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# Correlation between chain structures of corn starch and properties of its film prepared at different degrees of disorganization

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ABSTRACT

This study investigated the relationship between the chain structure of corn starch and the properties of corn starch-based films formed with starch pastes with different degrees of disorganization (70, 80, and 90 °C). The degree of gelatinization, chain length distribution, amylose content, and molecular weight of the corn starch were determined by the water absorption index, ion chromatography, spectrophotometry, and gel chromatography, respectively. The thickness, surface roughness, solubility, water content, water vapor permeability, mechanical properties, and maximum thermal degradation rate of corn starch-based films formed with starch pastes with different degrees of disorganization were evaluated. The moisture content, thickness and surface roughness of films formed with the starch pastes decreased. At the same time, the solubility, elongation at break, water vapor permeability, and molecular weight distribution increased with increasing heat treatment temperature. The maximum thermal degradation rate and tensile strength of the corn starch-based films formed with the starch pastes decreased with increasing heat treatment temperature. The gradual decrease in the amylose content of corn starch-based films formed with starch paste with increasing heat treatment temperature led to a change in the performance of the corn starch-based films.

## 1. Introduction

The global environmental pollution problem is becoming increasingly severe, leading to people's more vital awareness of the necessity of environmental protection [1]. Plastic pollution is already causing an increase in global pollution [2]. Therefore, current research on packaging materials focuses on developing biodegradable packaging materials that avoid environmental pollution, in which starch-based films have become a current research hotspot [3]. Starch-based films are a good substitute for petroleum plastics [3]. The main advantages of starch-based films are renewability, biodegradability, nontoxicity, and low cost [4]. However, the starches that can be used commercially are limited to corn, wheat, rice, cassava, and potatoes, among which corn starch is the most widely used [5].

Starch is mainly composed of amylose and a mylopectin. Amylose is a slightly branched linear polymer with α-D-glucose units linked by 1,4 glycosidic bonds. *In contrast,* amylopectin is a highly branched polymer made up of *α-D-glucose units* and linked linearly with α-1,4 as well as α-1,6 glycosidic *bonds at the branching points* [6]. The structures of amylose and amylopectin are essential to determine the physical and chemical properties of starch. Corn starch contains approximately 72 % amylopectin and 28 % amylose, white with light yellow powder, corn starch contains a small amount of fat and protein. In addition, corn starch hygroscopicity is strong, up to >30 % [4]. Starch gelatinization is a complex process involving the melting of crystals and the disintegration of starch particles. The essence of gelatinization is that when starch is heated with sufficient water, water molecules diffuse into starch particles and compete for hydrogen bonds [7]. Starch structures are

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usually less dense when the kinetic energy of water molecules exceeds the hydrogen bonds between starch molecules [8]. At this stage, starch molecules gradually absorb water until the granules break. The broken molecules gradually form a uniform viscous gel [8].

Presently, research on starch-based films has focused on adding different substances or using modified starch to improve starch's physical and chemical properties [9]. However, there have been few studies on how structural changes in starch affect the physical and chemical properties of starch-based films [9–11]. This is because the structural feature of starch is complex, and the starch must go through the process of gelatinization, during which plasticizer should be added [6,8,11]. These factors demonstrate that the formation mechanism of starch-based films is challenging. According to the literature, corn starch granules can be divided into four different structural levels: granule, growth ring, block, lamellar (composed of amorphous and crystalline regions), and molecular chain structures of amylopectin and amylose [12]. Therefore, the central themes of this study are as follows: 1. Corn starch-based films formed with starch pastes with different degrees of disorganization of 70, 80, and 90 °C were prepared. 2. The structure of amylose and amylopectin of corn starch-based films formed with the starch pastes were characterized at different degrees of disorganization. 3. The physicochemical indices of corn starch-based films were characterized at different degrees of disorganization. 4. The physical and chemical indices of corn starch-based films formed with starch pastes with different degrees of disorganization were assessed by analyzing different structures of amylose and amylopectin.

## 2. Materials and methods

### 2.1. Materials

Corn starch was purchased from COFCO Corporation (Beijing, China). Dimethyl sulfoxide, glycerol, isoamylase, sodium nitrate, sodium acetate, acetic acid, potassium iodide, and anhydrous ethanol were procured from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). A 0.45 μm organic membrane filter and sodium cyanomethyl borate were secured from Sigma (Shanghai, China).

### 2.2. Sample preparation process

Corn starch-based films were prepared by the casting method. First, 6 g of corn starch was weighed and mixed with 100 mL of distilled water in a conical flask. The conical bottle was placed in a magnetic hot plate agitator (B101S KeTai Company, Zhengzhou, China), the temperature was set at 70, 80, or 90 °C, the rotational speed was 800 rpm/min, and the time was set for 30 min. After stirring, the conical flask was removed, to which 30 % glycerol (based on starch weight) was added and then placed on a magnetic hot plate mixer to stir for 10 min. After stirring, the gelatinized corn starch-based film forming solution was poured into a particular polytetrafluoroethylene mold (PTFE, Shanghai Yuanye Co., Ltd., Shanghai, China, 15 cm × 20 cm). The mold was dried in a blast drying box at 45 °C for 7 h. After drying, the corn starch-based films were stripped from the polytetrafluoroethylene mold and kept at 25 °C and 54 % relative humidity (RH) for 48 h for further use (Bin Wang et al., 2021). Fig. 1 shows the appearance characteristics of corn starch-based films formed with starch pastes with different degrees of disorganization.

### 2.3. Water absorption

Herein, the gelatinization degree of corn starch formed with the starch pastes was characterized by determining the water absorption of the sample [13]. The starch sample used in this test was not supplemented with glycerin, and other production procedures are shown in Section 2.2. First, the weighing bottle was dried in a blast drying box at 105 °C to a constant weight. Then, 5 g samples were mixed with 30 mL distilled water in a conical flask. The flask was stirred in a water bath at 30 °C for 30 min, and then the solution was poured into a 50 mL centrifuge tube and centrifuged at 6000 rpm for 10 min to remove the supernatant ($M_A$). The residue in the centrifuge tube was dried to a constant weight ($M_B$) in a blast drying box at 60 °C. The water absorption was calculated according to the following formula:

$$\text{WAI} = \frac{M_A - M_B}{M_A} \times 100$$

where WAI is the water absorption, $M_B$ is the precipitation quality after drying, and $M_A$ is the precipitation quality before drying.

The results are represented as the mean value of 3 sampling units taken from different films.

### 2.4. Molecular-weight distribution

The chromatographic system used a gel chromatography-differential-multiangle laser light scattering system with an Optilab T-rEX differential detector (Wyatt Technology, CA, USA) and a DAWN HELEOS II laser light scattering detector (Wyatt Technology). Based on the properties of the compound, a gel exclusion column with an appropriate molecular weight range (Ohpak SB-805 HQ, Wyatt

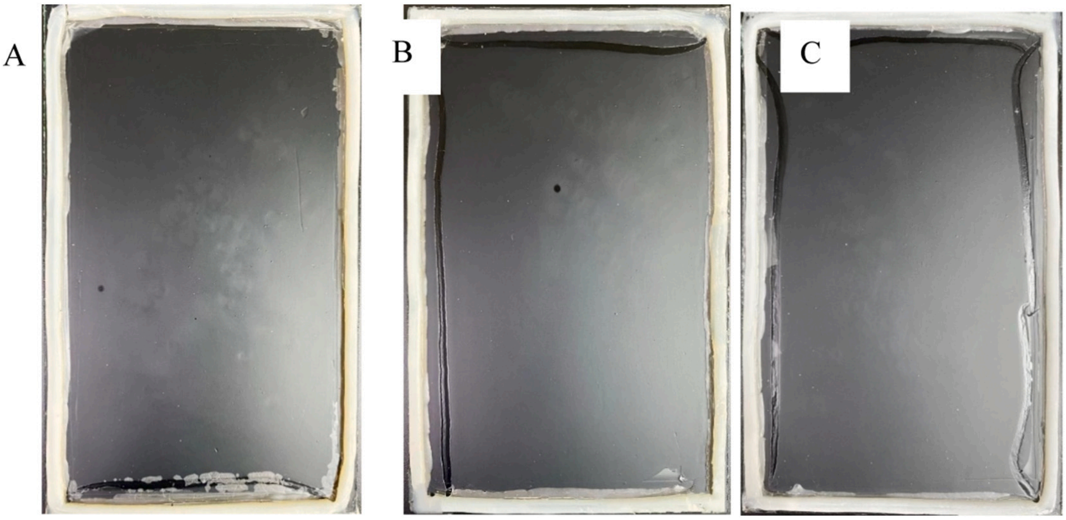

**Fig. 1.** Morphological characteristics of corn starch-based films formed with starch paste with different degrees of disorganization (A: 70, B: 80, and C: 90 °C).

Technology, 300 × 8 mm, Ohpak SB-804 HQ, 300 × 8 mm, Ohpak SB-803 HQ, 300 × 8 mm) was adopted, and the column temperature was set at 60 °C. The injection volume was 100 μL, and mobile phase A (0.1 M $NaNO_3$) was used.

One milliliter DMSO was added to a 5 mg starch sample, and the mixture was heated at 100 °C overnight. Then, 3 mL of anhydrous ethanol was added, the sample was centrifuged to remove the supernatant, and the residue was washed with anhydrous ethanol twice and air-dried. The sample was redissolved in 3 mL 0.1 M $NaNO_3$ solution and centrifuged at 12000 rpm for 10 min to obtain a 100 μL sample.

## 2.5. Starch chain length distribution

The chain length distribution of corn starch was analyzed by ion chromatography. First, a 10 mg starch sample was weighed and mixed with 2 mL 90 % DMSO solution. The mixture was heated and stirred for 20 min in a boiling water bath. After heating and stirring, 6 mL anhydrous ethanol (≥99 %) was added and then cooled to a low temperature, and the mixture was centrifuged at 3000 rpm for 15 min. The supernatant was discarded, and 2 mL 50 mM sodium acetate buffer solution (pH = 4) was added. The mixture was placed in boiling water for 20 min and equilibrated at 40 °C for 10 min, after which 10 μL isoamylase was added. After that, it was placed in a magnetic stirrer water bath (the temperature was set at 40 °C, the rotational speed was 150 rpm, and the stirring time was 24 h). After debranching was completed, the enzyme was denatured by heating for 10 min in a boiling water bath. One milliliter of the sample was diluted to 5 mL by adding 150 mM NaOH. (Shanghai Yuanye Biotechnology Co., Ltd., Shanghai, China).

The results are represented as the mean value of 3 sampling units taken from different films.

## 2.6. Amylose content

The target quantitative analysis was carried out using the MultiskanGO multifunctional enzyme indicator (Samufei, Shanghai, China) [14]. The best ultraviolet absorption wavelength was confirmed by scanning the absorbance of starch combined with iodine. The enzyme plate adopted the Corning method, which requires that the difference between holes be <0.02 at the target wavelength. First, the sample was removed from the water bath. Then, a 10 mg sample was weighed accurately and added to a clean EP tube, to which 100 μL alcohol and 900 μL NaOH solution were added and mixed well. The tube was placed in boiling water for 10 min, and the volume was adjusted to 10 mL after cooling. Afterwards, 0.5 mL supernatant, 0.1 mL acetic acid, and 0.2 mL potassium iodide solution were added to a clean 15 mL centrifuge tube. The volume was adjusted to a constant 10 mL, and the sample was kept for 10 min at room temperature. The absorbance was measured at 720 nm.

The results are represented as the mean value of 3 sampling units taken from different films.

## 2.7. X-ray diffraction (XRD)

The crystallinity of the samples was measured by X-ray diffraction (XRD) [15,16]. First, the sample was equilibrated at 25 °C and 53 % RH for 48 h. After the equilibration was completed, the sample was placed in a particular XRD template and was paved and flattened. The crystallinity of the samples was determined by an Ultima IV X-ray diffractometer (Tokyo, Japan). The test conditions were as follows: Cu - Kα radiation, 40 kV, 40 mA, step length 0.02, scanning speed 2°/min, scanning range 4°- 40°. The relative crystallinity of the samples was calculated by Jade 6.5 software.

## 2.8. Thermogravimetric analysis (TGA)

The thermal stability of the sample was determined by thermogravimetric analysis [17]. The relationship between the change in sample quality and the temperature was determined under programmed temperatures. Samples weighing <5 mg were put into a ceramic crucible for determination. The heating program was set at 30 °C ~ 600 °C, and the heating rate was 20 °C/min. The thermodynamic degradation curves (TGA curves) of the samples were recorded. The DTG curves were obtained by derivative thermogravimetric analysis, and the change in degradation rate with temperature was analyzed.

## 2.9. Thickness measurement

First, the prepared corn starch-based film was removed, and the thickness of the corn starch-based film was measured by a hand-held spiral micrometer (Mitutoyo No. 293–240–30, Tokyo, Japan). Each sample was measured at least ten times to take the average.

## 2.10. Moisture content and solubility in water

The method of [18] was modified to determine the moisture content of corn starch-based films. The prepared corn starch-based films were removed, and then a 0.5 g corn starch-based film sample ($M_1$) was weighed. The corn starch-based film sample was placed in an oven at 110 °C and dried to constant weight ($M_2$). The water content of the corn starch-based film samples was calculated according to the following formula:

$$MC = \frac{M_1 - M_2}{M_1} \times 100$$

MC: Moisture content, M1: Sample quality before drying, $M_2$: Sample quality after drying.

The prepared corn starch-based films were cut into 2 cm × 2 cm squares. The samples were weighed by an analytical balance (±0.0001 g, ZanWei Company, Shanghai, China) to determine the initial mass of corn starch ($M_3$). Next, the sample was placed into a conical bottle, and 100 mL of distilled water was added. The bottle was stirred in a shaker for 6 h at 180 rpm and 25 °C. After that, the sample was dried in an oven at 110 °C to a constant weight ($M_4$) [19]. The solubility of the corn starch-based film sample was calculated according to the following formula:

$$S = \frac{M_3 - M_4}{M_3} \times 100$$

S: Solubility in water, M3: Sample quantity before dissolution, M4: Sample quantity after dissolution.

Each test was repeated at least three times, and the results were averaged.

## 2.11. Water vapor permeability

The water vapor permeability of the corn starch-based film samples was measured by a water vapor permeability meter (PERME™W3/030, Lab Think Instruments Co., Ltd., Jinan, China) [20]. First, the sample was removed and equilibrated for 48 h and then cut into a round piece of 33 $cm^2$. The samples were analyzed 6 times in 30 min intervals at 38 °C and 90 % RH. Each sample was tested three times to take the average.

## 2.12. Atomic force microscopy

The surface roughness of corn starch-based films was observed by atomic force microscopy (AFM) [21,22]. The equipment parameters were set as follows: scanning range 5 μm × 5 μm, scanning frequency 0.977 Hz, tapping mode. The relevant image data were analyzed by NanoScope Analysis 1.5 software (Multimode 8, German Bruker Co., Ltd., Beijing, China). According to the analysis results, two indices for the roughness of the corn starch-based film were calculated: average roughness (Ra: the average value of the absolute deviation from the average surface height) and root mean square roughness (RQ: obtained from the root mean square of the average data plane height deviation).

### 2.13. Mechanical properties

The balanced corn starch-based films were cut into 100 mm × 15 mm pieces. Then, the mechanical properties (elongation at break (EAB, %) and tensile strength (TS, MPa)) were measured by an automatic tensile tester (Param Xlw Co., Ltd., Jinan, China) [23]. The speed of the crosshead was set at 50 mm/min. The experiments were carried out at least 6 times for each tested corn starch-based film.

### 2.14. Statistical analyses

SPSS (version 20.0, Statistical Package for the Social Sciences Inc., Chicago, USA) was used to analyze the experimental data, and Duncan's range test was used to compare the performance differences among the samples ($P < 0.05$).

## 3. Results and discussion

### 3.1. Water absorption

Water absorption can be used as an indicator of starch gelatinization [13]. As compiled in Table 1, the greater the water absorption is, the higher the starch gelatinization. The water absorption of corn starch was 11.25 % because it had not been gelatinized, so the water absorption of native corn starch was low. With increasing corn starch-based film gelatinization temperature, the water absorbance of the corn starch-based film samples gradually increased, indicating that corn starch was gelatinized during the film-forming process. As the gelatinization temperature increased, the degree of gelatinization of corn starch-based films increased, causing the water absorbance of the corn starch-based film samples to rise gradually. Therefore, we might prove that the gelatinization degree of corn starch-based films gradually increased with increasing heat treatment temperature.

### 3.2. Starch chain length distribution

The chain length distribution of corn starch and corn starch-based films was determined by ion chromatography [24]. The degree of polymerization (DP) refers to the total number of glucose molecules in each branched chain of starch. The chain length distribution of amylopectin refers to the hydrolysis of amylopectin into glucan straight chains of different lengths by hydrolyzing the α-1,6 glycosidic bonds by isoamylase. The content of glucan chains with different degrees of polymerization was analyzed by the HPAEC-PAD method to infer the average degree of polymerization [24]. According to the DP values, amylopectin was divided into A chains (DP = 6– 12), B1 chains (DP = 13– 24), B2 chains (DP = 25– 36), and B3 chains (DP ≥ 37) [25].

The percentage of the B2 chain was significantly decreased ($P < 0.05$). In contrast, the proportion of A and B1 chains was significantly increased ($P < 0.05$) in corn starch-based films formed with starch pastes with different degrees of disorganization than native corn starch (Table 1). This finding indicates that heat treatment destroyed the B2 chain structure of corn starch and facilitated the formation of A and B1 chains. Decreased with increasing temperature, the chain length distribution of corn starch gradually lengthened the B2 chain into a shorter chain and chain B1 and decreased with increasing temperature. The chain structure of corn starch was more seriously damaged. In the process of corn starch gelatinization, heating caused longer B2 chain breaks, and the preferred faults showed that the internal B2 chain may break at the α-1,4-glycosidic bond in the amorphous region rather than in the denser crystalline region. According to the cluster model proposed elsewhere [26], the B2 chain passes through two clusters, where each cluster is part of the crystalline and amorphous region.

### 3.3. Molecular-weight distribution

Table 2 provides information on the molecular weight of corn starch and corn starch-based film treated at different degrees of disorganization. The width index of the molecular weight distribution of corn starch was smaller than that of corn starch-based films formed with starch pastes with different degrees of disorganization. This finding could be attributed to the gelatinization of corn starch in developing corn starch-based films, which leads to the destruction of the structure of the corn starch chain and an increase in the width of the molecular weight distribution [27]. Table 2 shows increases in the width index of the molecular weight distribution of corn starch-based film samples with increasing temperature. This finding could be ascribed to the effect of the degree of gelatinization. With an increasing degree of gelatinization, the degree of destruction in the chain structure of corn starch increased. Hence, the width index of the molecular weight distribution of the corn starch-based films rose continuously [9].

### 3.4. Amylose content

Table 3 shows that the amylose content of corn starch-based film samples decreases with increasing heat treatment temperature. This is because the degree of gelatinization of corn starch increases with increasing heat treatment temperature. The essence of starch gelatinization is the rupture of corn starch granules, the disappearance of the crystal region, the destruction of amylose, and the dissociation and destruction of the amylopectin double helix [11]. With increasing heat treatment temperature, the degree of gelatinization of corn starch increased, and the degree of starch damage also increased, so the amylose content decreased with increasing temperature. Bao et al. [28]

**Table 2**
Structural properties of native corn starch and corn starch-based films formed with starch paste at different degrees of disorganization (native corn starch, 70, 80, and 90 °C).

| Sample | $M_w$ ($\times 10^3$ g/mol) | $M_n$ ($\times 10^3$ g/mol) | $M_n/M_w$ |
|---|---|---|---|
| Native corn starch | 11,406.2 | 15,697.9 | 1.376 |
| 70 °C | 1025.5 | 3394.9 | 3.345 |
| 80 °C | 2724.8 | 10,791 | 3.960 |
| 90 °C | 2109 | 12,343.6 | 5.853 |

**Table 1**
Chain length distribution, water absorption, and relative crystallinity of corn starch-based films formed with starch paste at different degrees of disorganization (native corn starch, 70, 80, and 90 °C).

| Sample | Chain A (DP = 6– 12) | Chain $B_1$ (DP = 13– 24) | Chain $B_2$ (DP = 25– 36) | Chain $B_3$ (DP ≥ 37) | Water absorption (%) | Relative crystallinity (%) |
|---|---|---|---|---|---|---|
| Native corn starch | $19.46 \pm 0.72^d$ | $56.02 \pm 0.06^c$ | $19.99 \pm 0.26^a$ | $4.53 \pm 0.05^a$ | $11.25 \pm 2.00^c$ | $19.46 \pm 0.34^a$ |
| 70 °C | $20.75 \pm 0.23^c$ | $57.77 \pm 0.08^b$ | $15.83 \pm 0.41^b$ | $5.65 \pm 0.04^a$ | $32.31 \pm 1.50^b$ | $13.17 \pm 0.35^b$ |
| 80 °C | $22.22 \pm 0.12^b$ | $58.10 \pm 0.15^b$ | $14.07 \pm 0.48^c$ | $5.61 \pm 0.11^a$ | $34.00 \pm 0.62^b$ | $8.84 \pm 0.30^c$ |
| 90 °C | $24.14 \pm 0.07^a$ | $59.26 \pm 0.45^a$ | $11.59 \pm 0.34^d$ | $5.01 \pm 0.01^a$ | $42.63 \pm 1.33^a$ | $4.14 \pm 0.21^d$ |

Different superscript letters in each column indicate a significant difference ($P < 0.05$).

**Table 3**
Moisture content, solubility in water, thickness, amylose content, AFM and mechanical properties of corn starch-based films formed with starch paste at different degrees of disorganization (70, 80, and 90 °C).

| Physical and chemical properties | 70 °C | 80 °C | 90 °C |
|---|---|---|---|
| Moisture content (%) | 20.10 ± 0.96$^a$ | 17.30 ± 0.45$^b$ | 13.21 ± 0.19$^c$ |
| Solubility in water (%) | 28.74 ± 1.29$^b$ | 32.61 ± 0.88$^a$ | 33.96 ± 0.93$^a$ |
| Thickness (μm) | 194.00 ± 1.46$^a$ | 179.00 ± 2.88$^b$ | 169.67 ± 2.46$^c$ |
| WVP (g mm$^{-2}$·s$^{-1}$Pa$^{-1}$) | 4.09 ± 0.11$^a$ | 3.30 ± 0.09$^b$ | 2.69 ± 0.09$^c$ |
| Amylose content (%) | 24.17 ± 0.15$^a$ | 22.11 ± 0.24$^b$ | 20.73 ± 0.15$^c$ |
| 5 μm$^2$ Rq | 170.50 ± 2.34$^a$ | 166.00 ± 3.56$^b$ | 111.15 ± 2.18$^c$ |
| 5 μm$^2$ Ra | 139.00 ± 3.31$^a$ | 126.25 ± 1.84$^b$ | 83.60 ± 2.94$^c$ |
| TS (MPs) | 22.03 ± 0.45$^a$ | 14.46 ± 0.48$^b$ | 11.32 ± 0.59$^c$ |
| EAB (%) | 14.18 ± 1.89$^c$ | 20.21 ± 2.03$^b$ | 25.34 ± 1.78$^a$ |

Different superscript letters in each line indicate a significant difference ($P < 0.05$).

found that the disintegration of starch molecules under the combined action of heat and water leads to the dissolution of amylose and an overall decrease in amylose content.

### 3.5. XRD

Amylopectin is the main component of the crystalline region, and amylose is the main component of the amorphous region [7] in starch. The crystal region of starch can be quantitatively analyzed by X-ray diffraction (XRD) [7]. At present, the crystal structure of starch can be divided into four types: A, B, C, and V [11]. Among them, corn starch belongs to the type A crystal, and there are four prominent characteristic peaks at 2θ = 15°, 17°, 18° and 23° [29]. The amylose-lipid complexes mainly form the V-type crystal, and its characteristic peaks occur at 2θ = 7.4°, 13.0°, and 20.1° [11].

As displayed in Fig. 2, the characteristic peaks of corn starch occurred at 2θ = 15°, 17°, 18°, and 23°, which proves that corn starch exhibits type A crystallization. Rocha et al. [30] concluded that cornstarch presents type A crystallization. The characteristic peaks of the corn starch-based film treated at different degrees of disorganization appeared at 20.1°, belonging to V-type crystallization. This is because amylose and lipids form complexes after gelatinization of starch, resulting in V-shaped crystals. Table 1 shows that the crystallinity of the corn starch-based films decreases with increasing heat treatment temperature, indicating that the lipid complex content continues to decline.

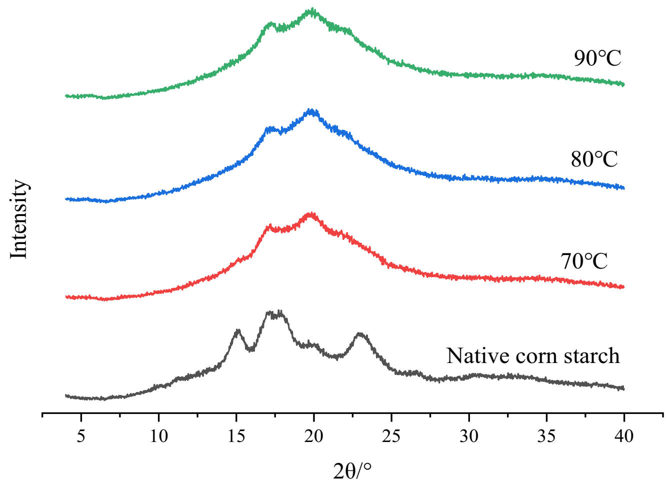

**Fig. 2.** XRD of corn starch-based films formed with starch paste at different degrees of disorganization (native corn starch, 70, 80, and 90 °C).

Our experiments showed that the gelatinization of corn starch led to a decrease in amylose content. Nevertheless, the degree of damage to amylose was different in corn starch-based films with varying degrees of gelatinization. The amylose content of corn starch-based films with high gelatinization degrees was lower. This results in fewer lipid complexes and fewer V-shaped crystals. It was reported that glycerol could form a stable single-chain V-conformational helix or V-shaped crystal with amylose. However, the amylose content decreases with increasing heat treatment temperature. The V-shaped crystals formed for this reason decrease with increasing heat treatment temperature [31]. Therefore, the crystallinity of corn starch-based films decreased continuously with the continuous increase in heat treatment temperature.

### 3.6. Thickness measurement

Table 3 shows that with increasing heat treatment temperature, the thickness of corn starch-based films decreased from 194.00 ± 1.46 to 169.67 ± 2.46 μm. We speculated that the degree of gelatinization of corn starch increased with increasing heat treatment temperature. During the gelatinization of corn starch, granule expansion and destruction of amylose and amylopectin occur. Therefore, the amylose content decreased continuously, and the resulting film thickness was correspondingly thinner. Some studies have shown that the amylose content is closely related to the thickness of starch-based films. Amylose easily forms rigid structures during film formation, and a higher amylose content increases the number of rigid structures. As a result, the thickness of corn starch-based films increases with increasing amylose content [32].

### 3.7. WVP

WVP is an important index to measure the quality of packaging materials. Food packaging materials can allow food to avoid contact and reduce material exchanges with the outside world to prolong the shelf life of food. Table 3 shows that the heat treatment temperature gradually increased the WVP of corn starch-based films. There were significant differences among the groups ($P < 0.05$). This might be because the amylose content of corn starch-based films decreased with increasing heat treatment temperature, leading to a decrease in the V-type crystallization of the prepared films [33]. The decrease in crystallization rate means that the amorphous layer increased. As the amorphous region of starch is loose, the zigzag path of water vapor is reduced, resulting in an increasing trend of WVP of corn starch. In this context, Donhowe and Fennema [34] found that the WVP decreased with the crystallization rate because permeation occurs across the amorphous layer of films. Furthermore, Mali et al. [35] reported that the WVP is affected by the *crystalline/amorphous ratio.*

### 3.8. Moisture content and solubility in water

Water content and solubility are important indices to evaluate packaging materials. Packaging materials with different moisture contents and solubilities were selected according to the characteristics of the packaged material. If the packaging has a high moisture content, the starch-based films should have low water solubility to ensure the integrity of the packaging material. Table 3 reveals that the water content decreases continuously from 20.10 ± 0.96 to 13.21 ± 0.19 % with increasing heat treatment temperature. Glycerol affects the moisture content of corn starch film. With the increase in the gelatinization degree of corn starch, the free hydroxyl group produced by corn starch will also increase. The free hydroxyl group can form a hydrogen bond with the hydroxyl group of glycerol [36]. Therefore, the amount of glycerol exerting a plasticizing effect increases with the gelatinization degree of corn starch. Glycerol itself has hygroscopicity and high water retention [37], so the moisture content of corn starch film increases with increasing gelatinization degree. Our experiments showed that the highest to the lowest degree of gelatinization was at heat treatment temperatures of 90, 80, and 70 °C. Therefore, the water content of corn starch-based films increases with increasing heat treatment temperature.

As exhibited in Table 3, with increasing heat treatment temperature, the solubility of the corn starch-based films increased from 28.7 to 33.9 %. The solubility of the corn starch-based films is related to crystallinity, where higher crystallinity corresponds to lower solubility. The crystallinity of corn starch-based films is related to amylose. The degree of gelatinization increased with increasing heat treatment temperature, which led to a gradual increase in the destruction of amylose in corn starch-based films. In the process of aging and regeneration of corn starch-based films, the formation of amylose lipid complexes (V-type crystallization) is increasingly less common. Therefore, with increasing heat treatment temperature, the crystallinity of corn starch-based films decreased, and the solubility of corn starch increased.

### 3.9. TGA

Thermogravimetric analysis was used to analyze the thermal decomposition behavior of corn starch samples [38]. Fig. 3 presents the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of corn starch and corn starch-based film samples treated at different heat treatment temperatures. The DTG curve is derived from the TG curve, representing the mass-loss rate during the degradation of corn starch samples [39]. The thermogravimetric curve can be divided into two stages. The first weight-loss stage occurs from 30 °C ~ 130 °C [38]. The weight loss in this stage is related to water evaporation. The second weight-loss stage occurs between 250 ~ 400 °C due to the weight loss of the starch sample itself [38].

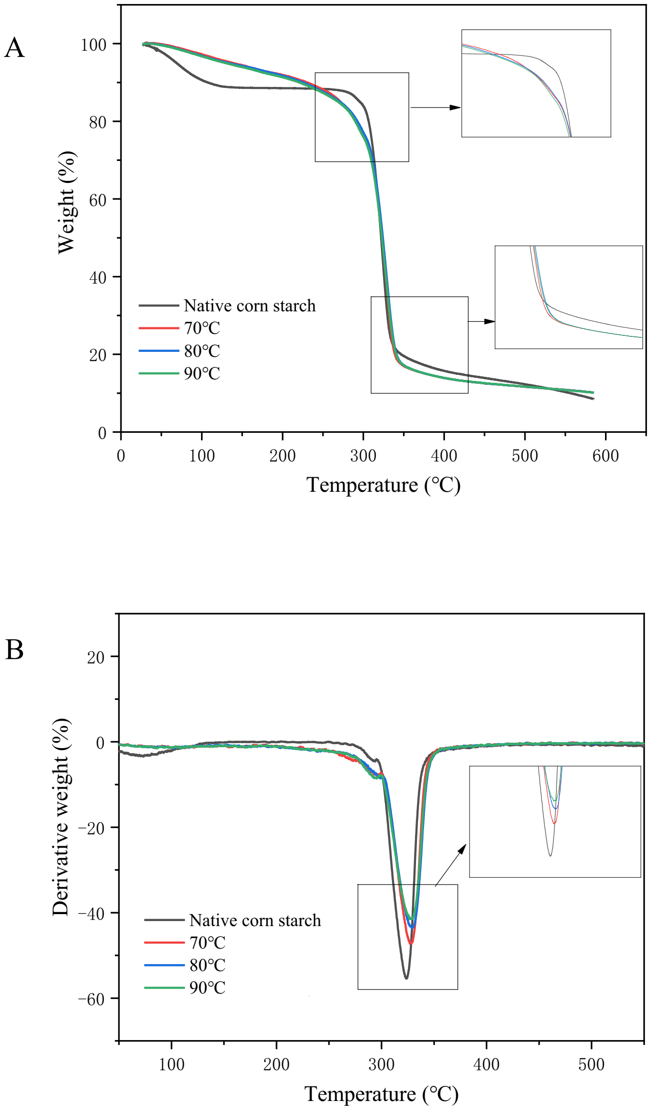

**Fig. 3.** TGA (A) and DTG (B) curves of corn starch-based films formed with starch paste at different degrees of disorganization (native corn starch, 70, 80, and 90 °C).

Fig. 3A shows that the degradation temperature of corn starch is higher than that of the corn starch-based film, indicating that the treated corn starch-based films have gelatinization reactions. This leads to the disruption of van der Waals forces and hydrogen bonds and the destruction of the chain structure of corn starch, which reduces the energy needed to destroy the internal structure of corn starch [11]. Therefore, the degradation temperature of the corn starch-based film treated at different degrees of disorganization is lower than that of corn starch. Fig. 3B shows that the maximum loss rate of the corn starch-based film sample decreases with increasing heat treatment temperature, denoting that the amylose molecular chain of starch is increasingly broken and destroyed during gelatinization with increasing heat treatment temperature. The experimental results correspond to the previous amylose content test results. It has been reported that there is a positive correlation between amylose content and thermal stability [40,41]. In starch-based film aging, amylose and lipids form V-shaped crystals, and amylose is positively correlated with V-shaped crystals. Therefore, a lower crystallinity results in a lower maximum loss rate. Therefore, the maximum loss rate decreases with increasing heat treatment temperature.

### 3.10. AFM

The surface morphology of corn tarch-based films was observed by atomic force microscopy (AFM). The surface roughness data (Rq and Ra) of corn starch-based films were calculated according to the results. Fig. 4 and Table 3 show that the surface roughness of corn starch-based film samples decreases with increasing corn starch-based film heat treatment temperature. This may be because the accumulation of amylose causes the roughness of corn starch-based films. Increasing the heat treatment temperature increases the degree of gelatinization of corn starch-based films, and the amylose content decreases. Hence, the accumulation of amylose decreases, which leads to a decrease in the surface roughness of the corn starch-based films. On the other hand, there is a possibility that the accumulation of starch granules that are not fully gelatinized may increase the surface roughness of corn starch-based films. Menzel et al. [42] declared that the thickness of corn starch increases with increasing amylose content. Wang et al. [11] stated that the structure of amylose was partially destroyed in gelatinized starch.

### 3.11. Mechanical properties

As shown in Table 3, the TS of corn starch-based films decreases, whereas the EAB increases with increasing heat treatment temperature. The TS was the lowest, and the EAB was the highest at 90 °C. The destruction of hydrogen bonds and van der Waals forces between corn starch molecules becomes more severe with increasing heat treatment temperature, decreasing intermolecular forces and increasing the sliding effect between molecular chains of corn starch-based films. Wang et al. [11] demonstrated that the intermolecular hydrogen bond and van der Waals force of starch were destroyed during the gelatinization process. In the amylose content experiment, we found that the amylose content decreased with increasing heat treatment temperature. Related literature has shown that the tensile strength of starch film is related to amylose; the higher the amylose content is, the greater the tensile strength of starch film, which is in direct proportion to the relationship, and the amylopectin content is in inverse proportion to the elongation at

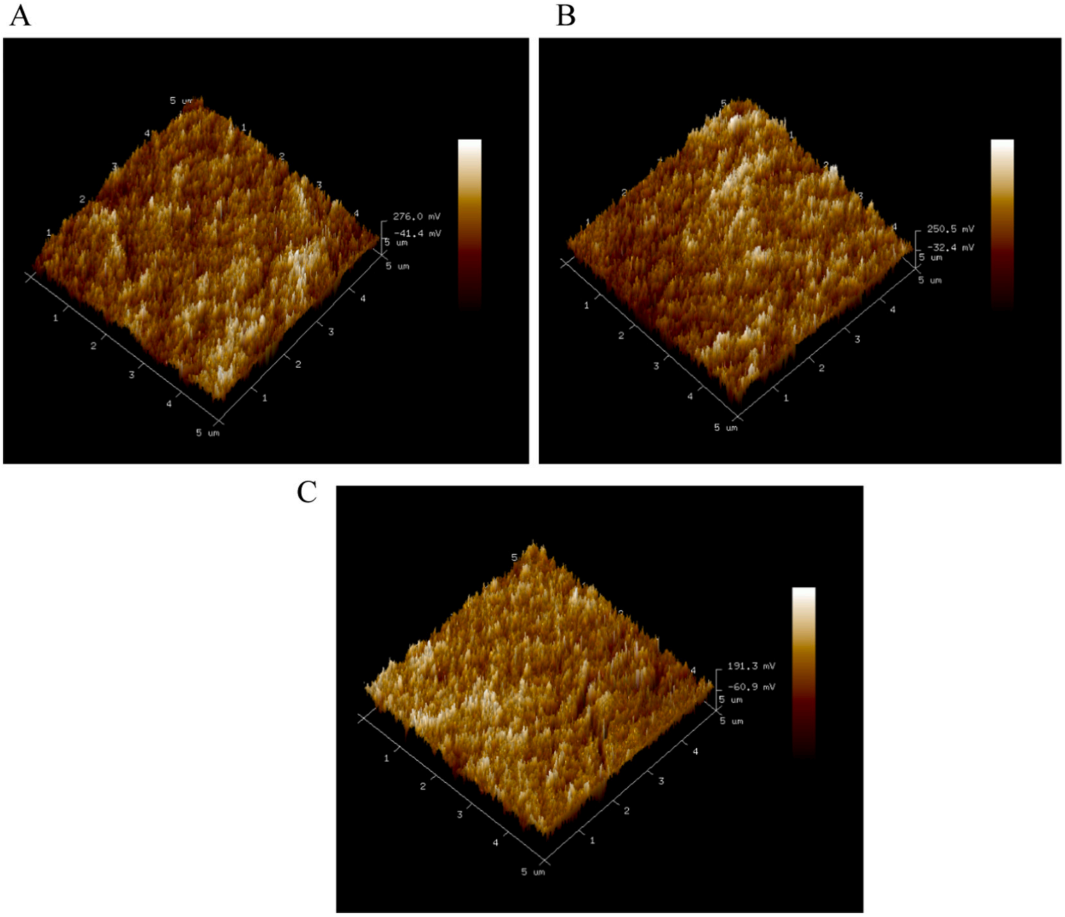

**Fig. 4.** AFM of corn starch-based films formed with starch paste at different degrees of disorganization (A: 70, B: 80, and C: 90 °C).

break [43]. With increasing treatment temperature, the relative crystallinity of cornstarch-based films decreased continuously. Koch et al. [44] found that the tensile strength of corn starch film decreased with the continuous decrease in crystallinity.

## 4. Conclusion

In this study, corn starch-based films formed with starch pastes with different degrees of disorganization (70 °C, 80 °C, and 90 °C) were prepared by the casting method, and the relationship between the changes in the chain structure of corn starch and the properties of corn starch-based films was investigated. The results revealed that with the increase in heat treatment temperature, the gelatinization degree of corn starch increased, and the increase in gelatinization resulted in the destruction of amylose and amylopectin structures, characterized by decreasing crystallinity and amylose content and increasing width index of the molecular weight distribution and the change of chain length distribution. With the increase in heat treatment temperature, the corn starch-based film thickness and surface roughness decreased gradually, while the solubility and water vapor permeability increased. In addition, the maximum thermal degradation rate and moisture content of corn starch decreased with increasing heat treatment temperature. With the increase in the heat treatment temperature, the elongation at break of the corn starch-based films increased, and the tensile strength decreased.

## CRediT authorship contribution statement

Bin Wang: investigation, software, visualization, and writing—original draft. Guixin Zhang and Chenxi Liu: supervision and project administration. Shouxin Yan, Xin Xu and Deyin Wang: formal analysis. Bo Cui: conceptualization, methodology, writing—review and editing, and supervision. A. M. Abd El-Aty: conceptualization, methodology, writing—review and editing, and supervision. All authors contributed to the article and approved the submitted version.

## Declaration of competing interest

The authors have declared no conflict of interest.

## Data availability

The data that has been used is confidential.

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