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Structural changes in corn starch granules treated at different temperatures

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ABSTRACT

The four structural levels of corn starch granules are as follows: particle structure, growth ring, crystalline region and chain structure. In this study, corn starch granules treated at different temperatures (50, 60, 70, 80, and 90 °C), then freeze-dried were evaluated. The corn starch granules remained largely intact in the control and at 50 °C and 60 °C, but with increasing temperature, the starch granules were broken. The growth ring structure and crystallization zone gradually broke up and disappeared with increasing temperature. Moreover, with increasing temperature, the degree of order (DO) and degree of the double helix (DD) of the crystalline region decreased gradually, indicating that the double helix structure of amylopectin in corn starch dissociated during heating. The molecular weight distribution index of corn starch was analyzed by gel permeation chromatography (GPC) and found that it increased with increasing temperature, indicating that the molecular chains of corn starch were broken during heating. In sum, the structural levels of corn starch granules, including the particle structure, growth ring, and crystalline region were damaged to varying degrees, whereas chain structure has been changed, after being processed at different temperatures. This study provides a model for theory of gelatinization in corn starch system.

1. Introduction

Due to environmental pollution and decline of petroleum resources, the development and application of biodegradable starch-based materials have strengthened (Ghasemlou et al., 2013). Starch is organic matter produced by green plants through photosynthesis and can be used for long-term energy storage (Jiang et al., 2020). It is a biodegradable and widely used polysaccharide molecule found in small particles in green plant stems, roots, grains, and fruits (Jiang et al., 2020). Starch consists mainly of amylose and amylopectin, in which amylose is composed of 1,4 glycoside bonds, and amylopectin consists of the glycoside chain of the ring-(1,4) glycoside bonds and the branch of the ring-(1,6) glycoside bonds. Corn starch is the most widely used starch type (Warren et al., 2016). In addition, corn starch is the world's largest source of starch, accounting for approximately 65% of the total amount worldwide (Šárka & Dvořáček, 2017).

The starch structure is much more complicated than conventional polymers. At present, few studies focus on starch microstructure (Wang et al., 2021). Starch-based polymer processing involves various chemical and physical reactions, including water diffusion, gelatinization, melting, and crystallization (Liu et al., 2009). The most significant reaction is starch gelatinization. According to previous studies, starch gelatinization can be divided into two stages. In the first stage, the starch molecule reversibly combines with water at 20–60 °C (Liu et al., 2009). At this time, the starch's molecular structure remains intact, and van der Waals forces and hydrogen bonds still exist. The polarization states of starch granules can still be observed under a polarizing microscope. In the second stage, between 60 and 90 °C, the hydrogen bond breaks, and the water molecule binds to the starch molecule hydroxyl group (Liu et al., 2009), eventually leading to crystal dissolution and the

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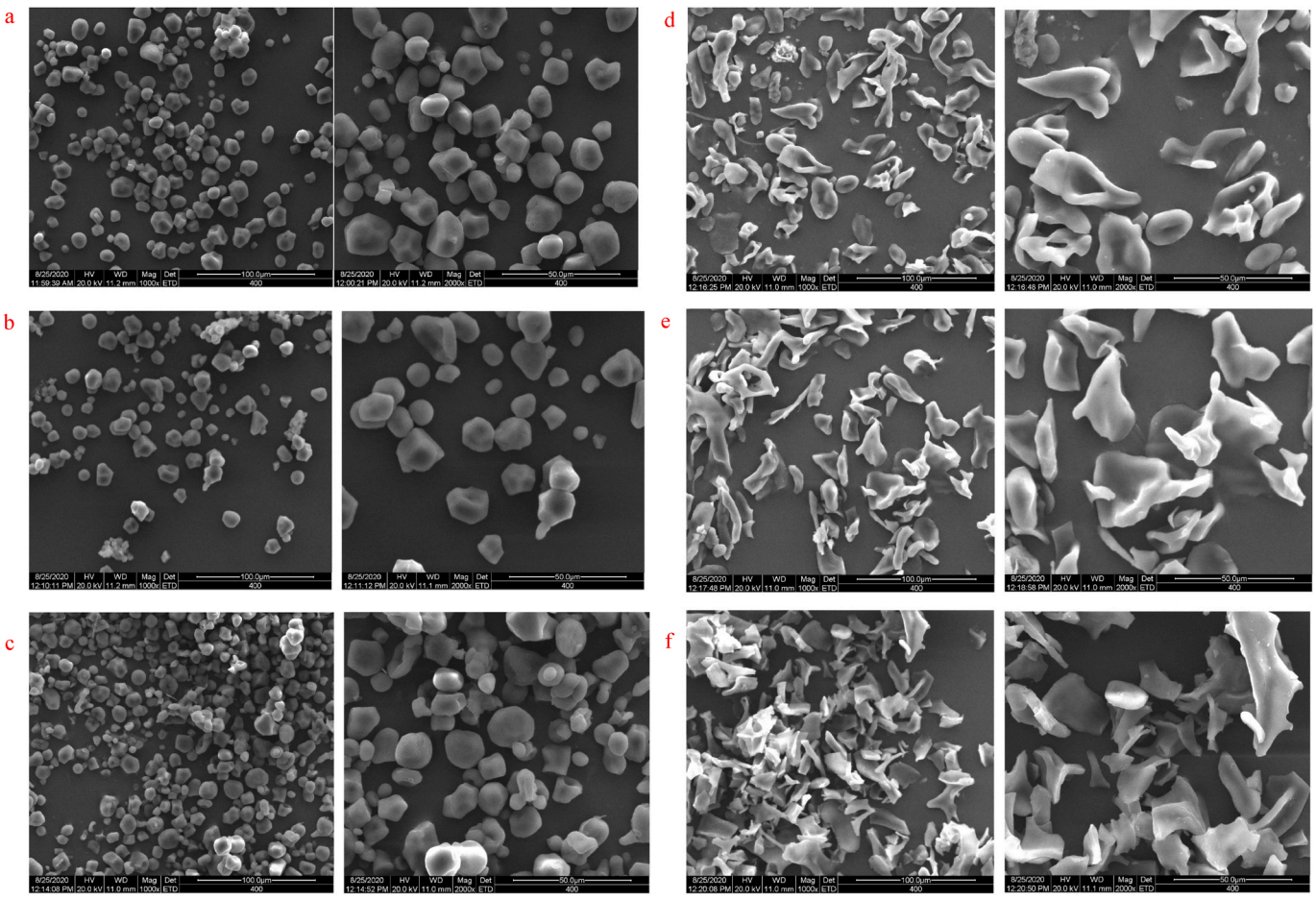

Fig. 1. Scanning electron microscopic images of corn starch: (a) control, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C, and (f) 90 °C.

destruction of starch granules (Liu et al., 2009). At this stage, the double helix structure of amylopectin is dissociated and destroyed.

Starch granules are aggregates composed of one or several starch molecules that are white and slightly shiny. Their key characteristics include morphology, size, rotation, polarized cross, and crystal structure (Zhang et al., 2019). Starch can be divided into four levels of structure: starch granules, growth rings (120–150 nm), amorphous and crystalline lamellae (9 nm), and amylopectin and amylose chains (0.1–1.0 nm) (Zhang et al., 2019). Through an experimental method of heating corn starch at different temperatures (50, 60, 70, 80, and 90), the present work tested various corn starch samples to reveal the structural changes of corn starch during gelatinization.

2. Materials

2.1. Materials

Corn starch was provided by COFCO Corporation (Beijing, China). Dimethyl sulfoxide and anhydrous ethanol were procured from Tianjin Kaitong Reagent Company (Tianjin, China). A 0.45 μm organic membrane filter and sodium cyanomethyl borate were secured from Sigma (Shanghai, China).

2.2. Preparation of starch solution

Corn starch (6 g) was weighed and dispersed in 100 mL distilled water, and six starch aqueous solutions were prepared under similar conditions. Afterward, the dispersed corn starch solution was placed into a magnetic stirrer (800 rpm) (B101S KeTai Company, Zhengzhou, China) at 50, 60, 70, 80, and 90 °C for 30 min; then the heated corn starch solution was poured into a Petri dish with a diameter of 15 cm. The Petri dishes were frozen in a refrigerator at −80 °C for 3 h and then removed and placed in a freeze-dryer for 48 h. The specimens were removed and put into a dryer for further study.

2.3. X-ray diffraction (XRD)

Before measurement, corn starch samples were balanced at 25 °C and 54% RH for 48 h (Suh et al., 2020). In this trail, an Ultima IV X-ray diffractometer (Tokyo, Japan) and CuKα (1.54 A, 45 kV and 200 mA) were used to scan corn starch treated at different temperatures. The crystallite peaks of corn starch (2θ) ranged from 4° to 40°, and the step length was 0.04982. The d spacing was estimated according to Bragg formula:

$$n\lambda = 2d \sin\theta$$

where n is an integer number, λ is the X-ray wavelength, d is the pitch between the polymer chains, and θ is the diffraction angle.

2.4. Scanning electron microscopy (SEM)

The microstructure of corn starch granules was observed by scanning electron microscopy (SEM, Hitachi SU3500, Tokyo, Japan) (Ghasemlou et al., 2013). Before observation, the corn starch was fixed on the support with double-sided adhesive tape and placed horizontally at 90°. Then, the vacuum sputtering instrument was gold-plated for 60 s at 15 mA. All corn starch granules were observed at 20 kV.

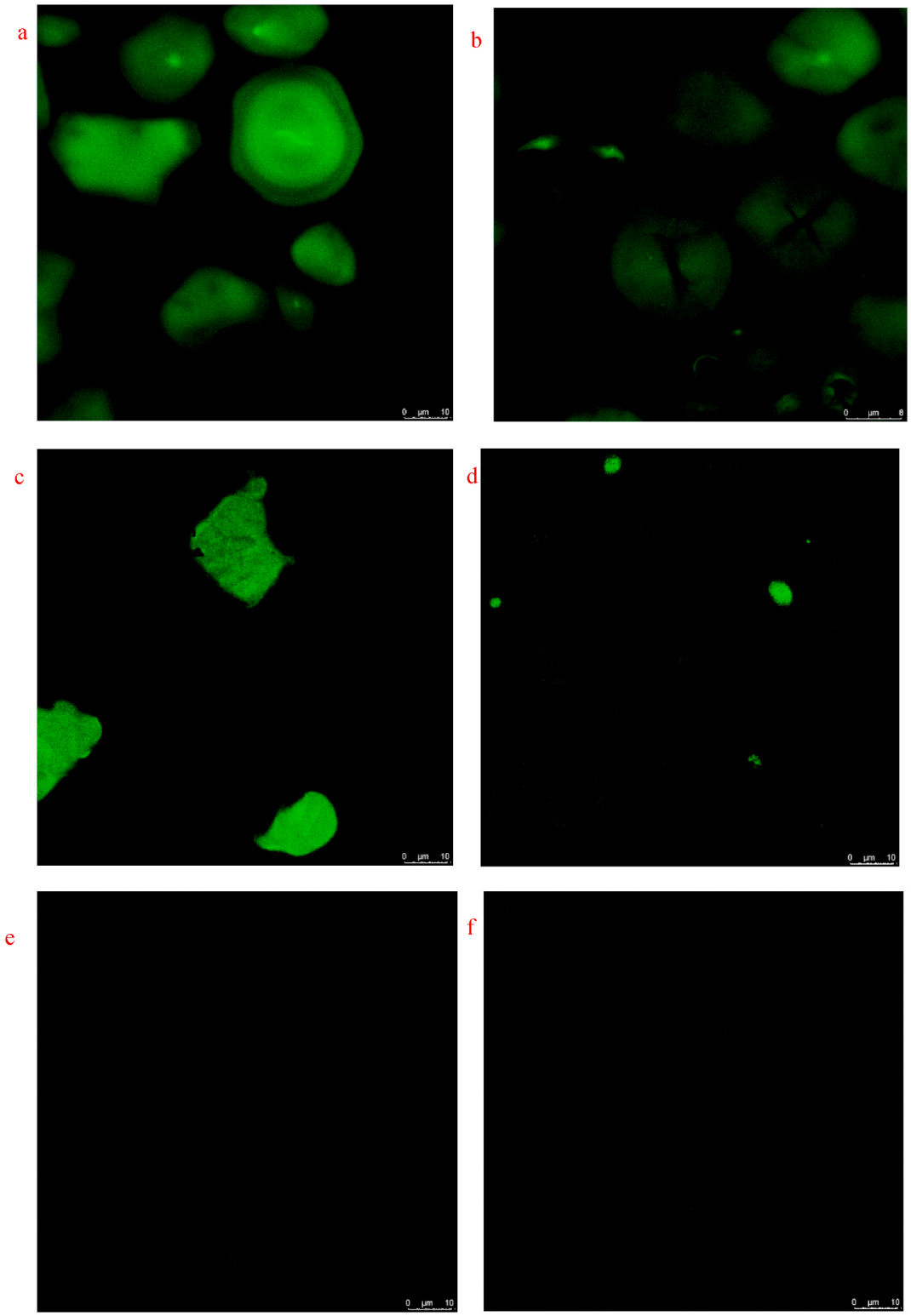

Fig. 2. CLSM optical sections of corn starch samples treated at different temperatures: (a) control, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C, and (f) 90 °C.

2.5. Hot stage polarized light microscope

Starch (0.6 g) was dispersed in 10 mL distilled water and then shaken for further use. The microscope and the hot stage were opened to add 1 mL sample, which was dropped into the slide, and then, the blank slide was repeatedly rolled on the liquid surface. Slides dripping into the sample were placed on the carrier table of the hot stage. The microscope settings were adjusted, the temperature was increased from 20 °C to 90 °C at a rate of 10 °C/min, and the material deformation process was video recorded.

2.6. Gel permeation chromatography (GPC)

In this section, the molecular weight distribution of corn starch at

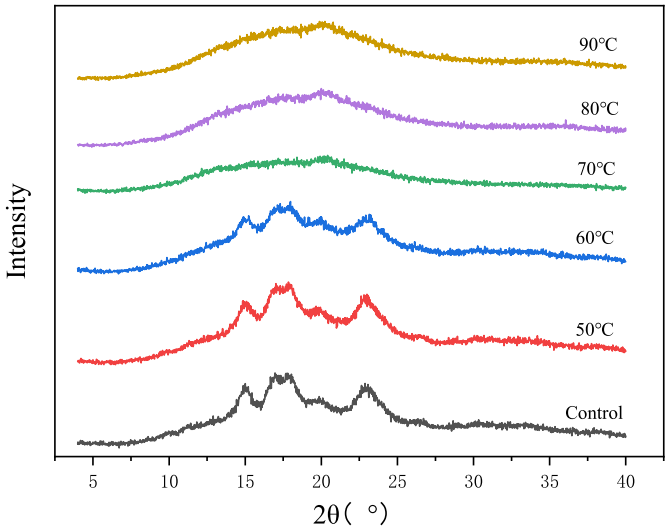

Fig. 3. X-ray diffraction of corn starch treated at different temperatures.

Table 1
ATR-FTIR spectra and crystallinity of corn starch treated at different temperatures.

Sample	Control	50 °C	60 °C	70 °C	80 °C	90 °C
Crystallinity (%)	30 ± 2.35^{a}	27 ± 1.53^{b}	13 ± 1.45^{c}	0^{d}	0^{d}	0^{d}
DO (1047/1015)	1.71 ± 0.13^{a}	1.53 ± 0.18^{b}	1.49 ± 0.20^{c}	1.47 ± 0.12^{cd}	1.38 ± 0.24^{e}	1.17 ± 0.11^{f}
DD (995/1015)	1.01 ± 0.11^{a}	0.92 ± 0.09^{b}	0.90 ± 0.07^{bc}	0.88 ± 0.07^{cd}	0.76 ± 0.08^{e}	0.71 ± 0.06^{f}

Values are presented as the mean ± standard deviation.
When analyzed by Duncan's multiple range test, different letters in the same column indicate significant differences ($P < 0.05$).

different temperatures was detected by gel permeation chromatography (GPC) following the method described by Zhu et al., 2011 with moderate modifications. First, 5 mg sample was weighed to which 1 mL dimethyl sulfoxide (DMSO) was added, and the sample was dissolved in a water bath adjusted at 100 °C for 10 h. Then, 3 mL absolute ethanol (≥99.7%) was added, the sample was centrifuged at 12,000 rpm for 10 min, the supernatant was removed, and the precipitate was washed twice with absolute ethanol and dried in an oven at 40 °C. Next, 3 mL 0.1 M $NaNO_3$ was added, the sample was placed in a water bath set at 120 °C for 20 min, then centrifuged at 12,000 rpm for 10 min; the dispersion was passed through a 0.45 μm organic filter membrane and injected into a sample bottle for measurement. This experiment used high-performance liquid chromatography (Agilent 1260) equipped with a differential detector (RID), with the following settings: chromatographic column, PL-aquagel-OH analytical column (Sigma St. Louis, MO, USA); mobile phase, 0.1 M $NaNO_3$; flow rate, 1 mL/min; column temperature, 35 °C; RID temperature, 35 °C; and injection volume, 20 μL.

2.7. Confocal laser scanning microscopy (CLSM)

According to (Chen et al., 2009), 10 mg corn starch was first weighed and dispersed into 15 μL APTS solution (20 mmol/L APTS, solvent is 15% acetic acid). Then, 15 μL sodium cyanoborate was added, and the reaction was incubated at 30 °C for 15–18 h. The cells were washed 5 times with 1 mL distilled water (while observing whether the precipitate was separated and stained). Lastly, the stained corn starch was suspended in a 20 μL mixture of glycerol and water (*v*/*v*, 1:1), pending further use.

Herein, confocal laser scanning microscopy (CLSM, TCS SP2, Leica Microsystems, Wetzlar, Germany) detected the fluorescence signal of stained starch treated at different temperatures. The instrument is equipped with an argon laser with the following specification: 100 × plan APO/1.40 oil UV. The wavelength was 488 nm with 52 capacities, and the image format was 512 × 512. Each line is scanned four times and averaged to reduce noise during image acquisition by the instrument.

2.8. ATR-FTIR spectroscopy analysis

ATR-FTIR was used to assess the molecular interplay between corn starch at varying temperatures (Liu et al., 2020). The ATR-FTIR (Bruker, V70FTIR, Berlin, Germany) machine carried out 32 scans and recorded the spectrum at a speed of 0.16 cm^{-1} in the wavelength range of 8000–350 cm^{-1}. The molecular interaction between corn starch at various temperatures was explored in detail through PeakFit, and the infrared absorbance at 1047/1015 cm^{-1} (DO) and 995/1015 cm^{-1} (DD) was mainly studied.

2.9. Statistical analyses

The data are expressed as the average ± standard deviation of each process. The experiment adopts a factorial design and uses analysis of variance (ANOVA) in SPSS (version 13.0, Statistical Package for the Social Sciences Inc., Chicago, USA) for a completely random design. Duncan's range test was applied to compare the average values of the corn starch physicochemical indexes.

3. Results and discussion

3.1. SEM

The size and shape of natural starch granules are related to their source. The morphology of starch granules is the most basic aspect in the study of the relationship between the structure and properties of starch, and it plays an important role in the processing of starch and starch-based materials. In this study, the microstructure of corn starch treated at different temperatures was analyzed by SEM (50 μm and 100 μm).

From the three sets of data in Fig. 1 (control, 50, and 60 °C), it is apparent that as the temperature increases, corn starch granules slowly absorb water and expand. Expansion mainly occurs at 60 °C (Thakur et al., 2019). concluded that starch granules initially swell at the onset of gelatinization. From the three sets of data at 70, 80, and 90 °C, it can be seen that the starch granules are broken and the starch is fragmented. With increasing temperature, the degree of rupture of the corn starch granules continuously increases. The reason is that when the temperature of starch is in the range of 70–90 °C, as the temperature continues to rise, hydrogen bonds are broken, and water molecules combine with the hydroxyl groups of starch molecules (Liu et al., 2009). This process ultimately leads to the dissolution of starch crystals and the destruction of starch granules (Liu et al., 2009). At this stage, the double helix structure of amylopectin is dissociated and destroyed, followed by starch fragmentation (Liu et al., 2009; Thakur et al., 2019).

3.2. CLSM

In this assay, laser confocal experiment was used to observe the growth ring structure of corn starch treated at different temperatures. The hot processing of corn starch is very complex, especially the gelatinization process Starch gelatinization is defined as the destruction of the ordered structure and crystal region. The heterogeneity and complexity of the internal structure of starch granules directly affect the starch gelatinization process. Understanding the morphology and changes of the corn starch growth ring structure with temperatures helps us further understand the gelatinization process.

Fig. 2 shows that the growth ring structure of starch granules

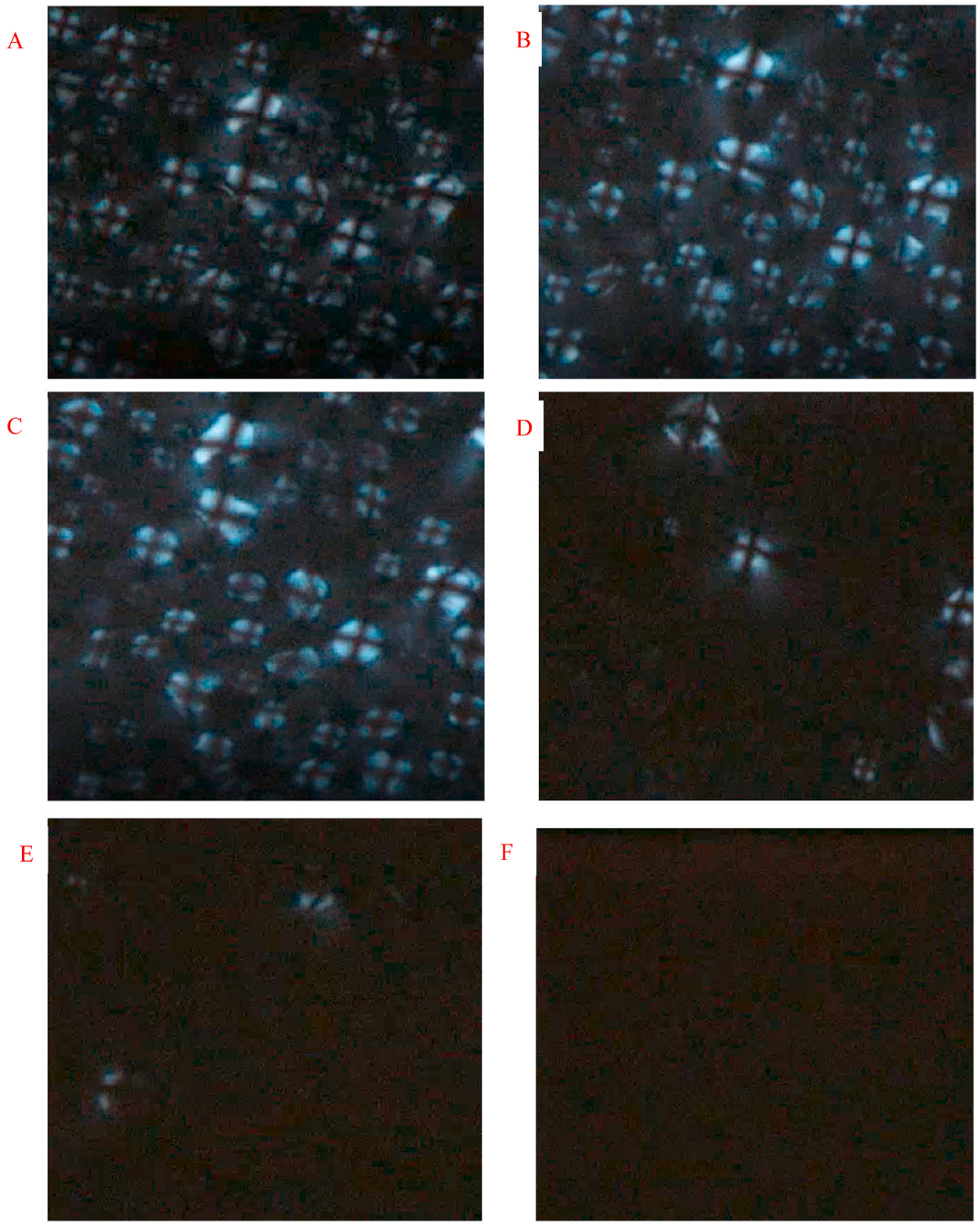

Fig. 4. Hot stage polarizing microscopy images of corn starch: (A) control, (B) 50 °C, (C) 60 °C, (D) 70 °C, (E) 80 °C, and (F) 90 °C.

gradually disappears with increasing temperature. The results showed that the starch growth ring was destroyed under high-temperature conditions, similar to our SEM results. The SEM analysis proved that the corn starch granules were destroyed with increasing temperature. The corn starch growth ring structure may be lost due to the destruction of corn starch granules. From the control group of Fig. 2 and the image at 50 °C, the gelatinization starts from the starch center and spreads rapidly to the periphery. It can be inferred that gelatinization begins in the center of corn starch granules. During this process, most amylose is exuded from the particles to form a gelatinized solution (Chen et al., 2009). concluded that the gelatinization of starch granules begins in the hilum or plant center of the granules and spreads rapidly to the periphery, and gelatinization begins in the intercellular region and the lowermost tissue area (CHUNG & LAI, 2006). observed this phenomenon as well in their study.

3.3. XRD and hot stage polarized light microscope

It is well accepted that the crystalline zones of starch are mostly composed of amylopectin, whereas the amorphous regions are composed of amylose (Parker & Ring, 2001). The crystal structure of starch can be divided into four types, including A, B, C, and V according to the characteristic X-ray diffraction (XRD) patterns. Starches from different sources differ widely in crystallinity and molecular structure. The crystal and amorphous structures of polymer films were quantitatively analyzed using X-ray diffraction analysis. Starch granules from various plant sources can be classified as a series of continuous crystal structures, including type A and B, and type C represents the intermediate crystal structure state (Xiao et al., 2020). Type A starch exhibited 4 obvious characteristic peaks at 15°, 17°, 18°, and 23°.

As shown in Fig. 3, type A crystal corn starch has four pronounced

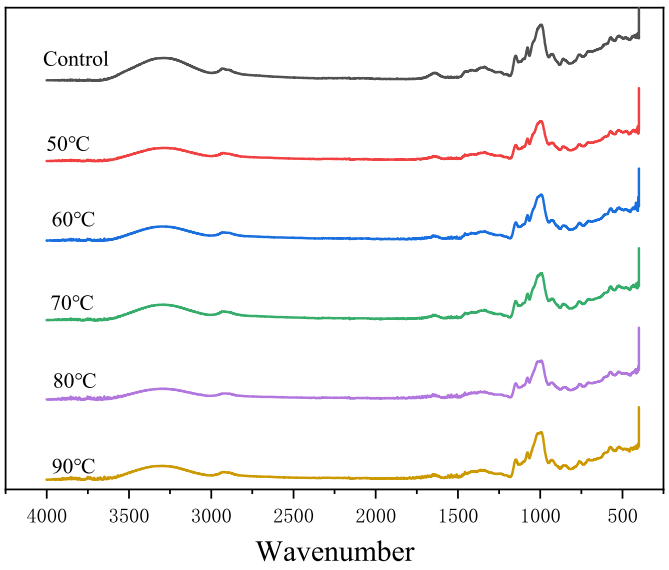

Fig. 5. ATR-FTIR spectra of corn starch treated at different temperatures.

Table 2
Structural properties of corn starch specimens treated at different temperatures.

Sample	M_w ($\times 10^3$ g/mol)	M_n ($\times 10^3$ g/mol)	M_w/M_n
Control	11406.2	15697.9	1.376
50 °C	13848.7	37,692	2.722
60 °C	13931.9	46600.4	3.311
70 °C	1025.5	3394.9	3.345
80 °C	2724.8	10,791	3.960
90 °C	2109	12343.6	5.853

characteristic peaks at 2θ = 15°, 17°, 18°, and 23° (Chen et al., 2017). Table 1 (0–60 °C) demonstrates that the crystallinity of corn starch decreased from 30% to 13% as the temperature continued to increase. Fig. 4 shows that the polarized cross of starch still existed in the control, 50, and 60 °C treatments. This temperature range is called the initial gelatinization temperature, the reversible binding of starch granules to water molecules, and particle swelling (Liu et al., 2009). However, the structure of the corn starch granules remained stable, and the spherulites remained intact by van der Waals forces and hydrogen bonds. At the same time, starch remains birefringent under the action of polarized light (Zhang et al., 2018). From Table 1, Figs. 3 and 4, it can be concluded that the starch polarization cross steadily decreases, and the crystallinity decreases during treatment at 70, 80, and 90 °C, indicating that the crystalline structure of starch is destroyed. Liu et al. (2009) showed that at high temperatures (70–90 °C), the crystalline structure in corn starch granules was destroyed. In particular, hydrogen bonds in corn starch granules were broken, and water attached to the free hydroxyl groups. During this process, the amylopectin double helix in the corn starch granules was completely opened, the crystal structure was completely eliminated, and the birefringence of the corn starch disappeared.

3.4. ATR-FTIR

Fig. 5 shows the ATR-FTIR spectra of corn starch treated at different temperatures. Through ATR-FTIR, we can determine the change in short-range molecular order of corn starch, especially the double helix structure (Yin et al., 2018). From Table 1, we found that corn starch treated at different temperatures had the same ATR-FTIR spectrum. The wideband at 3381 cm^{-1} corresponds to the stretching vibration of amylose and amylopectin hydroxyl groups (Ji et al., 2015). It can be seen from the ATR-FTIR spectra in Fig. 1 that the peak intensity in 3381 cm^{-1} decreases with increasing temperature, indicating that temperature treatment can reduce hydrogen bonding interactions between double helixes in corn starch, and the hydrogen bonding interaction between double helixes of corn starch decreases with increasing temperature (Liu et al., 2020). also reached similar conclusions.

It is proved in the literature that the characteristic peaks at 995 cm^{-1} and 1047 cm^{-1} represent the crystallinity and ordered structure of corn starch, and the absorbance at 1015 cm^{-1} represents the structure of the amorphous region (Liu et al., 2020). The degree of order of the double helix (DO) and the degree of double helix (DD) can be obtained by calculation. Through Table 1, we can see that the, DO of corn starch decreased with increasing temperature, and the XRD results showed the same trend. The crystallization zone of corn starch was destroyed with increasing temperature, leading to the decrease or even disappearance of crystallinity and the double helix order. From Table 1 it can be concluded that the DD of corn starch decreases with increasing temperature. The reason is that with increasing temperature, the gelatinization of corn starch leads to a decrease in the double helix content (Liu et al., 2009). concluded that gelatinization leads to the destruction of the crystallization region of starch, resulting in a decrease in starch crystallinity. (R. F. Tester & S. J. Debon, 2000) also concluded that the starch double helix opening causes a decrease in the double helix order in the gelatinization process.

3.5. GPC

The molecular weight distribution breadth index D measures the degree of dispersion of the molecular weight distribution. When D = 1, it corresponds to a polymer of uniform molecular weight. The larger the value of D is, the wider the molecular weight distribution and the greater the degree of polydispersity. We can obtain the structural changes of corn starch amylopectin and amylose at different temperatures through the molecular weight distribution breadth index D.

From Table 2, as the temperature gradually increases, the molecular weight distribution breadth index D of starch gradually increases (1.376–5.853), indicating that the molecular weight distribution widens as the temperature increases and the degree of polydispersity surges. During starch heating and gelatinization, amylose is freed from starch granules, and the amylopectin double helix is untied, resulting in a change in the starch molecular weight (Tester & Debon, 2000). (Liu et al., 2009) also discovered that the double helix structure of amylopectin was untied, and amylose was released during starch gelatinization at high temperatures (Roman et al., 2019). also reported that amylopectin tears during the extrusion process, causing a transformation in the starch molecular weight. The sample pretreatment in this experiment was carried out under a magnetic stirrer (800 rpm). We can infer that the amylopectin tearing of the corn starch by the magnetic stirrer causes a change in the corn starch molecular weight, leading to an increase in the molecular weight distribution breadth index D.

4. Conclusions

In this study, corn starches treated at different temperatures were freeze-dried, and the four structural layers were investigated. It was noticed that with increasing temperature, the corn starch granules expanded until they broke. This phenomenon also occurred in the corn starch crystallization zone, which decreased and disappeared with increasing temperature. Hot stage microscopy experiments confirmed this observation. By observing the growth ring of corn starch with confocal laser microscopy (CLSM), we found that the growth ring of corn starch gradually broke from the center and spread to the whole grain with increasing temperature. GPC tests helped determine the corn starch molecular weight at varying temperatures. The corn starch width index distribution gradually increased with temperature, and the amylose and amylopectin fragmented. Through ATR-FTIR studies, we detected the double helix DO and DD. This study contributes toward satisfactory

understanding of starch granule structures during hot processing.

CRediT authorship contribution statement

Bin Wang: Investigation, Software, Visualization, Writing – original draft. **Wei Gao:** Investigation, Data curation. **Xuemin Kang:** Formal analysis. **Yuqing Dong:** Investigation, Formal analysis. **Pengfei Liu:** Investigation, Formal analysis. **Shouxin Yan:** Investigation, Data curation. **Bin Yu:** Supervision, Project administration. **Li Guo:** Supervision, Project administration. **Bo Cui:** Conceptualization, Methodology, Writing – review & editing, Supervision. **A.M. Abd El-Aty:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors have declared no conflict of interest.

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