

Preparation and Characterization of Carboxymethyl Starch Under Ultrasound-Microwave Synergistic Interaction

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ABSTRACT: Using native cassava starch as raw materials, carboxymethyl starch (CMS) was prepared by ethanol solvent method under the ultrasound-microwave synergistic interaction. And the structure of CMS was characterized employing Fourier transform infrared (FTIR) spectrometer, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analyzer. Typically, the optimal synthesis conditions for the preparation process confirmed by orthogonal experiment $L_{18}(6^1 \times 3^6)$ were shown as follows: the ultrasonic treatment temperature was fixed to 35°C and two steps alkalization was employed; the ultrasonic time was 40 min before alkalizing and the ultrasonic power was 220 W; the amount of sodium hydroxide was 8.8 g, the microwave alkalization time was 2 min; the amount of monochloroacetic acid was 11.34 g; the amount of 95% (v/v) ethanol was 70 mL; the microwave etherification time was 3 min. The degree of substitution of prepared CMS was 1.089 ± 0.041 , which was increased 30.4% compared with the prepared sample without ultrasound-microwave synergistic treatment. FTIR results showed that the strong $-\text{COO}-$ characteristic absorption peaks of the stretching vibration were observed at 1613 and 1421 cm^{-1} , which proved that the carboxymethylation of cassava starch was occurred. SEM results suggested that there were many cracks and dents on CMS granules; and, XRD results indicated that the carboxymethylation of starch occurred both in amorphous region and crystalline region, the noticeable damage of crystalline region by carboxymethylation was observed. Thermogravimetric analysis (TG) and derivative TG showed that thermal stability of CMS changed better compared with native starch. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40906.

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INTRODUCTION

Starch is an environmentally friendly natural renewable resource, which is the abundant resource and with the property of biodegradation.¹ With the development of science and technology, starch is used in various industrial fields. The starch industry flourishes as the abundant resources and low cost of starch. However, most of the natural starches have many deficiencies, such as insoluble in cold water, easily aging of starch paste, and retrogradation at low temperatures, which have largely limited the applications of starch in the fields of food, paper, chemical, pharmacy, and so on. Therefore, the changes of the physical, chemical and other denaturation of starch are needed, which can result in the innovation of physicochemical properties. Such changes can be employed to adapt the requirement of modern new industrial technologies and new processes, which also broadens the scope of application of starch.² Usually, carboxymethyl starch (CMS) is an important chemical modified starch,³ which exhibits the advantages of strong hydrophilicity, easy pasting, weak retrogradation and freeze-thaw stability. The

performance of CMS is similar to that of carboxymethyl cellulose (CMC).⁴ However, the starch is more affordable, which can widely be used to replace expensive CMC in food,⁵ textile,⁶ medicine,⁷ chemical⁸ and other fields. Commonly, the synthetic methods of CMS can be divided into three types: dry method,^{9,10} aqueous method,¹¹ organic solvent method.^{12,13} The dry method can be occurred without alcohol or water as reaction medium (or small amount of alcohol or water). It can reduce the costs with high utilization of monochloroacetic acid (MCA) and its treating process has no pollution. However, this reaction is carried out in the solid phase system, and the small reagent molecules are difficultly penetrating into the starch granules. So the degree of substitution (DS) of the product is generally lower than 0.8; and, the DS along with the starch chains is uneven distribution. The substitution reactions are occurred on the particle surface, which result in the poor solubility of the product. Aqueous method is occurred using a lot of salt to prevent gelatinization of starch, which is generally functioned to prepare the products with DS less than 0.1. Most of organic solvent methods employ the mixed solvent

containing ethanol or propanol and a small amount of water, which can make the reaction mass exhibiting the form of dispersed particles state. The etherification reaction mainly occurs in the amorphous area of starch granule surface, which can make the DS increased to some extent. However, as the interleaved structures presented crystalline regions in starch granules limit the further occurrence of the denaturing reaction,^{14,15} the activity and efficiency of starch etherification reaction are decreased. Therefore, the exploration of the optimization of organic solvent method and the preparation of CMS with higher DS has become an important research topic.

Currently, ultrasonic and microwave can meet the requirement of the green food industry processing, the application of which in denaturation of starch have become research foci.^{16–18} It proved that the crystallization regions of starch granules were destroyed after the starches were treated under ultrasonic; and, many tiny holes were formed on the surface of starch granules,¹⁹ which would lead to increased chemical reactivity of the starches. Microwave has the feature of internal heating, which can result in the puffed starch and accelerate the chemical reaction process.²⁰ When the ultrasound-microwave synergistic interaction is used in the polarizing reaction system of starch, microwave can cause thermal effect by polarizing macromolecules and result in alignment with electromagnetic field poles that may cause the breakage of hydrogen bonds.²¹ Meanwhile, it can enhance mass transfer by the extreme pressure and temperature variations.²² The ultrasonic-microwave synergistic effect can further promote the effective collision of starch and denaturing agent. Herein, the ultrasonic-microwave synergistic interaction can enhance the efficiency of carboxymethylation.

In this study, CMS was prepared based on ultrasound-microwave synergistic interaction using MCA as the etherifying agent. As far as our knowledge, there are no related reports. Significantly, this research exploring a new modification method of starch provides experimental design basis for the synthesis of CMS with high DS.

EXPERIMENTAL

Materials

Cassava starch [food grade, (14.69 ± 0.14) wt % moisture] was bought from Guangxi Hongfeng Starch Co., Ltd., China. All other chemical used in this investigation were analytical grade. Sodium hydroxide and ethanol were purchased from Guangdong Guanghua Chemical Factory Co., Ltd., China. MCA was purchased from Hengyang Kaixin Chemical Reagent Co., Ltd., China. Glacial acetic acid was bought from Chengdu Kelong Chemical Reagent Factory, China. Methanol was supplied by Tianjin Fuchen Chemical Reagent Factory, China.

Synthesis of CMS

The synthesis of CMS was carried out based on the improved method according to the report of Wang et al.²³ Cassava starch (16.2 g) and a certain amount of 95% (v/v) ethanol were added into a 250 mL three-necked flask; and, the flask was placed in an ultrasonic reactor (SK6210LHC, Shanghai, China). While the mixture was stirred, the mixture was treated under ultrasonic interaction for certain time and the ultrasonic temperature was

fixed at (35 ± 1)°C. Then, 45 wt % sodium hydroxide solution was prepared. Two-third of 45 wt % sodium hydroxide solution of required amount was dropwisely added to the three-necked flask with stirring. The flask was moved into the microwave experiments furnace (NJL07-3, Nanjing, China) and treated under microwave radiation for a period of time. Then, the mixture was alkali treatment for a certain time (microwave treatment 15 s, interval 30 s, the alkalization reaction temperature was controlled not higher than 35°C). Then, one-third of 45 wt % sodium hydroxide solution of required amount and a certain amount of MCA were added. The intermittent microwave radiation was carried out under constantly stirring (radiation 30 s, intermittent 4 min, the reaction temperature was controlled at 35 ± 2°C). Then, the etherification reaction was occurred for some time. When the reaction was completed, the mixture was neutralized to neutral using glacial acetic acid. The product was filtered and washed several times with 85% (v/v) aqueous ethanol. The resulting CMS was then dried in a vacuum oven at 45°C.

Orthogonal Experimental Design for CMS

The synthesis of CMS was carried out both based on two steps alkalization as described earlier^{24,25} and according to our previous report.²⁶ The statistical analysis of the effects of reaction condition on DS was investigated by orthogonal design experiments. Seven relevant factors were investigated: ultrasonic time, ultrasonic power, sodium hydroxide, microwave alkalization time, MCA, ethanol 95% (v/v), microwave etherification time. The DS was used as evaluating indicator. The orthogonal table $L_{18} (6^1 \times 3^6)$ was designed (Table I), which suggested the optimal reaction conditions for CMS.

Determination of DS

The DS was determined based on the method reported by Stojanovic.²⁷ First, sample (0.50 g) was placed in a 100 mL small beaker. Second, 2 mol/L HCl methanol solution of 40 mL was added and stirred for 3 h. Third, the solution was filtered and washed using methanol solution of 80% (v/v) until no chlorine ions was detected (no white turbidity appears with AgNO_3 test). The filter cake was dissolved in 40 mL NaOH standard solution of 0.1 mol/L. And the solution was transparent under the micro-thermal conditions. Finally, the solution was immediately titrated using 0.1 mol/L HCl standard solution until the red color of phenolphthalein was just faded. The consumption volume of standard solution of HCl was recorded and the DS was calculated according to formula (1) and (2).

$$\text{DS} = \frac{162\omega_A}{5900 - 58\omega_A} \quad (1)$$

$$\omega_A = \frac{(c_{\text{NaOH}} \cdot V_{\text{NaOH}} - c_{\text{HCl}} \cdot V_{\text{HCl}}) \times 0.059}{m} \times 100 \quad (2)$$

The denotes of symbols in formula (1) and (2) are like these: ω_A is the mass fraction of acid carboxymethyl (%); V_{NaOH} is the volume of NaOH standard solution (mL); V_{HCl} is the volume of HCl standard solution consumed in titrating the excess NaOH standard solution (mL); c_{NaOH} is the concentration of NaOH standard solution (mol/L); c_{HCl} is the concentration of HCl standard solution (mol/L); m is the quantity of sample (g).

Table I. The Orthogonal Layout and the Results of Experiments

Experiment code	A Ultrasonic time (min)	B Ultrasonic power (W)	C Sodium hydroxide (g)	D Microwave alkalization time (min)	E MCA (g)	F Ethanol 95% (v/v) (mL)	G Microwave etherification time (min)	DS ^a
1	10	170	8.8	2	9.45	60	2	0.687 ± 0.014
2	10	220	7.2	1	7.56	70	1	0.937 ± 0.046
3	10	270	8.0	3	11.34	80	3	0.822 ± 0.133
4	20	170	8.0	1	9.45	80	1	0.654 ± 0.021
5	20	220	8.8	3	7.56	60	3	0.809 ± 0.044
6	20	270	7.2	2	11.34	70	2	0.996 ± 0.037
7	30	170	7.2	3	7.56	80	2	0.613 ± 0.043
8	30	220	8.0	2	11.34	60	1	1.070 ± 0.042
9	30	270	8.8	1	9.45	70	3	0.779 ± 0.055
10	40	170	7.2	1	11.34	60	3	1.088 ± 0.010
11	40	220	8.0	3	9.45	70	2	1.055 ± 0.033
12	40	270	8.8	2	7.56	80	1	1.042 ± 0.025
13	50	170	8.8	3	11.34	70	1	0.701 ± 0.013
14	50	220	7.2	2	9.45	80	3	0.876 ± 0.085
15	50	270	8.0	1	7.56	60	2	0.624 ± 0.086
16	60	170	8.0	2	7.56	70	3	0.783 ± 0.047
17	60	220	8.8	1	11.34	80	2	1.003 ± 0.067
18	60	270	7.2	3	9.45	60	1	0.398 ± 0.029
k_1	2.446	4.526	4.907	4.479	4.808	4.675	4.801	
k_2	2.459	5.750	5.007	4.578	4.448	5.250	4.978	
k_3	2.461	4.659	5.020	4.397	5.679	5.009	5.157	
k_4	3.184							
k_5	2.201							
k_6	2.184							
R	1.000	1.225	0.113	0.181	1.231	0.575	0.356	

^a Mean ± SD.

Each value was calculated from three repeats.

Characterization Methods

Infrared spectrum of sample was scanned using a Fourier transform infrared (FTIR) spectrometer (IRAffinity-1, Shimadzu, Japan). KBr compression method was used. The number of scanning was 17 /s and the scanning scope was 400–4000 cm^{-1} .

Morphological study was carried out in a scanning electron microscope (SEM) (S-3400N, Hitachi, Japan) operating at 20 kV. The samples were fixed on the sample table using conductive adhesive and sprayed gold in a vacuum.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer (Ultima IV, Japan). The test conditions were given as follows: the wavelength of Cu-K alpha ray was 1.527 nm, graphite monochromator, the tube pressure was 40 kV, the tube current was 40 mA, the scanning range was $2\theta = 5^\circ\text{--}60^\circ$, step was 0.02° , scan rate was $8^\circ/\text{min}$, continuous scanning. The crystallinities of starch were quantitative estimated according to the Hermans and Weidinger method.²⁸

The thermal stabilities of native cassava starch (NCS) and CMS were examined by using thermogravimetric analysis (TG) and

derivative TG (DTG) technique. Sample (9 mg) was placed in thermogravimetric analyzer (TGA-50, Shimadzu, Japan) and crucible material was Pt. The temperature increased to 550°C from room temperature with heating rate of 10 K/min under nitrogen flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Optimization of the Factors by Orthogonal Experimental Design

The preparation conditions of CMS with higher DS could be obtained by systematically analyzing each factor that influenced DS (Table I).

The range value (R) for each factor was the difference between the maximal and minimal value of the six or three levels. By analysis of R scales, the affection of the DS of product by seven factors can be determined. High R of variable means that this variable has strong effect on the response.²⁹ From the R value in Table I, the order of seven factors affecting the DS of product was determined and showed as follows: $E > B > A > F >$

G > D > C. Among seven factors, the amount of MCA was the largest factor and the amount of NaOH was the smallest factor.

The k value for each level of a parameter was the sum of three or six values shown in Table I, and the optimal level of variable could be obtained by comparing with k value. The optimum preparation conditions were obtained by the analysis of k values in Table I and were showed like these: the ultrasonic time was 40 min, the ultrasonic power was 220 W, the amount of NaOH was 8.8 g, two steps alkalization was used, the microwave alkalinization reaction time was 2 min, the amount of MCA 11.34 g, the amount of 95% (v/v) ethanol was 70 mL and the microwave etherification reaction time was 3 min.

The Validation and Comparison Experiment of Optimal Preparation Process

In the validation experiments, CMS was repeatedly prepared for three times using the optimal preparation process condition; and, the DS (1.089 ± 0.041) of product was obtained. In the contrast experiments, relatively low DS (0.835 ± 0.026) at the optimal reactions conditions was obtained without ultrasound-microwave synergistic interaction.

Therefore, compared with DS of CMS without ultrasonic-microwave synergistic interaction, the DS of CMS treated with ultrasonic-microwave synergistic interaction was increased by 30.4% under the optimal preparation process condition. This phenomenon might be resulted from the influence of ultrasonic radiation on the crystalline structure of starch granules. The ultrasonic radiation could result in the degradation of starch molecules.³⁰ Furthermore, the microwave heating could make the temperature of reaction system rapidly rise to a suitable temperature, which enabled the cassava starch particles to become loose. The contact area of MCA and starch granule was increased, which more easily drove the MCA into the starch grains and contacted with the starch molecules. Therefore, the etherification could be enhanced using less reaction time, and the DS was increased.^{31,32}

FTIR Characterization of Starches

The FTIR spectra of NCS and CMS samples were given in Figure 1.

As shown in Figure 1(a), the strong and broad peak in 3600–3100 cm^{-1} was the stretching vibration absorption peak of —OH in NCS and the characteristic peak of association hydroxyl hydrogen bond. The peak in 2929 cm^{-1} was the symmetric stretching vibration absorption peak of —CH₂— in NCS. The strong and broad peak in 1157–997 cm^{-1} was the stretching vibration absorption peak of C—O—C in NCS. Compared with the infrared spectra of NCS [Figure 1(a)] and CMS with 1.089 [Figure 1(b)], the symmetric stretching vibration absorption peak in 2929 cm^{-1} of —CH₂— and the stretching vibration absorption peak in 1157–997 cm^{-1} of C—O—C were similarly maintained. However, the stretching vibration absorption peak in 3600–3100 cm^{-1} changed weak and asymmetric; and, this peak shifted to the higher wavenumber region. Usually, there is associating hydrogen bond in NCS. The associating hydroxyl absorption peak appears in 3550–3200 cm^{-1} , and the free hydroxyl absorption peak appears in the 3640–3610 cm^{-1} .³³

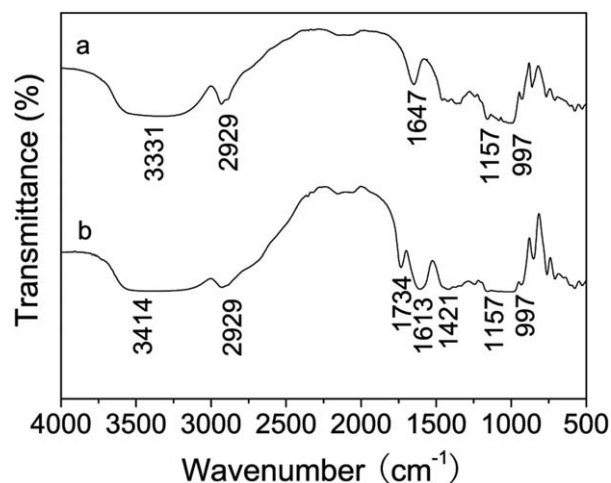


Figure 1. FTIR spectra of NCS (a) and CMS with DS = 1.089 (b).

Herein, the associating hydrogen bond was broke when the carboxymethyl etherification of associating —OH in starch was occurred; and, crystalline structure was damaged to a certain extent, which made the hydroxyl absorption peak shift to the high wavenumber region and changed to asymmetric peak. Meanwhile, the strong characteristic stretching vibration peaks of —COO— appeared around 1613 and 1421 cm^{-1} , which proved the carboxymethylation of native starch was enhanced under the ultrasonic-microwave synergistic interaction.³⁴

Morphological Characterization of the Starch Granules

The SEM images of granules of NCS, ultrasonic treated starch (UTS), alkaline treated starch (ATS), ultrasonic-ATS (UATS) and CMS were shown in Figure 2.

As shown in Figure 2(a-1,a-2), the morphology of native starch granules was circular, oval or polygonal. And native starch exhibited the varying sizes, smooth surface and slight dents of few starch granules. As shown in Figure 2(b-1,b-2), some grooves and caves were appeared on some starch granule when the ethanol suspension of starch was treated under ultrasonic field, which suggested that ultrasonic treatment was beneficial to denaturing agent penetrating into the inside of starch granules. Moreover, as shown in Figure 2(c-1,c-2), the surface of starch granules changed rough when the ethanol suspension of starch was treated using alkaline solution before the carboxymethylation. This treating process might promote the effective collision of starch and denaturing agent. Furthermore, as shown in Figure 2(d-1,d-2), compared with the starch treated just under ultrasonic treatment, more grooves and caves were appeared and the surface of starch granules were rougher when the starch was treated both under ultrasonic and alkaline treatment. And it also was favorable for the occurring of etherification reaction. Figure 2(e-1,e-2) showed the morphologies of CMS granule changed rough and exhibited grooves and caves, which suggested that the structures of the starch granules were damaged by a certain degree under ultrasound-microwave field;^{35–37} and, the chemical reactivity of the starch granules was enhanced. Therefore, MCA or sodium monochloroacetate and other small molecules could be easily penetrated into the starch granules and finished etherification reaction.

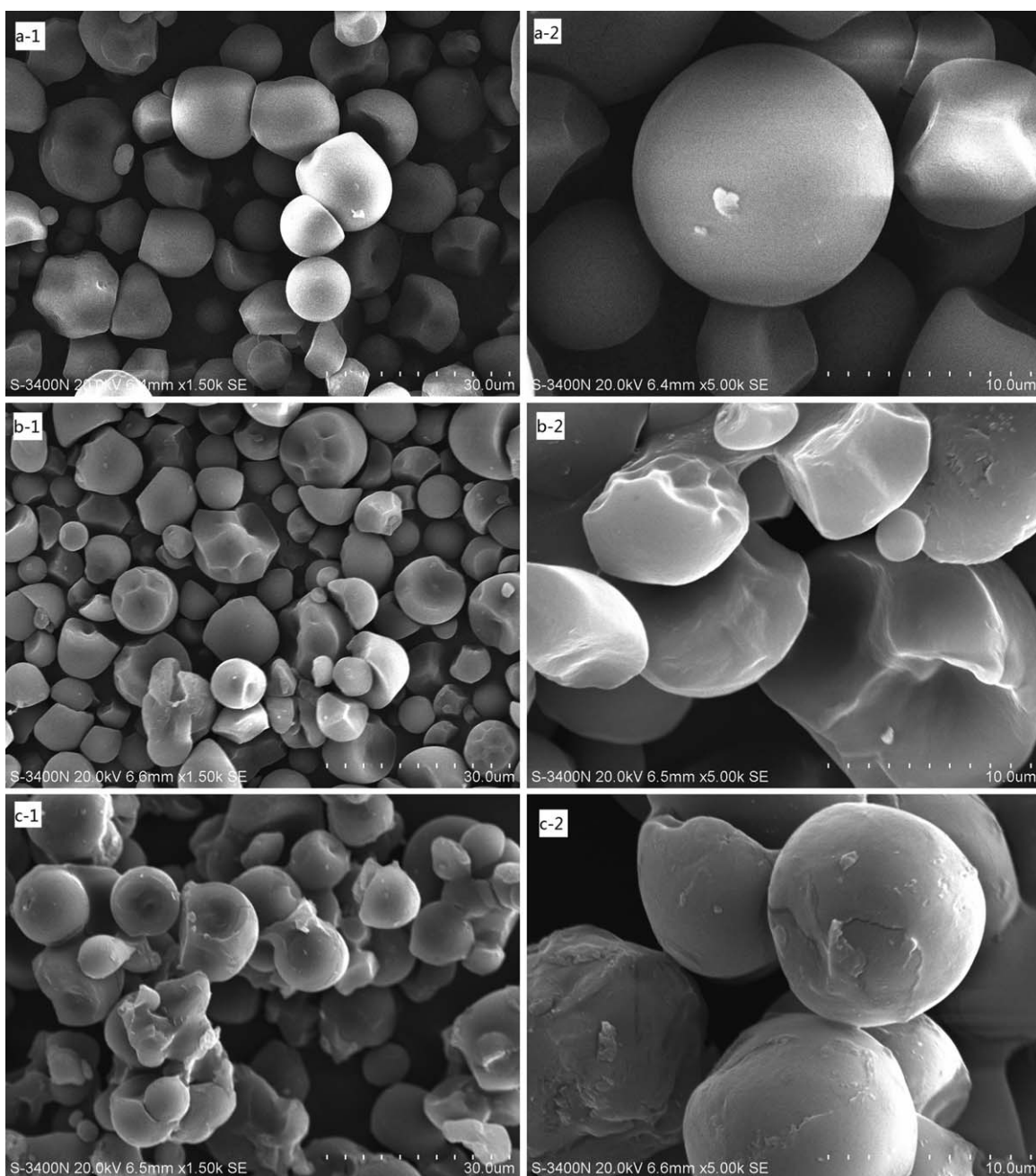


Figure 2. SEM images of starch granules: (a-1) NCS at magnification $\times 1500$ and (a-2) NCS at magnification $\times 5000$, (b-1) UTS at magnification $\times 1500$ and (b-2) UTS at magnification $\times 5000$, (c-1) ATS at magnification $\times 1500$ and (c-2) ATS at magnification $\times 5000$, (d-1) UATS at magnification $\times 1500$ and (d-2) UATS at magnification $\times 5000$, (e-1) CMS with DS = 1.089 at magnification $\times 1500$ and (e-2) CMS with DS = 1.089 at magnification $\times 5000$.

XRD Characterization of Starches

The XRD patterns of granules of NCS, UTS, ATS, UATS, and CMS were showed in Figure 3.

Seen from the XRD pattern of NCS [Figure 3(a)], the emergence of strong diffraction peaks ($2\theta = 15.1^\circ$, 17.1° , 18.1° , 23.1°) of native starch suggested that the native starch belonged to A-type crystalline structure,³⁸ and the crystallinity was 23.2%. Compared with the XRD pattern in Figure 3(b–d) with (a), the sharp diffraction peaks were appeared in $2\theta = 15.1^\circ$,

17.1° , 18.1° , 23.1° ; and, the crystallinities of UTS, ATS and UATS were changed to 15.6, 12.8, and 9.8%, respectively. It suggested that the crystallinities of starch under ultrasonic treatment, alkaline solution or synergistic treatment of ultrasonic-alkaline were decreased. However, the crystalline types were not changed. Additionally, the amorphous regions of UTS, ATS and UATS were increased, which was favorable for the occurring of etherification reaction. All of these observations were in accordance with the results obtained from SEM assay mentioned above.

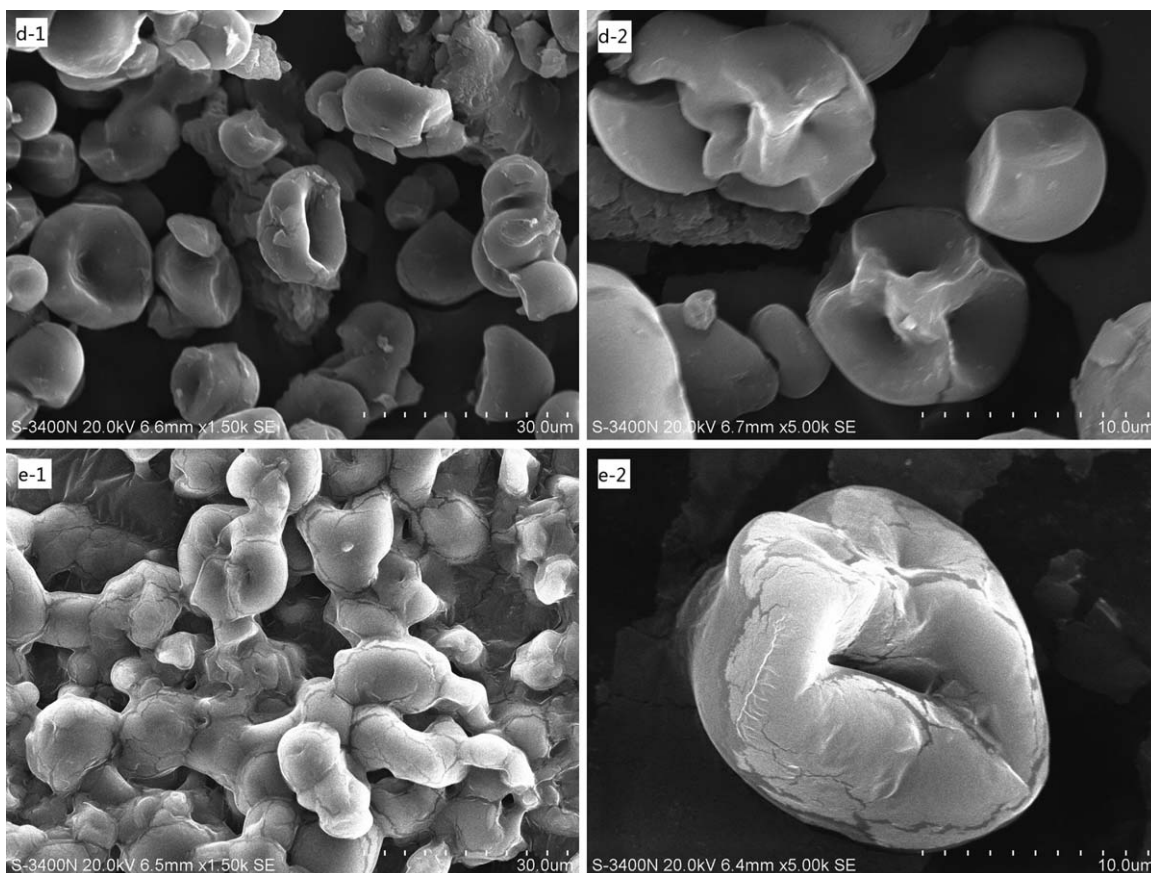


Figure 2. (Continued).

The XRD pattern of CMS with DS = 1.089 [Figure 3(e)] showed that the wide dispersion peaks appeared in the vicinity of $2\theta = 20.4^\circ$, the intensity of diffraction peak was decreased, and the crystallinity < 1%. The polycrystalline structure of starch granules changed into an amorphous structure, which proved that the carboxymethylation of starch occurred in both amorphous region and crystalline region under the ultrasound-

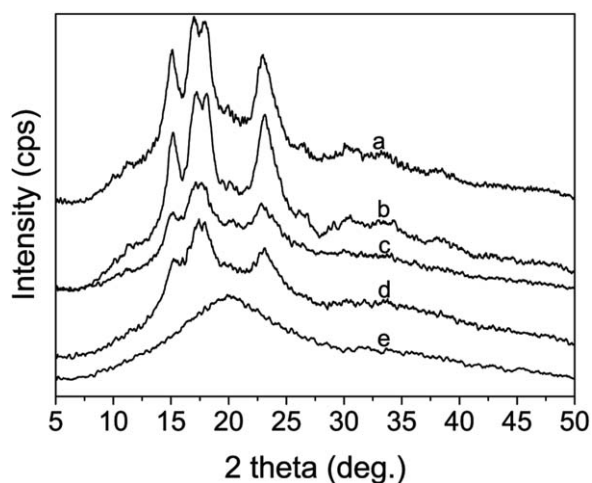


Figure 3. XRD patterns of NCS (a), UTS (b), ATS (c), UATS (d) and CMS with DS = 1.089 (e).

microwave synergistic interaction. And the crystalline region of starch granules was damaged obviously.³⁹

Thermal Stabilities of Starches

The TG and DTG thermograms of samples of NCS and CMS were shown in Figure 4.

From the curve of TG in Figure 4(a), the starting temperature of decomposition reaction of native starch was 279°C and the end temperature of decomposition reaction was 348°C . The temperature range span was 69°C . The DTG curve of Figure 4(a) proved that the maximum decomposition rate temperature of native starch was 322°C and the maximum decomposition rate was 20%/min. The TG curve in Figure 4(b) showed that the starting temperature of decomposition reaction of CMS with DS = 1.089 was 222°C . And the end temperature of decomposition reaction was 310°C . The temperature range span was 88°C . The DTG curve of Figure 4(b) proved that the maximum decomposition rate temperature of CMS with DS = 1.089 was 266°C ; and, the maximum decomposition rate was 8.5%/min. Therefore, we could draw a conclusion that the temperature region for the completing of decomposition reaction changed broad and the maximum decomposition rate decreased when the carboxymethylation of starch was occurred. Additionally, from room temperature to 550°C , the complete weight losses for NCS and CMS were 93.8 and 66.3%, respectively. So the weight loss of CMS was lower than that of NCS, which

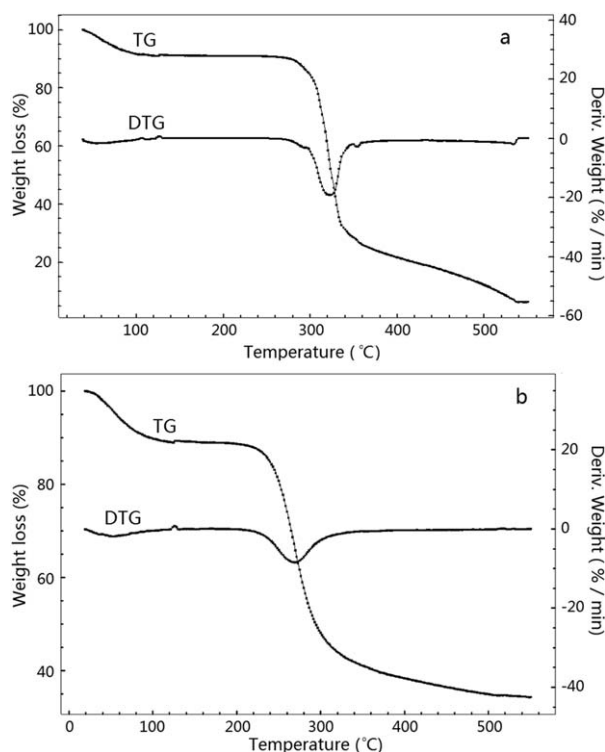


Figure 4. TG and DTG thermograms of NCS (a) and CMS with DS = 1.089 (b).

further proved that the thermal stability of CMS changed better compared with native starch. This result was in accord with the report of Li et al.⁴⁰

CONCLUSIONS

Compared with traditional process without ultrasonic-microwave synergistic interaction, the reaction time was shortened and the DS of CMS was increased when ultrasonic-microwave synergistic interaction was employed. The optimum preparation conditions were obtained and showed like these: the ultrasonic time was 40 min, the ultrasonic power was 220 W, the amount of NaOH was 8.8 g, two steps alkalization was used, the microwave alkalization reaction time was 2 min, the amount of MCA was 11.34 g, the amount of 95% (v/v) ethanol was 70 mL and the microwave etherification reaction time was 3 min. The DS of product under this condition was 1.089 ± 0.041 , which was increased by 30.4% compared with traditional process without ultrasonic-microwave synergistic interaction.

When the native starch was treated with carboxymethylation and ultrasonic-microwave synergistic interaction, the strong characteristic stretching vibration peaks of $-\text{COO}-$ appeared around 1613 and 1421 cm^{-1} , which proved the carboxymethylation of cassava starch was occurred. SEM analysis proved that the morphologies of CMS granules changed rougher and exhibited much more grooves and caves under ultrasonic-microwave synergistic interaction. The assay of XRD patterns suggested that the carboxymethylation of starch occurred in both amorphous region and crystalline region under the ultrasound-microwave synergistic interaction; and, the crystalline region of

starch granules was damaged obviously. The assay of the temperature range span, the maximum decomposition rate, and the complete weight losses based on TG and DTG thermograms proved that the thermal stability of CMS changed better compared with native starch.

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