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# Preparation of nano-sized flake carboxymethyl cassava starch under ultrasonic irradiation

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ABSTRACT

An efficient method was described for the synthesis of nano-sized flake carboxymethyl cassava starch (CMCS) with high-degree substitution under ultrasonic irradiation. The scanning electron micrographs (SEM) revealed that nano-sized CMCS flakes with the substitution degree of 1.15 were in shape of hexagon with smooth surface and with the size of 100–400 nm. The substitution degree of carboxymethylation had a great influence on the morphology and the size of these CMCS. In addition, the effect of reaction parameters on DS value of CMCS was also studied, including the influence of the molar ratio of NaOH/starch, the molar ratio of monochloroacetic acid (MCA)/starch, reaction temperature, ultrasonic power and sonication time.

## 1. Introduction

Starch is a natural abundant polysaccharide produced from many plants, which has gained considerable interest because it is inexpensive and has provided a viable alternative to replace synthetic polymers, decreasing in consequence the environmental pollution (Marques et al., 2006; Nagasawa, Yagi, Kume, & Yoshii, 2004). Starch is widely used in paper, textile, adhesive, food industries and medical materials (Che, Li, Wang, Chen, & Mao, 2007; Ren, Li, Wang, Ozkan, & Mao, 2010). However the properties of native starches do not meet the standards necessary for a wide range of industrial uses. For example, cassava starch is a major starch source, which has a unique granular property that exhibits considerably high single stage swelling and peak viscosity. However, the swollen granules lack the ability to retain the swollen structure and hence collapse instantaneously (John & Raja, 1999). Therefore, native starch granules can be modified to obtain the desired properties. Chemical modification is most often used, such as oxidation, hydrolysis, cross-linking and acetylating (Marinich, Ferrero, & Jiménez-Castellanos, 2009; Martinez-Bustos, Lopez-Soto, San Martin-Martinez, Zazueta-Morables, & Velez-Medina, 2007).

Among starch derivatives, carboxymethyl starches (CMS) have attracted a lot of attention in recent years (Lawal, Lechner, & Kulicke, 2008b). CMS are usually synthesized by the reaction of starch with monochloroacetic acid or its sodium salt based on Williamson's ether synthesis. Various methods have been used to prepare CMS such as dry method, semi-dry method, solvent method and water solvent method (Khalil, Beliakova, & Aly, 2001; Zhou, Yang, & Qu, 2007).

Ultrasonic irradiation was demonstrated to be an efficient synthetic technique for activating various organic reactions proceeding via single electron transfer mechanism or radical route (Zeng, Ji, & Wang, 2005). Ultrasound procedures generally displayed a beneficial role in terms of better rates, yields and chemo-, regio- and stereoselectivities for common depolymerization, glycosylation, and acetalization processes and the more sophisticated oxidations and C-heteroatom or C–C bond formations as well (Kardos & Jean-Louis, 2001). Therefore, sonochemical methods were also potentially useful in carbohydrate chemistry (Brochette-Lemoine et al., 2000).

In this letter, we described an efficient method for the synthesis of nano-sized flake carboxymethyl cassava starch (CMCS) with high-degree substitution under ultrasonic irradiation.

## 2. Experimental

### 2.1. Materials

Cassava Starch was provided by Guangxi Maple Leaf Starch Co. Ltd. Monochloroacetic acid (MAC) was purchased from Sinopharm Chemical Reagent. All other reagents were of analytical grade without further treatment.

### 2.2. Measurements

NMR spectra was acquired using a 300-Bruker spectrometer 300 MHz for $^{1}$H NMR and 75 MHz for $^{13}$C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spec-

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tra were recorded on a Bruker EQUINOX 55 spectrometer with the KBr-technique. Scanning electronic microscopy (SEM) images were taken on a Nova NanoSEM 200 scanning electron microscope. Powder X-ray diffraction measurements (XRD) were performed on a Bruker AXS D8 diffractometer using pressed pellets as samples with Cu Kα radiation (λ = 1.5418 Å) at a voltage of 40 kV and current of 200 mA.

### 2.3. Preparation of carboxymethyl cassava starch

0.1 mol cassava starch in 70 mL anhydrous ethanol was placed in a glass reactor. An aqueous solution of sodium hydroxide was added drop wise to the starch–solvent mixture under stirring until the whole amount of sodium hydroxide were added. The mixture was allowed to stirring for 1 h at 40 °C. Then, the solution of MAC was added drop wise to the starch–solvent–sodium hydroxide mixture under ultrasonic irradiation. Then, the temperature was kept between 25 °C and 55 °C for certain reaction time. The mixed solution of water and ethanol also could be used in preparation of carboxymethyl cassava starch, besides anhydrous ethanol.

### 2.4. Determination of degree of substitution

The degree of substitution of carboxymethyl cassava starch was determined using titrimetry according to the method presented by Lawal et al. (Lawal, Lechner, & Kulicke, 2008a; Li et al., 2010). CMCS (5 g) was dispersed in acetone (150 mL). 5 M HCl (15 mL) was added to this dispersion and stirred for 30 min. During this process, CMCS in sodium form was converted to H-CMCS (carboxymethyl cassava starch in hydrogen form). H-CMCS was washed with 80% (v/v) methanol until the solution became neutral. The neutral dispersion was filtered again, suspended in acetone and it was stirred for another 15 min, following which it was filtered and dried for 24 h in a desiccator over silica gel. 2 g of H-CMCS was dissolved in 1% (w/v) NaCl solution and it was titrated with 1 M NaOH. The DS was determined as follows.

$$DS = \frac{n_{\mathrm{NaOH}} \times M_0}{m_c - n_{\mathrm{NaOH}} \times M_R}$$

$$m_c = m_p - \left[\frac{m_p \times F}{100}\right]$$

where $M_0$ = molar mass of the anhydroglucose unit = 162 g/mol; $M_R$ = molar mass of carboxymethyl residue = 58 g/mol; $n_{\mathrm{NaOH}}$ = quantity of sodium hydroxide used (mol); $m_p$ = weight of polymer taken (g); $m_c$ = corrected weight of polymer (g); $F$ = moisture (%).

## 3. Results and discussion

### 3.1. FT-IR spectroscopy

The infrared spectra of native cassava starch and a representative carboxymethyl cassava starch (CMCS, DS 1.15) was presented in Fig. 1. The broad band stretch around 3420 cm$^{-1}$ was attributed to hydrogen-bonded hydroxyls on the starch molecules. The band at 2927 cm$^{-1}$ was assigned to CH$_2$ symmetrical stretching vibrations. In the native starch, the band at 1647 cm$^{-1}$ was assigned to scissoring of two O–H bonds of absorbed water molecules and the bands at 858 and 762 cm$^{-1}$ were due to skeletal stretching vibrations of starch. The carboxymethyl starch derivative showed new bands at $\nu$ = 1600, 1424, and 1251 cm$^{-1}$. Those new bands confirmed that carboxymethylation took place on the starch molecules. Similar observations were reported for carboxymethylated potato starch, corn starch, kudzu root starch and mungbean starches (Kittipongpatana, Sirithunyalug, & Laenger, 2006; Lawal et al., 2008b; Qiu & He, 1999; Wang, Pan, Hu, Miao, & Xu, 2010) (Scheme 1).

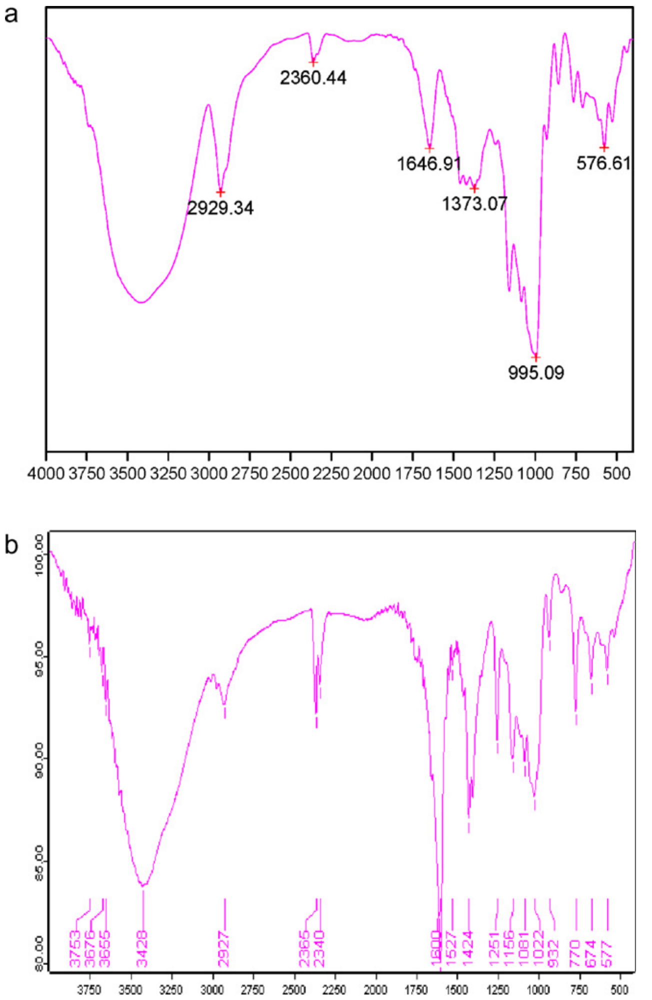


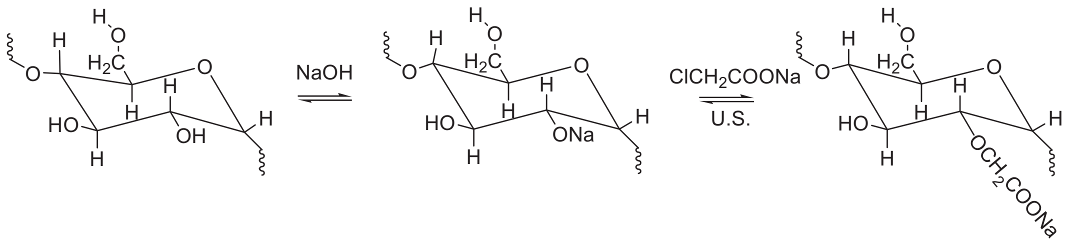
**Fig. 1.** FTIR spectra (a) native cassava starch (NS); (b) carboxymethyl cassava starch (CMCS).

### 3.2. $^{13}$C NMR characterization

The $^{13}$C NMR spectrum of the carboxymethyl cassava starch (CMCS, DS = 1.15) was shown in Fig. 2. The prominent peak at $d$ = 175.1 was assigned to the carbonyl carbon (C-8). The peak that appeared at $d$ = 97.3 was assigned to the anomeric carbon (C-1). This strong peak at 74.6 ppm was assigned to C-4. C-2s and C-3s were assigned peaks at 70.1 and 70.7 ppm, respectively. The signal at 69.0 ppm was assigned to C-5. The resonance at 57.7 ppm was assigned to C-6. The methylene carbon atoms of the carboxymethyl group (C-7) appeared 68.5 ppm (Lawal et al., 2008b; Wang et al., 2010).

### 3.3. X-ray powder diffraction

The wide-angle X-ray diffractograms obtained for both native cassava starch and the representative carboxymethylated derivative (DS = 0.36, 1.15, 1.3) were presented in Fig. 3. The native cassava starch gave the strongest diffraction on $2\theta$ = 14.97°, 17.72°, 23.05°. After carboxymethylation, a pronounced reduction in crystallinity was observed. This loss in crystallinity could be attributed to the effect of the replacement of the hydroxyl groups by the carboxymethyl groups. Hydrogen bonds maintained the stability of



**Scheme 1.** Synthesis procedures of carboxymethyl cassava starch (CMCS).

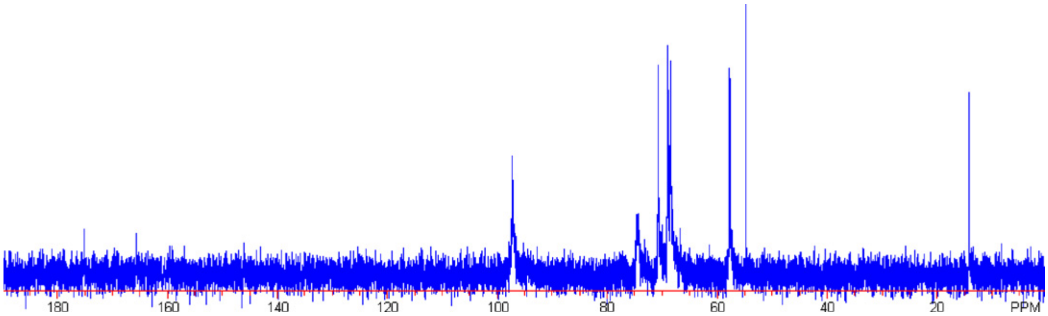


**Fig. 2.** $^{13}C$ NMR spectrum of carboxymethyl cassava starch (CMCS, DS = 1.15). S, carbon with carboxymethyl substituent; U, unsubstituted carbon.

starch crystal. When the hydroxyl groups were replaced, hydrogen bonds were broken. Therefore, more high DS value mean crystallinity reduced more significantly, as shown in Fig. 3(d). The rupture of starch granules may be also the possible reason of the loss of crystallinity. Since the presence of solvent, alkaline together with heat treatment caused the breakage of chemical bonds in starch molecules, which led to the rupture of starch granules (Sangseethonga, Ketsilp, & Sriroth, 2005; Wang, Gao, & Li, 2009). This observation corroborated the changes in the granule morphology revealed by the SEM.

The significance of the loss in crystallinity was important in applications such as the preparation of super-absorbent hydrogels since amorphous granules would facilitate water percolation (Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010).

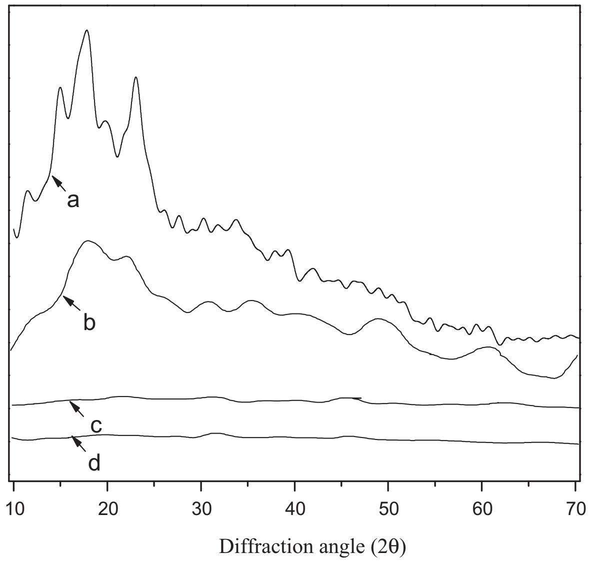


**Fig. 3.** XRD profile of native cassava starch and carboxymethyl starch: (a) native cassava starch; (b) CMCS, DS = 0.36; (c) CMCS, DS = 1.15; (d) CMCS, DS = 1.3.

### 3.4. *Starch granule morphology*

Scanning electron micrographs of the native cassava starch and carboxymethyl starch were presented in Fig. 4. SEM images of native cassava starch granules were round or oval in shape with smooth surface and wide distribution of size ranging from 2 μm to 20 μm, as shown in Fig. 4(a) (Lawal et al., 2008a). After carboxymethylation, significantly alteration of the granular structure of the carboxymethylated starch was observed. SEM images of CMCS with different substitution degree (DS = 0.36, 1.15, 1.3) were presented in Fig. 4.

The SEM images of the CMCS with relatively low substitution degree of 0.36 were shown in Fig. 4(b). CMCS granules were round in shape with the size of 8–28 μm. On the surface of CMCS granules, there were some small particles, which looked like surface corrosion. This led to the surface of CMCS granules look like much more coarse than that of native cassava starch. It was reported that the acid and alkali preferentially attacked the amorphous regions and then the high crystallinity regions (Wang, Yu, & Yu, 2008). The amorphous regions on the surface of native cassava starch granules being less compact than the crystalline regions resulted in the quick diffusion of hydroxyl ions ($OH^-$) into the amorphous regions in this experiment. This led to the surface carboxymethylation of starch granules and low DS value (Wang et al., 2010).

Furthermore, with the mole addition of sodium hydroxide during the substitution reaction of CMCS synthesis, the starch crystallinity was altered and thus allowing the etherifying agents to have more access to the starch molecules for the carboxymethylation processes. The alkaline environment during the carboxymethylation process accounted for the high DS value and thus the structural changes. With the increasing of the substitution degree to DS = 1.15, the granular structure of native starch was completely lost. And clusters of micron-sized flaky particles with uniform particle diameter were occurred in the whole field of view, as shown in Fig. 4(c). These micron-sized CMCS flakes were most in shape of hexagon with smooth surface and with the size of 100–400 nm, as shown in Fig. 4(c). However, with the further increasing of the degree of substitution to DS = 1.3, both the particles' size and morphology were much similar with that of the micron-sized CMCS flakes with DS = 1.15, as shown in Fig. 4(d).

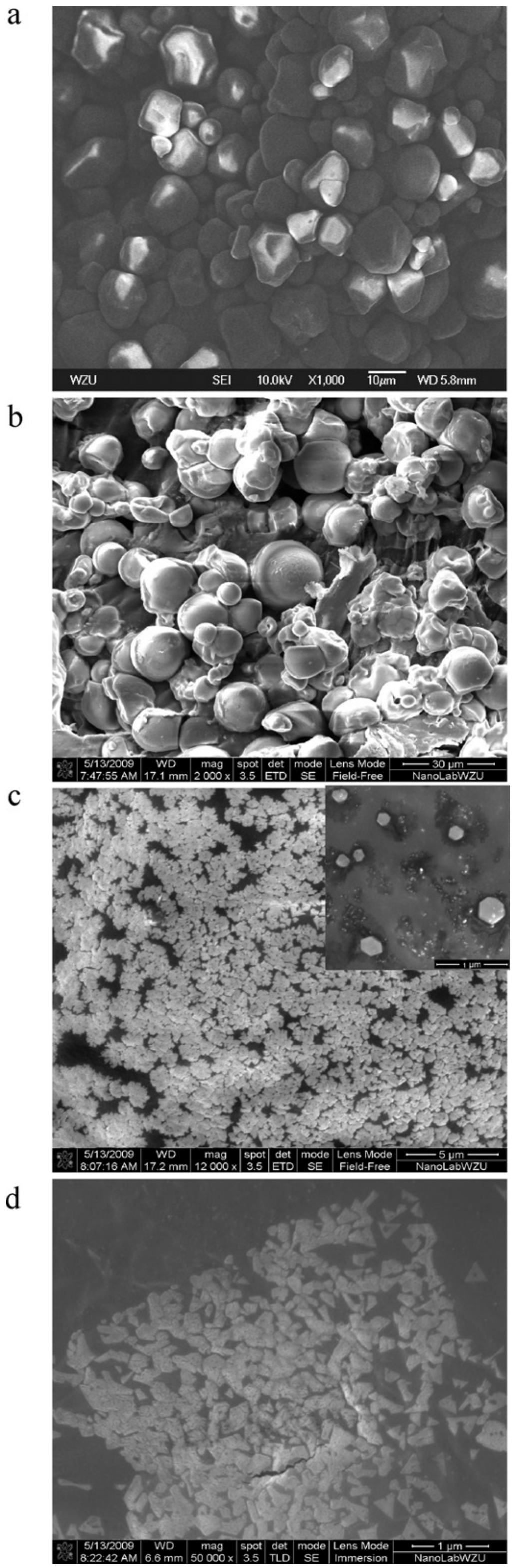


**Fig. 4.** SEM images of native cassava starch and carboxymethyl starch: (a) native cassava starch; (b) CMCS, DS = 0.36; (c) CMCS, DS = 1.15; (d) CMCS, DS = 1.3.

These results showed that the size of the CMCS particles reduced from micro- to nanometer, which was much smaller than that of native starch particles after modification.

Such a lamellar fragments were also reported by Yamagushi et al. to describe fragments of wet-mashed waxy maize starch granules and by Putaux et al. for acid-hydrolyzed fragments of waxy maize starch granules (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003; Z.F. Wang et al., 2009). It was reported that waxy maize starch nanocrystals consisted of platelet-like particles approximately 15–500 nm wide were obtained after long time hydrolyzing. And these nanocrystals were generally observed in the form of aggregates having an average size of 4.4 μm (Liu, Wu, Chen, & Chang, 2009). While in our study, the etherifying process was accelerated by ultrasonic irradiation to get starch nanocrystals. And these starch nanocrystals were carboxymethylated to get nanometer CMCS. Therefore, it was a good way to prepare nano-sized carboxymethyl starch under ultrasonic irradiation.

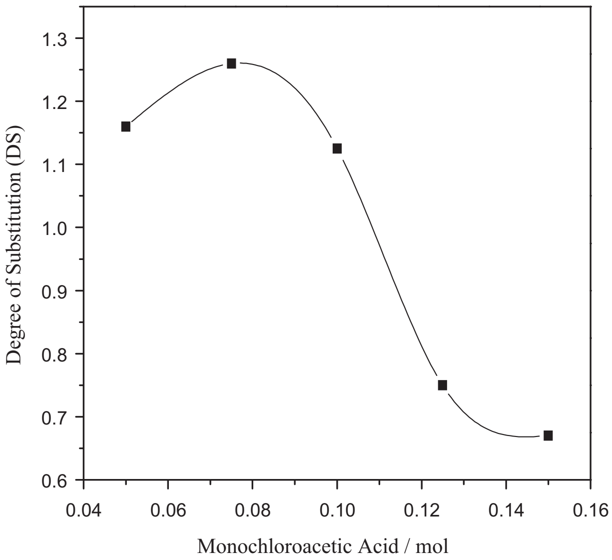


**Fig. 5.** Effect of different quantities of monochloroacetic acid (0.05–0.15 mol) on the DS (0.1 mol cassava starch, 0.25 mol sodium hydroxide, 70 mL anhydrous ethanol, ultrasonic irradiation (400 W, 20 min). reaction 80 min at 48 °C).

Given the different morphology carboxymethyl starch with different degree of substitution, there maybe an critical state of change from micrometer round granules of CMCS to nanometer flake of CMCS with the increasing of degree of substitution. Therefore, further research was undertaken in order to determine the optimal condition to prepare nano-sized carboxymethyl starch.

### 3.5. *Effect of reaction parameters on DS value of CMCS*

In the substitution reaction of CMCS synthesis, the main factors affecting the DS value were investigated, which included ultrasonic power, sonication time, reaction temperature, and the compounding ratio of MAC to starch and alkali to starch.

In Fig. 5, the influence of various molar ratios of MAC to starch on the DS was presented. 0.25 mol sodium hydroxide (in 20 mL distilled water) was added drop wise to the starch–solvent mixture (0.1 mol cassava starch in 70 mL anhydrous ethanol) under stirring. The mixture was allowed to be stirred for 1 h at 40 °C. Then different quantities of MAC (0.05–0.15 mol) were added to the starch, solvent and sodium hydroxide mixture under ultrasonic irradiation (400 w, 20 min). Then the temperature was kept at 48 °C for 80 min.

The DS increased to the maximal value of 1.26 with increment of MAC. However, the DS decreased when MAC was added more than 0.075 mol. This was because the increasing MCA/starch ratio would lead to consumption of NaOH, while under the reaction condition, the NaOH dosage was changeless. The more the MCA was, the less the NaOH can react with starch, so higher MCA/starch ratio led to lower DS (Zhou, Yang, & Qu, 2007).

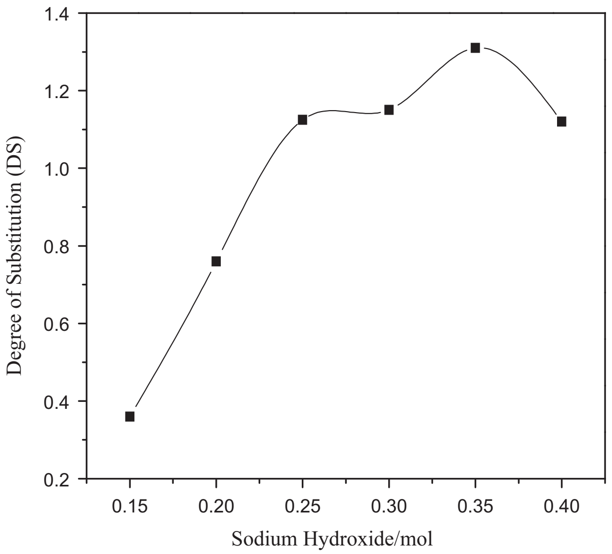


**Fig. 6.** Effect of different quantities of sodium hydroxide (0.05–0.40 mol) on the DS (0.1 mol cassava starch, 0.1 mol monochloroacetic acid, 70 mL anhydrous ethanol, ultrasonic irradiation (400 W, 20 min). reaction 80 min at 48 °C).

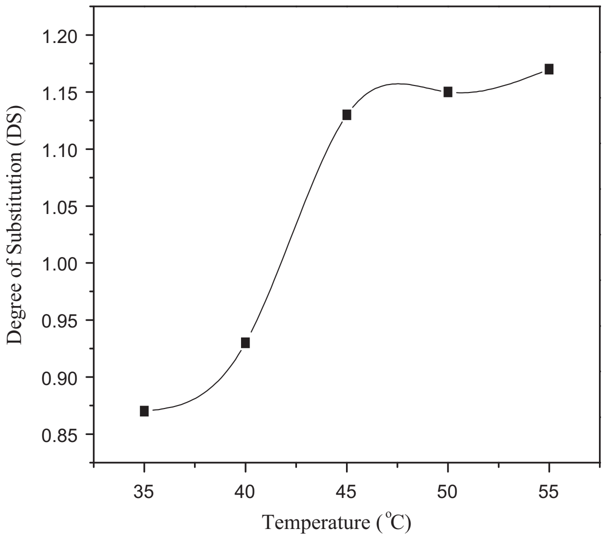


**Fig. 7.** Effect of temperature (30–55 °C) on the DS (0.1 mol cassava starch, 0.075 mol monochloroacetic acid, 0.25 mol sodium hydroxide, 70 mL anhydrous ethanol, ultrasonic irradiation (400 W, 20 min). reaction 80 min).

In Fig. 6, the influence of various molar ratios of sodium hydroxide to starch on the DS was shown. Different quantities of sodium hydroxide (0.15–0.40 mol) were investigated. All other reaction conditions were kept constant with the case above. The DS increased as the molar ratio of NaOH to starch increased from 1.5 to 3.5. NaOH added to this reaction was used to provide the alkaline environment for the reaction as well as served as the swelling agent to facilitate diffusion and penetration (Lawal et al., 2008b). Therefore, the starch crystallinity was altered, which allowed the etherifying agents to have more access to the starch molecules for the carboxymethylation processes, and thus accounting for the high DS value of 1.31. However, there was a reduction in the DS at higher ratio of NaOH to starch. These two reasons may account for this reduction in the DS. The increment in NaOH dosage would cause the consumption of MCA, and also the tendency for alkaline gelatinization which inhibited the contact between starch etherifying agents within the reaction mixture. Similar observation was reported for corn, amaranth, yam and pigeon pea starches (Lawal et al., 2008b; Y.L. Wang et al., 2009).

In Fig. 7, the effect of temperature (30–55 °C) on the DS was presented. The increment of the DS was obvious as the reaction temperature increasing from 35 to 45 °C. The increase in temperature enhanced solubility of the etherifying agents and it also facilitated both the swelling of the starch molecules and the diffusion of the reactants (Lawal et al., 2008b). However, the DS increased slowly when the temperature was higher than 50 °C. This was because the influence of carboxymethylation, particularly in alkaline medium, may cause the gelatinization at lower temperature (Lawal et al., 2008b; Y.L. Wang et al., 2009).

In Fig. 8, the effect of ultrasound power and sonication time on the DS was investigated. Three types of ultrasonic generators (180 W–40 kHz, 400 W–40 kHz and 500 W–40 kHz, Shanghai Zhi Sun Instrument, China) were involved to treat the reaction mixtures with ultrasound for 5, 10, 15, 20, 25, 30 and 35 min, respectively. All other reaction conditions were kept constant with the case above.

Both ultrasound power and sonication time had a great effect on the DS. The greater DS were gotten when using higher ultrasonic power, as shown in Fig. 8. While the effect of sonication time on the DS was relatively complex. The DS increased with the increment of sonication time within 15–20 min. DS could reach the maximum of 1.23 when the ultrasonic time was 15 min and ultrasound power was 500 W. Both the superficial and internal crystalline structure of starch were damaged after ultrasonic treatment. And the crystallinity was decreased with the interruption of the intermolecular hydrogen bonds in crystalline area, which led to chloroacetate group easily penetrating into the starch granules and thus greater DS value (Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008; Wu, Zivanovic, Hayes, & Weiss, 2008). Therefore, the DS increased with the decreasing of crystallinity of starch in certain time of ultrasonic treatment.

While after long time of ultrasonic treatment, too much starch crystalline were collapsed into dissociative moleculars with greater freedom and activity. These dissociative moleculars may rearrange to form new crystalline regions, which may inhibit the penetration of chloroacetic acid to the internal part of the crystallinity of particles, resulting in a decline in DS.

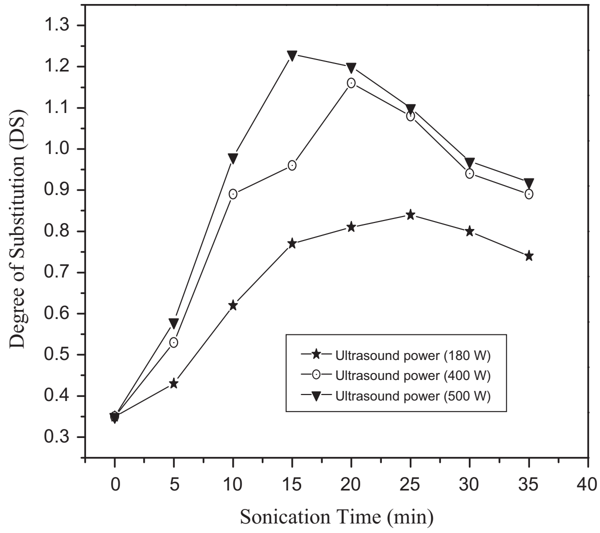


**Fig. 8.** Effect of ultrasound power and sonication time on the DS (0.1 mol cassava starch, 0.075 mol monochloroacetic acid, 0.25 mol sodium hydroxide, 70 mL anhydrous ethanol, reaction 80 min at 48 °C).

## 4. Conclusion

An efficient method was described for the synthesis of nano-sized flake carboxymethyl cassava starch (CMCS) with high-degree substitution under ultrasonic irradiation. The substitution degree of carboxymethylation had a great effect on the morphology and the size of these CMCS. CMCS granules gotten after carboxymethylation were round in shape with the size of 8–28 μm, different from the native cassava starch granules, which were round or oval in shape with smooth surfaces and wide distribution of size ranging from 2 μm to 20 μm. While with the increasing of the substitution degree to DS = 1.15, nano-sized CMCS flakes were obtained in shape of hexagon with smooth surface and with the size of 100–400 nm. These results showed that the size of the CMCS particles reduced from micro- to nanometer, which was much smaller than that of native starch particles after modification. It was because that the etherifying process was accelerated by ultrasonic irradiation to get starch nanocrystals, and then these starch nanocrystals were carboxymethylated to get nanometer CMCS. Therefore, it was a good way to prepare nano-sized carboxymethyl starch under ultrasonic irradiation.

In this paper, the influence of the molar ratio of NaOH/starch, the molar ratio of MCA/starch, reaction temperature, ultrasonic power and sonication time on the degree of substitution (DS) was also investigated. (1) The DS increased to the maximal value of 1.26 with increment of MAC to 0.075 mol, and then decreased for the increasing MCA/starch ratio would lead to consumption of NaOH. (2) The DS increased to 1.31 as the molar ratio of NaOH to starch increased from 1.5 to 3.5. However, there was a reduction in the DS at higher ratio of NaOH to starch, since the increment in NaOH dosage would cause the consumption of MCA. (3) The increment of the DS was obvious as the reaction temperature increasing from 35 to 45 °C, for good solubility of the etherifying agents under higher reaction temperature. However, the DS increased slowly when the temperature was higher than 50 °C. (4) Both ultrasound power and sonication time had a great effect on the DS. The greater DS were gotten when using higher ultrasonic power. And the DS also increased with the increment of sonication time within 15–20 min. DS could reach the maximum of 1.23 when the ultrasonic time was 15 min and ultrasound power was 500 W.

## Acknowledgements

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