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Article

Multiscale Structural Disorganization of *Indica* Rice Starch under Microwave Treatment with High Water Contents

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ABSTRACT: While the cooking of rice into porridge or similar foods is widely practiced, how microwave treatment, a rapid heating technology, changes the structure of rice starch with excess water remains largely unexplored. This work describes the multiscale structural changes of *indica* rice starch (IRS) with high water contents (70, 80, and 90 wt %, wet basis) subjected to microwave treatment for 1−3 min. Microwave treatment destructed crystalline lamellae, changed the crystalline type from A to B+V, and decreased crystallinity and double-helix content. While these changes depend on both water content and treatment time, the former had a stronger effect due to combined effects of water and heat for starch gelatinization. Interestingly, a highly porous material can be obtained simply upon microwave treatment of IRS for 3 min at a water content of 90 wt %. Thus, this work presents a simple method for creating such material promising for encapsulation and delivery applications.

KEYWORDS: *indica rice starch, starch microwave treatment, water content, starch multiscale structure*

1. INTRODUCTION

Starch is one of the most important sources of carbohydrates providing energy to humans.[1] Considering that starch-based products need to be cooked for consumption, it is indispensable to understand how a heating process affects the physicochemical and functional characteristics of starch−water systems.[2] The variations in starch hierarchical structures play a crucial role in determining the changes in physicochemical and functional properties.[3,4] Therefore, it is essential to understand starch structural alterations during cooking from an application point of view.

Starch is mainly composed of two types of biomacromolecules, namely, amylopectin and amylose. Amylopectin is generally considered to be the main component in starch and responsible for its structural organization, while amylose accounts for approximately 15−35% of the starch granule.[5,6] The structure of starch is complex and considered to be organized on different length scales, comprised of the whole granule, growth rings, and semicrystalline lamellae (with a 9−10 nm repeat distance), crystalline structure (the crystalline regions within the lamellae), and double and single helices.[7−9] The multiscale structural characteristics of starch, such as the granule surface and molecular and crystalline structures, significantly affect starch physicochemical and functional properties such as pasting properties and digestibility.[3,10,11] Thus, it is highly interesting to tailor starch properties by manipulating the multiscale structures of starch.

Different methods have been used to modify starch properties, including physical cooking, chemical cross-linking, and enzymatic hydrolysis.[12] Among different methods, microwave treatment is considered to be a simple, cost-effective, physical method without the use of chemical reagents.[13] Microwave is a kind of non-ionizing radiation electromagnetic wave and highly efficient at thermal processing.[14] Therefore, microwave treatment has been widely applied in food engineering processes such as drying, heating, cooking, and sterilization.[13,15] Moreover, microwave is also an effective method for physical modification, which can change the structure and physicochemical and functional properties of starch.[16] The literature indicates that microwave treatment can disrupt the original crystalline structure and helical order of starch and induce starch chain rearrangement, changing thermal and pasting properties, viscosity, swelling power, and digestibility.[4,11,17−19] The effect of microwave on starch is determined by two main factors: microwave parameters and starch characteristics. Microwave parameters include frequency, power level, and irradiation time. Starch characteristics include the type of starch, water content, and dielectric properties.[13,20] Only polar substances (e.g., sugar, salt, and water) with suitable dielectric properties can be heated in a microwave field.[13,14] Among them, water is an important factor affecting the dielectric properties of overall starch systems, and the dielectric properties of starch−water systems determine the degree of change in the starch structure.[20]

Most research focused on the effect of microwave irradiation on starch at low moisture contents (15−45%).[18,19,21−23] For example, it was reported that microwave treatment (0.5 W/g, 60 min) led to reduced crystallinity for wheat and normal maize starches with 30% water content (wet basis), while not affecting the crystallinity of waxy maize starch with the same water content.[23] Szepes et al.[24] found that, for native potato

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starch (9.66% water content), microwave irradiation (450 W, 15 min) increased the degree of crystallinity and changed the X-ray diffractogram pattern from B type to A type whereas, under the same treatment, the crystalline fraction of native maize starch (6.84% water content) decreased drastically with its crystalline type unchanged.

There have been limited studies concerning the changes in the structure and properties of rice starch with a high water content (especially ≥90%) under microwave. Zhong et al.[16] demonstrated that microwave pretreatment (540 W, 20 min) significantly promoted the annealing of *indica* rice starch (IRS) with a 90% water content (wet basis). However, Fan et al.[25] revealed that microwave heating (800 W) did not significantly affect the *japonica* rice starch structure (94% water content, wet basis), unlike under oil-bath or hot-plate heating. In addition, Fan et al.[26] studied the change in dielectric properties of rice starch (concentration of 6%, wet basis) by comparing two different heating methods (e.g., microwave heating and hot-plate heating). Their results indicated that at temperatures below the gelatinization temperature, microwave-induced dielectric rearrangement and changes in the polarization characteristics of starch suspensions reduced the absorption properties; at temperatures above the gelatinization temperature, these characteristics became consistent with conventional heating. Despite these previous efforts, the structural changes of rice starch with a high water content (especially 70−90%) under short-time microwave treatment (within minutes) have received only limited focus. Nonetheless, the understanding of these changes has significant practical and scientific importance, as such microwave treatment conditions today represent a common situation of fast starch food cooking, especially for producing porridge or similar foods.

As one of the most widely used staples, rice is an important energy source for humans. *Indica* and *japonica* rice are two main subspecies cultivated in Asia.[27] *Indica* rice is far more widely consumed, and its starch hydrolysis is slower than that of *japonica* rice.[27,28] Thus, *indica* rice was selected as the raw material in this current study. We aim to understand the effect of microwave cooking on the multiscale structural changes of IRS for different lengths of time (1, 2, and 3 min) and with high water contents (70%, 80%, and 90%, wet basis) by specifically analyzing its granule morphology, crystalline, lamellar, and helical structures, and short-range order.

2. MATERIALS AND METHODS

2.1. Materials and Equipment. *Indica* rice grains were purchased from Xiangyang Saiya Rice Co., Ltd. (Xiangyang, China). All other reagents were of analytical grade. An MKX-J1A microwave instrument with a frequency of 2450 MHz and a maximum electric power of 1000 W was supplied by Qingdao Microwave Creative Technology Co., Ltd. (Qingdao, China).

2.2. Starch Isolation. Rice starch was isolated from *indica* rice grains by an alkali method described previously.[29] In brief, the rice grains were soaked in distilled water at room temperature for 3 h, which were then ground with a laboratory GM-WZ150 colloid mill (Shishou, China) for 3 min. The ground sample was centrifuged (SF-TDL-5A, Shanghai Feiqiaer Analytical Instrument Co., Ltd., Shanghai, China) for 15 min at 3000*g* and then dried overnight at 35 °C to afford dried crude starch. Purification was achieved by soaking and stirring the crude starch with a 0.2% (w/v) NaOH solution (pH 11.7) for 2 h and then centrifugation at 3000*g* for 5 min. The supernatant and residue above the starch layer were discarded, and this process was repeated three times. Afterward, the sediment was washed three times by being resuspended in distilled water and adjusted to pH 7.0 with 0.1 mol/L HCl. After centrifugation at 3000*g* for 10 min, purified starches were suspended in 95% ethanol and then transferred to an open container after centrifugation (10 min at 3000*g*). The starch obtained was dried at 35 °C for 48 h. The amylose content of *indica* rice starch was 14.56 ± 0.39%, which was determined by the iodine colorimetric method.[30]

2.3. Microwave Treatment. The powder starch (moisture content of 7 wt %) was adjusted to different water levels (70, 80, and 90 wt %, wet basis, the original moisture content considered) by the addition of distilled water. The mixtures were stirred well in conical flasks and kept at room temperature for 10 min to allow the starch to absorb water sufficiently. Before microwave treatment, the starch slurry was stirred again until there was no sediment at the bottom and then placed into a triangle bottle. The mouth of the bottle was covered with kitchen cling film, which was pierced to create holes. Microwave cooking was carried out for 1, 2, or 3 min, and the microwave power was fixed at 8 W/g. The obtained samples were denoted as MC-70%-1 min, where "MC" is the abbreviation for microwave cooking, 70% is the water content, and 1 min indicates the heating time. Microwave cooking was carried out for 1, 2, or 3 min, and the end temperatures of the samples were approximately 30−40, 60−70, and 95−100 °C, respectively.

After microwave treatment, the samples were immediately transferred to plastic dishes, frozen by liquid nitrogen, and vacuum freeze-dried. The lyophilized sample was crushed and sieved through an 80-mesh screen.

2.4. Scanning Electron Microscopy (SEM). Micrographs of native and microwaved starches were obtained with a scanning electron microscope (JSM-6390, NTC). Starch samples were scattered on double-sided carbon adhesive tape and sputter-coated with gold. An acceleration voltage of 15 kV and a magnification of 5000× were used for imaging.

2.5. X-ray Powder Diffraction (XRD). The crystalline features of native and microwaved starches were analyzed by an X-ray diffractometer (JDX-10P3A, JEOL) at 40 kV and 40 mA with Cu Kα radiation (λ = 0.154 nm). Measurements were carried out from 5° to 40° 2θ values at a speed of 0.5°/s and a step size of 0.02° following our previous method.[4]

2.6. Small-Angle X-ray Scattering (SAXS). Lamellar structures of native and microwaved starches were studied using SAXS at a wavelength (λ) of 1.03 Å on the BL19U2 BioSAXS beamline at the Shanghai Synchrotron Radiation Facility (Shanghai, China). Distilled water was added to obtain a starch slurry with a water content of 80 wt% and equilibrated for 2 h at room temperature before SAXS tests. A Pilatus 1 M detector (effective area of 169 mm × 179 mm; pixels of 172 μm × 172 μm) was used to collect the two-dimensional scattering patterns of the sample, and the RAW software was used to obtain the one-dimensional small-angle scattering curve. The scattering vector q was defined as $q = 4\pi \sin\theta/\lambda$, where 2$\theta$ is the scattering angle and λ is the wavelength of the X-ray source.[29] All data were recorded in a q range of 0.09−5.5 nm^{-1}, subject to background subtraction, and normalized.

2.7. Solid-State ^{13}C Cross-Polarization Magic-Angle Spinning Nuclear Magnetic Resonance (^{13}C CP/MAS NMR) Spectroscopy. Solid-state ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) spectroscopy was conducted using an Advance AV spectrometer (Bruker) at a ^{13}C frequency of 100.613 MHz and 295.6 K. NMR spectra were obtained with a cross-polarization (CP) accessory and a 4 mm broad-band double-resonance MAS probe. Approximately 400 mg of the starch sample was placed into the sample rotor with tight push-fitting caps. At least 3000 scans were recorded for each spectrum with a recycle delay of 2 s to obtain a satisfactory signal:noise ratio.[31] The spectra of amorphous starch and the starch samples were recorded. The spectra were fitted using PeakFit version 4.12. The percentages of amorphous, single helices, and double helices in starch were calculated according to a previous method.[32]

2.8. Fourier-Transform Raman Spectroscopy (FT-Raman). Raman spectra were recorded using an iS50 FT-Raman spectrometer (Thermo Fisher Scientific) with a $\lambda_{Nd/YAG}$ = 1064 nm laser source.[33] Native and microwaved starches were placed on an aluminum holder,

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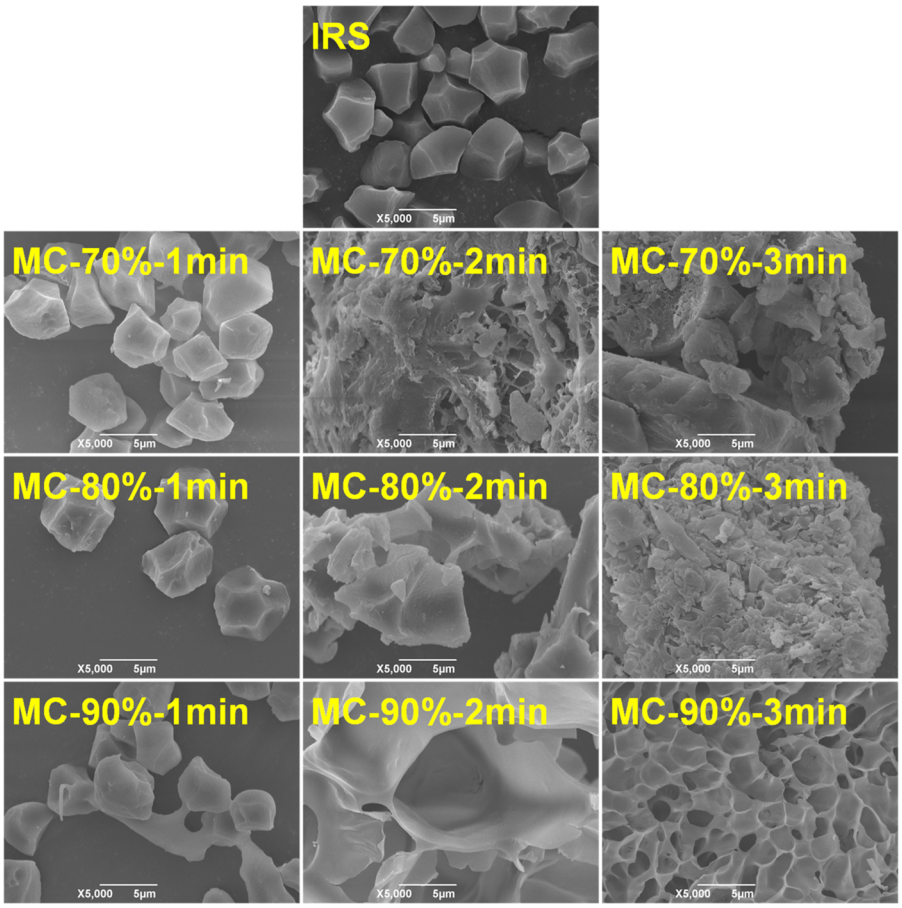

Figure 1. SEM images of native rice starch and the different microwaved rice starch samples immediately followed by liquid nitrogen freezing and vacuum freeze-drying.

and 256 scans were accumulated and co-added. The spectra were recorded over a wavenumber range of 200−1600 cm^{-1} with a 4 cm^{-1} spectral resolution. All FT-Raman measurements were analyzed using OMNIC version 8.2. Values of the full width at half-maximum (FWHM) of the 480 cm^{-1} characteristic peak were calculated using PeakFit version 4.12 to study the short-range molecular order of starch.[34]

2.9. Statistical Analysis. All data were expressed as means ± the standard deviation. The significant differences were determined using one-way analysis of variance (ANOVA) performed by Duncan's test ($p < 0.05$) with SPSS 19.0 statistical software (SPSS Inc., Chicago, IL).

3. RESULTS AND DISCUSSION

3.1. Microscopic Morphology. SEM micrographs of native and different microwaved starch samples are shown in Figure 1. Native IRS granules are polyhedral with sharp edges and smooth surfaces, consistent with previous findings.[29,35] Microwave cooking caused starch granule edges to become blunt and even disappear. After treatment for 2 min, the starch granules were destroyed and covered by a molten polymer film.[16,36] The change in granule morphology could be mainly caused by microwave-induced gelatinization.[16,26] The dielectric properties and microwave absorption capability of starch could change significantly during gelatinization due to the migration of water into starch granules.[14,26] However, Zhong et al.[16] found that the edges and angles of IRS granules without added water were also destructed to some extent with increasing microwave treatment time.

SEM images show that a higher water content significantly increased the degree of gelatinization (as reflected by granule damage). At a 90% water content, IRS starch granules were swollen significantly with the original granule morphology destroyed, leading to a highly porous material. Xie et al.[19] observed that microwave treatment caused fracturing and collapse of potato starch granules (water content of 67%, wet basis) under 700 W for 20 s, but no porous structure was formed. Here, the porous structure formation probably resulted from bubbles due to the continuous boiling of starch slurry under excessive water. In comparison, no such porous structure was found for rice starch samples with 70−90% moisture content subjected to conventional heating (boiling water bath for 30 min) still immediately followed by liquid nitrogen freezing and vacuum freeze-drying (Figure S1). Thus, we found a simple method based on microwave treatment to impart IRS with a porous network structure, while elsewhere, porous starch is usually prepared by enzyme/acid hydrolysis, freezing and thawing, cross-linking, and solvent exchange.[37] This porous IRS prepared by microwave treatment could be promising for the encapsulation and delivery of flavors, bioactives, and drugs.

3.2. Crystalline Structure. The crystalline structures of native rice starch and the different microwaved rice starch samples were studied by XRD with results shown in Figure 2. Native IRS presents the typical A-type crystalline pattern, with strong diffraction peaks at 2θ values of 15.6° and 23.5° and a doublet at 17.5° and 18.0°.[13,38] Microwaved starch samples

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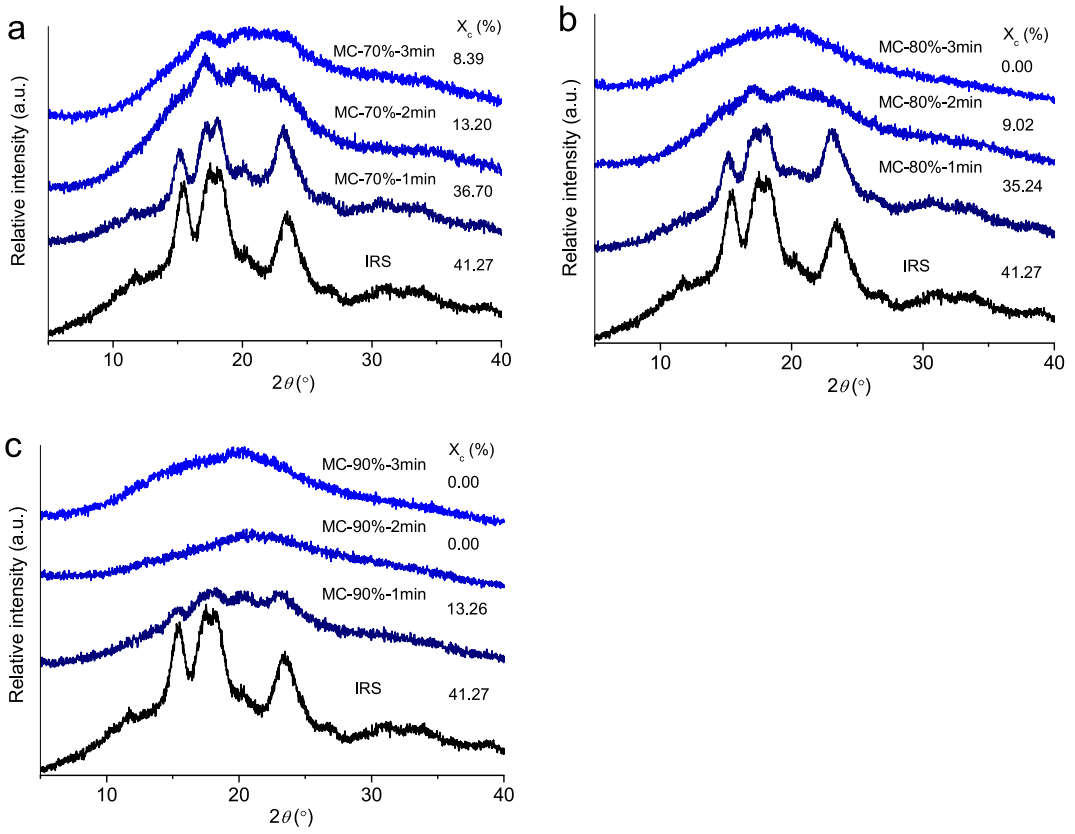

Figure 2. X-ray diffractograms for native rice starch and the different microwaved rice starch samples.

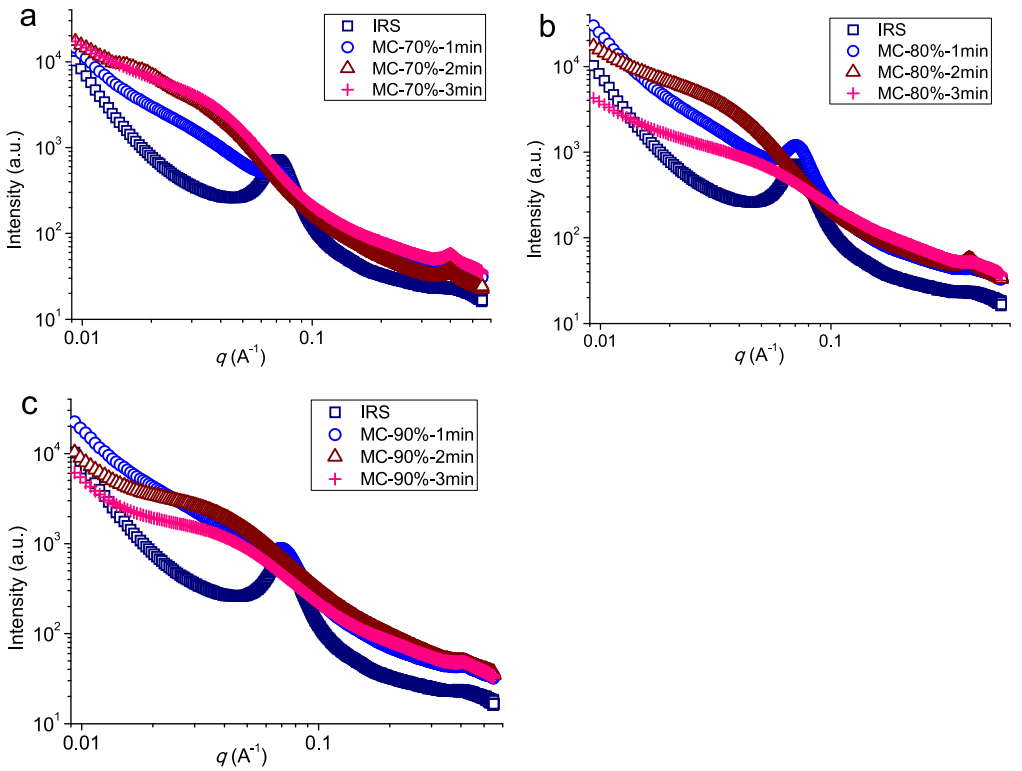

Figure 3. SAXS curves for native rice starch and the different microwaved rice starch samples.

displayed peaks at 2θ values of 17°, 20°, and 22°, indicative of a B+V-type polymorph.[4] In all cases, microwave treatment reduced the relative crystallinity of IRS. This means that under microwave irradiation, the vibrations of polar water molecules and the rapid temperature increase destroyed the original starch crystalline structure and led to chain re-arrangement and

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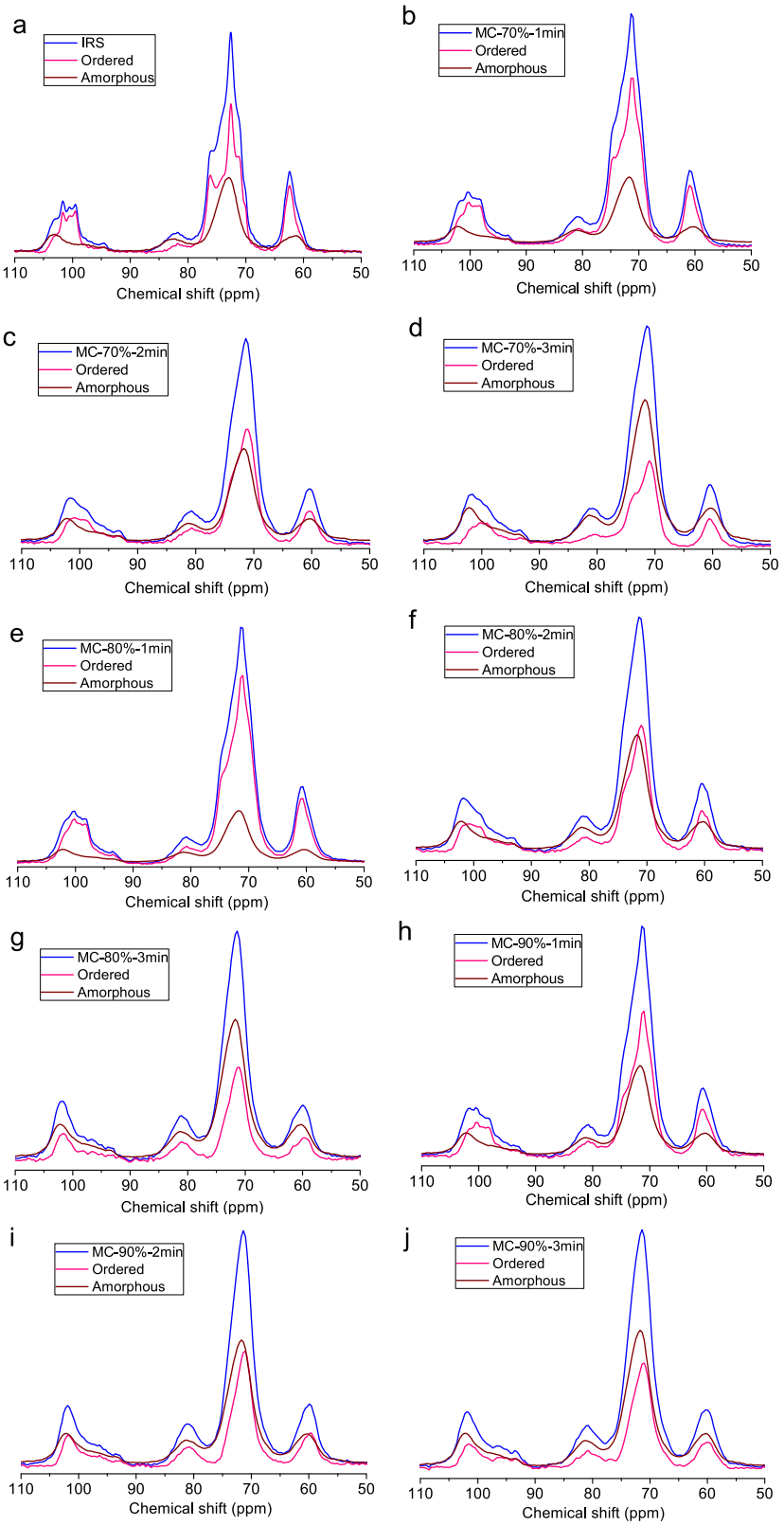

Figure 4. ^{13}C CP/MAS NMR curves for native rice starch and the different microwaved rice starch samples.

the formation of new crystallites (recrystallization).[36] The time of microwave treatment had a great impact on the major peak intensities. Specifically, with prolonged (2−3 min) microwave treatment, the peak intensities were significantly suppressed, indicating a predominantly amorphous structure. Previous studies[19,21] showed that the crystallinity of microwaved starch increased with water content (≤40%, wet basis), suggesting that starch molecular chains rearranged to form crystallites under a low water content. However, when the water content was >45% (wet basis), increasing the water content resulted in

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a progressive decrease in crystallinity for microwaved starch. With regard to this, likely, excess water could hinder recrystallization.[19,21] With regard to our results here, the higher content of water facilitates heating, enhances the effect of microwave on starch, and results in reduced crystallinity or increased amorphous content.[13]

3.3. Lamellar Structure. SAXS is an efficient method for investigating the semicrystalline lamellar structure of starch.[4,39] Figure 3 shows the double-logarithmic SAXS curves for native and different microwaved rice starch samples. Native IRS displayed a strong scattering peak around q = 0.07 Å^{-1}, corresponding to the 9 nm repeat distance of the starch semicrystalline lamellar structure, based on Bragg's law ($d = 2\pi/q$).[1,40] With a longer duration microwave treatment, this peak gradually weakened and became a shoulder peak at ∼0.03 Å^{-1}, indicating a significant disruption of the lamellar structure during starch gelatinization.

The electron density ($\Delta\rho = \rho_c - \rho_a$) represents the difference between crystalline lamellae (ρ_c) and amorphous lamellae (ρ_a). For microwaved rice starch, an increase in scattering intensity of the lamellar peak at low q was observed after heating for 1−2 min. This suggests that in the early stage of gelatinization, water molecules enter amorphous lamellae, allowing crystalline regions to evolve from a nematic phase to a smectic phase, resulting in increased electron density.[39,41,42] With a 3 min microwave treatment, combined effects of heat and water destructed crystalline lamellae, as reflected by the reduced SAXS peak intensity and thus the decreased electron density between crystalline and amorphous lamellae.

One can see in Figure 3 that for microwaved starch samples, there was a second 100 interhelix peak at ∼0.39 Å^{-1}, which represents the hexagonal units of the B-type starch crystalline structure.[29,43] With a longer treatment time and a higher water content, this lamellar peak gradually disappeared. This result is consistent with the XRD data (see Figure 2).

3.4. Helical Structure. NMR is a useful tool for studying the short-range ordered structures of starch (i.e., single and double helices).[32] Figure 4 shows the ^{13}C NMR spectra for native and different microwaved rice starch samples. All samples showed C1−C6 resonance signals. The C1 signals in the NMR spectra reflected the crystalline and amorphous structures in starch.[44] For native IRS, there was an unresolved triplet peak at approximately 100, 101, and 102 ppm in the C1 signal region for the double helix, characteristic of A-type crystallites,[8,33,44] which is consistent with the XRD results. After microwave treatment, the shapes of the peaks representing C1−C3 and C5 were altered largely, while the shapes of the peaks associated with C4 and C6 remained unchanged. With microwave heating from 1 to 3 min, the triplet peak signal gradually weakened and then disappeared, and only a single peak at 102 ppm in the C1 region was left, indicating that IRS was gradually gelatinized.[44]

The relative proportions of amorphous, single-helical, and double-helical conformations of native and microwaved starches calculated are listed in Table 1. The percentages of single helices, double helices, and amorphous content of native IRS were 2.2%, 62.3%, and 35.5%, respectively. These data, especially the high content of double helices, indicate that native IRS possesses a highly ordered molecular structure. Some researchers[45,46] used ^{13}C NMR spectra to investigate whether the changes in long-range crystalline order were consistent with that in short-range molecular order. They found that the amount of double helices was higher than the degree of crystallinity in native starches, which is in agreement with the results here. This indicates that not all double helices are involved in the crystalline structure of starch.[45,46] Irrespective of starch water content, with the microwave treatment time increasing from 1 to 3 min, the fraction of double helices decreased gradually while more amorphous content appeared, indicating that microwave hydrothermal treatment destroyed the intermolecular hydrogen bonds in starch.[4,7] Water was found to be the most important factor affecting the dielectric properties of starch.[20] With a higher water content, the double-helix fraction of microwaved starch samples was lower while the percentage of amorphous starch was higher. In this case, more water contained in starch means more microwave energy can be converted into heat through the vibrations of polar water molecules, and thus, the double-helix ordered structure can be disrupted more easily. Compared with native starch, MC-80%-1 min even showed higher proportions of double and single helices and a lower amorphous content. For this phenomenon, with microwave treatment for 1 min at an 80% water content, the starch underwent mainly annealing effects (temperature of starch slurry, <40 °C) that facilitate the alignment of amorphous chains into double- and single-helical components. With prolonged microwave treatment, the content of single helices decreased gradually.

Table 1. ^{13}C CP/MAS NMR and FT-Raman Characteristic Parameters for Native Rice Starch and the Different Microwaved Rice Starch Samples

sample	single helices (%)	double helices (%)	amorphous content (%)	FWHM$_{\lambda_{480}}$ [a]
IRS	2.2	62.3	35.5	14.7 ± 0.1 ^{cd}
MC-70%-1 min	12.0	58.0	30.1	14.5 ± 0.0 ^{cd}
MC-70%-2 min	7.7	46.3	46.0	16.7 ± 0.6 ^{a}
MC-70%-3 min	4.8	30.7	64.6	15.6 ± 0.2 ^{acd}
MC-80%-1 min	11.5	65.0	23.45	14.2 ± 0.4 ^{d}
MC-80%-2 min	6.8	42.3	50.9	16.2 ± 0.1 ^{acd}
MC-80%-3 min	4.9	32.1	63.0	16.7 ± 0.9 ^{a}
MC-90%-1 min	9.6	49.2	41.3	16.0 ± 0.1 ^{acd}
MC-90%-2 min	5.4	37.9	56.6	16.6 ± 0.7 ^{ac}
MC-90%-3 min	4.4	3.7	58.4	17.4 ± 1.3 ^{a}

[a]Values of the mean ± standard deviation with different superscript letters are significantly different ($P < 0.05$).

3.5. Short-Range Order Structure. Raman spectroscopy is an effective method to study the vibrations of starch molecules. The full width at half-maximum (FWHM) of the Raman band at 480 cm^{-1} is sensitive to the degree of structural order in starch while being less affected by the amount of sample and other experimental variables and thus can be an ideal parameter for spectral evaluation.[33] A smaller FWHM value indicates a higher degree of short-range molecular order.[47] Figure 5 shows the Raman spectra for native and microwaved rice starches, and the values of FWHM of the Raman band at 480 cm^{-1} (FWHM$_{\lambda_{480}}$) are listed in Table 1. Native IRS showed an intense band at 480 cm^{-1}, indicating a

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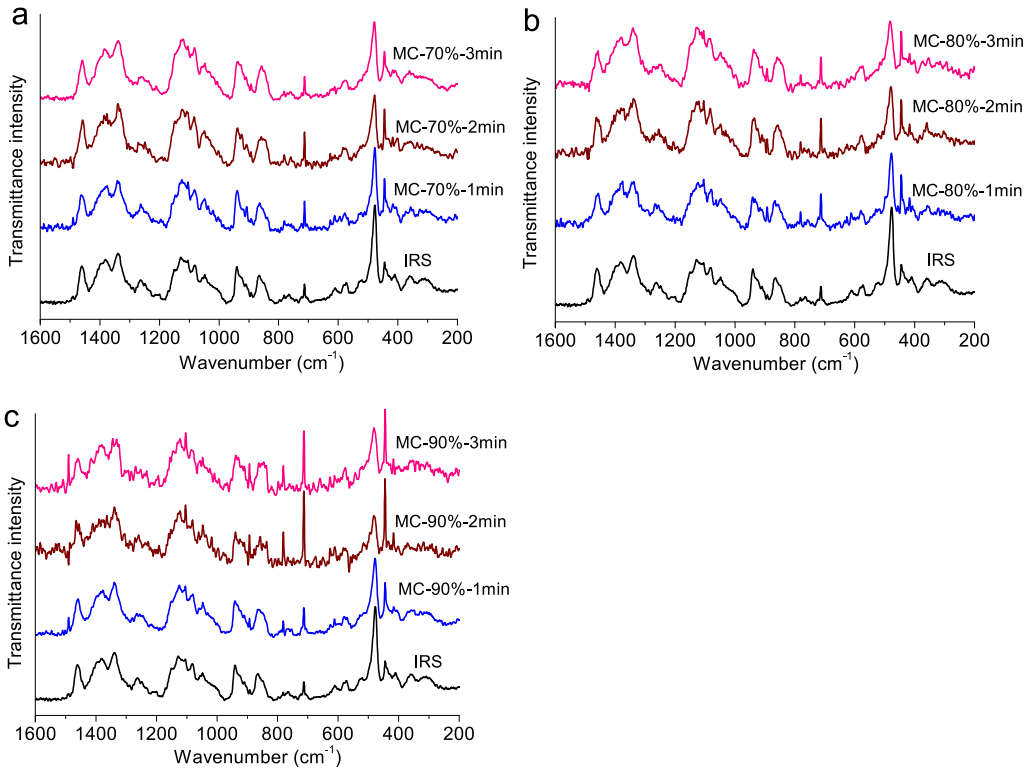

Figure 5. FT-Raman patterns for native rice starch and the different microwaved rice starch samples.

high degree of starch structural order, which is positively correlated with its crystallinity.[48] As shown in Table 1, irrespective of the starch water content, with an increasing microwave treatment time, the $FWHM_{\lambda_{480}}$ values increased, indicating the loss of molecular order during starch gelatinization. This change in $FWHM_{\lambda_{480}}$ corresponds to the reduced starch crystallinity (see Figure 2). In this regard, extending the microwave treatment time allows starch to absorb more microwave energy, which facilitates the motion between chains and promotes the destruction of molecular order.[33,49] Compared with MC-70% and MC-80% samples, MC-90% samples had a higher $FWHM_{\lambda_{480}}$ value, suggesting a lower degree of structural order at a short-range scale. This is consistent with the ^{13}C NMR spectroscopy results representing double helices. A higher water content means more intense vibration of water molecules in starch crystalline regions under microwave treatment, which causes more intense destruction to the lamellar structure and a reduced level of molecular order.[20,36] However, MC-80%-1 min had the lowest $FWHM_{\lambda_{480}}$ value, followed by MC-70%-1 min and native IRS, indicating that the former had a higher degree of structural order. This phenomenon could be attributed to the rearrangement of gelatinized starch chains during sample preparation.

3.6. Mechanism Regarding Starch Gelatinization during Microwave Treatment. According to the discussions described above, it is evident that the effect of microwave treatment strongly depends on treatment time and water content. The differences could be attributed to the dielectric properties of starch−water systems, which affect the heat generation or increase in temperature in the systems and, thus, gelatinization. Under microwave irradiation, original hydrogen bonds are broken, leading to hydration, swelling or breakage of rice starch. Regardless of the starch water content, with microwave treatment for only a short time (1 min), there may be not enough energy to swell starch granules significantly, and in this case, the morphology of starch granules is largely maintained (Figure 1). A longer time of microwave treatment leads to a greater extent of starch gelatinization, along with which the granule surface is damaged, the mobility of water molecules in crystalline and amorphous regions is increased, the content of double helices is reduced, and crystallites are destroyed.

Our results show that the damage to the starch structure under microwave was more intensive with a higher water content. It was indicated previously that the heating rate for starch suspensions under microwave treatment was positively correlated with water content.[50] Water is the main substance that transforms microwave energy into heat due to its high molecular polarity and the matching of dielectric properties to microwave frequency. Water is also indispensable for starch gelatinization under heat treatment. The highest water content (90%) resulted in the greatest extent of starch gelatinization, and in this case, the microwave-induced vibrations of the largest amount of water molecules led to the greatest extent of input of energy to the starch−water system. We can conclude that a higher water content provides dual effects of heating and hydration, benefiting starch granule swelling, the hydration of amorphous regions, the destruction of crystalline regions, and the disaggregation of double helices, all leading to a more disordered structure.

In conclusion, this work shows that the multiscale structural changes of IRS under microwave treatment depend on treatment time (1, 2, and 3 min), which can be apparently influenced by water content (70, 80, and 90 wt %). All treated starch samples displayed a reduction in crystallinity and double-helix content and a change in crystalline type from A to B+V. With a prolonged treatment time, microwave disrupted

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the hydrogen bonds between starch chains, resulting in a reduced degree of molecular order and fewer double helices. In addition, the original microscopic morphology of rice starch granules disappeared gradually and large gel blocks with a porous structure formed. The water content had a stronger effect than treatment time to disrupt the starch structure as water could enhance the effect of microwave on starch based on dual effects of heating and hydration. The knowledge from this work could guide our design of microwave processes for treating IRS especially at a high water content (≥70%).

Moreover, we present a simple and rapid process based on microwave treatment to create a highly porous starch material based on IRS, which could be used for encapsulation and delivery applications (e.g., flavors, bioactives, and drugs).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsfoodscitech.0c00080.

SEM images of *indica* rice starch samples with different water levels (70, 80, and 90 wt %, wet basis) subjected to conventional heating (boiling water bath for 30 min) immediately followed by liquid nitrogen freezing and vacuum freeze-drying (Figure S1) (PDF)

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■ REFERENCES

(1) Chen, P.; Xie, F.; Zhao, L.; Qiao, Q.; Liu, X. Effect of acid hydrolysis on the multi-scale structure change of starch with different amylose content. *Food Hydrocolloids* **2017**, *69*, 359−368.

(2) Bello Perez, L. A.; Agama-Acevedo, E. Chapter 1 - Starch. In *Starch-Based Materials in Food Packaging*; Villar, M. A., Barbosa, S. E., García, M. A., Castillo, L. A., López, O. V., Eds.; Academic Press, 2017; pp 1−18.

(3) Qiao, D.; Tu, W.; Zhang, B.; Wang, R.; Li, N.; Nishinari, K.; Riffat, S.; Jiang, F. Understanding the multi-scale structure and digestion rate of water chestnut starch. *Food Hydrocolloids* **2019**, *91*, 311−318.

(4) Li, N.; Cai, Z.; Guo, Y.; Xu, T.; Qiao, D.; Zhang, B.; Zhao, S.; Huang, Q.; Niu, M.; Jia, C.; Lin, L.; Lin, Q. Hierarchical structure and slowly digestible features of rice starch following microwave cooking with storage. *Food Chem.* **2019**, *295*, 475−483.

(5) Liu, K.; Zhang, B.; Chen, L.; Li, X.; Zheng, B. Hierarchical structure and physicochemical properties of highland barley starch following heat moisture treatment. *Food Chem.* **2019**, *271*, 102−108.

(6) Pérez, S.; Bertoft, E. The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review. *Starch - Stärke* **2010**, *62* (8), 389−420.

(7) Wang, H.; Liu, Y.; Chen, L.; Li, X.; Wang, J.; Xie, F. Insights into the multi-scale structure and digestibility of heat-moisture treated rice starch. *Food Chem.* **2018**, *242*, 323−329.

(8) Huo, Y.; Zhang, B.; Niu, M.; Jia, C.; Zhao, S.; Huang, Q.; Du, H. An insight into the multi-scale structures and pasting behaviors of starch following citric acid treatment. *Int. J. Biol. Macromol.* **2018**, *116*, 793−800.

(9) Qiao, D.; Yu, L.; Liu, H.; Zou, W.; Xie, F.; Simon, G.; Petinakis, E.; Shen, Z.; Chen, L. Insights into the hierarchical structure and digestion rate of alkali-modulated starches with different amylose contents. *Carbohydr. Polym.* **2016**, *144*, 271−81.

(10) Jeong, D.; Han, J.-A.; Liu, Q.; Chung, H.-J. Effect of processing, storage, and modification on in vitro starch digestion characteristics of food legumes: A review. *Food Hydrocolloids* **2019**, *90*, 367−376.

(11) Xu, X.; Chen, Y.; Luo, Z.; Lu, X. Different variations in structures of A- and B-type starches subjected to microwave treatment and their relationships with digestibility. *LWT* **2019**, *99*, 179−187.

(12) Han, Z.; Shi, R.; Sun, D.-W. Effects of novel physical processing techniques on the multi-structures of starch. *Trends Food Sci. Technol.* **2020**, *97*, 126−135.

(13) Li, Y.; Hu, A.; Wang, X.; Zheng, J. Physicochemical and in vitro digestion of millet starch: Effect of moisture content in microwave. *Int. J. Biol. Macromol.* **2019**, *134*, 308−315.

(14) Chandrasekaran, S.; Ramanathan, S.; Basak, T. Microwave food processing—A review. *Food Res. Int.* **2013**, *52* (1), 243−261.

(15) Guo, Q.; Sun, D. W.; Cheng, J. H.; Han, Z. Microwave processing techniques and their recent applications in the food industry. *Trends Food Sci. Technol.* **2017**, *67*, 236−247.

(16) Zhong, Y.; Xiang, X.; Zhao, J.; Wang, X.; Chen, R.; Xu, J.; Luo, S.; Wu, J.; Liu, C. Microwave pretreatment promotes the annealing modification of rice starch. *Food Chem.* **2020**, *304*, 125432.

(17) Zeng, S.; Chen, B.; Zeng, H.; Guo, Z.; Lu, X.; Zhang, Y.; Zheng, B. Effect of Microwave Irradiation on the Physicochemical and Digestive Properties of Lotus Seed Starch. *J. Agric. Food Chem.* **2016**, *64* (12), 2442−2449.

(18) Stevenson, D. G.; Biswas, A.; Inglett, G. E. Thermal and Pasting Properties of Microwaved Corn Starch. *Starch - Stärke* **2005**, *57* (8), 347−353.
(19) Xie, Y.; Yan, M.; Yuan, S.; Sun, S.; Huo, Q. Effect of microwave treatment on the physicochemical properties of potato starch granules. *Chem. Cent. J.* **2013**, *7* (1), 113.
(20) Braşoveanu, M.; Nemţanu, M. R. Behaviour of starch exposed to microwave radiation treatment. *Starch - Stärke* **2014**, *66* (1-2), 3−14.
(21) Zhang, J.; Wang, Z.-W.; Shi, X. M. Effect of microwave heat/moisture treatment on physicochemical properties of Canna edulis Ker starch. *J. Sci. Food Agric.* **2009**, *89*, 653−664.
(22) Guo, Y.; Xu, T.; Li, N.; Cheng, Q.; Qiao, D.; Zhang, B.; Zhao, S.; Huang, Q.; Lin, Q. Supramolecular structure and pasting/digestion behaviors of rice starches following concurrent microwave and heat moisture treatment. *Int. J. Biol. Macromol.* **2019**, *135*, 437−444.
(23) Lewandowicz, G.; Jankowski, T.; Fornal, J. Effect of microwave radiation on physico-chemical properties and structure of cereal starches. *Carbohydr. Polym.* **2000**, *42* (2), 193−199.
(24) Szepes, A.; Hasznos-Nezdei, M.; Kovács, J.; Funke, Z.; Ulrich, J.; Szabó-Révész, P. Microwave processing of natural biopolymers—studies on the properties of different starches. *Int. J. Pharm.* **2005**, *302* (1), 166−171.
(25) Fan, D.; Ma, W.; Wang, L.; Huang, J.; Zhang, F.; Zhao, J.; Zhang, H.; Chen, W. Determining the effects of microwave heating on the ordered structures of rice starch by NMR. *Carbohydr. Polym.* **2013**, *92* (2), 1395−1401.
(26) Fan, D.; Wang, L.; Zhang, N.; Xiong, L.; Huang, L.; Zhao, J.; Wang, M.; Zhang, H. Full-time response of starch subjected to microwave heating. *Sci. Rep.* **2017**, *7* (1), 3967.
(27) Schwanz Goebel, J. T.; Kaur, L.; Colussi, R.; Elias, M. C.; Singh, J. Microstructure of indica and japonica rice influences their starch digestibility: A study using a human digestion simulator. *Food Hydrocolloids* **2019**, *94*, 191−198.
(28) Spaeth, S. Jasmine, Basmati, Sticky, and Beyond: The Serious Eats Guide to Rice. https://www.seriouseats.com/2019/10/guide-to-rice.html.
(29) Li, N.; Wang, L.; Zhao, S.; Qiao, D.; Jia, C.; Niu, M.; Lin, Q.; Zhang, B. An insight into starch slowly digestible features enhanced by microwave treatment. *Food Hydrocolloids* **2020**, *103*, 105690.
(30) Sowbhagya, C. M.; Bhattacharya, K. R. A Simplified Colorimetric Method for Determination of Amylose Content in Rice. *Starch - Stärke* **1971**, *23* (2), 53−56.
(31) Miao, L.; Zhao, S.; Zhang, B.; Tan, M.; Niu, M.; Jia, C.; Huang, Q. Understanding the supramolecular structures and pasting features of adlay seed starches. *Food Hydrocolloids* **2018**, *83*, 411−418.
(32) Tan, I.; Flanagan, B. M.; Halley, P. J.; Whittaker, A. K.; Gidley, M. J. A Method for Estimating the Nature and Relative Proportions of amorphous, single, and double-helical components in starch granules by C-13 CPMAS NMR. *Biomacromolecules* **2007**, *8*, 885−891.
(33) Mutungi, C.; Passauer, L.; Onyango, C.; Jaros, D.; Rohm, H. Debranched cassava starch crystallinity determination by Raman spectroscopy: Correlation of features in Raman spectra with X-ray diffraction and 13C CP/MAS NMR spectroscopy. *Carbohydr. Polym.* **2012**, *87* (1), 598−606.
(34) Chao, C.; Yu, J.; Wang, S.; Copeland, L.; Wang, S. Mechanisms Underlying the Formation of Complexes between Maize Starch and Lipids. *J. Agric. Food Chem.* **2018**, *66* (1), 272−278.
(35) Guo, Y.; Xu, T.; Li, N.; Cheng, Q.; Qiao, D.; Zhang, B.; Zhao, S.; Huang, Q.; Lin, Q. Supramolecular structure and pasting/digestion behaviors of rice starches following concurrent microwave and heat moisture treatment. *Int. J. Biol. Macromol.* **2019**, *135*, 437−444.
(36) Palav, T.; Seetharaman, K. Impact of microwave heating on the physico-chemical properties of a starch-water model system. *Carbohydr. Polym.* **2007**, *67* (4), 596−604.
(37) Liu, L.; Shen, W.; Zhang, W.; Li, F.; Zhu, Z. Porous Starch and Its Applications. In *Functional Starch and Applications in Food*; Jin, Z., Ed.; Springer Singapore: Singapore, 2018; pp 91−117.
(38) Sun, Q.; Han, Z.; Wang, L.; Xiong, L. Physicochemical differences between sorghum starch and sorghum flour modified by heat-moisture treatment. *Food Chem.* **2014**, *145*, 756−764.
(39) Blazek, J.; Gilbert, E. P. Application of small-angle X-ray and neutron scattering techniques to the characterisation of starch structure: A review. *Carbohydr. Polym.* **2011**, *85* (2), 281−293.
(40) Chen, L.; Ma, R.; McClements, D. J.; Zhang, Z.; Jin, Z.; Tian, Y. Impact of granule size on microstructural changes and oil absorption of potato starch during frying. *Food Hydrocolloids* **2019**, *94*, 428−438.
(41) Gebhardt, R.; Hanfland, M.; Mezouar, M.; Riekel, C. High-Pressure Potato Starch Granule Gelatinization: Synchrotron Radiation Micro-SAXS/WAXS Using a Diamond Anvil Cell. *Biomacromolecules* **2007**, *8* (7), 2092−2097.
(42) Vermeylen, R.; Derycke, V.; Delcour, J. A.; Goderis, B.; Reynaers, H.; Koch, M. H. J. Structural Transformations during Gelatinization of Starches in Limited Water: Combined Wide- and Small-Angle X-ray Scattering Study. *Biomacromolecules* **2006**, *7* (4), 1231−1238.
(43) Cameron, R. E.; Donald, A. M. A small-angle x-ray scattering study of starch gelatinization in excess and limiting water. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31* (9), 1197−1203.
(44) Shen, H.; Fan, D.; Huang, L.; Gao, Y.; Lian, H.; Zhao, J.; Zhang, H. Effects of microwaves on molecular arrangements in potato starch. *RSC Adv.* **2017**, *7* (24), 14348−14353.
(45) Zhang, B.; Wang, K.; Hasjim, J.; Li, E.; Flanagan, B. M.; Gidley, M. J.; Dhital, S. Freeze-drying changes the structure and digestibility of B-polymorphic starches. *J. Agric. Food Chem.* **2014**, *62* (7), 1482−91.
(46) Cooke, D.; Gidley, M. J. Loss of crystalline and molecular order during starch gelatinisation: origin of the enthalpic transition. *Carbohydr. Res.* **1992**, *227*, 103−112.
(47) Wang, S.; Zheng, M.; Yu, J.; Wang, S.; Copeland, L. Insights into the Formation and Structures of Starch-Protein−Lipid Complexes. *J. Agric. Food Chem.* **2017**, *65* (9), 1960−1966.
(48) Wang, S.; Zhang, X.; Wang, S.; Copeland, L. Changes of multi-scale structure during mimicked DSC heating reveal the nature of starch gelatinization. *Sci. Rep.* **2016**, *6* (1), 28271.
(49) Fan, D.; Ma, W.; Wang, L.; Huang, J.; Zhao, J.; Zhang, H.; Chen, W. Determination of structural changes in microwaved rice starch using Fourier transform infrared and Raman spectroscopy. *Starch - Stärke* **2012**, *64* (8), 598−606.
(50) Ndife, M.; Şumnu, G.; Bayındırlı, L. Differential Scanning Calorimetry Determination of Gelatinization Rates in Different Starches due to Microwave Heating. *LWT - Food Science and Technology* **1998**, *31* (5), 484−488.

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