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Determining the effects of microwave heating on the ordered structures of rice starch by NMR

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ABSTRACT

The effects of microwave heating on the double helices, single helix and amorphous structures and the relative crystallinity of rice starch were studied by ^{13}C CP/MAS NMR method, with rapid heating in an oil bath and conventional slow heating as controls. The results indicated that compared with rapid heating, microwave heating did not significantly change the ordered and disordered structures. All of the heating methods exhibited similar content changes to the double helices, V-type single helix and amorphous structures with rising temperature. The rapid heating effects caused by microwave and oil bath accelerated the destruction of the V-type single helix in the starch granules. The electromagnetic effect of microwave heating did not affect the decrease of the double helices or the amorphous content of the starch.

1. Introduction

Based on the principle of dielectric loss, microwave heating acts on materials through high-frequency electric fields to generate the micromovement and friction of molecules, which convert electromagnetic energy into thermal energy and produce simultaneous internal and external heating (Galema, 1997). Microwave technology has been widely used in the food processing and consumption industries for applications that include reheating, baking, defrosting, enzyme deactivation, modification, puffing and sterilization (Cui, Xu, & Sun, 2002; Lewandowicz et al., 2000; Satge et al., 2002). The use of microwave technology depends on the dielectric properties of the food product, which determine the microwave response characteristics of the food and the penetration depth (Piyasena, Dussault, Koutchma, Ramaswamy, & Awuah, 2003). Starch is an important macromolecule in food composition and contains a large number of hydroxyl groups, which specifically bind to water in conventional heat treatment processes and induce gelatinization (Tester & Morrison, 1990). Because water has a high dielectric constant, it accelerates the gelatinization of starch in a microwave field and helps unwind the chain structure of starch, which has a significant impact on the response of the food material to heating (Palav & Seetharaman, 2007; Roebuck, Goldblith, & Westphal, 1972). Studying the effects of the microwave heating process on the structure of starch will lay a theoretical foundation for further investigation into the reaction mechanisms of electromagnetic waves on carbohydrates and provide information regarding the application of new processing technologies for starchy foods.

Starch is a semi-crystalline macromolecular carbohydrate that consists of amylose and amylopectin. The ordered structures in a starch granule are primarily composed of two types of helical structures from amylopectin side chains. The ordered arrangement of these helical structures forms a crystalline structure in starch (Atichokudomchai, Varavinit, & Chinachoti, 2004). Information regarding the ordered and disordered structures within starch granules can be obtained primarily through X-ray diffraction (XRD) and solid-state nuclear magnetic resonance (NMR) technology. XRD is generally used to study the long-range ordered structures of starch granules, and ^{13}C CP/MAS NMR is used to evaluate the short-range ordered structures in starch granules (Cooke & Gidley, 1992). The chemical structures of starch and its derivatives are similar. The only differences are the number of repeating units or the order of atomic arrangements. As a result, these analogs cannot

Abbreviations: NS, native rice starch sample; MS, microwaved rice starch sample; RS, traditional rapid heating rice starch sample.

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be distinguished using infrared spectroscopy or other analytical approaches. However, ^{13}C-NMR can clearly detect small differences in structures and has advantages in assessing the double helical structure in starch (Liu, Wu, & Mao, 2008). Researchers have performed extensive research on starch hydrolysis, aging and modification by using ^{13}C CP/MAS NMR to analyze the changes that occur in the double helical structures and relative crystallinity during these processes (Spěváček & Brus, 2008; Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). Cooke and Gidley (1992) compared the results of XRD and NMR before and after starch gelatinization and found that the molecular (double helical) order was significantly greater than the crystalline order in native starches and that both structures were disrupted concurrently during gelatinization because the enthalpy of gelatinization primarily reflects the loss of molecular (double helical) order. Morrison, Tester, Gidley, and Karkalas (1993) studied the double helical structures and amorphous state of starch during acidic hydrolysis by using ^{13}C CP/MAS NMR. The NMR results showed that the initial increase in the relative proportion of double helical structures and crystallinity was due to hydrolytic destruction in the amorphous domain, the retrogradation of the partially hydrolyzed amylose and the crystallization of free amylopectin double helices. Błaszczak, Valverde, and Fornal (2005) employed ^{13}C CP/MAS NMR to examine the effects of high pressure on the amorphous state of potato starch. However, few studies have examined the changes to the amorphous state and double and single helical structures within starch granules during gelatinization following heating and radiation processes.

The present study utilized a conventional rapid heating method to simulate the rapid heating effect of a microwave and investigated the impact of the microwave heating process on the relative crystallinity and content of ordered and disordered structures in rice starch by using ^{13}C CP/MAS NMR technology.

2. Materials and methods

2.1. Preparation of starch

Thirty grams of rice (QiuShouBao Rice Products Co., Ltd., AnHui, China) were pulped intermittently for 30 s after being soaked for 18 h. The residue was suspended in distilled water and adjusted to a pH of 5 with 0.1 mol/L HCl (Sinopharm Medicine Holding Co., Ltd., Shanghai, China). The suspension was added to 0.04 g of cellulase (XueMei enzymatic preparation Sci. Co., Ltd., Wuxi, China) and heated at 50 °C for 2 h. The mixture was adjusted to a pH of 7 with 0.1 mol/L NaOH (Sinopharm Medicine Holding Co., Ltd., Shanghai, China). A total of 0.9 g of liquefaction type protease (Neutrase 0.8Au/g, Novo Nordisk A/S, Denmark) was added, and the suspension was stirred at 50 °C for 4 h. The slurry was centrifuged at 10,000 × *g* for 30 min. The surface proteins on the sediment were scraped, and the sediment was dissolved in distilled water. The centrifugation process was repeated 5 times.

The protein-free rice flour was suspended in 100 mL of 63% (v/w) n-butyl alcohol (Sinopharm Medicine Holding Co., Ltd., Shanghai, China) and stirred for 18 h to extract the lipids. The supernatant was discarded. The sediment was washed 3 times with distilled water, centrifuged at 10,000 × *g* for 30 min and dried by lyophilization (Labconco Corporation, KS, USA). The dried starch sample was crushed with an analysis grinding apparatus (IKA A11 basic, Guangzhou, China).

2.1.1. Methods

2.1.1.1. Preparation of microwave-treated samples (Vandeputte et al.). A total of 3.00 g of the rice starch was dispersed in 47.00 g of deionized water and heated at 800 W in a microwave work station (Sino Tech Manufacture Co., Ltd., Nanjing, China) (Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). An optical fiber temperature probe (FISO Technologies Inc., Québec, Canada) was used to measure the temperature of the starch sample during the heating process, and the change in temperature over time was recorded.

2.1.1.2. Preparation of samples via rapid heating in an oil bath (RS). The starch (3 g of the rice starch sample dispersed in 47 g of deionized water) was heated in a Thermo Scientific AC200 oil bath (Pierce, IL, USA), and the change in temperature over time was recorded using an optical fiber temperature probe. The microwave power and/or oil temperature was altered until the two temperature curves coincided.

2.1.1.3. Preparation of samples via a traditional heating method (Putseys et al.). The starch (6 g of the rice starch sample dispersed in 94 g of deionized water) was heated on a hot plate (Xingshui Scientific Instrument Company, Tianjing, China), and the change in temperature over time was recorded using an optical fiber temperature probe (Putseys, Gommes, Puyvelde, Delcour, & Goderis, 2011).

The starch samples were heated by microwave or oil bath to 40 °C, 50 °C, 60 °C, 65 °C, 70 °C, 75 °C and 80 °C before being cooled with ice and lyophilized. Each dried starch sample was crushed and passed through a 75-μm sieve to create a powder.

2.1.2. Preparation of samples in an amorphous state

Amorphous starch was prepared using a Rapid Visco-Analyzer (RVA) (Newport Scientific, Australia). Briefly, a 6% (w/v) rice starch solution was heated from 25 °C to 95 °C at a rate of 0.25 °C/s and maintained at 95 °C for 5 min, followed by cooling to 50 °C at a rate of 0.25 °C/s. Completely gelatinized starch samples were passed through a 75-μm sieve after freeze-drying. The water content was approximately 10%.

2.1.3. Water equilibration

A saturated $BaCl_2$ solution was used to equilibrate the water content of the samples for two weeks at 25 °C until the water activity of the samples (a_w = 0.686) was constant and consistent.

2.1.4. ^{13}C CP/MAS NMR

The ^{13}C CP/MAS NMR spectra were recorded at room temperature at 100 MHz by using a Bruker AVIII-400 equipped with a 7 mm CP/MAS detection probe (Bruker Instrument, Inc., Billerica, MA). The samples were spun at 20 kHz, and 4096 scans were accumulated. The spectral width was 38 kHz, and the contact time was 13 ms.

2.1.5. Sub-peak fitting and data processing

In accordance with the method described by Tan et al. (2007), the Solver data analysis tool in Excel was used to calculate the decomposition rate of the obtained spectra. The ordered subspectrum was obtained by subtracting the subspectrum of the amorphous component from the original spectra of the sample. PeakFit version 4 for Win 32 (Jandel Scientific Software, CA) was used to fit the peaks of the spectra.

The proportions of double and single helical structures in the starch samples were calculated using the method of Tan et al.

3. Results and discussion

3.1. Comparing the three heating methods

In the microwave heating process, the thermal and electromagnetic effects of the microwave act on the material simultaneously. In this study, rapid heating in an oil bath was used to simulate the rapid heating process of a microwave to investigate the thermal

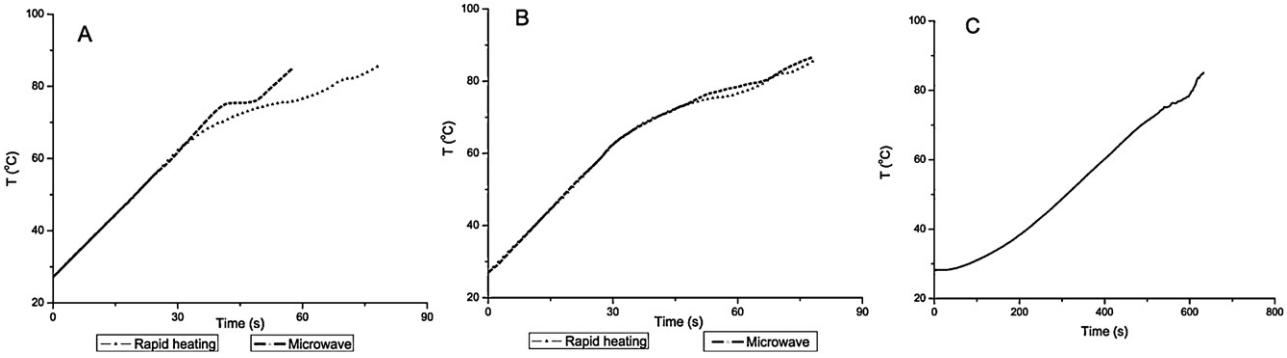

Fig. 1. (A) Temperature curves of the samples heated using a microwave at a power of 1000 W and a 200 °C oil bath. (B) Temperature curves of the samples heated using a microwave at powers of 1200 W – 32 s, 600 W – 20 s, 300 W – 14 s and 600 W – 12 s and a 200 °C oil bath. (C) Temperature curve of the samples treated with the slow heating method.

and electromagnetic effects of microwave heating on the structure of starch. The starch samples treated with rapid heating were compared with samples treated using a conventional slow heating conduction method.

At temperatures below 65 °C, the temperature curve resulting from 1000 W of microwave power completely overlapped with the temperatures due to heating in a 200 °C oil bath. When the temperature reached 65 °C and higher, a rapid temperature increase followed by a temperature plateau was observed in the samples treated with the microwave because of the concurrent electromagnetic and thermal effects. The conventional heat conduction method exhibited a slow heating rate and a sluggish rise in temperature without a temperature plateau, as shown in Fig. 1A.

The microwave power level was altered after the temperature reached 65 °C such that the temperature curves of the two methods were identical. The final temperature used for rapid heating in an oil bath was 200 °C. The microwave program was set at 1200 W for 32 s, 600 W for 20 s, 300 W for 14 s and 600 W for 12 s. The heating curves of the two methods are shown in Fig. 1B. The correlation coefficient of the two curves was calculated to be 0.9989, and the heating rate was approximately 1.5 °C/s. The temperature curve of the samples treated with the conventional slow heating method (with a heating rate of 0.05 °C/s) is shown in Fig. 1C.

3.2. Total analysis of the ^{13}C CP/MAS NMR spectra

Fig. 2A–C shows the ^{13}C CP/MAS NMR spectra of the starch samples subjected to microwave heating, rapid heating in an oil bath and conventional slow heating, respectively, at 40 °C, 50 °C, 60 °C, 65 °C, 70 °C, 75 °C and 80 °C along with the spectra of the raw and amorphous starches. The chemical shifts of each major peak are presented in Table 1, which shows that the peak locations were consistent with the results of previous studies (Gidley & Bociek, 1985, 1988). The signal at 94–105 ppm was associated with C1, the signal at 58–65 ppm was associated with C6, and the overlapping signal at 68–78 ppm was associated with C2, C3 and C5.

In the NMR spectra of the raw starch, distinct triplet peaks were observed in the C1 signal region. The crystalline content indicated that the starch used in this study was an A-type starch. The two broad peak shoulders near 103 ppm in the C1 and 82 ppm in the C4 regions provided information on the amorphous components in the starch (Liu et al., 2008; Paris, Bizot, Emery, Buzaré, & Buléon, 1999). As shown in Fig. 2, as the duration of heating increased, the signal representing the amorphous state gradually intensified in the C1 and C4 regions, whereas the intensity of the triplet peaks in the crystalline state gradually decreased. When the temperature was higher than 65 °C, the signal from the triplet peaks became weak, and the spectra were similar to the spectra of fully gelatinized amorphous starch. As shown in Fig. 2, the signal from the triplet peaks dropped significantly when the temperature was above 60 °C. The rice starch treated with the three heating methods exhibited a marked elevation in amorphous content between 60 °C and 80 °C. This finding indicates that the gelatinization temperature range was consistent for the rice starch subjected to the three heating methods.

The C1 (99–102 ppm) signals in the NMR spectra contained information related to the crystalline and amorphous structures in the starch (Delval et al., 2004; Gidley & Bociek, 1985). In an A-type starch, maltotriose is the smallest repeating unit, and the double helical structures are formed from two-fold axisymmetric helical

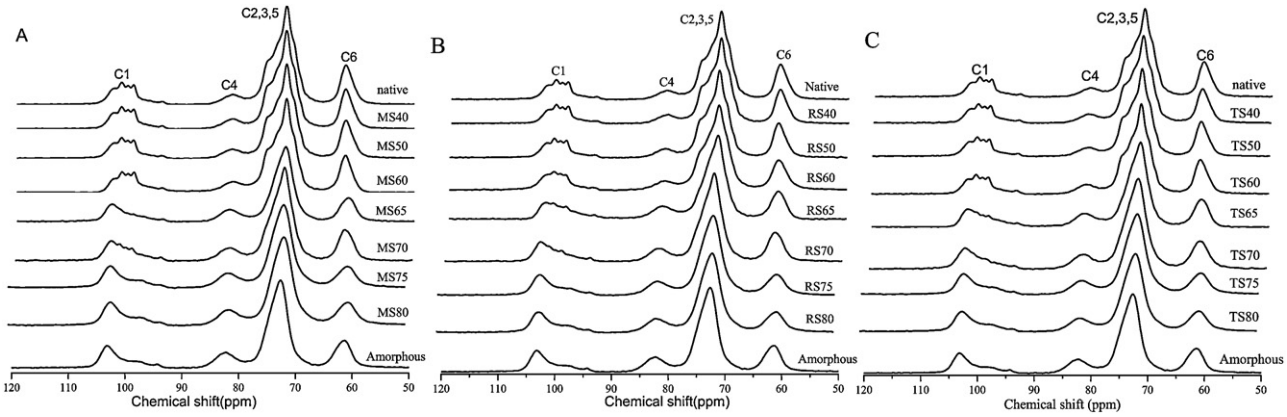

Fig. 2. NMR spectra of MS, RS and TS (A – MS; B – RS; C – TS).

Table 1
Chemical shift in the NMR spectra of the samples using three heating methods.

Starch sample	Chemical shift (ppm)			
	C1	C2, C3, and C5	C4	C6
Raw starch	99.38, 100.37, 101.48, 103.02	71.2, 72.4, 73.9	82.0	61.9
Amorphous	103.13	72.4, 74.2	82.3	61.5
MS40	99.38, 100.38, 101.50, 103.03	71.2, 72.4, 73.9	82.1	61.9
MS50	99.40, 100.41, 101.48, 102.99	71.2, 72.4, 73.9	82.1	61.9
MS60	99.36, 100.41, 101.43, 103.86	71.1, 72.4, 74.0	81.9	62.0
MS65	99.36, 100.49, 101.51, 103.03	71.1, 72.4, 73.9	82.1	61.9
MS70	99.36, 100.53, 101.55, 103.18	71.1, 72.4, 74.0	82.3	61.8
MS75	99.37, 100.51, 101.52, 103.15	72.4, 74.0	82.2	61.8
MS80	99.34, 100.52, 101.55, 103.21	72.4, 74.0	82.3	61.8
RS40	99.41, 100.42, 101.46, 102.94	71.2, 72.4, 73.9	82.0	61.9
RS50	99.40, 100.46, 101.49, 102.85	71.2, 72.4, 73.8	82.0	61.9
RS60	99.30, 100.33, 101.62, 103.02	71.1, 72.4, 74.0	82.1	61.8
RS65	99.40, 100.41, 101.47, 102.96	71.1, 72.4, 74.0	82.0	61.8
RS70	99.39, 100.44, 101.46, 103.12	71.1, 72.4, 74.0	82.2	61.7
RS75	99.40, 100.42, 101.53, 102.88	72.4, 74.0	82.1	61.7
RS80	99.39, 100.37, 101.49, 103.07	72.4, 74.0	82.1	61.8
TS40	99.37, 100.40, 101.50, 103.03	71.1, 72.4, 73.9	82.1	61.9
TS50	99.38, 100.41, 101.48, 102.94	71.2, 72.4, 73.9	82.0	61.9
TS60	99.39, 100.41, 101.49, 102.99	71.1, 72.4, 73.9	82.1	61.9
TS65	99.40, 100.40, 101.49, 102.99	71.2, 72.4, 74.9	82.1	61.9
TS70	99.29, 100.69, 101.43, 103.38	72.4, 74.6	82.3	61.6
TS75	99.41, 100.55, 101.48, 103.27	72.4, 74.7	82.2	61.7
TS80	99.39, 100.67, 101.45, 102.99	72.4, 74.8	82.3	61.7

The number following each starch sample (e.g., MS40, RS40 and TS40) indicates the final temperature of the sample.

structures, which form a triplet in the C1 peak. In a B-type starch, maltose is the smallest repeating unit, and the double helical structures are formed from three-fold screw axes, which form a doublet in the C1 peak (Gidley & Bociek, 1985). As shown in Fig. 2, triplet peaks were observed in the C1 region, which indicates that the double helical structures in rice starch are A-type double helices in a two-fold axisymmetric helical structure. The ratio of the sub-peak areas of the triplet peaks was nearly 1:1:1. However, the intensity of the triplet peaks gradually decreased when the temperature increased. When the temperature reached 70 °C, the triplet peaks at 99–101 ppm nearly disappeared, indicating that the rice starch was completely gelatinized. The relative intensities of the signals in the C4 region increased with increased temperatures. This data suggest that the amorphous content in the starch granules substantially increased, which indicates a higher level of gelatinization with a rise in temperature.

3.3. Analysis of the single and double helical structures and amorphous structure in starch treated with microwave heating

Morrison, Tester, et al. (1993) classified the signals in several C regions based on the analysis of ^{13}C CP/MAS NMR for acid-hydrolyzed waxy barley starch and conventional barley starch. The signals at 99–102 ppm in the C1 region (90–110 ppm) represented information on the double helices, and the signals at 93–99 ppm represented several of the signals from the non-ordered material. The broad peak at 103 ppm contained information from the non-ordered material. The C2, C3 and C5 regions (70–79 ppm) mainly showed the B-type double helices resulting from the residues of free amylase from waxy starch, whereas the C4 region (80–84 ppm) represented information on the amorphous state. A small proportion of left-handed single-stranded V-type single helices is present in starch and primarily occurs in the transition layer between lipids and amylopectin and the amorphous and crystalline regions in starch (Morrison, Law, et al., 1993; Snape, Morrison, Maroto-Valer, Karkalas, & Pethrick, 1998). In this analysis, the NMR spectra obtained from the starch treated with the three heating methods were decomposed. Changes in the V-type single helices, double helices, amorphous structures with respect to temperature were calculated to investigate the effects of heating on these structures in rice starch. Microwave heating was compared with rapid heating in an oil bath and a conventional slow heat conduction method to further elucidate the principles of the effect of microwave heating on starch structures.

Using MS as an example, this study utilized the Solver data analysis tool to analyze the spectra of each MS sample and the spectra of the amorphous content in the samples at different temperatures. The ordered subspectrum was obtained by subtracting the subspectrum of the amorphous component from the original spectra of the sample. The three spectra of the MS samples are shown in Fig. 3. The NMR spectra of RS and TS samples were also analyzed.

Based on the decomposed NMR spectra of the samples, the intensity and area of the spectra from the amorphous structures gradually increased with a rise in temperature, while the intensity and area of the spectra from the ordered structures gradually declined. The subspectrum of the ordered structures was weak and highly unstable at temperatures higher than 65 °C.

As shown in Fig. 3, the C1 region contained signals from a V-type single helix component and a double helix component (A- or B-type polymorph), whereas the C4 region contained signals from the amorphous and V-type single helix components (80–85 ppm) while the signals for double helical were presumably hidden under the C2, C3, and C5 peak. By comparing the area of the C1 signals in the ordered subspectrum and the area of the C4 signals in the amorphous subspectrum with the area of the C1 and C4 signals at the beginning of the starch spectrum, this study calculated the proportions of amorphous, single helical, and double helical structures in the starch samples.

Sub-peak fitting was performed for the spectra of ordered and disordered structures in the samples by using PeakFit software. A combination (50/50) of Lorentzian and Gaussian profiles provided an acceptable fitting ($r^2 \geq 0.9990$). The peak fitting results of the sub-spectrum of MS are shown in Fig. 4, and the calculated proportions of amorphous, single helix and double helices structures are summarized in Table 2.

As shown in Table 2, the contents of amorphous, double helices and V-type single helix all changed with the rising temperature, especially when the temperature was near the gelatinization point.

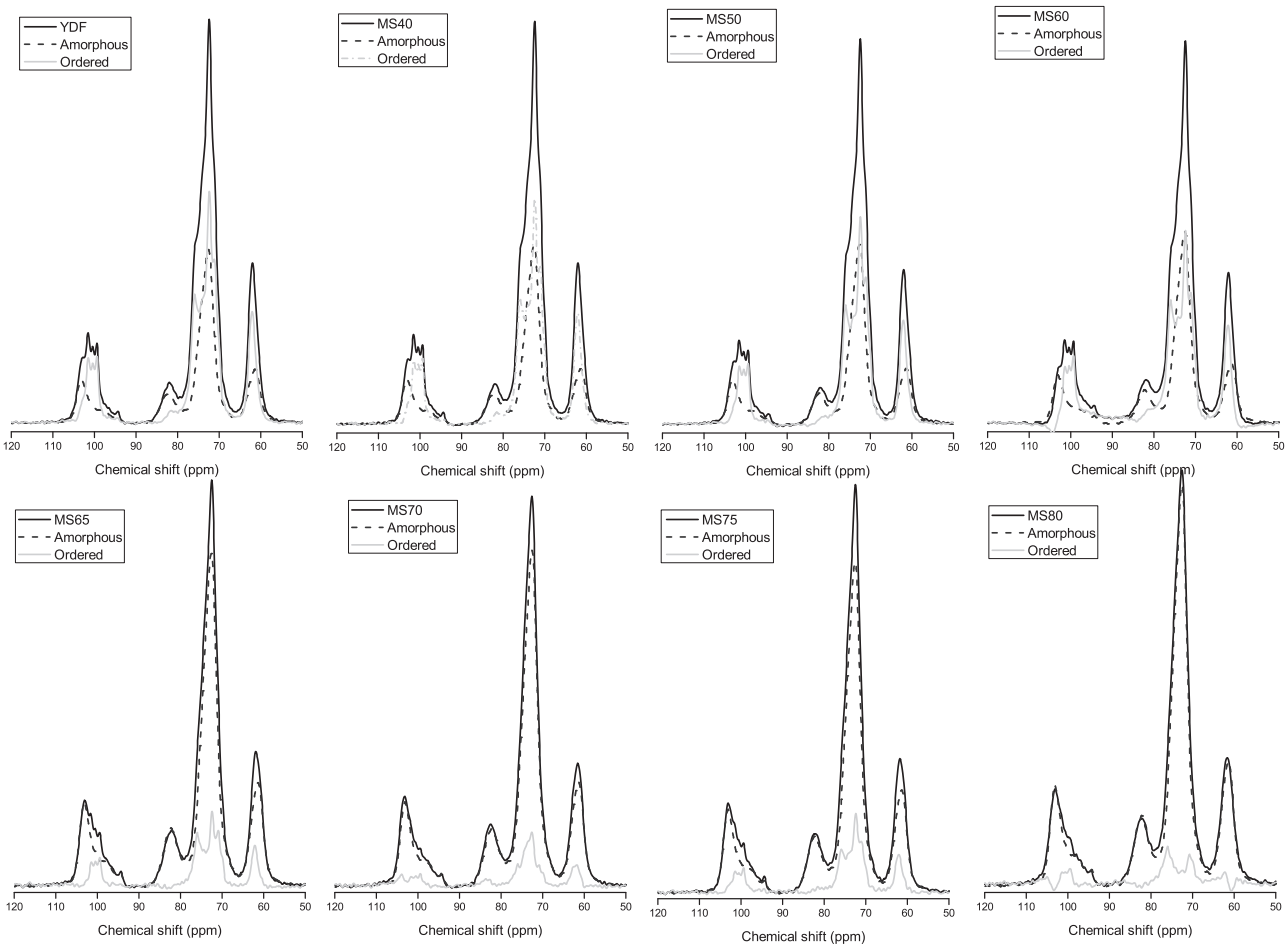

Fig. 3. Decomposition of the MS ^{13}C CP/MAS NMR spectra into the amorphous and ordered phases by subtracting the subspectrum of the amorphous phase of gelatinized rice starch. The number following MS indicates the final temperature of the sample.

Table 2
Proportions of amorphous, double helical and V-type single helical structures in starch samples treated with three different heating methods.

Sample	Amorphous content (%)	Single helix content (%)	Double helix content (%)
Raw starch	43.30	5.18	51.52
MS40	45.08	5.09	49.83
MS50	47.93	3.30	48.77
MS60	53.22	2.45	44.33
MS65	82.81	0.60	16.59
MS70	86.49	0	13.51
MS75	96.30	0	3.70
MS80	96.64	0	3.36
RS40	45.37	4.93	49.70
RS50	48.48	3.05	48.47
RS60	52.51	2.17	45.32
RS65	81.18	0.56	18.26
RS70	91.73	0	8.27
RS75	96.07	0	3.93
RS80	96.69	0	3.31
TS40	47.26	4.99	47.75
TS50	51.42	4.28	44.30
TS60	52.75	3.77	43.48
TS65	88.77	0.71	10.52
TS70	93.99	0	6.01
TS75	95.66	0	4.34
TS80	96.13	0	3.87

When the temperature was below 60 °C, the contents of the ordered and disordered structure changed very slightly. While when the temperature was between 60 °C and 80 °C, the variations of the amorphous and double helices reached 45% and 40%, respectively. Furthermore, the content of double helices was stable when the temperature was over 75 °C.

The samples treated with three different heating methods exhibited similar trends with respect to the changes in the proportions of amorphous starch and double helices. MS and RS showed gradually increase in the amorphous at the growth rate of 2%, and the double helical content of MS and RS both decreased at the rate of 1%. However, the change rate of the amorphous and the double helical contents of TS were slightly larger than MS and RS. The number of double helices quickly dropped when the temperature exceeded 60 °C. The V-type single helices decreased with a rise in temperature until they disappeared. RS and MS displayed similar trends with respect to the proportion of V-type single helices, which decreased at a higher rate than TS. The effect of microwave heating on the changes in the amorphous, double and single helical structures in starch granules is primarily related to the rapid increase in heat. The content of V-type single helices decreased more rapid than the double helices. However, it cannot be determined whether the extent of damage to the single helices was greater than the damage to the double helices during the heating and gelatinization process because of the low content of single helices in starch. The microwave electromagnetic energy absorption capacity of the

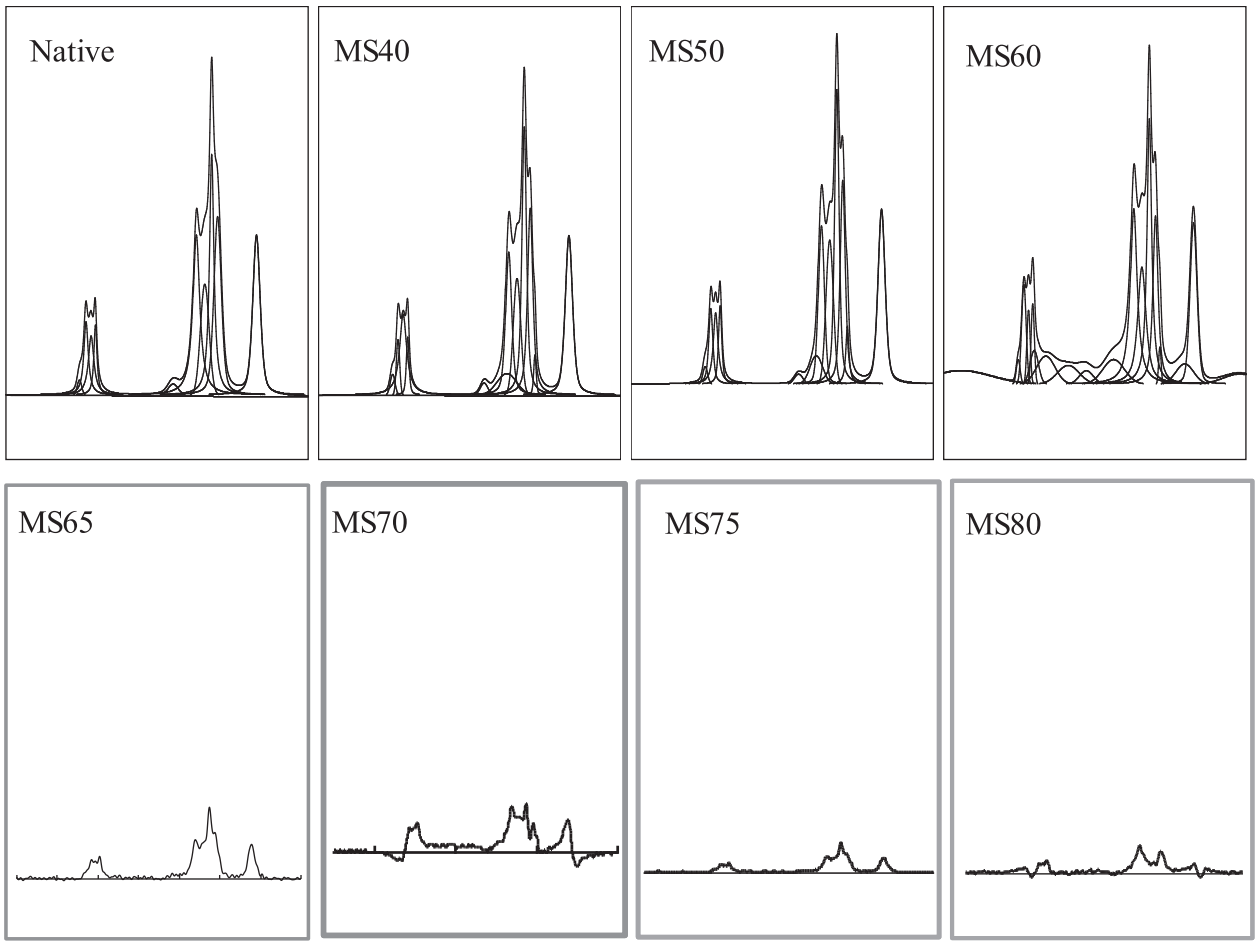

Fig. 4. Peak fitting results of the sub-spectrum of ordered structures in MS samples. The number following MS indicates the final temperature of the samples.

starch suspension increased with gelatinization. The extent of this increase in capacity was directly related to the concentration of the starch suspension and the water content of the starch samples because water has a much larger dielectric constant and a higher microwave energy absorption capacity than starch. At the beginning of the microwave treatment, the water molecules in the suspension absorbed the microwave electromagnetic energy and continuously converted the electromagnetic energy into kinetic and thermal energy. The rapid movement of the water molecules caused constant collisions between the water molecules and the starch granules, which accelerated the movement of the starch granules. The water molecules entered the starch granules to generate thermal energy, resulting in a rapid increase in the temperature of the samples. At this stage, the destruction of the internal structure of the starch had not commenced, and the contents of the examined structures were relatively stable. It was inferred that in the low temperature process, the starch particle gradually absorbed water, swelled prior to gelatinization and the temperature of samples rose quickly, which may lead to the strengthen of H-bond and the loss of ordered structure such as double helices. When temperature reached 60 °C, starch particle swelled rapidly and the hydration rate and particle swelling rate of starch rapidly increases if a large number of water molecules enter the starch granules, and the gelatinization process begins. All the above process may lead to a slow down on the heating rate above 60 °C (Fig. 1). When the temperature approached 60 °C, the water molecules in the starch granules absorb a large amount of microwave energy and create continuous movement and vibration, which leads to an increased interaction within the starch granules. The absorption capacity of the microwave electromagnetic energy in hydrated starch granules also increases, which leads to a higher kinetic energy and promotes the transformation from ordered to disordered structures. The degree of starch gelatinization increased as the temperature increased and the dielectric loss in the starch samples increased, which improved the microwave electromagnetic energy absorption capacity. The continuous movement of the starch granules following energy absorption hindered the continuous transformation of the ordered structures. Consequently, MS exhibited a lower amorphous content than TS and RS after the heating was stopped.

4. Conclusions

The effects of microwave heating on the ordered structures in starch granules were remarkably similar to the effects of rapid heating in an oil bath. The rate of heating determined the differences in the proportions of amorphous starch, double helices and V-type single helices, while the electromagnetic effects of microwave heating did not have a significant impact on the ordered structures in starch granules.

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