Chapter 3
Physicochemical Properties of Starch

Binjia Zhang, Yabin Guo, Zihang Cheng, and Dongling Qiao

Abstract Starch is a major biopolymer in many flour-based foods consumed worldwide and a crucial material in various industrial areas. The starches from different botanical origins often show differences in the composition and structure, and thus in the physicochemical properties (e.g., thermal, rheological, solubility, swelling, hydrolysis, and degradation features), which stands at the core of the design and production of starch-based products. This chapter summarizes the physicochemical properties of starch and related influencing factors, providing a foundational information for other chapters.

Keywords Thermal · Rheological · Hydrolysis

3.1 Introduction

Starch, typically a naturally occurring carbohydrate in many plants (e.g., cereals, tubers, roots, legumes, and some immature fruits like mangos or bananas) (Alcázar-Alay and Meireles 2015), is a major food component providing energy for the human body and has been used in various industrial areas (Cai et al. 2021). Starch is composed of two D-glucan polymers, including amylose, a mostly linear 1,4-α-D-glucan, and amylopectin, mainly 1,4-α-D-glucan having 1,6-α linkages at branching points (Zhang et al. 2013; Pratiwi et al. 2018). These two kinds of biopolymers can form multi-scale structures inside the starch granule mainly through hydrogen bonding, involving the granule (<1–100 μm), alternating semicrystalline and amorphous shells (100–400 nm), amorphous-crystalline lamellae (9–10 nm), and macromolecular chains (~nm) (Oates 1997; Xie et al. 2012).

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Z. Sui, X. Kong (eds.), *Physical Modifications of Starch*,
https://doi.org/10.1007/978-981-99-5390-5_3

The composition (e.g., amylose content) and structure of starch have important influences on its physicochemical properties such as thermal (gelatinization and pasting) and rheological (e.g., steady state, dynamic, and textural) features, which are closely related to the processing performance of starch-based products. For instance, potato and tapioca starches, with low gelatinization temperature, a quick swelling rate and a high viscosity, can endow noodles with increased elasticity and chewiness (Obadi and Xu 2021). Starch hydrogels with different amylose contents and crystalline types display different mechanical performances, and a higher amylose content can produce a higher hardness value (Cui et al. 2022). Apart from the abovementioned physicochemical properties, other properties such as starch digestibility also show close links to the starch structure (Zhu 2018). To widen the application of starch in food and industry, it is essential to understand the physicochemical features of starch. This chapter summarizes the current knowledge on the starch physicochemical properties (including thermal, rheological, and other properties), which provides fundamental information for the rational usage of starch resources.

3.2 Thermal Properties

Starch usually needs to be processed before it is turned into usable forms. Among them, the thermal processing (e.g., steaming, cooking, and extrusion) for aqueous starch systems has been widely practiced. While heated in water, the semi-crystalline architecture of starch could be gradually disrupted, resulting in disordered starch matrices (sol/gel forms) (Fig. 3.1a). This process is well known as "gelatinization", which is an irreversible process that involves starch granule swelling, crystallite melting, and molecule solubilization (Sullivan and Johnson 1964).

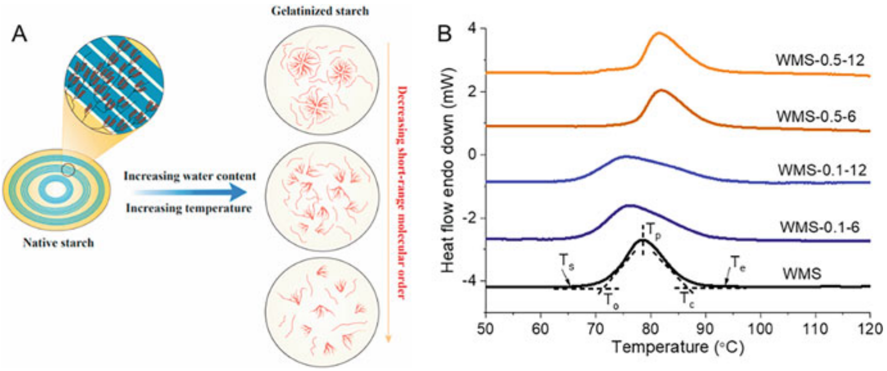

Fig. 3.1 Thermal transition of starch during hydrothermal treatment (**a**), and DSC thermograms of waxy maize starch (WMS) and its alkali-treated samples (**b**). (**a**) is reprinted from Huang et al. (2021) with permission from Elsevier, Copyright 2021; (**b**) is adapted from Qiao et al. (2017) with permission from Elsevier, Copyright 2017

The thermal properties of starch are affected by a series of factors such as starch source, moisture content, additives, heating time, and temperature. Understanding the gelatinization and pasting properties of starch can help us in better regulate the thermal processing of starch-based products and eventually their quality attributes (Wang et al. 2021).

3.2.1 Gelatinization

The gelatinization of starch can be divided into three stages (Copeland et al. 2009): (1) at the reversible water absorption stage, the amorphous part of starch granules absorbs a small amount of water and produces a limited expansion; (2) at the irreversible water absorption stage, a large amount of water enters the interior of the starch granules, the volume of the starch granules expands significantly, some amylose overflows on the surface, and the viscosity of the system increases rapidly; (3) at the final granule disintegration stage, the starch granules break and lose their original shape, the viscosity begins to decrease, and the starch molecules overflow and disperse in the solution. The gelatinization of starches plays a key role in their food and non-food applications (Genkina et al. 2014). The gelatinization process can be inspected using the differential scanning calorimeter (DSC). Several investigations also characterized the degree of starch gelatinization using optical microscopy, synchrotron X-ray scattering, and nuclear magnetic resonance (Gonera and Cornillon 2002; Carlstedt et al. 2015).

The DSC enables us to acquire the gelatinization temperatures (starting (T_s), onset (T_o), peak (T_p), conclusion (T_c), and end (T_e)), enthalpy (ΔH), and gelatinization temperature range (R) of starch (Fig. 3.1b) (Qiao et al. 2017). In general, starch gelatinization occurs at a temperature range of 60–80 °C (Liu et al. 2019), which depends on the composition, starch molecular weight and structure, moisture content, and the addition of substances (Schirmer et al. 2015). The starch granule size also affects the gelatinization behaviors (Puncha-arnon et al. 2008). Amylopectin with a high degree of polymerization (DP) could exhibit high crystallinity, thus providing a more stabilized starch structure and limiting the hydration of amorphous regions; this could enhance the resistance of the granules to gelatinization (Shevkani et al. 2016). The gelatinization temperature normally increases as the amylose content increases (Genkina et al. 2014); T_o and T_p are positively correlated with the relative length of amylopectin short chains, and T_c is related to the relative length of the medium chains of amylopectin (Li and Gong 2020).

The starch gelatinization parameters can be changed by various treatments. For instance, annealing treatment at 50 °C increased the starch gelatinization temperature by stabilizing the starch crystals and increasing the amylose-amylopectin interactions, but had little effect on the enthalpy (Wang et al. 2017a, b). The pressure treatment disrupted the starch structure and promoted water migration during gelatinization, decreasing gelatinization enthalpy but not changing it linearly (Liu et al. 2009).

The reduction of water content for starch can allow increases in T_o, T_p, and T_c and a decrease in ΔH. As indicated by previous findings, T_p increased and then decreased with the increase of NaCl concentration (Li et al. 2014), since the presence of a small amount of NaCl could protect the hydrogen bonding between starch molecules and delay the destruction of starch crystallization; the addition of protein and protein fibrils enhanced the gelatinization temperature and reduced the enthalpy (Chen et al. 2020; Wang et al. 2020); the lipids on the surface of starch affect starch gelatinization, and the removal of lipids could decrease the crystallinity, gelatinization temperature, and enthalpy (Li et al. 2016); sugars and sugar alcohols could form intermolecular interactions with starch in the amorphous regions, suppressing starch gelatinization (Allan et al. 2018).

3.2.2 Pasting Properties

The pasting properties represent changes in the viscosity of starch during pasting. The pasting process is usually studied using an amylograph, Rapid Visco Analyzer (RVA), a Brabender Amylograph, an Ottawa Starch Viscometer, or a dynamic Rheometer. These instruments are used to record the viscosity changes of the starch pastes/suspensions under shear with temperature. Among these, RVA has been used extensively to study the pasting properties of starches and related foods, due to its fast testing speed and the small sample size required (Sneh et al. 2020). A typical pasting profile with common parameters measured by RVA is included in Fig. 3.2a. The temperature at which the viscosity starts to increase indicates the pasting temperature (PT). The peak time or maximum viscosity time is the heating time at which the maximum paste viscosity occurs. The maximum viscosity reached during heating is defined as the peak viscosity (PV). The breakdown viscosity (BD) refers to the difference between the peak viscosity and the minimum viscosity. The difference between the final viscosity and the minimum viscosity represents the setback viscosity (SB), closely related to the retrogradation of gelatinized starch. The final viscosity (FV) corresponds to the viscosity value at the end of a cooling stage (Balet et al. 2019).

The pasting properties of thermally processed starches or related food matrices are determined by several factors, such as the moisture content, the starch source, additives, and the temperature and time of thermal treatment (Xia et al. 2021). For instance, the paste viscosity of wheat and rice flours apparently depends on the water content, attributed to the gradual disruption of starch granules followed by interactions between starch, protein, and lipid (Guo et al. 2018). The relationship between rice starch structure and pasting properties after citric acid treatment could be understood in Fig. 3.2b (Huo et al. 2018). The effect of thermal processing on the paste viscosity of starchy foods is also associated with the starch source. The paste viscosities (PV, FV, TV, SB, and BD) of cooked japonica flour or indica hybrid flour were lower than those of its raw flour, but waxy flour showed an opposite phenomenon (Wang et al. 2016). The paste viscosities of waxy rice flour decreased

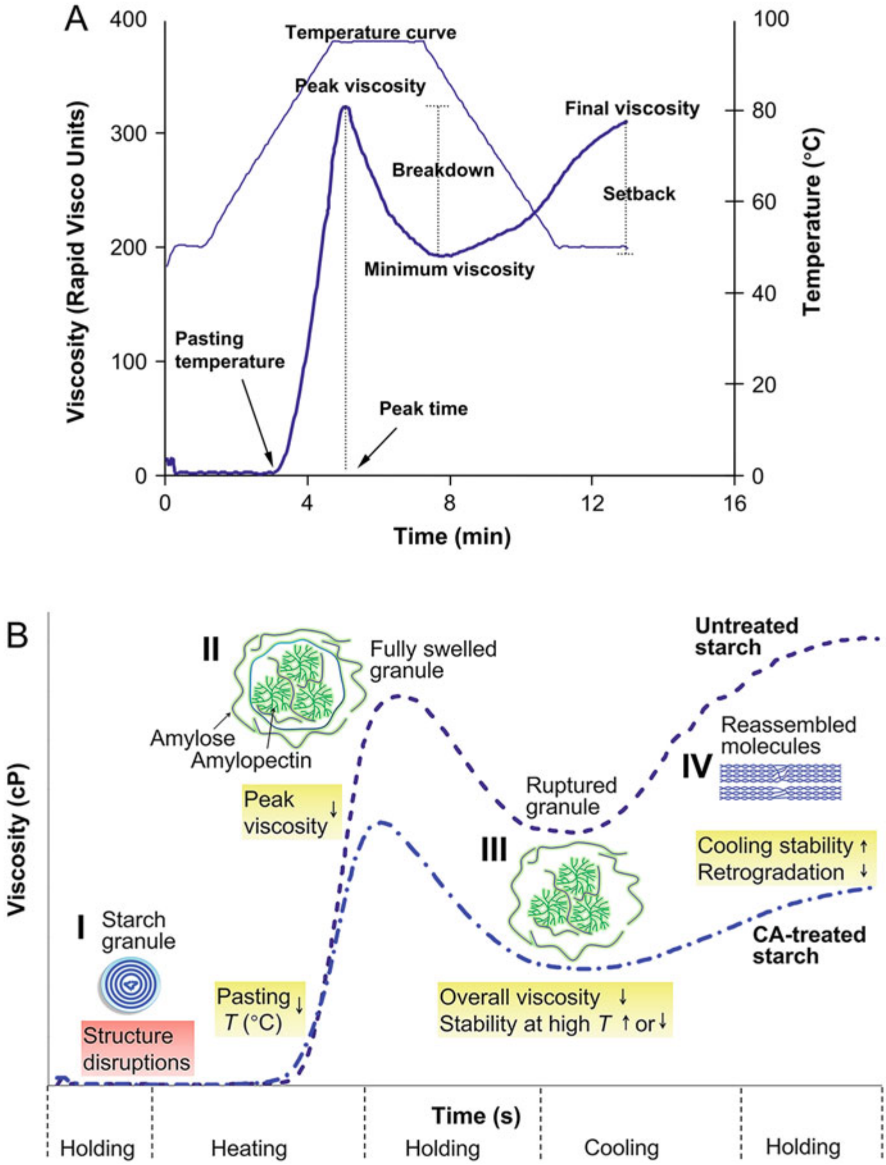

Fig. 3.2 Pasting profile of rice starch measured by RVA (**a**), and effect of citric acid treatment on rice starch pasting (**b**). (**a**) is reprinted with permission of the Royal Society of Chemistry (Copeland et al. 2009), permission conveyed through Copyright Clearance Center, Inc; (**b**) is adapted from Huo et al. (2018) with permission from Elsevier, Copyright 2018

significantly as the oven-heating temperature increased from 140 to 180 °C, attributed to the degradation of starch molecules at high temperatures (a decrease in the capacity of the starch to swell) (Xla et al. 2020). The peak viscosity and breakdown viscosity of the steamed noodles were significantly lower than those of the non-steamed noodles, and this phenomenon was more obvious as the steaming time increased (Luo et al. 2015).

Physical treatments also affect starch gelatinization, such as high hydrostatic pressure treatment (HHP) and heat-moisture treatment (HMT) modification. Research has shown that HHP affected the pasting behavior of various types of starch differently. This treatment could induce a transformation of the crystalline type of corn starch, and alter the pasting temperature and the paste viscosity (Katopo et al. 2002). The effect on rice starch pasting was not significant at low-pressure values (120 and 480 MPa), and the peak viscosity decreased significantly at 600 MPa (Li et al. 2012). Investigations on the pasting properties of HMT-treated starches showed that HMT increased the pasting temperature and thermal stability of the starch but decreased the peak viscosity and breakdown (Gunaratne and Corke 2007). The pasting temperature for normal and waxy maize starches increased as the HMT moisture level increased, but remained constant with the increase of HMT time (Ai et al. 2015).

3.3 Rheological Properties

Rheological properties play vital roles in the processing and quality regulation of starch-based products. The rheological properties could be used to predict and explain the flow and deformation of starch systems, as well as the conditions of texture changes for different starch-based foods. The rheological properties of starch mainly include steady state, dynamic rheological, and texture features. Relative to shear rheology, the knowledge on the extensional rheological behaviors of starch is insufficient.

3.3.1 Steady-State Features

The rheological features of starch under steady state are usually studied using a rotational rheometer to discuss the variations of flow behaviors of starch under shear, and the methods mainly include rotational flow shear and dynamic oscillation shear (Evans and Haisman 1980) (Table 3.1).

The flow behavior describes the rotationally shearing features of starch under the geometry, and the shear rate, shear stress, and apparent viscosity can be recorded. Flow shear mode is often conducted under steady shear state. During flow shear, the viscosity of starch paste decreases when shear rate increases (a shear-thinning feature), indicating that starch paste belongs to a pseudoplastic fluid, as the network of entangled starch molecules is disrupted during shear process (Ahuja et al. 2020). Usually, the viscosity of starch paste decreases in a wide range of sections of increasing shear rate but keeps almost constant when the shear rate is very low or

Table 3.1 Rheological modes and parameters of starch

Modes		Parameters	Models	Parameters via fitting
Flow shear	Steady flow shear	γ, σ, η	Ostwald-de Waele model	K, n
			Herschel-Bulkley model	σ_0, K, n
			Carreau model	η_0
	Transient flow ramp	γ, σ	Ostwald-de Waele model	S
Oscillation shear	Frequency sweep	ω, G', G''		
	Temperature sweep	T, G', G'''		

Note: γ shear rate, σ shear stress, η apparent viscosity, ω angular frequency, T temperature, G' storage modulus, G'' loss modulus, K consistency coefficient, n flow index, σ_0 yield stress, η_0 zero shear viscosity, S area of hysteresis hoop

very high, since the deformation and recombination of network structure keep a dynamic equilibrium at very low or high shear rate.

To better understand the starch flow behaviors, the Ostwald-de Waele (Power law) model (Eq. (3.1)) and the Herschel-Bulkley model (Eq. (3.2)) are widely used in data analyses (Silva and Lucas 2018):

$$\sigma = K \times \gamma^n \tag{3.1}$$

$$\sigma = \sigma_0 + K \times \gamma^n \tag{3.2}$$

In these equations, σ is shear stress (Pa), σ_0 is yield stress (Pa), γ is shear rate (s^{-1}), K is consistency coefficient (Pa s^{-1}), and n is flow index. The coefficient K reflects the average viscosity of a non-Newtonian fluid (e.g., starch paste), and the flow index n indicates the deviation degree of the fluid from Newtonian flow. While the pseudoplastic fluid (e.g., starch paste) shows a shear-thinning behavior ($n < 1$), the dilatant fluid (e.g., starch suspension) has a shear-thickening behavior ($n > 1$) (Pang et al. 2020). For a starch paste, the n value ranges from 0 and 1, and the lower the n value the trend of shear-thickening is stronger. The K and n values are commonly determined by the solid content of starch paste, the amylose content, and the temperature of the environment. The addition of exogenous additives (e.g., hydrocolloids) also influences the flow behavior of starch pastes. In addition, the yield stress σ_0 is defined as the minimum shear stress required to initiate flow (Genovese and Rao 2003), and it is usually achieved via increasing solid content or adding polysaccharides into starch pastes.

Previous investigations also discussed the zero shear viscosity and infinite shear viscosity of starch pastes, as deduced from models such as the Carreau model:

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\lambda\gamma)^2\right]^{\frac{n-1}{2}} \tag{3.3}$$

In which, η is apparent viscosity (Pa s), η_0 is zero shear viscosity (Pa s), η_∞ is infinite shear viscosity (Pa s), λ is relaxation time (s), γ is shear rate (s^{-1}), and n is power-law index. Among these parameters, the zero shear viscosity η_0 is used to represent the linear region of Newtonian compliance in which the units flow past one another for the rapture of bonds, and this value normally increases as the average molar mass of unlinked flowing chains increases.

Thixotropy is another important rheological parameter of starch paste as it simultaneously has time-dependent and shear-thinning characteristics. The thixotropy is usually measured via a two-stage flow ramp test, including a stage of increasing shear rate and the other stage of decreasing shear rate through transient continuous variation. The area of hysteresis hoop (S) of up curve and down curve in the shear stress-shear rate graph reflects the thixotropic degree of starch systems (pastes), and the larger the area the stronger thixotropic behavior starch possesses (Liu et al. 2021). In fact, the thixotropy reflects the deformation and recombination of starch chains and network structures, significantly depending on factors such as the botanical source, starch concentration, amylose/amylopectin ratio, exogenous additives, and temperature (Ma et al. 2019; Zhang et al. 2019). Generally, increasing the concentration of starch pastes enhances the thixotropy.

3.3.2 Dynamic Rheological Features

The dynamic rheological analysis is used to determine the viscoelasticity of materials (Rao and Cooley 1992). The dynamic viscoelastic nature of starch involves the mechanical response law of starch pastes or gels under the action of periodic stress (strain). Such dynamic behavior is frequency-dependent and temperature-dependent. The dynamic viscoelasticity test can be conducted by fixing two of control variables (e.g., oscillation frequency, oscillation amplitude, test temperature, and test time) and changing the third one. The basic test modes include strain sweep, frequency sweep, temperature sweep, and event sweep. During a sweep mode, the related parameter is continuously changed in selected steps. Using dynamic measurements, we can obtain several key rheological parameters of starch matrices such as storage modulus G' (Pa) and loss modulus G'' (Pa), loss tangent ($\tan\delta = G''/G'$), and complex viscosity (η^*) (Kamweru 2020).

G' indicates the ability of starch material to recover during a deformation period, representing its elastic behavior. G'' shows the amount of energy dissipated during a deformation period, which is used to represent its viscous behavior (Tabilo-Munizaga and Barbosa-Cánovas 2005). The $\tan\delta$ indicates the relative effect of elasticity or viscosity in the system viscoelastic behavior (Gunasekaran and Ak 2000). The intersection of the storage modulus and the loss modulus curves generally is used to show the gel point of starch ($G' = G''$ and $\tan \delta = 1$). The starch system has occurred at this point from viscosity to elasticity. The frequency and modulus corresponding to the intersection reflect the structure information inside starch matrices (Whistler et al. 2012). When the complex viscosity (η^*) is high (e.g., 39.8–97.5 Pa s), the starch gel is suitable as a good thickener or stabilizer (Yousefi and Razavi 2015).

The dynamic rheological properties of starch pastes and gels are affected by different factors, including starch particle size, concentration, gelatinization conditions (e.g., temperature and heating rate), and storage conditions (e.g., temperature and time) (Punia et al. 2020). In particular, when the starch was heated in water, the viscoelastic change of the starch system normally involves several stages (Fonseca-Florido et al. 2018). For instance, (1) at an early stage of heating, the G' and $\tan \delta$ of the starch slurry are small, and amylose molecules leach from starch granules; (2) at or above the gelatinization temperature, the amylose matrix interacts with the low molecular weight amylopectin to strengthen the continuous network, resulting in a sharp increase in G' and G''. The $\tan \delta$ value decreases at the same time (Wu et al. 2016).

3.3.3 Texture Features

The texture is an important quality aspect of starch-based products, since it is closely related to the practical performance (e.g., sensory and other attributes). There are some basic testing modes, including compression, puncture, shear, bending, and tensile analyses, in addition to texture profile analysis (TPA).

TPA and puncture tests are important for investigating starch texture. TPA simulates the chewing process by compressing the sample (mainly gel form) two times (Yu et al. 2020). Several texture parameters of starch matrices could be obtained using TPA, including hardness, springiness, gumminess, chewiness, cohesiveness, and adhesiveness (Wu et al. 2017). Among these parameters, (1) hardness is positively correlated to starch retrogradation and springiness shows a opposite trend (Yang et al. 2021); (2) cohesiveness is a parameter related to elasticity and intramolecular interactions, which determines the internal resistance of the starch under compression (Nishinari et al. 2019); (3) adhesiveness has been reported to correlate with sensory of many starch-based matrices such as rice (Nishinari et al. 2019); (4) gumminess (product of hardness and cohesiveness) is the energy required to disintegrate a gel; (5) chewiness (product of hardness, cohesiveness, and springiness) is the energy required to masticate a starch matrix (Mehboob et al. 2015). In addition, the strength, breaking stress, brittleness, and breaking distortion rate of starch could be obtained from puncture test and compression test.

These texture properties can be varied by multiple factors, such as amylose content, molecular weight, and additives (Ong and Blanshard 1995; Tao et al. 2019; Zhao et al. 2021). Tao et al. (2019) reported a positive correlation between the amylose content and the hardness of cooked rice. Starches of different sources (such as rice, quinoa, corn, and potato) could show significant differences in the texture features (Adawiyah et al. 2013; Wu et al. 2017). Adawiyah et al. (2013) confirmed that the gel from arenga starch was more rigid than that of sago starch at high concentrations, despite having a similar amylose content. The same results were seen for rice starch due to the molecular weight of amylopectin (Peng et al. 2021). The additives (e.g., sugars and tea derivatives) could affect the retrogradation of starch matrix and thus its hardness, springiness, and cohesiveness (Zhang et al. 2015, 2017).

3.4 Solubility and Swelling Power

Solubility and swelling power are key indicators to present the interaction between starch and water molecules. Solubility is the percentage of dissolved starch molecules at a certain temperature, corresponding to the degree of dissolution of starch molecular chains. Swelling power is the amount of water absorbed by per unit of starch, when it is heated in excess water at a certain temperature. This hydration (water-holding) property of starch is generally expressed as swelling power (*SP*) (Eq. (3.4)) and solubility (S_o) (Eq. (3.5)) in water at a certain temperature:

$$SP\ (\text{g/g dry starch}) = m_1/(m_0 - m_2) \tag{3.4}$$

$$S_o\ (\text{g/100 g dry starch}) = (m_2/m_0) \times 100 \tag{3.5}$$

Here, m_0 means the weight of starch in dry basis, m_1 is the weight of swollen starch, and m_2 is the weight of dissolved starch.

The *SP* and S_o values of starch are greatly influenced by the temperature. More specifically, starch granules are highly robust and impermeable to water at ambient temperature, which prevents starch-water interaction to absorb water and increase viscosity. In contrast, when heated in excess water above the melting point of starch crystallites, gelatinization occurs to sharply increase the solubility and swelling power. Other influencing factors include the amylose and amylopectin features (e.g., ratio, molecular weight, and chain length), the presence of other components (lipids and phosphates), and the granule structure. Also, processing (e.g., shearing and cooking) and storage can change starch solubility and swelling power (Majzoobi and Farahnaky 2021; Li et al. 2022). For instance, it was shown that the swelling power of wheat starch was correlated negatively with amylose content. An analysis of the amylopectin structure showed that starch with a higher swelling power tended to contain a higher proportion of long chains with a degree of polymerization ≥35 (Ge et al. 2022).

3.5 Hydrolysis and Degradation

Starch may be hydrolyzed and degraded under numerous conditions. This section presents the knowledge on the hydrolysis (by enzyme, acid, or alcohol acid) of starch and its degradations during processing (plasma, dry heat, heat-moisture, or thermomechanical treatment).

3.5.1 Enzyme Hydrolysis

In recent years, the enzyme hydrolysis (in vitro digestion) of starch has been widely investigated. The hydrolysis features of starch can be quantitatively studied based on the first-order kinetic functions (Eqs. (3.6) and (3.7)) and the associated logarithm of the slope (LOS) plot (Fig. 3.3) (Li et al. 2020):

$$C_t = C_\infty \left(1 - e^{-kt}\right) \tag{3.6}$$

$$\ln \frac{dC_t}{dt} = -kt + \ln(C_\infty \times k) \tag{3.7}$$

In which, C_t (%) represents the amount of starch hydrolyzed at a time point t (min); C_∞ (%) represents the estimated percentage of starch hydrolyzed at the end of a hydrolysis (digestion) period; k (min^{-1}) stands for the rate coefficient of the hydrolysis (digestion). Such hydrolysis (digestion) parameters of starch are often varied by influencing factors. For instance, the enzyme hydrolysis of starch granules tends to be largely affected by the polymorph type; the A-type starch can show a higher enzyme susceptibility than that of B-type starch, and an intermediate susceptibility between A- and B-type starches could be seen for C-type starch (Zhu 2018). Additionally, the presence of lipids and proteins could mitigate the enzyme hydrolysis (digestion) of starch associated with the complexation between starch chains and lipid/protein molecules (Zhang et al. 2022).

The enzymes commonly used for starch hydrolysis include α-amylase, glucoamylase, and pullulanase. The presence of ingredients like lipid, protein, and polyphenol usually has a negative influence on starch hydrolysis (Yu et al. 2018; Zhang et al. 2022). The protein especially the water-insoluble protein could retard the hydrolysis (digestion) of starch by α-amylase due to protein-enzyme binding events (Yu et al. 2018). Zhang et al. (2022) studied the effects of non-starch components and starch molecular structure on the α-amylase hydrolysis of starch; they found that the differences in the structure of amylose did not show significant effects on the hydrolysis, and a higher molecular density of corn amylopectin resulted in a lower hydrolysis degree, as compared to the counterpart in cassava and potato starch. In addition, the removal of protein had a significant promotion effect on starch hydrolysis but lipid removal only showed a slight effect (Zhang et al. 2022). However, the traditional hydrolysis of starch by enzymes may have

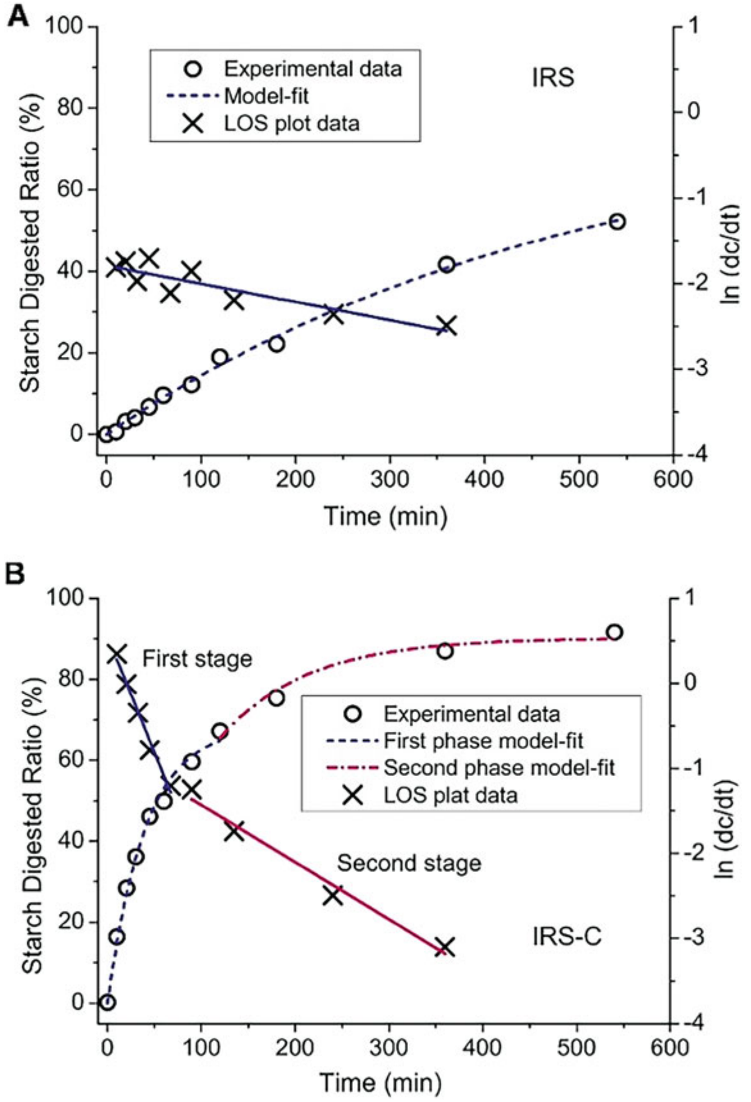

Fig. 3.3 Enzyme hydrolysis (in vitro digestion) data and related LOS plots of native indica rice starch (IRS) (**a**) and its cooked counterpart (**b**). Adapted from Li et al. (2020) with permission from Elsevier, Copyright 2020

disadvantages, such as high cost and slow kinetics; researchers tend to combine other techniques (such as ultrasound) with enzyme hydrolysis to make the starch hydrolysis cost-effective and efficient (Wang et al. 2017a, b). Activation of amylase with ultrasonication and Ca^{2+} ions could significantly increase the enzyme

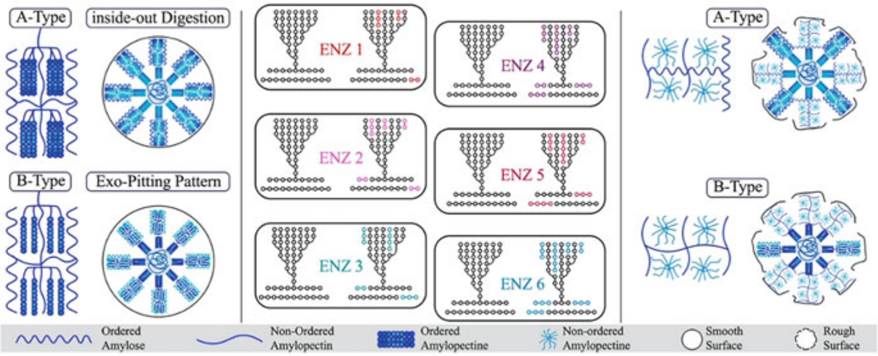

Fig. 3.4 Schematic representation of how activated amylase affects the enzyme hydrolysis of starch. Reprinted from Abedi et al. (2022) with permission from Elsevier, Copyright 2022

hydrolysis rate toward starch suffered from freezing-thawing pre-treatment (Fig. 3.4) (Abedi et al. 2022).

3.5.2 Acid Hydrolysis

To overcome the shortages of native starch (e.g., poor solubility and low shear resistance), acid hydrolysis has been widely practiced to improve the performance of starch and thus widen its industrial applications. The acid-treated starch shows changes in the features of gelatinization, retrogradation, and digestion (enzyme hydrolysis) (Li and Hu 2021). The acid treatment is conducted by exposing starch to mineral acids such as HCl, H_2SO_4, HNO_3, and H_3PO_4 at low temperature below the gelatinization point, and the degree of hydrolysis varies as a function of treatment time (Pratiwi et al. 2018). The acid hydrolysis of starch preferably starts from amorphous growth rings, followed by slow hydrolysis of semi-crystalline growth rings (Li and Hu 2021). Size-exclusion chromatography (SEC) can be used to characterize the chain lengths and molecule sizes of starch suffering from acid hydrolysis.

To inspect the hydrolysis patterns of amylose and amylopectin molecules, a first-order reaction model (Eq. (3.8)) and a linear model (Eq. (3.9)) are used to describe the acid hydrolysis data and the multiple steps during hydrolysis (Pinto et al. 2021):

$$C_p = C_0\left(1 - e^{-kt}\right) \tag{3.8}$$

$$\ln\frac{C_0}{C_0 - C_p} = kt \tag{3.9}$$

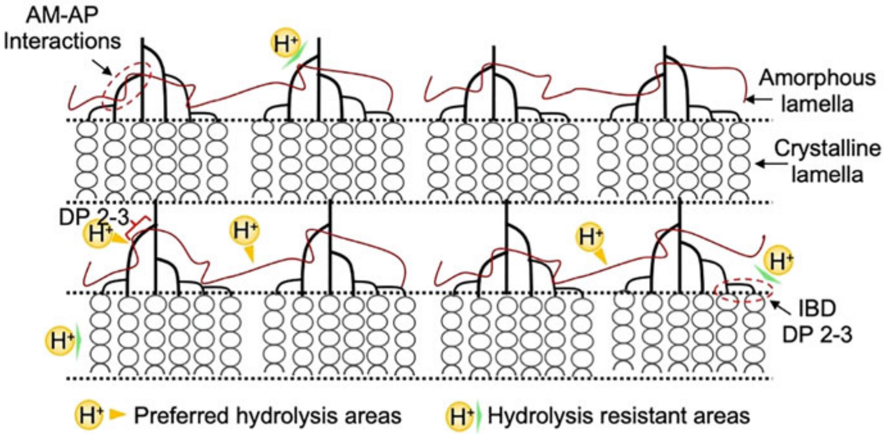

Fig. 3.5 Schematic representation for the hydrolysis pattern of hydrochloric acid on the amylose and amylopectin molecules in starch semi-crystalline lamellae. Reprinted from Li and Hu (2021) with permission from Elsevier, Copyright 2021

In these equations, C_p reflects the starch hydrolyzed at a time point; C_0 represents the initial percentage of starch hydrolysates; t and k stand for the reaction time (d) and the first-order rate constant (d^{-1}), respectively. Using the HCl hydrolysis pattern of amylose and amylopectin molecules as an example (Fig. 3.5), H^+ tends to hydrolyze the amylose long chains with DP $> \sim 300$ and the 2 or 3 glucose units away from the branching points of amylopectin long intra-cluster branches (Li and Hu 2021). The acid type, concentration, and hydrolysis time could affect the structure and functional properties of starch (Chen et al. 2017). The hydrolysis process exhibits two stages, including a first rapid stage (ascribed to the hydrolysis of amorphous layers of starch granules) and a second slower stage (related to the degradation of crystallites in starch granules) (Genkina et al. 2009). The acid hydrolysis pattern of starch is largely affected by amylose content; an exo-corrosion pattern for high amylose starch (G80) and an endo-corrosion pattern for waxy starch could be seen (Chen et al. 2017).

3.5.3 *Processing-Induced Degradation*

Starch may undergo degradation during processing, which plays a crucial role in determining the product processibility and quality. The starch chains have been found to be degraded by specific treatments such as extrusion, plasma treatment, and heat-moisture treatment.

It was found that starch underwent significant degradation during typical thermomechanical processing (extrusion) (Liu et al. 2010). While being extruded, the presence of high shear stress and temperature causes gelatinization and degradation of starch, while the rigid amylopectin crystallites are more susceptible to shear degradation than the flexible amorphous amylose (Liu et al. 2010). From a previous finding, the molecule degradation of starch during extrusion possessed the following features: (1) the size distribution of starch molecules gradually narrowed down as degradation proceeded; (2) the degradation was rapid at the beginning of extrusion and then slowed down with the size of the starch molecules decreased; (3) the sizes of amylopectin molecules (mainly larger than amylose molecules in size) became smaller and thus presented an apparent overlapping region with amylose molecules (Fig. 3.6a) (Liu et al. 2010). The molecule degradation of starch during extrusion predominantly occurred at the center of the chains, rather than the case that the outer chains were cleaved from the parent chain (Fig. 3.6b). For the same size, amylose was more stable than amylopectin with a given shear environment (Liu et al. 2010).

Plasma (the fourth state of matter) contains a variety of active substances (e.g., ions, electrons, and free radicals) (Wu et al. 2022), and has attracted great attention in the modification of starch. Plasma treatment (cold plasma) could alter the multi-scale structures (e.g., molecular structure, morphology, and crystallinity) of starch, and its properties (e.g., gelatinization and rheological features) (Gao et al. 2021; Okyere et al. 2022). In particular, the active species of plasma could not only endow starch with various chemical groups such as carboxyl, carbonyl, and peroxide groups (Gao et al. 2021), but also cause an evident degradation of starch chains (Okyere et al. 2022). Accompanying the starch degradation, plasma treatment could allow an increase in the proportion of linear chain fragments (Zhu 2015; Gao et al. 2019).

Heat-moisture treatment (HMT) is a typical modification method for starch, which is normally conducted at limited water levels (typically <35% w/w) and controlled temperature (below gelatinization point) and for 15 min to 16 h (Pratiwi et al. 2018). HMT could result in degradation of starch molecules, and the treatment effectiveness largely related to the starch features (e.g., botanical source, structure, and amylose content) and processing parameters (such as water content, temperature, and heating time) (Fonseca et al. 2021). In addition, dry heat treatment is a green method for starch physical modification and is conducted by heating starch at high temperatures (>100 °C) and low moisture content (<10%) for several hours, which can degrade starch chains into smaller parts and increased the flexibility of starch branches (Chi et al. 2019).

3.6 Summary

To rationally use starch resources, great efforts have been made to understand their physicochemical properties, mainly including gelatinization, pasting, solubility and swelling power, as well as hydrolysis and degradation characteristics. Multiple techniques (methods) (e.g., DSC, RVA, XRD, and rheometer) and theoretical models (e.g., Herschel-Bulkley model and first-order kinetic function) have been applied to inspect the starch properties mentioned above. Such physicochemical

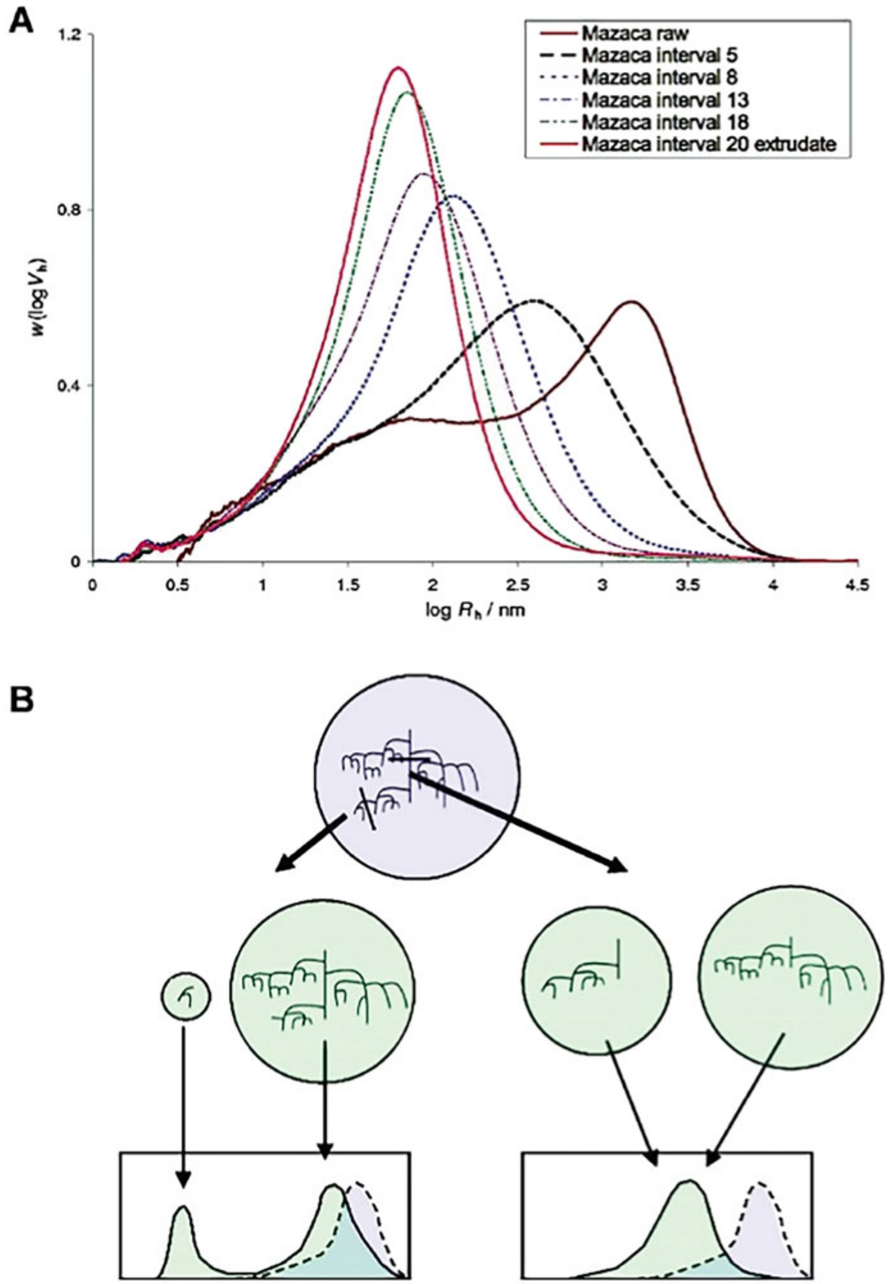

Fig. 3.6 Evolution of the size distribution of fully branched Mazaca starch that collected along the barrel of the extruder (**a**), and the different size distributions caused by the extrusion of intact starch molecules with different bond breaking positions (**b**). Reprinted with permission from Liu et al. (2010). Copyright (2010) American Chemical Society

features have close links to starch composition (e.g., amylose content) and structure (e.g., crystalline structure and granule structure), processing conditions (e.g., water content, temperature, and shear stress), and additives (e.g., alkalis, hydrocolloids, and lipids). Despite these advances, it is still highly necessary to disclose more correlations among processing conditions, starch-component interaction, starch-based matrix structure, and the resulting physicochemical properties.

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