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Synthesis and properties of carboxymethyl kudzu root starch

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ABSTRACT

Carboxymethyl kudzu root starch was synthesized for the first time under different reaction conditions. Optimal degree of substitution (DS) of 0.92 and reaction efficiency (RE) of 66.1% were obtained at 40 °C, 3 h in isopropanol–water reaction mixture ratio 1:0.08. The ratio of sodium hydroxide and sodium monochloroacetate moles to anhydroglucose unit moles for the optimal DS and RE were 2.02 and 1.39. The influence of sodium hydroxide concentration, sodium monochloroacetate concentration, and water content, type of organic solvent, reaction time, and temperature were evaluated for degree of substitution (DS) and reaction efficiency (RE). Wide angle X-ray diffractometry revealed that starch crystallinity was reduced after carboxymethylation. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) results show that thermal stability improved after carboxymethylation. IR spectrometry showed new bands at $v = 1597$, 1415, and 1323 cm^{-1} when starch underwent carboxymethylation. The broadband ^{13}C NMR spectra of the ultrasonically degraded carboxymethyl starch showed a peak at $\delta = 177.85$ ppm which was assigned to carbonyl carbon.

1. Introduction

Starch and starch derivatives play important roles in the growing biopolymer industries because they are source extensive, cheap, non-toxic, renewable, and compatible with many other materials in the industrial applications. Applications in food, environmental management, agriculture, pharmacy, biomedical engineering, and textiles have been reported widely in the literature (Thomas & Andreas, 2005). However, native starch forms have many certain undesirable characteristics such as poor solubility, poor resistance to mechanical shear and instability at high temperature, which limit their applications. Hence, modified starch is ideal for specific industrial processes. Chemical modification of starch involves reaction of the hydroxyl groups (C2, C3, C6) on the AGU and these have been used to produce starch derivatives based on oxidation (Lawal, Adebowale, Ogunsanwo, Barba, & Llo, 2004), acetylation, hydroxyl propylation, carboxymethylation, and cross-linking (Seidel, Kulicke, Hess, & Hartmann, 2001). Among the starch derivatives, carboxymethylated starch is very important because it covers a wide range of industrial applications such as food, pharmaceuticals, textile, paper, plastics as well as biomedical (Lawal, Lechner, & Kulicke, 2008a).

Many kinds of starch, such as corn starch, potato starch, cocoyam starch, pea starch, water yam starch, have been used as materials for carboxymethylation. It is well known that the properties (viscosity of solution, film forming, interaction with cations, the formation of supramolecular aggregates, etc.) are mainly determined by the total DS, i.e., the average number of carboxymethyl groups in the polymer (Stojianovic, Jeremic, Jovanovic, & Dieter Lechner, 2005). Technically, DS is defined as the average number of substituent per AGU. In the present investigation, kudzu root starch was used as the source of starch for carboxymethylation. Kudzu root is a unique plant root in china, with a high starch content.

Kudzu is a perennial leguminous vine of the genus *Pueraria* native to East Asia. It is believed to have originated in China and is one of the earliest medicinal plants used in traditional Chinese medicine. The success of kudzu is due in part to its production of large underground storage roots (Rowan, 2009). Starch is a main component of the root of kudzu. The yield of starch is about 15–34.2% of the fresh roots (Pham, 2007). There are no previous publication on synthesis and characterization of carboxymethyl kudzu root starch in the literature. Therefore, we present in this study, the synthesis as well as the influences of reaction parameters on synthesis and characterization of carboxymethyl kudzu starch. We are convinced that the information presented in this paper will contribute significantly to the literature and will be useful for further research in this area.

2. Materials and methods

2.1. Materials

Sodium hydroxide and sodium monochloroacetate (SMCA) were purchased from Sinopharm Chemical Reagent, China. Methanol,

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Table 1
Reaction conditions used for the carboxymethylation of kudzu root starch.

Sample	Organic solvent	Time (h)	Temperature (°C)	H_2O/solvent	*n*NaOH/*n*AGU(s)	*n*SMCA/*n*AGU(s)	DS	RE (%)
CMKS1	Isopropanol	3	60	0.08	1.62	1.39	0.86 ± 0.02	62.1 ± 0.3
CMKS2	Isopropanol	3	50	0.08	1.62	1.39	0.91 ± 0.01	65.3 ± 0.3
CMKS3	Isopropanol	3	30	0.08	1.62	1.39	0.53 ± 0.01	38.1 ± 0.4
CMKS4	Isopropanol	3	40	0.08	1.62	1.74	0.82 ± 0.01	50.4 ± 0.3
CMKS5	Isopropanol	3	40	0.08	1.62	1.39	0.73 ± 0.01	52.8 ± 0.3
CMKS6	Isopropanol	3	40	0.12	1.62	1.39	0.75 ± 0.02	53.7 ± 0.1
CMKS7	Isopropanol	3	40	0.16	1.62	1.39	0.76 ± 0.02	54.9 ± 0.1
CMKS8	Isopropanol	3	40	0.08	1.21	1.39	0.72 ± 0.02	59.5 ± 0.3
CMKS9	Isopropanol	3	40	0.08	0.81	1.39	0.68 ± 0.02	83.9 ± 0.1
CMKS10	Isopropanol	3	40	0.08	1.62	1.04	0.35 ± 0.01	33.9 ± 0.2
CMKS11	Isopropanol	3	40	0.08	1.62	0.69	0.26 ± 0.01	37.7 ± 0.2
CMKS12	Isopropanol	3	40	0.20	1.62	1.39	0.81 ± 0.02	58.2 ± 0.1
CMKS13	Methanol	3	40	0.08	1.62	1.39	0.07 ± 0.01	5.30 ± 0.3
CMKS14	Ethanol	3	40	0.08	1.62	1.39	0.55 ± 0.01	39.4 ± 0.1
CMKS15	Acetone	3	40	0.08	1.62	1.39	0.58 ± 0.02	42.1 ± 0.1
CMKS16	Isopropanol	3	40	0.08	1.82	1.39	0.82 ± 0.02	59.0 ± 0.3
CMKS17	Isopropanol	3	40	0.08	2.02	1.39	0.92 ± 0.02	66.1 ± 0.2
CMKS18	Isopropanol	2	40	0.08	1.62	1.39	0.65 ± 0.02	46.8 ± 0.4
CMKS19	Isopropanol	1	40	0.08	1.62	1.39	0.36 ± 0.01	26.0 ± 0.2
CMKS20	Isopropanol	4	40	0.08	1.62	1.39	0.78 ± 0.02	56.3 ± 0.1

ethanol, acetone were of technical grade. All other reagents were of analytical grade. Kudzu root starch was isolated and purified from raw materials in the laboratory. For this isolation method, the harvested kudzu root were peeled and homogenized with 1 M NaCl solution using a commercial blender. The mixture was filtered through triple layered cheesecloth and starch washed through using water. The granules were allowed to settle and water decanted followed by centrifugation at 3000*g* for 10 min. Starch was allowed to air dry overnight at room temperature.

2.2. Preparation of carboxymethyl starch

Carboxymethyl reaction of kudzu root starch was carried out in aqueous-organic liquid media. Organic solvents used in this experiment were ethanol, methanol, acetone, and isopropanol. The reaction was carried out in a 500 mL three necked round-bottom flask, equipped with motor-driven stirrer (Tijsen, Kolk, Stamhuis, & Beenackers, 2001). Sodium hydroxide of different weight (3.24–8.08 g) was added to water in the flask and the mixture was stirred at 300 rpm until dissolution of sodium hydroxide was complete. Solvent was added to the solution and the temperature was raised to 30 °C. The water content in the reaction mixture was varied between 13.50 and 37.45 mL, taking into consideration the moisture content of kudzu root starch (13.6%). Starch (18.75 g) was added to the mixture and it was stirred at 300 rpm while nitrogen gas was flushed through the reaction mixture. After stirring for 1 h, SMCA was added to the mixture and the reaction time was varied between 1 and 4 h. At the end of the reaction, the starch slurry was filtered, suspended in ethanol, and was dispersed again in 85% ethanol and was washed several times until the silver nitrate test for chloride of the filtrate was negative (Pfeiffer, Heinze, & Lazik, 2002). The slurry obtained was suspended in absolute ethanol, washed five times, and dried in an oven at 40 °C for 48 h. Reaction conditions are given in Table 1.

2.3. Determination of degree of substitution and RE

The interaction of the carboxymethyl groups with salt ions leading to quantitative precipitation of the polymers with copper salt and back titration of the excess of copper ions allows for quantification of the DS. The DS was determined by a method described elsewhere (Whistler, 1963).

DS_t is the theoretical degree of substitution. It is the maximal degree of substitution when the limiting reactant either sodium monochloroacetate or sodium hydroxide is totally used without the formation of sodium glycolate as indicated.

$$DS_t = \frac{n\text{SMCA}}{n\text{AGU}}, \quad \text{if } n\text{NaOH} \geqslant n\text{SMCA},$$

$$DS_t = \frac{n\text{NaOH}}{n\text{AGU}}, \quad \text{if } n\text{NaOH} < n\text{SMCA},$$

where *n*SMCA, number of moles of sodium monochloroacetate; *n*AGU, number of moles of anhydroglucose unit; *n*NaOH, number of moles of sodium hydroxide.

RE is a measure of the amount of carboxymethyl group bonded to the starch.

RE is defined as:

$$RE = \frac{DS}{DS_t} \times 100.$$

2.4. FT-IR spectroscopy

The IR spectra of starches were run as KBr pellets using a 470 Nicolet FT-IR spectrometer (Nicolet Instrument Corporation, USA) in the frequency range 4000–400 cm^{-1}.

2.5. Starch granule morphology

Starch granule morphology was examined with a JSM-6390LV scanning electron microscope (JEOL, Tokyo, Japan). The samples were mounted on studs, sputter coated with gold (Balzers, JFC-1600), and examined under the scanning electron microscope.

2.6. X-ray diffraction

The X-ray diffraction pattern of native kudzu root starch and its carboxymethylated derivatives were recorded using a Rigaku D/Max-IIIA X-ray diffractometer (Rigaku Corporation, Japan). The diffractograms were registered at Bragg angle (2θ) = 5–40° at a scan rate of 5°/min, while step with = 0.02° (Kittipongpatana, Chaitep, Kittipongpatana, Laenger, & Sriroth, 2007).

2.7. ^{13}C NMR spectroscopy

^{13}C NMR spectra were obtained on an Avance 400 MHz spectrometer (Bruker, Rheinfelden, Germany) in D_2O as a solvent with TMS (3-(trimethylsilyl) propionic 2,2,3,3-d_4 acid, sodium salt) as internal reference. Prior to the measurements, the samples were degraded by ultrasonic degradation (Lawal, Lechner, & Kulicke, 2008b) with a sonifier W-250 ultrasonic degradation device (Branson Schallkraft GmbH, Heusenstamm, Germany) equipped with ¾″ titanium resonator.

For this experiment, 300 mL of 0.5% w/w solution was used. The sound frequency and max output of the device was 20 kHz, 400 W, respectively. Thermostat bath was used to cool the solution below 0 °C during degradation. The density of the ultrasonic output was approximately 80 W/cm^2. Following degradation for 3 h, ultracentrifugation (10,000 rpm, 1 h) was carried out to remove abraded metal fines from the ultrasonic resonator in order to avoid broadening of the NMR signals. The clear solutions obtained were lyophilized (Beta 2-8 LD plus, Christ, Osterode, Germany).

3. Results and discussion

3.1. Influence of reaction parameters

The effects of the parameters including amount of NaOH and SMCA, temperature, time of reaction, solvent type, on DS and reaction efficiency (RE) were investigated. The DS_t is the theoretical DS and it is the maximal DS when the limiting reactant (either SMCA or NaOH) is completely converted without formation of sodium glycolate.

3.1.1. Effect of NaOH concentration

As shown in Table 1, the effect of sodium hydroxide on DS and RE was studied by varying the concentration of the sodium hydroxide. It was observed that the DS of CMKS increased with sodium hydroxide concentration and attained a maximum DS of 0.92 at *n*NaOH/*n*AGU of 2.02. However, a minimum RE of 52.8% at *n*NaOH/*n*AGU ratio of 1.62 was observed. This observation can be explained by considering the carboxymethylation process, where two competitive reactions take place simultaneously. The first involves reaction of the starch hydroxyl with sodium monochloroacetate in the presence of sodium hydroxide to give CMKS. The second step involves sodium hydroxide reacting with sodium monochloroacetate to form sodium glycolate.

3.1.2. Effect of water content

Several articles have reported that water could play significant roles in aiding dissociation, diffusion, and adsorption of etherifying agents as well as facilitation of starch swelling during carboxymethylation. By varying the ratio of water to isopropanol solvent, and the other reaction conditions were 40 °C, 3 h, *n*NaOH/*n*AGU = 1.62, *n*SMCA/*n*AGU = 1.39, we obtain the effect of water content in the reaction mixture. At the beginning, it was suspected that there may exit a critical ratio at which both the DS and the RE are maximal. After the critical ratio, further increase in water content reduces the RE and the DS. However, our results suggest that a critical ratio not exist. Both the DS and the RE increased slowly as the ration of water to organic solvent increased from 0.08 to 0.20. But agglomeration and starch gelation also occurred at a high water content of the reaction mixtures. These phenomena reduced contact of the etherifying agent with starch molecules. In addition, the granular nature of the starch was lost and product recovery was difficult.

3.1.3. Effect of sodium monochloroacetate

In the starch carboxymethylation, sodium monochloroacetate (SMCA) provides all carboxymethyl groups. DS increased with increasing SMCA concentration while a maximum (RE = 52.8%, *n*SMCA/*n*AGU = 1.39) in RE was observed as the *n*SMCA/*n*AGU ratio increased between 0.69 and 1.74, while the other conditions were 40 °C, 3 h, *n*NaOH/*n*AGU = 1.62, *n*SMCA/*n*AGU = 1.39, water/isopropanol = 0.08. Higher SMCA concentration could cause side reactions, such as the sodium glycolate reaction, which decrease DS and RE (Pushpamalar, Langford, Ahmad, & Lim, 2006). This finding is supported by reports in the literature (Bhattacharyya, Singhal, & Kulkarni, 1995; Khalil, Hashem, & Hebeish, 2006). This observation is however inconsistent with the article on carboxymethylation of cocoyam starch (Lawal, Dieter Lechner, Hartmann, & Kulicke, 2007).

3.1.4. Effect of duration of reaction

Increases in both DS and RE were observed as the duration of the reaction increased within the time frame studied (1–4 h), while the other conditions were 40 °C, *n*NaOH/*n*AGU = 1.62, water/isopropanol = 0.08. This is attributed to enhanced swelling of the starch which improved the accessibility of the etherifying agents. It is also reasonable that longer reaction time enhanced starch swelling and ultimately improved homogeneity of the reactants (Lawal et al., 2007). However, longer time (more than 3 h) resulted in no further increases in both DS and RE. We can speculate that the accessibility of etherifying agents have a maximum value no matter how long it takes.

3.1.5. Effect of temperature

The temperature points of 30, 40, 50, 60 °C were selected to determine the effect of temperature on DS and RE. An 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. Solubility and diffusion of the etherifying agents can be enhanced by high temperature (Kittipongpatana et al., 2007). Increasing the temperature increases the proportion of molecules with higher energy than the activation energy, and consequently the rate of reaction increases and thus DS and RE. However, at temperature 60 °C gelatinization occurred, stirring was difficult and it was also difficult to remove the product and agglomeration was observed. Lawal's study indicates the gelatinization temperature of native cocoyam starch was 76 °C. The gelatinization temperature is higher in organic liquids; however, the influence of carboxymethylation, particularly in alkaline medium, obviously caused gelatinization to occur at lower temperature. Slight declines in DS and RE were observed above 50 °C. Increase of temperature inhibits reaction due to the exothermic reaction system.

3.1.6. Comparison of organic solvent media

Carboxymethylation was carried out in methanol, ethanol, acetone, and isopropanol when other parameters were kept constant, while the other conditions were 40 °C, 3 h, *n*NaOH/*n*AGU = 1.62, *n*SMCA/*n*AGU = 1.39, water/solvent = 0.08. The results indicate optimal DS and RE were obtained on isopropanol–water reaction medium when H_2O/isopropanol was 0.2. A similar result was reported for maize starch (Khalil et al., 2006) and pea starch (Ma, Chang, & Yu, 2007) in isopropanol–water reaction medium. However, when methanol–water was used, minimal DS and RE were obtained. In carboxymethylation of pea starch, a methanol–water reaction medium was more effective than an ethanol–water reaction medium (Lawal et al., 2008b).

3.2. FT-IR spectroscopy

The infrared spectra of native and a representative carboxymethylated starch (CMKS-7) derivative are presented in Fig. 1. The broad band between 3600 and 3000 cm^{-1} is assigned to O–H stretching and it is due to hydrogen bonding involving the hydroxyl groups on the starch molecules. The band at 2922 cm^{-1} is assigned to CH_2 symmetrical stretching vibrations. The band at 1597 cm^{-1} is attributed to the scissoring of two O–H bonds of water molecules, while the bands at $v = 860$ and 767 cm^{-1} are due to skeletal stretching vibrations of starch. The carboxymethyl starch derivative shows new bands at $v = 1597, 1415$, and 1323 cm^{-1}. Those new bands confirm that carboxymethylation took place on the starch molecules. Similar observations were reported for carboxymethylated potato starch, corn starch, and maize starch (Bhattacharyya et al., 1995; Zeljko, Katarin, & Slobodan, 2000).

3.3. Starch granule morphology

Scanning electron microscopy was used to investigate the granule morphology of the native starch and carboxymethylated kudzu starch (Fig. 2A/B). Studies revealed that the native kudzu root starch granules were round in shape with sizes ranging from 2 to 45 μm. This result is larger than Pham Van Hung's study on SEM of Thanh Hoa, Nara Prefecture, and Seoul kudzu. The fractions observed are due to the process of extraction and drying.

As observed, the conditions of modifications significantly altered the granular structure of the carboxymethylated starch. The alkaline environment during the carboxymethylation process accounts for the structural changes. This result also suggests that starch crystallinity was altered and thus allowing the etherifying agents to have more access to the starch molecules for the carboxymethylation processes. We could find crackles in the starch granule surface, which would reduce the shear properties and stability of the products. This case suggests that etherification and drying processing need more mild conditions.

3.4. Wide angle X-ray diffractometry

The wide angle X-ray diffraction patterns of a native kudzu starch and a representative carboxymethyl starch (CMKS 7) is presented in Fig. 3. The kudzu starch exhibited B-type crystal as classified by Zobel (1988) with the major peaks 5.89, 5.19, 4.92 Å and a medium peak 15.68 Å. The result is similar to kudzu starch from

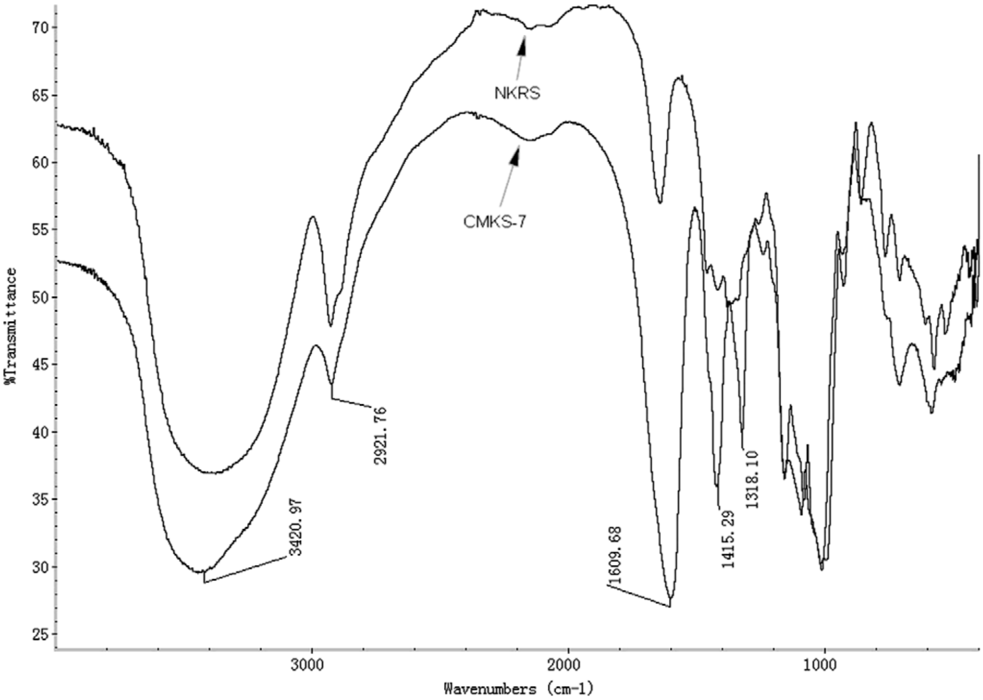

Fig. 1. The infrared spectra of native kudzu root starch (NKRS) and a representative carboxymethylated starch (CMKS-7, DS = 0.76).

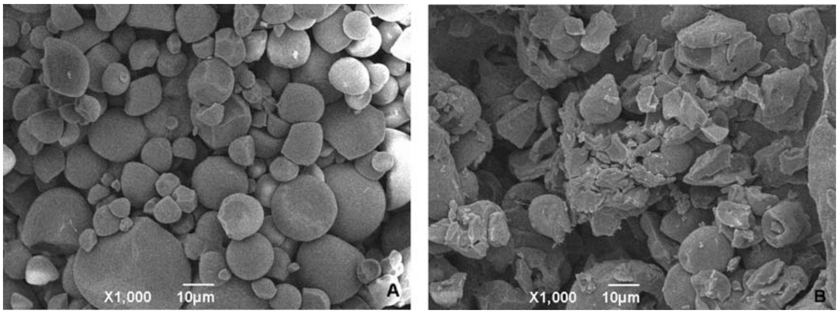

Fig. 2. Scanning electron micrographs of (A) unmodified kudzu root starch, magnification 1000×; (B) of carboxymethyl starch (CMKS-7, DS = 0.76). Only the micrograph of one CMS is shown here because no pronounced differences were observed among the micrographs of all CM starches prepared; magnification 1000×.

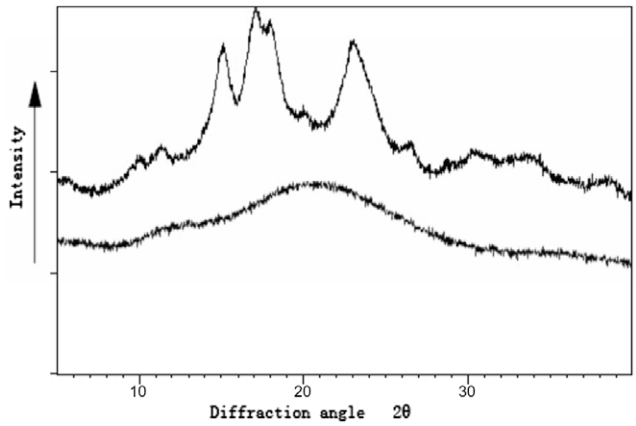

Fig. 3. Wide angle X-ray diffraction pattern of native and a representative carboxymethylated kudzu root starch (CMKS-7, DS = 0.76).

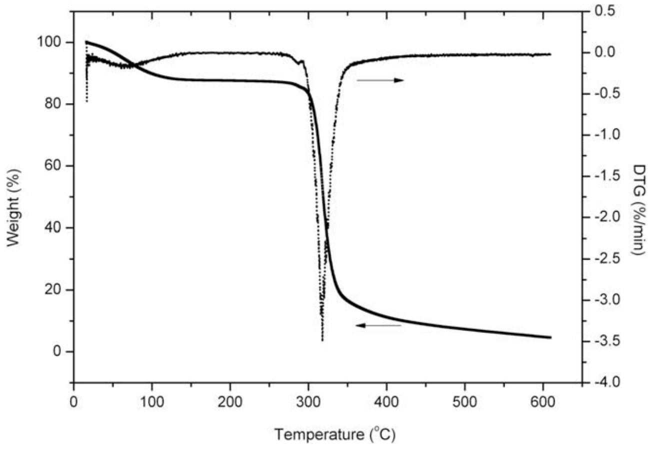

Fig. 4. Thermogravimetry (TG) and derivative thermogravimetry (DTG) of native kudzu starch.

Nara Prefecture of Japan (Pham, 2007). Remarkable changes were observed after carboxymethylation because crystallinity reduced significantly. This observation also corroborates the morphological studies (Kittipongpatana, Chaitep, Kittipongpatana, Laenger, & Sriroth, 2006). Hydrogen bonds maintain the stability of starch crystal, when carboxymethyl groups replace hydrogen atoms of hydroxyl groups, hydrogen bonds are broken. Hence more high DS value mean crystallinity reduced more significantly. The rupture of starch granules may be also the possible reason of the loss of crystallinity, which in the presence of water together with heat treatment caused the breakage of chemical bonds in starch molecules. The significance of the loss in crystallinity is important in applications such as the preparation of hydro gels for diverse industrial utilization like super absorbents since amorphous granules would facilitate water percolation.

3.5. Thermogravimetry (TG) and derivative thermogravimetry (DTG)

Thermogravimetry (TG) and derivative thermogravimetry (DTG) can give us samples thermal information in Figs. 4 and 5. At the range of 295–366 °C (DTG_{max} = 317 °C), maximum decomposition was observed. At 500 °C, 92.6% of native starch was decomposed. But for carboxymethylated kudzu starch, at the range of 254–321 °C (DTG_{max} = 292 °C), maximum decomposition was observed. At 500 °C, nearly 57.99% of carboxymethylated starch was decomposed. In the beginning of both native and carboxymethylated starches, we can find out a small gravimetry loss, which are due to water evaporation (Thomas, Liebert, Heinze, & Schwikal, 2004).

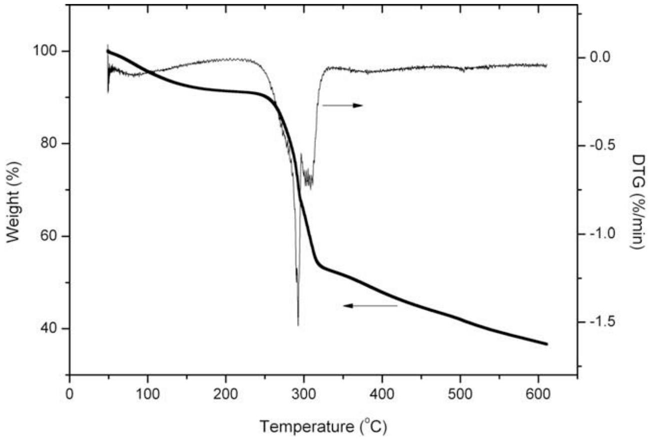

Fig. 5. Thermogravimetry (TG) and derivative thermogravimetry (DTG) of a carboxymethylated kudzu starch.

3.6. ^{13}C NMR characterization

The ^{13}C NMR spectrum of carboxymethyl kudzu starch (CMKS-2, DS = 0.91) is shown in Fig. 6 (range between 182 and 60 ppm). The prominent peak at d = 177.85 is assigned to the –CO carbon (C-8) of the carboxymethyl group. At 99.6 and 96.4 ppm, two peaks appear together because C-2 causes a downfield shift of ~3 ppm on C-1. At 79.9 ppm, this strong peak is assigned to C-4. Compared with C-1, this peak is single. C-2u and C-3u were assigned peaks at 71.5 and 72.5 ppm, respectively. The signal at 73.3 ppm is assigned to C-5. As a result of the electron withdrawing effect imposed by oxygen in the carboxymethyl substituent, C-6s (68.8 ppm) have a downfield shift of ~4.5 ppm compared to C-6 (64.2 ppm). The methylene carbon atoms of the carboxymethyl group (C-7) appear at three major peaks (71.1, 70.2, 69.5 ppm), because carboxymethyl substitution can occur in three different positions (C-2, C-3 or C-6) (Lawal et al., 2008b).

4. Conclusions

The synthesis and the characterization of carboxymethyl derivatives of kudzu root starch are presented for the first time. Various reaction parameters and characteristics were investigated. Optimal DS of 0.91 was achieved with a reaction efficiency of 65.3% after 3 h in isopropanol/water reaction medium when H_2O/isopropanol was 0.08. The broad-band ^{13}C NMR spectra of carboxymethyl starch showed a peak at δ = 177.85 ppm which was assigned to carbonyl carbon. Wide angle X-ray diffractometry revealed that starch crystallinity was reduced after carboxymethylation. Thermogravimetry (TG) and derivative thermogravimetry (DTG) show that thermal stability improved after carboxymethylation. IR spectrometry showed new bands at v = 1597, 1415, and 1323 cm^{-1} presentative of starch that has undergone carboxymethylation. This new starch source is plentiful and it has a reasonably wide distribution, particularly in the hilly region in southern of China. The authors are inclined to believe this new raw material is useful for production and industrial applications of carboxymethyl starch. More related research is warranted for kudzu root starch.

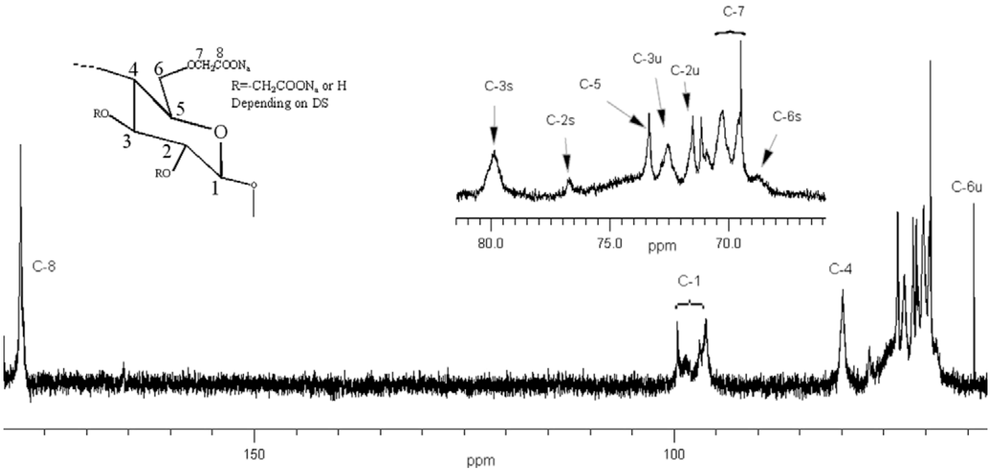

Fig. 6. The broad-band ^{13}C NMR spectrum of carboxymethyl kudzu starch (CMKS-2, DS = 0.91). Inset map: the enlarged range of 66–82 ppm. S, carbon with carboxymethyl substituent; U, carbon without carboxymethyl substituent.

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