



## Effect of annealing and pressure on microstructure of cornstarches with different amylose/amylopectin ratios

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### ABSTRACT

This work focuses on the effect of annealing and pressure on microstructures of starch, in particular the crystal structure and crystallinity to further explore the mechanisms of annealing and pressure treatment. Cornstarches with different amylose/amylopectin ratios were used as model materials. Since the samples covered both A-type (high amylopectin starch: waxy and maize) and B-type (high amylose starch: G50 and G80) crystals, the results can be used to clarify some previous confusion. The effect of annealing and pressure on the crystallinity and double helices were investigated by X-ray diffraction (XRD) and <sup>13</sup>C CP/MAS NMR spectroscopy. The crystal form of various starches remained unchanged after annealing and pressure treatment. XRD detection showed that the relative crystallinity (RC) of high amylopectin starches was increased slightly after annealing, while the RC of high amylose-rich starches remained unchanged. NMR measurement supported the XRD results. The increase can be explained by the chain relaxation. XRD results also indicated that some of the fixed region in crystallinity was susceptible to outside forces. The effect of annealing and pressure on starch gelatinization temperature and enthalpy are used to explore the mechanisms.

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### 1. Introduction

Starch gelatinization is critically important for cooking of cereal foods and processing of starch-based polymeric materials. Various chemical and physical modifications have been developed to improve gelatinization behaviors. Annealing and pressure treatment are two important techniques to modify the microstructure and physicochemical properties of starch.<sup>1–5</sup> Previous studies have shown that the gelatinization behaviors of starches were significantly affected by these two kinds of treatments. Pressure treatment generally facilitates gelatinization processing.<sup>6–9</sup> Furthermore, when gelatinized at a certain temperature, some of the starch samples treated with high pressure did not show any extensive swelling and retained their granular character, which resulted in a weaker gel.<sup>8,10,11</sup> On the other hand, starch annealing is defined as a physical reorganization of starch granules in excess and intermediate water at a temperature above glass transition but below gelatinization temperature.<sup>12–14</sup> Previous studies have shown that annealing could increase the initial temperature of gelatinization and narrow the gelatinization temperature range for all starches regardless of their molecular structure and the ratio of amylose and amylopectin.<sup>15–20</sup>

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Mechanisms of the effect of annealing and pressure treatments on starch gelatinization have also been discussed. Effect of annealing has been studied by DSC, microscopy observation, swelling factor (SF), viscometry, and <sup>13</sup>C CP/MAS NMR.<sup>16,20–26</sup> These results showed that annealing treatment modified starch structure and increased granular stability, which resulted in properties changes, such as elevation of gelatinization temperature and narrowing gelatinization range, a decrease in SF and amylose leaching, and an increase in hot and cold paste viscosities. Moreover, in post-annealing treatment, the amount of double helices increased for high amylose starches, whereas the amount remained constant, but registration was optimized for high amylopectin starches. XRD is another powerful tool to detect the changes of pattern and crystallinity for annealed starches. A polymorphic structure change from 'A+B' type to 'A' type during annealing has been found in sweet potato and barley starch.<sup>2,27</sup> Waduge et al.<sup>2</sup> observed an increase in relative crystallinity (RC) of waxy and normal starches but an unchanged RC for the high amylose starches, using a barley family of varying amylose content (up to ~50%). On the other hand, pressured gelatinization is significantly different from the traditional gelatinization,<sup>1,28</sup> as the pressure treatment could cause an irreversible distortion of the crystalline region in starch granules prior to a reversible hydration of the amorphous phase, which in turn leads to the destruction of the granule structure. Previous studies using XRD have shown that high-pressure treatment

converts starches that display the A-type pattern into B-type like starches, whereas B-type starches remain in their original B-type pattern.<sup>10,29</sup> A DSC thermogram of A-type starch exhibited a new retrograded peak right after high hydrostatic pressure treatment ( $\sim 700$  MPa), indicating that the rearrangements occurred for the crystalline transformation.<sup>30</sup> Furthermore, in the case of the NMR spectrum of pressurized waxy cornstarch, an increase in the signal intensity of C4 ( $\sim 83$  ppm) resonances, which revealed the presence of amorphous material, was observed.<sup>31</sup>

This work focuses on the effect of annealing and pressure treatment on the microstructure of starches, in particular the crystal structure and crystallinity to further explore the mechanisms of annealing and pressure treatment. Cornstarches with different amylose/amylopectin ratios were used as model materials. Since the samples covered both A-type (high amylopectin starch: waxy and maize) and B-type (high amylose starch: G50 and G80) crystals, the results will be used to check some previous assumptions and clarify some previous confusions. The effect of annealing and pressure treatment on the crystallinity and double helices were investigated by X-ray diffraction (XRD) and NMR spectroscopy. The effect of annealing and pressure on starch gelatinization temperature and enthalpy are used to explore the mechanisms.

## 2. Experimental

### 2.1. Materials

Cornstarches with different amylose/amylopectin contents (waxy 0/100, corn 23/77, Gelose 50 50/50, Gelose 80 80/20) were used in the experimental work as model materials. All the starches were commercially available and kindly supplied by Penford (Australia). An infrared heating balance (Model DHS-20, Shanghai Company) was used to measure moisture content through heating samples to  $110^\circ\text{C}$  for 20 min.

### 2.2. Annealing treatment and normal DSC measurement

Starch suspensions (1:10 w/w) were heated in a sealed container in a water bath kept at a constant temperature of  $50^\circ\text{C}$ . After an incubation period of 72 h, the suspensions were centrifuged, and the precipitates were dried over phosphorus pentoxide. Annealed starches were stored for 10 days in a desiccator containing satd magnesium nitrate, as described by Kohyama and Sasaki.<sup>32</sup>

The annealed samples were mixed with desired water for DSC measurement. Sample preparation for DSC can be found in a detailed description.<sup>33</sup> After a 24-h equilibration, the mixed material was scanned by DSC. The total moisture content of the mixture was taken as the original moisture content of the starch together with added water. DSC measurements were performed in triplicate, and the results are presented as the mean.

### 2.3. Pressure treatment and high-pressure DSC

A Mettler Toledo high-pressure DSC 827e with a pressure chamber was used for pressure treatment and thermal characterization. The pressure cell allows measurement up to a maximum working pressure of 10 MPa from room temperature up to  $700^\circ\text{C}$ . The defined pressure was created by introducing compressed air or carbon dioxide into the measuring chamber by controlling the pressure gauge. On reaching the desired pressure conditions, the DSC heating program was immediately started at a heating rate  $15^\circ\text{C}/\text{min}$  from 25 to  $110^\circ\text{C}$ . The enthalpy of gelatinization was calculated on the dry mass of the starch. DSC measurements were performed in triplicate, and the results are presented as the mean.

Starch–water suspension was prepared in a 40- $\mu\text{L}$  aluminum DSC pan. Starch (about 5 mg) was weighed in the pan, and then distilled water was injected by a microsyringe. The ratio of starch/water is approximately 1:3 and 1:1 (w/w), respectively. Effects of the annealing process on starch suspensions were also detected online by the HP-DSC. The samples were initially heated to  $60^\circ\text{C}$  for various times, and then rescanned from 25 to  $110^\circ\text{C}$ .

The samples for XRD and NMR were also treated by the HP-DSC. A starch–water suspension was treated in the pressure chamber under 5.0 MPa for 5 h at room temperature (about  $23^\circ\text{C}$ ). Then samples were air dried and kept in desiccators for XRD and NMR measurements.

Food grade compressed air (99.9%) and carbon dioxide (99.9%) were used as pressure sources.

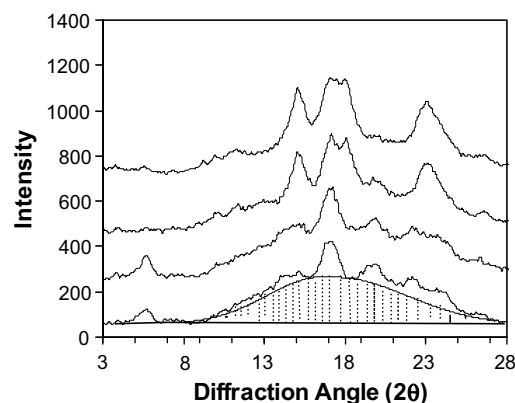
### 2.4. X-ray diffraction (XRD) studies

XRDs of the native and treated starch granules were detected using a Bruker D8 Diffractometer operating at 40 kV, and 40 mA, with Cu K $\alpha$  radiation monochromatized with a graphite sample monochromator. To ensure that starch samples had almost identical moisture content in order to minimize the influence of different water contents on crystallinity, uniform experimental conditions were adopted. The moisture content of all samples was adjusted to  $\sim 16\%$  by being kept in a desiccator over satd  $\text{BaCl}_2$  solution ( $25^\circ\text{C}$ ,  $a_r = 0.9$ ) for 3 weeks.<sup>2,34</sup> No increase in moisture content was found after further exposure time.

Relative crystallinity (RC) of the samples was quantitatively estimated by calculating the relative peak intensity. A smooth curve connected with the peak baseline was computer-plotted on the diffraction. It is noted that some of the points were not joined to the smooth curve. The area above the smooth curve was regarded as the crystalline portion, while the lower area between the smooth curve and a linear baseline that connected the two points of intensity at  $2\theta$  of  $4\text{--}28^\circ$  in amylopectin-rich cornstarches, as well as three points of  $4^\circ$ ,  $6^\circ$ , and  $28^\circ$  in amylase-rich starches, was taken as the amorphous section (Fig. 1). The upper diffraction peak area and the total diffraction area were integrated by conventional mathematics software, ORIGIN 7.5. The ratio of upper area to total diffraction area was taken as the relative crystallinity (RC).

### 2.5. Solid-state NMR studies

High-resolution solid-state NMR experiments were conducted using a Varian Unity plus spectrometer at resonance frequencies of 75 MHz for  $^{13}\text{C}$ . Experiments were carried out under CP/MAS/



**Figure 1.** X-ray diffraction patterns of cornstarches with different amylose contents (from top to bottom: waxy, normal corn, G50, and G80). The portion of the dashed line indicates the amorphous area.

DD (cross-polarization, magic angle sample spinning, and high power decoupling) conditions or using a single 90° pulse excitation (SPE) method with high-power decoupling. The 90° pulse was 4.5  $\mu$ s for  $^{13}\text{C}$ , whereas the spinning rate of MAS was set at a value in the range of 6–7 kHz. A contact time of 1.2  $\mu$ s was used for measuring the CP/MAS spectra, and the relaxation delay time was 2 s. The chemical shifts in the  $^{13}\text{C}$  CP/MAS spectra were determined by taking the carbonyl carbon of solid glycine (176.03 ppm) as an external reference standard. High-resolution solid-state  $^1\text{H}$  NMR spectra were obtained under MAS conditions with a spinning rate at a value of 6–7 kHz using TMS as an external reference. All of the NMR experiments were conducted at room temperature.

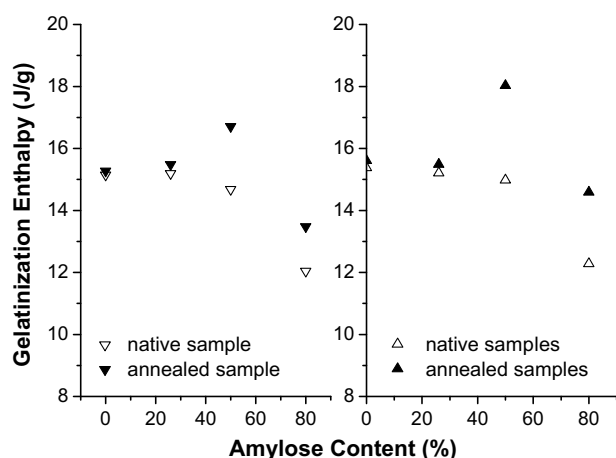
### 3. Results and discussion

Figure 2 shows the effect of annealing on the gelatinization enthalpy of cornstarch with different amylose/amylopectin ratios under intermediate (50%) and excess (75%) water conditions. It can be seen that annealing significantly increased the gelatinization enthalpy of high amylose cornstarch regardless of the environmental water conditions, but only a small increase was observed for high amylopectin starches. In addition, there was a higher increase rate for Gelose 50 (G50) than that for Gelose 80 (G80) recorded in the present work. Previous studies have found that the strongest interactions during annealing treatment occurred when the amylose and amylopectin concentrations are approximately equal,<sup>16</sup> which can be used to explain this phenomenon. Table 1 displays the effect of pressure treatment on the gelatinization of waxy cornstarch under various annealing times. It is seen that the gelatinization enthalpy was not influenced (examined by *t*-test;  $P > 0.05$ ) by the annealing process no matter what the pressure applied. The gelatinization temperatures (both onset  $T_o$  and peak  $T_p$ ) were increased

after pressure treatment. Thevelein et al.<sup>35</sup> also reported an upward shift of gelatinization temperature within applied pressure range 0–150 MPa, and no further influence was observed thereafter. A subsequent fall in gelatinization temperature at higher pressure (>200 MPa) was also reported.<sup>9,36</sup> As a higher pressure system is built-up, it even evokes starch gelatinization at room temperature, zero, or even subzero temperatures.<sup>5,7</sup>

The X-ray diffraction spectra of a native cornstarch family with different amylose contents are shown in Figure 1. It is seen that high amylopectin (waxy and normal corn) starches exhibited typical A-type pattern, while high amylose (G50 and G80) show the strong B-type pattern signal. As the amylose content increases, the scanning intensity becomes progressively weaker except for the peaks around  $2\theta$  values of 5° and 20°, which is characteristic for B-type and V-type starches, respectively. These results are in accord with previous reports.<sup>37,38</sup> The increase in amylose content lowered the relative crystallinity (RC) of starch. The RC dropped significantly from 42.3% to 28.3% (see Table 2). A similar trend has been reported by Cheetham and Tao.<sup>38</sup>

The effect of annealing on the X-ray diffractograms of cornstarches with varying amylose content is presented in Figure 3. It is seen that the scanning intensity slightly increased post-annealing process for high amylopectin starches. The effect of annealing depended on the ratio of amylose and amylopectin. For example, the RC was increased from about 42.3% to 45.9% for waxy starch (Table 2) (examined by *t*-test;  $P < 0.001$ ). The influence became weaker with increasing amylose content. There was no discernable variation in RC for annealed amylopectin starches (G50 and G80). Similar results have been reported for barley starches.<sup>37</sup> However, Waduge et al. observed an increase in intensity at 20°  $2\theta$  for all annealed barley starches, which indicated the enhanced order of amylose–lipid complexities within the starch granules.<sup>2</sup> The tendency of an increase in RC did not appear in our experimental work. The results in Table 2 clearly show that the influence of annealing on RC is inversely proportional to the amylose content. The higher the amylose content in starch, the weaker the increase in RC.



**Figure 2.** Effect of annealing treatment on the gelatinization enthalpy of cornstarch with different amylose contents in intermediate (left) and excess (right) water conditions.

**Table 2**  
X-ray powder diffraction characteristics of native and annealed cornstarches with different amylose contents

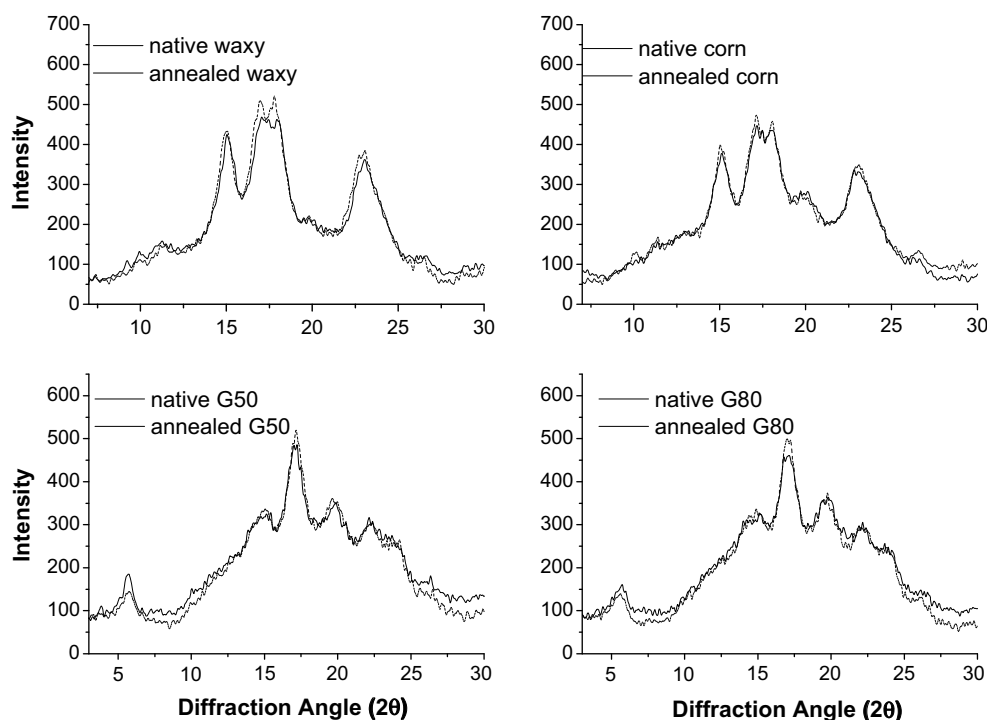
Sample <sup>a</sup>	Amylose content (%)	Crystal pattern	Relative crystallinity (100%)
Waxy	0	A	42.3 ± 0.3
Waxy (pressured)	0	A	39.4 ± 0.2
Waxy (50)	0	A	45.9 ± 0.2
Corn	23	A	38.3 ± 0.4
Corn (50)	23	A	40.1 ± 0.3
G50	50	B	31.3 ± 0.2
G50 (50)	50	B	31.6 ± 0.3
G80	80	B	28.3 ± 0.4
G80 (50)	80	B	28.5 ± 0.3

<sup>a</sup> (pressure) means pressure under 5 MPa for 5 h; (50) means annealing at 50 °C for 72 h.

**Table 1**

Effect of annealing time at 60 °C on gelatinization temperatures (on set  $T_o$  and peak  $T_p$ ) and enthalpy of waxy cornstarch under (a) 1 atm and (b) 5 MPa pressure

Annealing time (min)	Gelatinization temperature (°C)				Gelatinization enthalpy $\Delta H$ (J/g)	
	$T_o$		$T_p$			
0	67.3 ± 0.4 <sup>a</sup>	69.9 ± 0.6 <sup>b</sup>	72.2 ± 0.7 <sup>a</sup>	75.6 ± 0.5 <sup>b</sup>	15.22 ± 0.42 <sup>a</sup>	9.64 ± 0.71 <sup>b</sup>
10	69.5 ± 0.5 <sup>a</sup>	72.0 ± 0.5 <sup>b</sup>	73.9 ± 0.6 <sup>a</sup>	76.7 ± 0.7 <sup>b</sup>	15.16 ± 0.23 <sup>a</sup>	9.52 ± 0.34 <sup>b</sup>
60	71.3 ± 0.9 <sup>a</sup>	73.5 ± 0.4 <sup>b</sup>	74.9 ± 0.6 <sup>a</sup>	77.3 ± 0.8 <sup>b</sup>	15.31 ± 0.29 <sup>a</sup>	9.34 ± 0.52 <sup>b</sup>
300	73.5 ± 0.3 <sup>a</sup>	75.6 ± 0.7 <sup>b</sup>	76.6 ± 0.3 <sup>a</sup>	79.0 ± 0.5 <sup>b</sup>	15.08 ± 0.84 <sup>a</sup>	9.47 ± 0.51 <sup>b</sup>
900	75.9 ± 0.2 <sup>a</sup>	77.1 ± 0.5 <sup>b</sup>	78.1 ± 0.4 <sup>a</sup>	80.4 ± 0.5 <sup>b</sup>	15.43 ± 0.31 <sup>a</sup>	9.39 ± 0.39 <sup>b</sup>



**Figure 3.** X-ray diffraction patterns of native and annealed cornstarches with different amylose content.

Figure 4 shows the comparison of X-ray diffractograms of native and pressured waxy cornstarches. It is seen that the intensity of waxy samples post-pressure treatment was decreased. It is generally considered that A-type starch exhibits strong deflections at about 15° and 23° 2 $\theta$ , and an unresolved doublet at 17° and 18° 2 $\theta$ .<sup>38</sup> After pressure treatment, no polymorphic transformation was observed, which corresponds with previous reports.<sup>2,27</sup> However, the unresolved peaks and the peak at 23° 2 $\theta$  became weaker, whereas the peak at 15° 2 $\theta$  remained unchanged. The decreased intensity was supported by the declined RC, which dropped about 2.9% (see Table 2) (examined by *t*-test; *P* < 0.001). By comparison of the X-ray diffractograms, it is interesting to find that the unresolved doublet at 17° and 18° 2 $\theta$  and the peak at 23° 2 $\theta$  were more sensitive to the outside force such as the pressure and annealing process, while the peak at 15° 2 $\theta$  was kept stable. It has been suggested that some fixed region in crystalline zone was not stable and thus susceptible to outside forces. The inherent mechanism will be explored in future research.

The results of a solid-state <sup>13</sup>C CP/MAS NMR survey of native and annealed G80 and waxy starches are provided in Figure 5. Signals at 99–104 and 59–62 ppm are assigned to C-1 and C-6, respectively, while the partially resolved resonance at 80–83 ppm is attributed to C-4, which showed the presence of amorphous material in the spectrum.<sup>39–41</sup> The proportion of the area of this peak to the total area under the spectrum of the native and amorphous starches was usually used for calculating the ratio between the content of the amorphous and ordered parts in starches. In Figure 5, it is seen that the peak of C-4 weakened slightly after annealing treatment, indicating that the amount of amorphous material was decreased. As one of two carbon sites is involved in glycosidic bonds, it would be expected to be the most sensitive to polysaccharide conformation as it is defined by the geometry of glycosidic linkages.<sup>40</sup> The result is consistent with previous results that showed optimized registration for annealed waxy starches.<sup>21,22,42</sup> The amorphous regions hydrate and allow amylopectin exterior chains to optimize the helical associations and structure during annealing in unrestricted water.

Due to the complexity of starch and the limitation of every available technology, it is extremely vital to choose at least two methods for the studies so that the results derived from one method can be verified and compared with other methods.<sup>43</sup> Investigations on starch gelatinization as a function of annealing treatment using DSC<sup>21–23,44</sup> and hot-stage microscopy<sup>15</sup> have shown higher gelatinization temperatures with much narrower ranges. In this work, the DSC results (see Fig. 2) have shown that under either intermediate or excess water conditions, annealing only increased the gelatinization enthalpy of the high amylose starches, in which amylose molecules interact with other amylose or amylopectin molecules to form new double helices. However, through X-ray diffraction detection, the RC of annealed high amylopectin starch was shown to be intensified, which meant that either a new crystalline area was built-up or native crystalline regions became more ordered, whereas that of high amylose starch remained unchanged. Combined, the results of DSC and NMR studies, which showed an increase in both gelatinization enthalpy and double helices content for high amylose cornstarch, indicated that the new helices were formed by ‘free’ amylose that occurred in non-crystalline domains which could not be detected by XRD.

An increase in RC, together with the unchanged gelatinized enthalpy, leads to another annealing mechanism proposed for the high amylopectin starch. During the annealing process, the helices in the crystalline regions are ordered with a minor optimization of double-helical length.<sup>12,22</sup> The enhancement was elongated from incomplete pre-existing double helices. Previous researchers<sup>21,42,45</sup> have found that A-type starches contain amylopectin of shorter average chain length, and a larger proportion of short chains than B-type starches. It is noteworthy that the optimization of helical length may also occur in amylocorn, but the elongation is limited due to the smaller proportion of the short-chain fraction. This could be used as an explanation for the unchanged RC of annealed amylocorn. In addition, the relative intensity of waxy samples after post pressure is decreased, which indicates that some fixed region in crystallinity was susceptible to outside forces. The results in this work also support the comment that the gelatinization definition

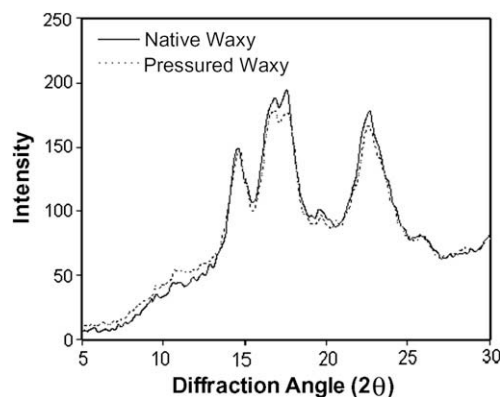


Figure 4. X-ray diffraction patterns of native and pressured waxy cornstarches.

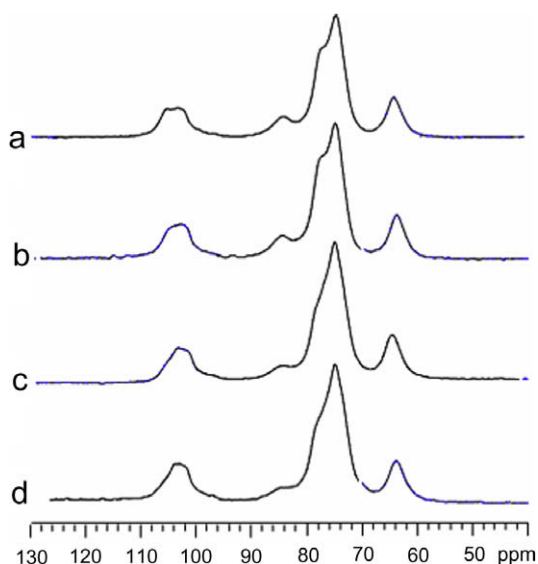


Figure 5.  $^{13}\text{C}$  CP/MAS NMR spectrum of native and annealed cornstarches (from top to bottom): (a) native G80, (b) annealed G80, (c) native waxy, (d) annealed waxy, respectively.

could be different by different measurement techniques.<sup>46–49</sup> DSC thermograms primarily reflect loss of double-helical order rather than loss of crystalline register.

#### 4. Conclusions

Cornstarches with different amylose contents were utilized to study the effect of annealing and pressure treatment on the microstructure, in particular the crystal structure and crystallinity. Annealing treatment significantly increased the gelatinization enthalpy of high amylose cornstarch regardless of the environmental water condition, but no discernable change was found for high amylopectin starches. The gelatinization enthalpy was decreased by pressure treatment. The gelatinization temperature (both onset  $T_0$  and peak  $T_p$ ) was increased slightly after pressure treatment.

There was an increase in RC for high amylopectin starches, but no discernable changes for high amylose starches after annealing as detected by XRD. Combining the results of both DSC and NMR studies, it is confirmed that there are two annealing mechanisms that exist in the A- and B-type cornstarches: for B-type starch, the annealing treatment formed some new double helices by 'free' amylose in amorphous area, whereas the elongation of amylopec-

tin double helices predominated in A-type starches. The XRD results for annealed and pressure-treated starch samples also indicated that some fixed region in the crystalline state is not stable and is easily affected by outside forces.

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