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Effects of sodium chloroacetate concentration on the physicochemical properties of carboxymethyl tapioca

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Abstract

The role of reaction variables on the carboxymethylation of commercial tapioca was investigated using a statistically experimental design approach. The reaction was carried out in an isopropanol-water mixture at 25°C for 1 hr. The influence of the etherification reaction parameter on the degree of substitution (DS), moisture content, ash content, syneresis, swelling power, and solubility was determined to be the best concentration of sodium chloroacetate based on the effect on carboxymethyl tapiocas. Using FT-IR techniques allowed us to evaluate the changes in modified starch when compared to native starch. The results showed that the treatment of sodium chloroacetate concentration caused a shift in chemical properties where the values of DS (0.18-0.38), moisture content (6.65-12.96%), and ash content (0.82-1.54%) were higher than native tapioca. The syneresis of carboxymethyl tapioca (80.33-84.16%) was lower than that of native tapioca (87.91%). The new bands in Fourier transform infrared at 1597-1604 cm^{-1} and 1450 cm^{-1} indicated that the starch granules were substituted. The concentration of sodium chloroacetate caused an increase in the swelling power of carboxymethyl tapioca (0.19-2.45 g/g) and an increase in solubility (58.91-74.44%). The best concentration of sodium chloroacetate was 20%, which produced carboxymethyl tapioca with a DS of 0.38; a moisture content of 6.65%; an ash content of 1.17%; a syneresis of 80.33%; a swelling power of 2.45 g/g; and a solubility of 74.44%. The correlation analysis showed that very close relationship ($R^2 > 0.8$). Generally, carboxymethyl tapioca has changed its chemical and physical properties.

1. Introduction

Tapioca is a native starch with several disadvantages compared to other native starches in general. These are limited by specific undesirable characteristics such as a long cooking time (thus requiring high energy), a stiff and not transparent paste, being too sticky, low thickness, low solubility, and low swelling strength (Charoenthai *et al*., 2018; Sumardiono *et al*., 2020). Hence, it is always reasonable to modify it to suit a specific process. Technological developments in starch processing have shown that native starch can be changed to have the desired properties. Important properties wanted from modified starch (which native starch does not have) include higher brightness (whiter starch), lower retrogradation, lower viscosity, clearer formed gel, softer gel texture, lower tensile strength, more easily broken starch granules, higher gelatinisation time and temperature, and lower time and temperature of starch granules to break down. Tapioca showed variations in chemical and physical properties; however, they generally showed similar crystallinity type (type C) (Polnaya *et al*., 2021). Starch modification can be done by physical or chemical treatment or by combining the two as appropriate (Herawati, 2012). One method that can be used to modify starch is chemical modification.

Chemical modification of starch involves the reaction of hydroxyl groups on an anhydrous glucose unit (AGU), and these have been used to produce starch derivatives based on carboxymethylation (Ganorkar and Kulkarni, 2013). Carboxymethyl starch is a cold-water-soluble starch derivative having wide applications in pharmaceuticals (Charoenthai *et al*., 2018; Lefnaoui and Moulai-Mostefa, 2015), textiles, paper making, adhesive, and absorbent (Li *et al*., 2011), medicine, cosmetics, and food (Spychaj *et al*., 2013). Carboxymethylation is a starch modification method based on the etherification reaction to enter the hydrophilic group into the AGU or replace the hydroxyl group with sodium chloroacetate

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($ClCH_2COONa$). The first step of carboxymethylation is alkalisation, in which the hydroxyl group (-OH) of the starch molecule is activated and converted into a more reactive alkoxide form (Starch-O_2). In the second step, an etherification reaction occurs (Adeyanju *et al*., 2016).

Carboxymethyl starch is a modified starch with different properties from other modified starches. This is due to the negatively charged functional group (CH_2COO). Carboxymethyl starch is soluble in cold water (Li *et al*., 2011), has a lower gelatinisation temperature (Lefnaoui and Moulai-Mostefa, 2015), increases swelling power and solubility (Agwamba *et al*., 2016; Ganorkar and Kulkarni, 2013), and prevents starch retrogradation at low temperatures (Kittipongpatana *et al*., 2006). According to Li *et al*. (2011) and Rusman *et al*. (2017), the degree of substitution of carboxymethyl starch will increase with an increasing concentration of sodium chloroacetate. However, a higher concentration of sodium chloroacetate can cause side reactions, such as the sodium glycolate reaction, which reduces the degree of substitution and reaction efficiency of the resulting carboxymethyl starch. This study aimed to determine the best sodium chloroacetate concentration based on its effect on the resulting carboxymethyl tapioca's physicochemical properties.

2. Materials and methods

2.1 Materials

The tapioca (Rose Brand, Indonesia) used in this study was obtained from the local market.

2.2 Preparation of carboxymethyl tapioca

The synthesis of carboxymethyl tapioca was carried out using Kittipongpatana *et al*. (2006). Four hundred mL of isopropanol was added to 100 g of tapioca and then alkalised using 100 mL of 35% NaOH solution for 1 hr at 25°C. This alkalisation was carried out using a water bath (Memmert, Germany) and stirred during the alkalisation process. After the alkalisation time ended, sodium chloroacetate was added according to the treatment (10, 20, or 30% w/v based on starch weight).

The following process is the carboxymethylation process, where this process time is 20 mins at a temperature of 50°C. This carboxymethylation process is also carried out using a water bath and continuously stirred until the carboxymethylation process ends. After the carboxymethylation process was completed, the suspension was cooled to room temperature (27°C) and then neutralised using glacial acetic acid. After the slurry is neutral, it is filtered to separate the solid from the solution, and then it is washed four times using 95% ethanol.

The solid obtained was then dried using a cabinet dryer at 50°C for 17 hrs. The dry carboxymethyl tapioca was crushed and sieved using an 80-mesh sieve. Furthermore, the degree of substitution, moisture content, ash content, syneresis, swelling power, and solubility were carried out.

2.3 Determination of degree of substitution

Titrimetric was used to determine the DS, according to Yanli *et al*. (2009). Carboxymethyl starch (5 g) was dispersed in acetone (150 mL), and 5 M HCl (15 mL) was added and stirred for 30 mins. The sodium-carboxymethyl starch (Na-CMS) form was converted to H-CMS (carboxymethyl starch in hydrogen form) during this process. The H-CMS was washed several times with 80% ethanol until the solution became neutral with a pH test. The neutral dispersion was filtered again, suspended in acetone, and stirred for 15 mins, after which it was filtered and dried for 24 hrs in a silica gel desiccator. H-CMS (2 g) was dissolved in 1% (w/v) NaCl solution, and it was titrated with 1 M NaOH. The DS was determined as follows:

$$DS = \frac{162 \times n_{NaOH}}{m_c - N_{NaOH} \times 58}$$

$$m_c = m_p - \left(\frac{m_p \times F}{100}\right)$$

Where 162 is the molar mass of anhydrous glucose units (g/mol); 58 = molar mass of carboxymethyl residue (g/mol); n_{NaOH} (in mol) is the quantity of sodium hydroxide used; m_p is the weight of polymer taken (g); m_c is corrected weight of polymer (g); F is water content (%).

2.4 Fourier transform infrared (FT-IR) spectroscopy

The tapioca and carboxymethyl tapioca of different DS were blended with KBr powder, respectively, and pressed into tablets before measurement on an IR spectrophotometer IRPrestige-21 (Shimadzu, Japan) in the wavenumber range 4000-400 cm^{-1}.

2.5 Moisture content

Moisture content analysis refers to the AOAC method (AOAC, 2012). As much as 1 g of the sample is put into a weighing bottle with a known weight. Samples were heated in an oven (Memmert, Germany) at 105°C until a fixed weight was obtained. The sample's moisture content is based on the difference in sample weight before and after drying.

2.6 Ash content

Ash content analysis refers to the AOAC method (AOAC, 2012). A total of 5 g of the sample was put in a dried porcelain dish, and its weight was known. Samples

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were burned with an electric heater until the samples were smokeless and then ignited in a furnace (Vulcan A-550 Ney, USA) at a temperature of 650°C until the ash was produced was greyish-white, and its weight was constant. The ash content of the sample is determined by weighing the remaining minerals from the organic matter's combustion.

2.7 Syneresis

Syneresis analysis refers to the method proposed by Pal *et al*. (2002). A total of 1.2 g of the sample was suspended with 15 mL of distilled water, heated in a water bath (Memmert, Germany) at 85°C for 15 mins, and then cooled at room temperature (27° C). After that, 4 g of the starch suspension was weighed into a 10 mL centrifuge tube, frozen at -18° C for 18 hrs, and then thawed at room temperature for 6 hrs. The starch suspension was then centrifuged (Hermle, Germany) at 6000 rpm for 20 mins. The percentage of water separated after the freeze-thaw cycle is measured and expressed as a percentage of water with the following formula:

$$Syneresis\ (\%) = \frac{Total\ water\ separated\ (g)}{Total\ sample\ weight\ (g)} \times 100\%$$

2.8 Swelling power and solubility

The analysis of starch's swelling power refers to the method proposed by Picauly *et al*. (2017). Starch was dissolved in distilled water (1%, w/v) in a test tube of known weight (W1). Then it was heated in a water bath (Memmert, Germany) at a temperature of 95°C for 30 mins, then cooled to room temperature (27°C). Furthermore, the starch suspension was separated by centrifugation (Hermle, Germany) at 6000 rpm for 20 mins for the residue and supernatant to separate and solubilise. The residue from the centrifugation was then weighed (W2). The swelling power (based on dry weight) was determined as follows:

$$Swelling\ power\ \left(\frac{g}{g}\right) = \frac{W1 - W2}{Sample\ weight\ (g)}$$

The supernatant was dried to a constant weight for 12 hrs at 120° C. The residue that is present after drying the supernatant shows the amount of starch dissolved in water (%), which can be determined as follows:

$$Solubility\ (\%) = \frac{Dry\ weight\ supernatant\ (g)}{Sample\ weight\ (g)} \times 100\%$$

2.9 Statistical analysis

Data were statistically analyzed using the analysis of variance test procedure. Analysis of variance was used to determine the effect of sodium chloroacetate concentration on each observed variable and then tested by Tukey's test (α = 0.05) using Minitab 18 software.

A correlation analysis was used to see the presence and strength of the correlation between the results of the analysis of the effect of sodium chloroacetate concentration on each observed variable with the correlation coefficient strength scale: 0 = no correlation; 0.25 = very weak; 0.25-0.5 = moderate; 0.5-0.75 = tight; 0.75-0.99 = very close; 1 = perfect correlation.

3. Results and discussion

3.1 Degree of substitution carboxymethyl tapioca

The degree of substitution of carboxymethyl tapioca will increase by up to 20% and decrease with the increasing concentration of sodium chloroacetate (Table 1). The correlation coefficient analysis results showed that the concentration of sodium chloroacetate and the degree of substitution of carboxymethyl tapioca had a very close correlation (0.99) (Figure 1).

Table 1. Carboxymethyl tapioca DS based on treatment

The concentration of sodium chloroacetate	DS
Native	0±0[d]
10	0.31±0.02[b]
20	0.38±0.02[a]
30	0.18±0.02[c]

Values are presented as mean±SD. Values with different superscripts are statistically significant different using the Tukey test (α = 0.05).

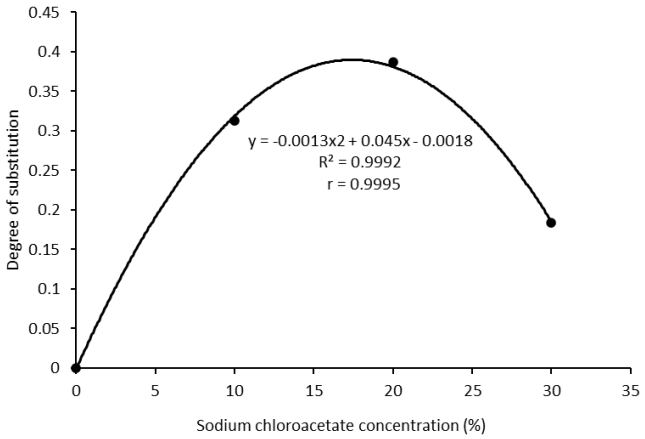

Figure 1. Correlation curve of the relationship between sodium chloroacetate concentration to the DS of carboxymethyl tapioca

The degree of substitution of carboxymethyl tapioca produced was 0.18-0.39, higher than native tapioca (Table 2). The DS value obtained is relatively the same as in several other studies. The DS values of carboxymethyl starch ranged from 0.24-0.40 for rice starch (Kittipongpatana *et al*., 2006), and 0.05-0.45 for Chinese yam starch (Yanli *et al*., 2009).

The DS value of carboxymethyl tapioca increased with increasing sodium chloroacetate concentration up to

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20%. The increase in the DS value is due to the rise in sodium mono-chloroacetate concentration at optimal conditions, which will cause an increase in dissolved sodium chloroacetate, thereby accelerating the diffusion of the chloroacetate salt into the hydroxyl group as the reaction centre. Li *et al*. (2011) and Rusman *et al*. (2017) also showed a tendency to increase the DS value as the concentration of sodium chloroacetate increased to a certain extent, and then decreased. The decrease in DS value at high sodium chloroacetate concentrations (> 20%) can be caused by the reaction of NaOH with sodium chloroacetate. Li *et al*. (2011) showed that the initial increase in the molar ratio of sodium monochloroacetate (SMCA) to AGU from 0.5 to 1.5 resulted in the elevation of DS, but further increases in the molar ratio of SMCA to AGU resulted in the decrease of the DS carboxymethyl starch. At a lower molar ratio of SMCA to AGU, an increase in the contact between the molecules of starch and SMCA leads to the enhancement of the DS. However, the available reactive sites on starch molecules become saturated, and the glycolate formation increases at a higher molar ratio of SMCA to AGU (Liu *et al*., 2012). This causes the DS to decline.

Table 2. Chemical characteristics of carboxymethyl tapioca based on DS

DS	Water Content (%)	Ash Content (%)
0	11.70±0.32^{a}	0.55±0.08^{b}
0.18	12.96±1.57^{a}	0.82±0.03^{b}
0.31	11.98±0.38^{a}	1.54±0.77^{a}
0.38	6.65±0.09^{b}	1.17±0.14^{ab}

Values are presented as mean±SD. Values with different superscripts are statistically significant different using the Tukey test (α = 0.05).

Li *et al*. (2011) and Anirudhan and Parvathy (2014) suggested that the NaOH used in the alkalisation process reacts further with excess sodium chloroacetate in the etherification stage to form sodium glycolate ($HOCH_2COONa$) and sodium chloride (NaCl) as side reactions that result in a decrease in DS. The reaction fits the equation:

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl$$

3.2 FT-IR spectroscopy

The infrared spectra of tapioca (DS = 0.00) and carboxymethyl tapioca (DS = 0.18, 0.31, and 0.38) are presented in Figure 2. The broadband between 3600 and 3000 cm^{-1} is assigned to O–H stretching due to hydrogen bonding involving the hydroxyl groups on the starch molecules. The band at 2924 cm^{-1} is assigned to CH_2 symmetrical stretching vibrations. Compared with tapioca, it is indicated that strong absorption peaks for asymmetric and symmetric vibrations of COO^{-} occur at 1597-1604 and 1450 cm^{-1}, respectively, in all infrared spectra of carboxymethyl tapioca (Akarsu and Dolaz, 2019; Li *et al*., 2011; Lv *et al*., 2016). These bands confirm introducing the -CH_3COO^{-} group into the starch molecule.

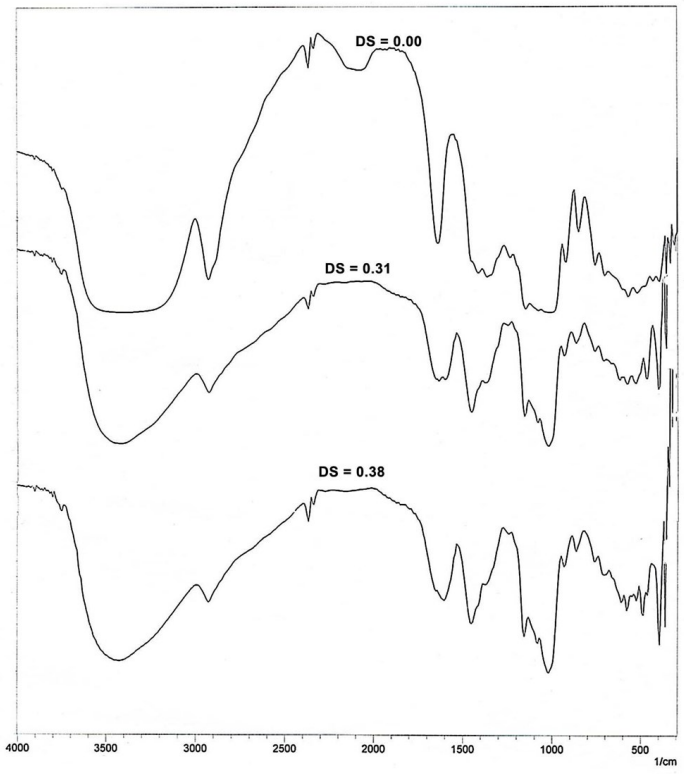

Figure 2. FT-IR spectra of native tapioca and carboxymethyl tapioca with different DS

3.3 Carboxymethyl tapioca chemical characteristics

The variables analysed for carboxymethyl tapioca's chemical characteristics included water (%) and ash (%). The analysis of the chemical characteristics of carboxymethyl tapioca based on the value of the degree of substitution (DS) for each variable is presented in Table 2.

3.3.1 Carboxymethyl tapioca moisture content

The moisture content of carboxymethyl tapioca with DS values of 0.31 and 0.18 (11.98% and 12.96%) was relatively higher than DS 0.00 (native tapioca). Still, carboxymethyl tapioca's moisture content with the highest DS value (0.38) was somewhat lower than native tapioca, 6.65% (Table 2). The correlation coefficient analysis results showed that the DS value and the moisture content of carboxymethyl tapioca had a very close correlation (0.87) (Figure 3).

The difference in moisture content of carboxymethyl tapioca can be because the carboxymethyl starch is hygroscopic and absorbs water from the air. The amount of water absorbed depends on the relative humidity, temperature, and degree of substitution and is also influenced by the degree of chain-breaking, represented

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by the DS value.

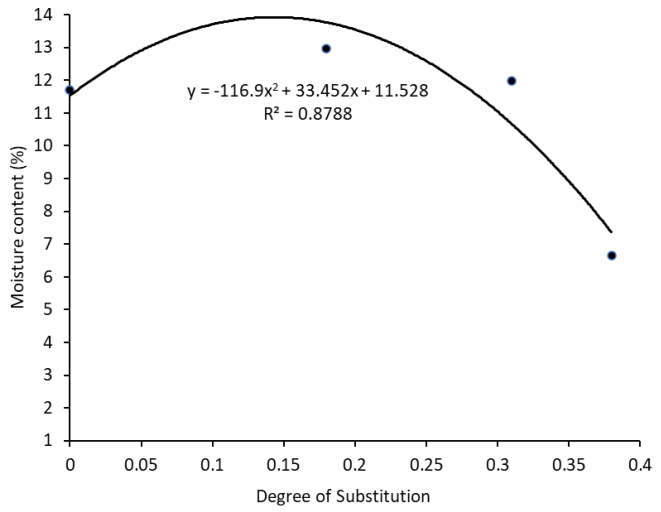

Figure 3. The regression curve and correlation of the DS on the moisture content of carboxymethyl tapioca

3.3.2 Carboxymethyl tapioca ash content

The ash content of carboxymethyl tapioca with a DS value of 0.18-0.31 (0.82-1.54%) was higher than that of native tapioca (0.55%) (Table 2). This can be caused by the use of NaOH in the tapioca alkalization process, which can increase the amount of Na^+ ions, which then react with the tapioca to form alkaline tapioca. Therefore, there will be an ion exchange; namely, Na^+ ions easily soluble in water will bond with Cl^- ions from chloroacetate from NaCl salts. Tapioca, which has released Na^+ ions, will be reactive to the carboxyl group of chloroacetate to form carboxymethyl tapioca, which will increase carboxymethyl's ash content.

The correlation coefficient analysis results showed that the DS value and the ash content of carboxymethyl tapioca had a strong correlation (0.71) (Figure 4).

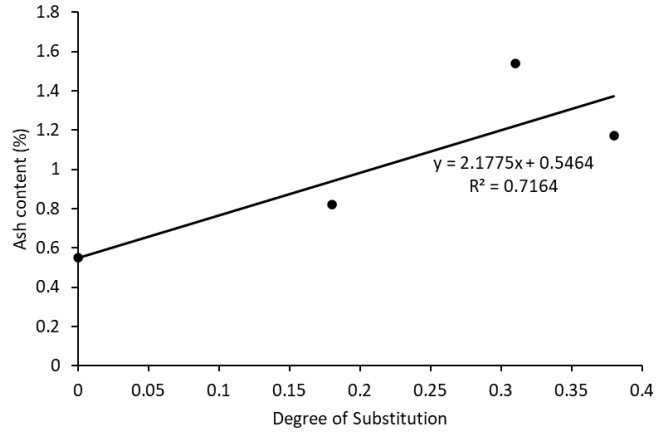

Figure 4. The regression curve and correlation between the DS and the ash content of carboxymethyl tapioca

3.4 Physical characteristics of carboxymethyl tapioca

The variables analysed for the physical characteristics of carboxymethyl tapioca included syneresis (%), swelling power (g/g), and solubility (%). The analysis of the physical characteristics of carboxymethyl tapioca based on the DS value for each variable is presented in Table 3.

Table 3. Physical characteristics of carboxymethyl tapioca

DS	Syneresis (%)	Swelling power (g/g)	Solubility (%)
0	87.91±1.23[a]	0.18±0.04[c]	25.11±3.25[c]
0.18	84.16±0.87[b]	0.19±0.04[c]	58.91±0.93[b]
0.31	81.41±0.87[c]	1.28±0.07[b]	72.19±0.72[a]
0.38	80.33±0.52[c]	2.45±0.35[a]	74.44±0.01[a]

Values are presented as mean±SD. Values with different superscripts are statistically significant different using the Tukey test (α = 0.05).

3.4.1 Syneresis

The syneresis of carboxymethyl tapioca will decrease to DS 0.38 and increase with the decreasing value of DS. The correlation coefficient analysis results showed that the DS value and the syneresis of carboxymethyl tapioca had a close correlation (0.99) (Figure 5).

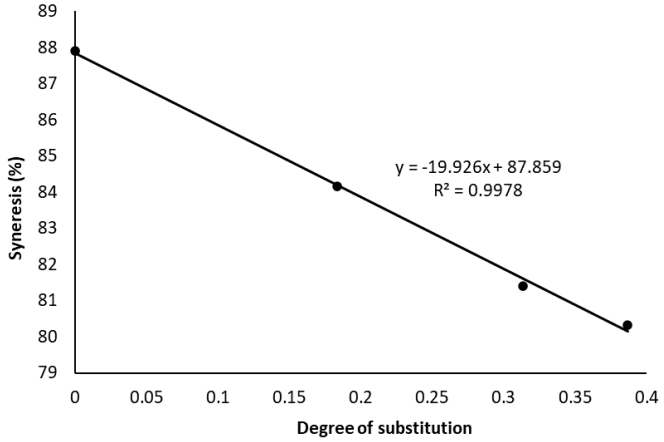

Figure 5. The regression curve and correlation of the DS on the syneresis of carboxymethyl tapioca

The syneresis with a DS value of 0 was 87.91%, while the resulting syneresis range of carboxymethyl tapioca was 80.33-84.16%. Carboxymethyl tapioca produced with a DS value of 0.38 showed a lower syneresis (80.33%) when compared to carboxymethyl with a DS value of 0-0.31.

Tapioca (DS 0) and two samples of carboxymethyl tapioca (DS 0.18 and 0.31) showed higher syneresis (Table 3). This indicates that extensive retrogradation has occurred when starch is stored at very low temperatures. Amylopectin isn't completely carboxymethylated, so when it's stored for a long time, things start to break down again. This makes syneresis values higher (Noor Fadzlina *et al*., 2005).

The low syneresis of carboxymethyl tapioca with a

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DS value of 0.38 can be caused because amylose and amylopectin are completely carboxymethylated during the etherification of starch; therefore, retrogradation can be inhibited during the storage process. Retrogradation handles the syneresis of starch pastes and gels when they last a long time. Lian *et al*. (2014) suggested that the physicochemical properties of starch pastes change during a long storage time due to retrogradation. The starch's retrogradation properties are indirectly influenced by the structural arrangement of the starch chains in the amorphous and crystalline regions of the non-gelatinized starch granules, which affects the extent of starch granules' breakdown during gelatinisation and the interactions that occur between the starch chains during gel storage.

3.4.2 Swelling power and solubility

The ability to swell measures the product's hydration capacity because the estimated starch weight is related to expanding starch granules in the water. The lower the DS value, the greater the carboxymethyl tapioca's ability to bubble up to a DS of 0.38 which decreased as the DS value decreased. The correlation coefficient analysis results showed that the DS value and the bubbling ability of carboxymethyl tapioca had a very close correlation (0.82) (Figure 6).

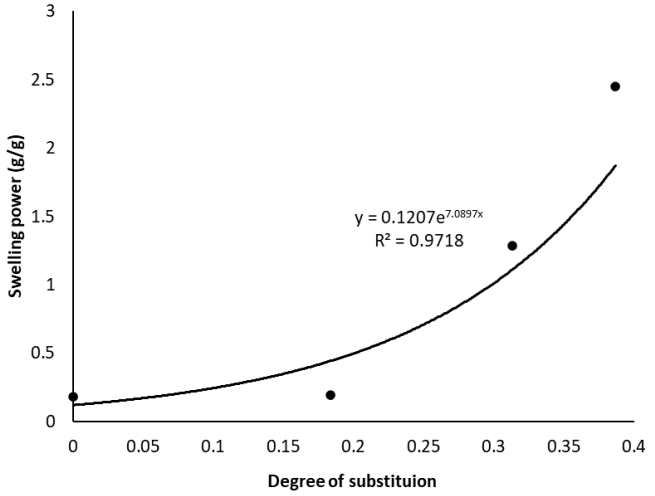

Figure 6. The regression curve and correlation of the DS on the swelling power of carboxymethyl tapioca

Inflation of starch occurs in the amorphous regions of the starch granules. Weak hydrogen bonds between starch molecules in the amorphous area will be broken when heating, resulting in water hydration by the starch granules. The starch granule will continue to expand to increase the viscosity to the maximum hydration volume that the starch granule can achieve.

The swelling power of carboxymethyl tapioca with DS 0.18-0.38 (0.19-2.45 g/g) is higher than native tapioca with DS 0 (0.18 g/g). Agwamba *et al*. (2016) also showed an increase in swelling power and DS carboxymethyl mango starch. This was due to a decrease in the high proportion of soluble dextrins of small and medium-chain lengths in the modified starch granules, increasing the modified starch's capacity to absorb more water and expand with increasing DS.

The result showed that the DS influences the solubility of carboxymethyl tapioca. The correlation coefficient analysis results showed that the DS value and the swelling power of carboxymethyl tapioca had a very close correlation (0.94) (Figure 7).

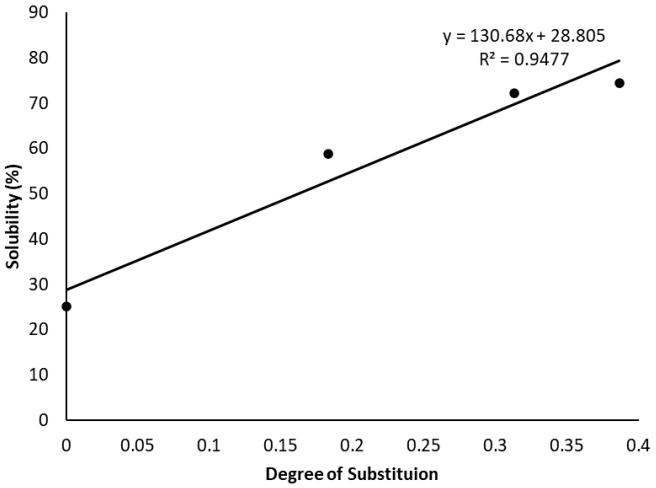

Figure 7. The regression curve and correlation of the DS on the solubility of carboxymethyl tapioca

The solubility of carboxymethyl tapioca with DS 0.18-0.38 (58.91-74.44%) was higher than that of native tapioca with DS 0 (25.11%) due to differences in granule characteristics. These results are from the research proposed by Agwamba *et al*. (2016). The increased solubility of carboxymethyl starch is due to the brittle granule structure resulting from carboxymethylation. The brittle nature of granules can make it easy for water molecules to interact with the starch granules and replace the hydrogen interactions between molecules to more easily absorb water and have high expansion. This expansion will press the granules from the inside so that the starch granules will break and dissolve.

Spychaj *et al*. (2013) suggest that the carboxymethyl group can reduce the bond strength between starch molecules to increase starch's swelling power and solubility. Carboxymethyl starch's swelling power and solubility are higher than native starch (Ganorkar and Kulkarni, 2013) due to hydrophilic substitution groups ($CH_2C=O$) which form hydrogen bonds to increase and store water molecules in starch granules.

4. Conclusion

The modification resulted in significant changes in the physicochemical properties of the carboxymethyl tapioca. The DS and FT-IR patterns demonstrated that

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carboxymethylation occurred. Moisture content increased after modification, and high ash content was also observed because of enhanced hygroscopic components and ion exchange. The carboxymethyl tapioca samples exhibited improved swelling power and solubility but decreased syneresis. The swelling power and the solubility of the starch samples increased as the DS increased. The results of the correlation analysis show that there is a very close relationship between the concentration and the properties measured ($R^2 > 0.8$).

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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