwulan N, 2014). The highest breakdown value is the pH 3 MOCAF sample, it shows that under acidic conditions the viscosity stability is not good when compared to the pH 7 MOCAF sample which has the lowest breakdown value. This shows that the viscosity of starch is stable at neutral compared to acidic conditions. pН Breakdown viscosity defined as the difference between peak viscosity and minimum viscosity, while stability ratio was the ratio of viscosity at the onset of cooling to peak viscosity before cooling (Shafie et al., 2016). The stability explained the hydration, starch swelling power and shear resistance of starch paste during heating.

Setback (SB)

The highest setback value was in the MOCAF pH 3 sample, while the highest setback was in the control MOCAF sample. viscosity indicated Setback starch retrogradation tendency after gelatinization and cooling at 50°C. The viscosity changes while cooling were mainly due to amylose molecular re-association, and low setback viscosity indicated a low rate of starch retrogradation (Shafie et al., 2016). The lowest setback viscosity could be a good thickener and stabilizer for food processing industries (Corke, 1997).

Peak Time (Ptime) and Pasting Temperature (PT)

Peak time is the time required to reach peak viscosity, while pasting temperature is the temperature required for the sample to undergo the gelatinization process (Putri, 2015). The value of the peak time and pasting temperature of the sample decreased with the lowering of the pH. This shows that under acidic conditions, starch will be gelatinized faster and requires lower energy.

CONCLUSION

From the results of the recent study, it can be concluded that the gelatinization profile of MOCAF is influenced by acid treatment. From the measurement results using RVA, an increase in the value of peak viscosity and breakdown, as well as a decrease in the value of minimum viscosity, final viscosity, setback, time to peak and pasting temperature occur along with the lower pH (acid conditions).

The peak viscosity value indicates the ability of starch granules to expand, the breakdown viscosity indicates the viscosity stability during the heating process, and the setback viscosity indicates the level of retrogradation. Thus, the MOCAF processed at acidic conditions has the lowest viscosity stability and retrogradability.

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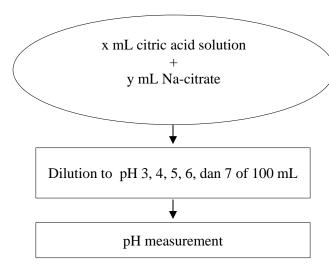
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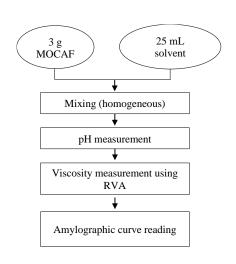


Figure 1. Preparation of citrate buffer solution

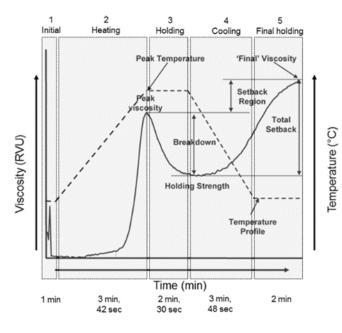


Figure 2. RVA running process stage

Time (hh:mm:ss)	Function Type		Value	
00:00:00	Temp	-	50	
00:00:00	Speed	-	960	
00:00:10	Speed	-	160	
00:01:00	Temp	-	50	
00:04:42	Temp	-	95	
00:07:12	Temp	-	95	
00:11:00	Temp		50	
00:13:00	End			

Figure 4. Flour methode on RVA setting

Figure 3. RVA temperature setting (Balet et al., 2019)

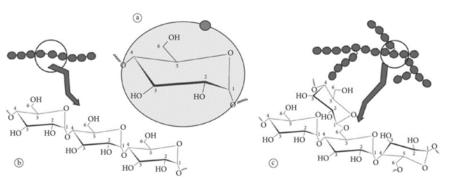


Figure 5. Starch chain structure (a), amylose (b), amylopectin (c) (Alcázar-Alay and Meireles, 2015)

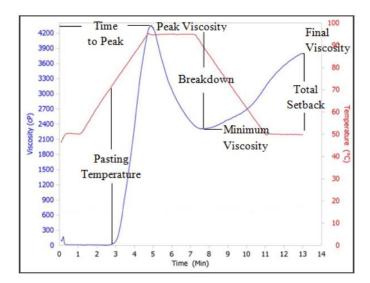


Figure 6. Amylographic curve of measurement results using RVA (Manaois, 2009)

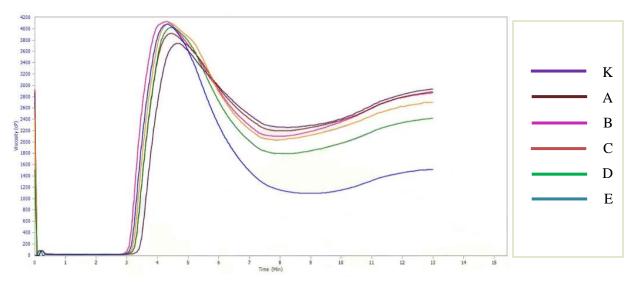


Figure 7. MOCAF amylograph curve with distilled water (K) and citrate buffer solution pH 7 (A), pH 6 (B), pH 5 (C), pH 4 (D), pH 3 (E)

Components	Total (%)
Water	$12,\!15 \pm 0,\!07$
Starch	$83,\!63 \pm 3,\!60$
Amylose	$16,22 \pm 1,29$
Amylopectin	$83,78 \pm 1,29$

Table 1. Chemical content of MOCAF

Table 2. MOCAF gelatinization profile with different types of solvents and acidity conditions

Sample	PV (cP)	MV (cP)	BD (cP)	FV (cP)	SB (cP)	Ptime (minute)	PT (°C)
K	3983.4 ± 129.16	1959.0 ± 84.90	2024.4 ± 76.75	2644.6 ± 125.62	685.6 ± 44.85	4.28 ± 0.03	73.65 ± 0.34
А	3741.0 ± 90.63	2248.6 ± 11.72	1492.4 ± 83.36	2924.0 ± 16.11	675.4 ± 12.66	4.60 ± 0.07	77.32 ± 0.38
В	3861,6 ± 33.95	2148.8 ± 9.65	1674.4 ± 27.84	2878.6 ± 7.83	674.6 ± 19.55	4.45 ± 0.04	75.65 ± 0.38
С	4106.8 ± 74.31	2038.4 ± 33.81	2068.4 ± 64.98	2706.4 ± 26.48	671.5 ± 9.14	4.40 ± 0.00	74.86 ± 0.34
D	4138.4 ± 95.66	1816.8 ± 22.47	2270.0 ± 59.46	2235.2 ± 13.41	631.8 ± 8.29	4.39 ± 0.11	74.74 ± 0.79
Е	4206.4 ± 133.97	1158.6 ± 45.77	3047.6 ± 95.62	1604.0 ± 54.69	445.2 ± 11.17	4.31 ± 0.33	74.28 ± 0.06

Note: the value in the table is the average value of three measurements