Zhongquan Sui · Xiangli Kong *Editors*

Physical Modifications of Starch

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Preface

Starch is one of the most abundant biopolymers in nature. It has wide applications in food and nonfood products. However, native starch has limitations that restrict its applications to a certain extent. Generally, starch was firstly modified to improve its functionality by physical, chemical, enzymatic, and biotechnological methods. Physical modification attracted more interests to the food industry in recent years because the starch product does not need to be labeled as a modified starch.

This book summarizes recent progresses achieved in starch modifications by physical methods; each chapter focuses on one thermal treatment (i.e., pregelatinization, heat-moisture treatment, annealing, microwave heating) or one non-thermal treatment (i.e., gamma irradiation, ultrahigh pressure treatment, ultrasonic treatment, milling), except the first chapter that gives basic information about structural and functional properties of starches. Mechanism of each treatment and changes in starch structure, functionalities, and potential applications of modified starch in industry are reviewed in chapters.

We would like to thank all the contributors who wrote the chapters that made this book come into reality. We sincerely hope this book will be a useful reference for graduate students, researchers, and product developers in related fields.

Shanghai, China
Hangzhou, China
January 2018

Zhongquan Sui
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Chapter 1
Structure and Physicochemical Properties of Starch

Fan Zhu and Qian Xie

Abstract Starch is a major component of many food products. It is also an important industrial ingredient for many different applications. Understanding the composition, molecular and granular structure, and physicochemical properties of starch contributes to the processing of starch for different uses. There are great variations in properties and structure of starches from different sources. This chapter reviews the basics of starch structure and physicochemical properties, providing a fundamental basis to better understand the contents of the other chapters of this book.

Keywords Cluster structure · Genetic variation · Starch · Structure · Physicochemical property

1.1 Introduction

Starch is a major component of many food products such bread and rice. The properties and structure of starch are critical for quality of the food products. Starch is also an important industrial ingredient for many different applications. Starches with industrial significance are from maize, potato, cassava, wheat, and rice. There are other starches from other botanical sources such as sweet potato and quinoa with local significance and commercial potential. These “new” starches have been gaining interest both from academia and industries. Native starch has limited functionalities and is commonly modified for desired properties. Understanding the composition, structure, and physicochemical properties of starch contributes to the processing and applications of starch for different uses. This chapter reviews the basics of starch structure and physicochemical properties, providing a fundamental basis to better understand the contents of the other chapters of this book. This chapter is useful for researchers without a starch chemistry background. Sweet potato starch is often employed as an example starch system after a general introduction of an aspect of starch due to its unique yet typical position among diverse starches.

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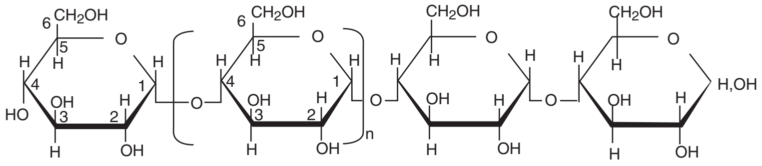
1.2 Starch Composition

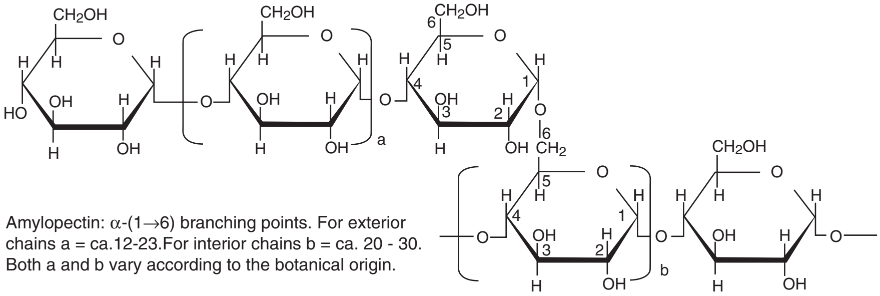
1.2.1 Main Components of Starch

Starch is an abundant biomolecule found in many crops. Amylose and amylopectin are the two major components of starch. Amylose is a linear polymer with small side branches, which are composed of glucan chains joined by α-(1–4) linkages. The molecular weight of amylose ranges from 10^5 to 10^6 Da (Hoover 2001). Amylopectin is a highly branched polymer that consists of short chains of glucan joined by α-(1–4) linkages and α-(1–6) linkages at their branches (Zhu and Wang 2014). The average molecular weight of amylopectin ranges from 10^7 to 10^9 Da (Tester et al. 2004). Figure 1.1 summarises amylose and amylopectin structure. Starch's amylose content is highly dependent on the botanical origin and can range from less than 1% to 80% (Zhu et al. 2017).

Amylose and amylopectin properties have a great impact on starch properties. For example, the amount of amylose as well as the entanglement between amylose/amylose and amylose/amylopectin greatly affect the water-binding capacity, thermal properties, and enzyme susceptibility (Naguleswaran et al. 2010; Zhu and Wang 2014; Li et al. 2016; Zhu et al. 2017).



Amylose: α-(1→4)-glucan; average n = ca. 1000. The linear molecule may carry a few occasional moderately long chains linked α-(1→6).



Amylopectin: α-(1→6) branching points. For exterior chains a = ca.12-23.For interior chains b = ca. 20 - 30. Both a and b vary according to the botanical origin.

Fig. 1.1 Structure of amylose and amylopectin. (Reprinted with permission from Tester et al. (2004). Copyright 2004, with permission from Elsevier)

1.2.2 Amylose Content of Starch

Amylose is one of the major components in a starch granule, which contributes greatly to the starch's functional properties. For example, it has been reported that amylose content is significantly associated with swelling power, gel strength, pasting, enzyme susceptibility, and thermal properties (Zhu and Wang 2014; Chen et al. 2003; Waramboi et al. 2011).

Amylose concentration in starch can be measured using several methods. One of the most popular ways is an iodine-binding based technique. It is well known that the formation of iodine-amylose complexes exhibits a blue colour, which can be measured by colorimetry. However, this technique is not consistently accurate for many reasons such as the presence of long-chain polymers, the selection of standards, and the degree of polymerisation (Gibson et al. 1997; Zhu et al. 2008). As a result, the amylose content of starch as measured by the iodine-binding technique in this study is referred to as apparent amylose content. Gel permeation chromatography is another way to measure the amylose content of starch. Gel permeation chromatography not only measures the amylose content of starch but also allows determination of different chain distributions such as long-chain amylopectin and amylose. However, this method is labour-intensive and time-consuming (Zhu et al. 2011b, 2013a). The Megazyme amylose kit is also used to determine the amylose content of starch. The principles of the method are based on the amylopectin precipitation with concanavalin A lectin. However, this method requires precise experimental control and can be costly (Zhu et al. 2008).

Great variations in amylose content among different starches have been reported by many studies (Abegunde et al. 2013; Zhu et al. 2011b; Waramboi et al. 2011). For example, in general, the amylose content of sweet potato starches can vary from 8.5% to 37.4% (Chen et al. 2003). This significant variation is attributed to many factors, including genotypic difference, growing conditions, and measurement techniques. Table 1.1 shows a good example that the amylose contents of sweet potato starches vary between different genotypes and measurement techniques.

1.2.3 Minor Components of Starch

Besides amylose and amylopectin, starch also contains some minor components such as proteins, lipids, and minerals. The amount of minor components is not only related to the botanical source of the starch but is also affected by other factors such as growing season and isolation techniques (Zhu 2015).

Although the concentration of minor components is usually low in starch, they may dramatically affect starch's properties. The phosphorus is found in different starches in the form of phospholipids, inorganic phosphates, and phosphate monoesters (Pérez and Bertoft 2010; Tester et al. 2004). For example, the phosphorus content of sweet potato starch ranges widely from 9 to 22 mg per 100 g (Tian

Table 1.1 Amylose contents of sweet potato starches

Genotype	Geographic origin	Category	Code	Moisture (%)	AAM content (i)[a] (%)	True AM content (i)[b] (%)	AAM content (g)[c] (%)
E6107b	Hubei	Landrace	1	10.9	25.6a	22.5a	19.8b
E6107a	Hubei	Breeding line	2	9.5	25.5a	19.3b	23.0a
Yuzi263	Chongqing	Cultivar	3	10.0	26.5a	20.1b	19.4b
Xuzi13–4	Jiangsu	Cultivar	4	10.2	24.9ab	19.5b	22.3ab
E5306	Hubei	Breeding line	5	9.9	25.9a	17.1c	21.3ab
Eshu–6	Hubei	Cultivar	6	9.9	24.8ab	18.3bc	21.8ab
Ea2	Hubei	Landrace	7	9.8	25.8a	22.0a	22.2ab
Ea3–1	Hubei	Landrace	8	10.0	26.3a	22.1a	23.9a
Ea4	Hubei	Landrace	9	10.8	25.4a	21.1ab	21.5ab
Ea3–2	Hubei	Breeding line	10	10.4	26.0a	20.1b	22.5ab
Xushu22	Jiangsu	Cultivar	11	10.0	23.3b	15.9d	17.5c
Mean				10.1	25.6	19.8	21.4

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Values in the same column with the different letters differ significantly ($p < 0.05$)

[a] Amylose content measured by iodine-binding method

[b] Amylose content measured by concanavalin A-binding method

[c] Amylose content measured by gel permeation chromatography of debranched starch

et al. 1991). In comparison with starches from other crops, the phosphorus content of potato starch is much higher (Tian et al. 1991; Moorthy 2002). The amount of phosphorus is highly related to some starch properties. High phosphate levels increase starch viscosity, clarity, and swelling but impede starch retrogradation (Tester et al. 2004; Chen et al. 2003). The high phosphorus content can also improve gel strength, which is preferable for some food applications such as jelly (Moorthy 2002). However, the phosphorus in the form of phospholipids has been reported to reduce starch gel clarity (Pérez and Bertoft 2010).

Lipids, in the form of free fatty acid and phospholipid, are also found in most starches (Pérez and Bertoft 2010). The fatty acid chain of lipids can form a lipid-amylose complex with the amylose. The lipid-amylose complex has been reported to result in low clarity and slow swelling of the starch (Chen et al. 2003). Moreover, the presence of the complex can also reduce starch's iodine-binding capacity (Tester et al. 2004). In general, the amounts of lipid present in cereal starches are higher than starches found in potatoes and legumes (Pérez and Bertoft 2010). The proportion of lipid-amylose complexes presented in cereal starch ranges from 15% to 55% of amylose fraction as reported in a previous study (Tester et al. 2004).

The protein content of starch is often in the range of 0.1–0.7% by weight and can be found at both the surfaces and interior parts of the starch granule (Pérez and

Bertoft 2010). High protein content can increase hardness of cereal grains and often leads to a high cost of starch isolation, which is not suitable for some food applications (Pérez and Bertoft 2010; Tester et al. 2004). The browning reaction of some starches (e.g. sweet potato) is also partially related to its high levels of polyphenol oxidase in addition to phenolic compounds. This reaction may affect starch quality and reduce its commercial value (Chen et al. 2003).

1.3 Starch Structure

1.3.1 Molecular Structure of Amylopectin

The structure of amylopectin is considered to be one of the important factors that affects the physicochemical properties of starch. Amylopectin chains are often classified into three main groups called A, B, and C chains (Peat et al. 1952). A chains are the external chain that form links to other chains but do not carry other chains, whereas the B chains link to and also carry other chains. The C chain is a single long chain that has one reducing end group in the amylopectin molecule (Bertoft et al. 2008; Srichuwong and Jane 2007; Eliasson 2004).

The molecular structure of amylopectin can be detected by several methods such as size-exclusion chromatography, high-performance liquid chromatography, and high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Hanashiro et al. 1996). Amylopectins can be debranched by isoamylase and/or pullulanase, and their unit chain profiles can be estimated by HPAEC-PAD. The proportions of unit chains are categorised into four main fractions by weight or molar concentration (Zhu et al. 2011a). Beta-limit dextrins (β-LDs) can be produced by removing amylopectin's external part using β-amylase. The internal molecular structure of amylopectins is estimated by HPAEC-PAD after β-LDs debranching. Based on the parameters obtained from unit chain length compositions of β-LDs, the proportions of A and B chains can be estimated, and various amylopectins can be characterised into groups 1–4 as proposed in previous studies (Bertoft et al. 2008). It has been reported that the A-type starch often belongs to the group 1, whereas the B-type starch often belongs to the group 4 due to its high proportion of long B chains (Bertoft et al. 2008).

The branches of amylopectin are clustered and organised into "building blocks". The structure of building blocks and clusters can be studied by using α-amylase of *Bacillus amyloliquefaciens*. A procedure is schematically illustrated in Fig. 1.2 (Zhu et al. 2013b). There has been increasing evidence to support the building block and backbone model of amylopectin. Bertoft (2017) systematically reviewed this model.

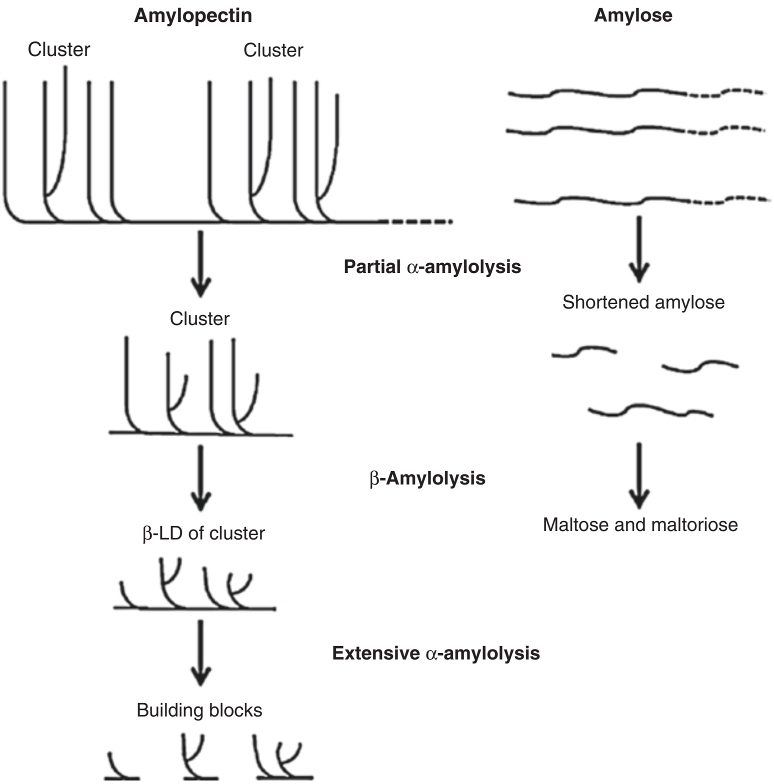

Fig. 1.2 Enzymatic studies of clusters and building blocks from starch without amylose and amylopectin separation. (Reprinted with permission from Zhu et al. (2013b). Copyright 2013, with permission from Elsevier)

1.3.2 Morphology of Starch Granule

The starch granule structure has been well investigated in many studies. In general, the semi-crystalline starch granule consists of amylopectins and amylose (Jane et al. 2003). The starch granules are often described according to many characteristics, including their shape, size, distribution, polymorphism, and crystallinity (Zhu and Wang 2014). These features are highly related to a range of factors such as botanical origin, growing conditions, and plant physiology (Abegunde et al. 2013; Zhu 2015).

The particle size analyser and scanning electron microscope (SEM) are often used to analyse the starch granule's size and form (Huang et al. 2006; Zhu 2015). The granule size of starches varies widely, ranging from 1 to 100 μm in diameter (Tester et al. 2004; Pérez and Bertoft 2010). The granule sizes of starches from different plants differ (Peroni et al. 2006). For example, in general, the granule size of sweet potato starch is similar to that of cassava starch but much smaller than the potato starch (Chen et al. 2003; Moorthy 2002). The starch's granule size is related to some functional starch properties such as the swelling, solubility, and enzyme susceptibility (Moorthy 2002; Qi and Tester 2016).

Many shapes can be found in starch granules. In general, most of the starch granules are oval, round, and spherical in shape, but polygonal and irregular shapes are also found (Hoover 2001). For example, the shapes of the sweet potato starch granules are diversely round, spherical, oval, and polygonal which are more irregular than potato and amaranth starch granules (Zhu et al. 2011a; Kim et al. 2013). Jane et al. (1994) systematically documented the starch granule morphology of many different types by SEM.

1.3.3 Starch Polymorphism

Starch granules are semi-crystalline, which consists of amorphous and crystalline lamellae. Amylopectin chains are packed in clusters, which contribute to the formation of these amorphous and crystalline lamellae (Srichuwong and Jane 2007). Figure 1.3 exhibits the semi-crystalline structure of starch described above.

The polymorphism of starch is determined by the mode of amylopectin and water packaging. The A-type starch has relatively compact double-amylopectin helices with low water content, while the double helices of the B-type starch have a looser structure and high water content (Tester et al. 2004). The C-type polymorph, which consists of a combination of A and B types, has also been observed in many studies (Lee and Lee 2017; Moorthy 2002). The C-type polymorph is further divided into C_a, C_c, and C_b based on whether the C-type polymorph is similar to the A- or B-type polymorph (Kim et al. 2013). Sweet potato starches have been reported to possess A, C_a, and C_b by many investigators (Moorthy 2002; Lee and Lee 2017; Kim et al. 2013).

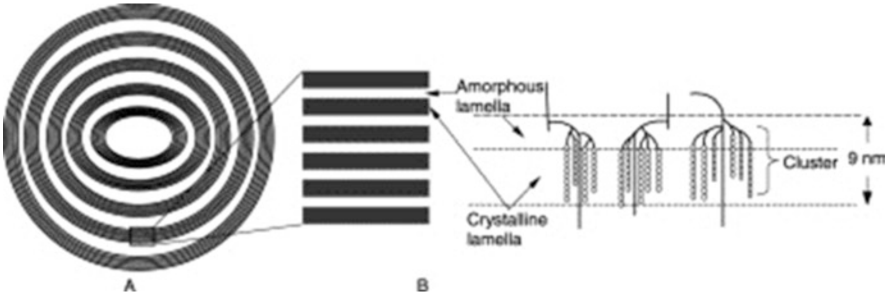

Fig. 1.3 The semi-crystalline structure of starch granule. (**a**) Growth rings formed by repeating crystalline and amorphous lamellae; (**b**) packing of amylopectin in the cluster. (Adapted from Tester et al. (2004); reprinted with permission from Elsevier)

1.4 Physicochemical Properties of Starch

1.4.1 Starch Swelling

Starch can become swollen by heating the starch with an excess amount of water. The water-holding properties of starch is generally expressed as swelling power (SP) and water-soluble index (WSI) (Abegunde et al. 2013; Zhu and Wang 2014). Starch swelling is highly temperature dependent in that both SP and WSI tend to increase with a corresponding increase in temperature (Lawal and Adebowale 2005). High temperatures tend to disrupt the crystalline structure of the starch, which promotes hydrogen bonding between water molecules and amylose/amylopectin (Hoover 2001).

There is great diversity in SP and WSI among starches as reported by many studies (Zhu et al. 2011b; Abegunde et al. 2013; Zhu and Wang 2014). Differences in SP and WSI among starches reflect the variation in their water-holding capacities. The variation can be affected by many factors, including amylose and amylopectin properties (ratios, molecular weight, chain length, and others), the presence of minor components (lipids, phosphates), and the granular structure of starch (Beta et al. 2001; Li and Yeh 2001; Abegunde et al. 2013). Different sample pretreatments could also contribute to variations observed among various studies (Beta et al. 2001). A two-stage swelling pattern of some starches has been reported, which suggests that the starches have some different mechanisms of interacting forces related to its swelling behaviour (Chen et al. 2003).

1.4.2 Gelatinisation and Retrogradation of Starch

When starch granules are heated to a specific temperature with sufficient water, the starch granules swell and rapidly lose their semi-crystalline structure. This process is called gelatinisation. The process is vital for the utilisation of starch in both food and non-food applications (Genkina et al. 2014). The loss of crystalline structure within the starch granule can result in many changes in their functional properties including starch swelling, pasting, and birefringence (Singh et al. 2003).

The enthalpy change of gelatinisation and gelatinisation temperatures of starch can be quantified by differential scanning calorimetry (DSC) during heating in excess water, which has been commonly used in many related studies. Gelatinisation transition temperatures such as onset (T_o), peak (T_p), conclusion temperatures (T_c), and the gelatinisation enthalpy (ΔH) are the common parameters measured by DSC (Vamadevan and Bertoft 2015). Techniques such as polarised light microscopy and nuclear magnetic resonance spectroscopy have also been used in some studies (Ai and Jane 2015). Great variations in gelatinisation properties have been reported for different starches from previous studies. In general, most of the starches have the gelatinisation temperatures between 60 and 80 °C, and A-type starch often has higher gelatinisation temperatures than B type (Copeland et al. 2009; Tian et al. 1991). However, some exceptions have been reported in a recent study in which starches with an extremely high amount of amylose exhibit much higher gelatinisation temperatures (Ai and Jane 2015). The gelatinisation temperature of starch is affected by multiple factors, including molecular structure, minor components, and growing environment of the crop (Abegunde et al. 2013; Singh et al. 2003; Ai and Jane 2015).

Starch retrogradation can be measured by the same techniques used for gelatinisation of starch. Retrogradation of starch is a phenomenon that the structure of gelatinised starch is partially reordered and recrystallized over a period of storage. The variation in retrogradation of starches is related to many factors, including amylose/amylopectin ratio, the presence of lipids, molecular size, and temperature (Tian et al. 1991; Singh et al. 2003). The amylose/amylopectin ratio is one of the most important factors for the starch retrogradation because amylose retrogrades much faster than the amylopectin (Copeland et al. 2009). Starch retrogradation is an important feature for the applications of starch because the properties of starchy food such as stickiness, digestibility, and hardness can be affected by starch retrogradation (Copeland et al. 2009; Ishiguro et al. 2000). It has been reported that bread containing sweet potato flour has a slower staling rate than other breads due to its relatively low rate of retrogradation (Rosario and Pontiveros 1983).

1.4.3 Rheological Properties of Starch

1.4.3.1 Pasting Property of Starch

Pasting is a process that measures the sample viscosity during and after gelatinisation. For the analysis of starch pasting, a starch suspension is stirred and examined with a viscometer under programmed heating and cooling conditions (Collado et al. 1999). During heating, the starch granules swell, lose their granular structure, and eventually rupture. Paste viscosity increases to a maximum when the percentage of swollen starch granules is at maximum but decreases as the starch granules rupture. During cooling, a gel is formed due to starch retrogradation (Copeland et al. 2009; Ai and Jane 2015). A typical pasting profile with common parameters measured by rapid visco analyser (RVA) is displayed in Fig. 1.4. Starch pasting can be classified as types A, B, C, and D based on their pasting characteristics. Multiple types of sweet potato starch pasting have been observed in previous studies (Chen et al. 2003; Waramboi et al. 2011). There are many factors that can affect the pasting properties of starch, including particle size, presence of impurities, and amylose content. Different methodologies and experimental parameters used in various studies such as pH, sample concentration, temperatures, and shear rates can also affect the results of pasting properties (Waramboi et al. 2011; Chen et al. 2003).

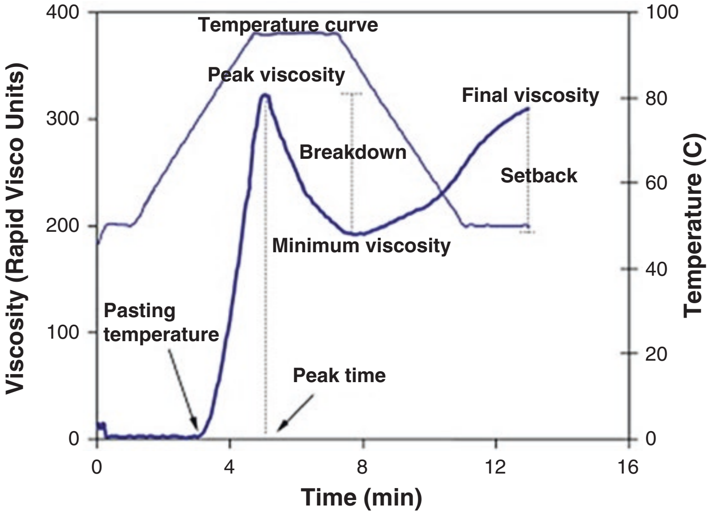

Fig. 1.4 Pasting profile of rice starch measured by RVA. (Adapted from Copeland et al. (2009); reprinted with permission from Elsevier)

1.4.3.2 Flow Behaviour of Starch

Starch's flow behaviour can be determined from the relationship between starch shear rate and apparent viscosity of starch paste (Nurul et al. 1999). The power law, Herschel-Bulkley and Bingham models are the common models used to express the flow behaviour of starch (Ai and Jane 2015; Kong et al. 2010). Starch's flow behaviour is critical to many applications as it relates to the suspending properties of product at different shear rate (Nurul et al. 1999). Starch pastes are reported to have a non-Newtonian and shear-thinning behaviour by previous studies (Zhu et al. 2016; Kong et al. 2010). The differences in viscosity among starch pastes are significantly related to their starch concentration, amylose content, and temperature (Ai and Jane 2015).

1.4.3.3 Dynamic Oscillatory Analysis of Starch

Dynamic rheological analysis can be used to characterise the viscoelastic properties of starch by continuous modulus analysis during heating and frequency sweep testing (Singh et al. 2003). The storage modulus (G'), loss modulus (G''), and the loss tangent (*tan* δ = ratio of G''/G') are commonly used to represent the viscoelastic properties of starch. The energy stored in and recovered from the starch gel per cycle of deformation is measured by G', while the energy dissipated or lost per cycle of deformation is measured by G'' (Wu et al. 2016; Ai and Jane 2015). The *tan* δ is used to represent the relationship between G' and G'' in which a starch gel with low tan δ is harder and more solid than the starch gel with high *tan* δ (Singh et al.

2003). The values of G' and G'' are related to multiple factors such as the granule size, amylose/amylopectin ratio, and the methodologies (Zhu et al. 2016; Ai and Jane 2015; Singh et al. 2003).

1.4.3.4 Gel Textural Properties of Starch

Starch gel produced after the pasting analysis can be further studied by using texture profile analysis (TPA). The starch gel is compressed and the texture is evaluated by using a probe. Parameters such as hardness, adhesiveness, and cohesiveness are recorded or calculated to evaluate the textural properties of starch gel (Karunaratne and Zhu 2016). Variations in the textural properties of starches (sweet potato, amaranth, maca, and quinoa starches) have been reported in some studies. These findings suggest that textural properties of starches are related to multiple factors including amylose content, cultivar differences, molecular weight of amylopectin, and gel pretreatment (Zhu et al. 2011a, b; Zhu 2017; Li et al. 2016).

1.4.4 Enzyme Hydrolysis of Starch

Hydrolysis of starch is an important way to gain energy for metabolism in plants and animals. The starch can be hydrolyzed into low-molecular carbohydrates such as glucose and maltose (Djabali et al. 2009). The rate of starch digestion is highly related to the blood glucose level, which is important for the human health (Zhou et al. 2010). The starch susceptibility to enzyme hydrolysis has been reported to be affected by several factors, such as the starch crystalline, polymorph, morphology of starch granules, amylose/amylopectin content, and starch origins (Djabali et al. 2009; Srichuwong and Jane 2007; Zhou et al. 2004). The digestibility of sweet potato starch exhibits great variations from 27.3% to 41.2% or 48–75 g per 100 g in different studies (Yussof et al. 2013; Zhu et al. 2011a, b; Liu et al. 2010). However, the direct comparison of the results of different studies is impeded by the various methodologies applied in the studies. The digestibility of starches is much related to the starch polymorph. C-type starch tends to have a lower digestibility than A-type starches but higher than B-type starches (Jane et al. 2003).

1.5 Concluding Remarks

Starch is simple and complex. It is simple in the sense that it is made of only glucose unit. It is rather complex due to the multiple levels of structures from the glucose, to the molecules, and finally the granules. Some of the detailed structure of starch remain to be better explored. There are many different techniques to explore different aspects of starch gelatinisation and retrogradation. There is a great variation in the composition, chemical and granular structure, and physicochemical properties of starches from different botanical sources. Such a variation should be taken into consideration as it contributes to the outcomes of modifications of starch functionalities.

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Chapter 2
Heat-Moisture Treatment of Starch

Anil Gunaratne

Abstract Heat-moisture treatment (HMT) is a physical modification method that can be employed to modify the starch structure and functional properties without destroying the starch granular structure. In HMT, starch is exposed to a high temperature, commonly above the gelatinization temperature with insufficient water to gelatinize. Changes in X-ray pattern, crystallinity, starch chain interactions, swelling, amylose leaching, gelatinizing, pasting, gelling and digestible properties of starch have been shown to occur during HMT. These changes have been found to vary with the source of starch, moisture content, incubation temperature and time. During HMT, structural arrangement that occurred in starch chains within the crystalline and amorphous domains of starch granule modifies the physicochemical properties of starch.

Keywords Heat-moisture treatment · Starch · Properties

2.1 Introduction

Starch is a polysaccharide stored in plant tissues such as tubers, roots, stems, seeds, and grains and is the second largest biomass produced on Earth next to cellulose. Starch is widely used in food and non-food industry. Granules are the basic physical structural units of starch. Functionality is the key to utilizing starches in the wide range of food applications such as specific viscosity, mouth feel, freeze-thaw stability, clarity, emulsion stability, color, and film-coating properties. These properties have shown to be influenced by composition, morphology, and molecular arrangement amylose and amylopectin (Hoover 2010). The granules are partially crystalline and insoluble in cold water, and their size shape and composition are essentially genetical. Starch granule may be spherical, oval, polygonal, disk, kidney, or elongated (Jane et al. 1994). In general cereal starch granules are small and polyhedric,

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whereas tuber and root starch granules are large and spherical or ellipsoid. Native starches usually do not possess desirable functional properties such as thermal, shear, and acid stability and solubility in cold aqueous liquids and resistant to phase separation (retrogradation) and thus need some sort of value addition through the modification. Modified starch plays a major role in food applications as functional ingredients. Starch is modified mainly either by chemically or physically to improve the functionality. But most starches presently used in food applications are chemically modified. Physical modification is favored with the growing demand generated for nontoxic consumer safety foods. Hydrothermal treatments, mainly heat-moisture treatment and annealing, can modify functional properties of starch without destroying the starch granular structure. In heat-moisture treatment, starch is incubated at low moisture level (<35% water w/w) to a certain period of time, at temperature higher than the glass transition temperature but lower than the gelatinization temperature, and thus, heat-moisture treatment occurs below the onset of starch gelatinization.

2.2 Properties of Amylose and Amylopectin and Starch Structure

Amylose and amylopectin are the major constituents of starch. Minor component of amylose containing about 20–30% is consisted mainly of α-(1–4) linked glucose units and thus often refers as linear polymer. However the presence of slight degree of branching has been reported having α-(1–6) branch points. Hizukuri et al. (1981) reported slight degree of branching (9–20 branch point per molecules) in amylose from starches of several plant sources. The side chains range in chain length from 4 to over 100 (Hizukuri et al. 1981; Takeda et al. 1987), and a decrease in β-amylolysis limit has been shown with increase in molecular size of amylose (Greenwood and Thompson 1959). The degree of polymerization (DP) which is differed both between and within plant species is more frequently used to denote the size of the polymers than molecular weight (Perez and Bertoft 2010). The DP of this linear molecule is about 500–600 units (Jacobs and Delcour 1998). The molar fraction which varies from 0.1 to 0.7 in branched amylose generally has higher molecular weight than linear polymer (Takeda et al. 1987). Incomplete conversion of amylose to maltose by the exoenzyme β-amylase indicates the presence of branch points (Morrison and Karkalas 1990). Though slight branching is present, amylose essentially behaves like a linear polymer forming films and complexes with ligands (Biliaderis 1998). The confirmation of amylose has been the subject to controversy and has been shown to vary from helical to an interrupted helix to a random coil. Two important features of amylose in solution that determine the applicable functionality of this polymer in starch-based food products are its ability to form helical inclusion complexes when an appropriate ligand is present and the interchain associations mediated by local ordering of the polysaccharide chains (Biliaderis 1998). Single amylose chains have unique ability to complex with ligands such as monoacyl lipids and emulsifiers and smaller ligands such as alcohol and flavor. When amylose forms complexes with various ligands crystalographically distinct structure of starch, the V polymorph is formed (Biliaderis 1998). Depending on the size of the complexing agents, the amylose helices of six, seven, and eight glucose residues per turn can be seen (Perez and Bertoft 2010). When the ligand is bulkier than a hydrocarbon chain, helices of seven or eight glucose residues per turn are also formed (French and Murphy 1977). The typical chain conformation of V-amylose is a left-handed single helix with six residues per turn, and the pitch height varies between 7.92 and 8.04 Å (Perez and Bertoft 2010). X-ray diffraction patterns of granular starches do not usually show the presence of V-structure with the exception of wrinkled pea starch, amylomaize, and some other maize genotypes (dull, au) (Zobel 1988, 1992; Gernat et al. 1993). The lack of V-type characteristics is not because of the absence of amylose-lipid complex but due to the fact that the absence of organized helices into well-defined three dimensional structures (Biliaderis 1998). Development of V-type polymorph can be induced by heat-moisture treatments of starch (Zobel 1988) and by extrusion cooking (Mercier et al. 1980) or by simply gelatinization and cooling of starch dispersions. In the solution behavior, interchain association of amylose occurs forming double helices over chain segments less than 100 units (Biliaderis 1998). Concentration and chain length of amylose play important roles in the solubility and molecular association/crystallization of amylose (Gidley and Bulpin 1989; Pfannemuller et al. 1971). In the location and state of amylose within the starch granules, it has been reported that amylose is more concentrated at the periphery of the starch granules (Boyer et al. 1976). According to the cross-linking studies done on maize and potato starch by Jane et al. (1992), amylose was cross-linked with amylopectin and that there was no cross-linking between amylose molecules. After critically analyzing the current wisdom of the location and state of amylose in the starch granules, Perez and Bertoft (2010) explained that individual radial-oriented amylose is randomly distributed among the radial amylopectin chains.

Amylopectin, the major extensively branched component of starch granule, is reported to have *Mw* 60-10^6 -110×10^6 (Aberle et al. 1994). The polymer is composed of linear chains [glucose residues contented with α-(1,4) glycosidic bonds] contacted through α-(1,6) linkages (4–5%) forming a highly branched compact molecule (Biliaderis 1998). The molecular structure of the highly branched large molecule of amylopectin is more complex than that of amylose. The amylopectin chains are grouped into certain categories in order to distinguish the unit chain composition. According to Hizukuri (1996) amylopectin unit chains can be categorized into A-, B-, and C-chains. The unbranched A-chains are linked to B-chains and do not carry any other chains; the B-chains (B1–B4) carry one or more A-chains and/or B-chains, while the C-chain contains the reducing end group of the molecule. The shortest chains (A and B1) have chain length (CL) of 14–18, while the longest B2–B4 have CL of 45–55. For most amylopectin, the average chain length ranged 17–26 depending on the type of crystallinity (Perez and Bertoft 2010). The reported values for weight-average chain length of amylopectin of A-, B-, and C-type starches were in the ranges 23–29, 30–44, and 26–29, respectively, and, in general, A-crystalline starch contains shorter CL than B-types (Hizukuri 1985). The average CL of amylopectin poorly reflects the true structure since all samples (normal types of starch) of amylopectin pose at least two major groups: long and short chains (Perez and Bertoft 2010). The shortest reported CL for any amylopectin sample is six (Koizumi et al. 1991)

Though detailed information of structural properties of starch polymers have been extensively studied and characterized, the molecular order of the starch granules (arrangement of amylose and amylopectin within the granule), which governs the physicochemical properties of native starch, is still under investigation. In the semicrystalline structure of starch granule, the crystalline lamellae exist in the granule alternatively with amorphous lamellae (Donald et al. 1997). The combined thickness of crystalline lamellae plus amorphous lamellae is 9 and 9.2 nm for A-type starches and B-type starches, respectively (Jenkins et al. 1993; Jane et al. 1997). Clusters of amylopectin short chains occur within the crystalline domains of the granule (Yamaguchi et al. (1979). The amorphous region that has been shown to be very susceptible to chemical and enzymatic modification (Hood and Mercier 1978; Robyt 1984) accounts for 70% of the starch granule (Oostergetel and Van Bruggen 1993) and consists of free amylose, lipid-complexed amylose, and some branch points of amylopectin (Hizukuri 1996). Amylopectin molecules are involved in the granule crystallinity intertwining short linear chains of the branches forming double helices and clusters, and α-(1,6) branch points are located in more amorphous region between the clusters of double helices (Robin et al. 1975; Perez and Bertoft 2010). The double-helical clusters are packed together to form alternating crystalline and amorphous lamellae. Starch is classified according to the packing arrangement of the amylopectin double-stranded helices in the granules, namely, A-, B-, and C-type as determined by X-ray diffraction patterns. The A-type crystallinity is found mainly in cereal starches and is characterized by peaks at 15, 17, 18, 20, and 23 2θ angles (Zobel 1988; Cheetham and Tao 1998). Typical B-type X-ray pattern can be seen from most of the tuber and root starches (Zobel 1988) with peaks that are both broad and weak with two main reflections centered at 5.5 and 17 angles. The C-type starches are mixtures of A-type and B-type starches having special properties according to the distribution and proportion of A- and B-type polymorphs (He and Wei 2017). Bogracheva et al. (1998) showed that in C-type starches, the B polymorphs are arranged centrally, while the A polymorphs are located peripherally within the granules. The amylopectin of A-type starches has a close packing arrangement compared with that of B-type starches. The calculation of starch crystallinity and the correlation of double-helical content to the crystallinity have been developed combined with the use of X-ray diffraction with solid NMR (Lopez-Rubio et al. 2008). The contribution of different crystal polymorphs of starch to the total crystallinity can be calculated from this novel method.

2.3 Heat-Moisture Treatment

Heat-moisture treatment of starches is defined as a physical modification that involves incubation of starch granules at low moisture level (<35% water w/w) during a certain period of time, at a temperature above the glass transition temperature but below the gelatinization temperature (Hoover 2010).

2.3.1 Impact of HMT on Granule Morphology

Granule morphology, size and distribution, and surface characteristics play an important role in some food and non-food applications. Changed or unchanged granular morphology of HMT starches seems to be affected by the heating temperature, the moisture content, and the type of starch. Granule morphology of maize, wheat, potato, yam, lentil, and breadfruit starches has shown to remain unchanged after HMT (Kulp and Lorenz 1981; Stute 1992; Hoover and Vasanthan 1994; Franco et al. 1995; Hoover and Manuel 1996; Tan et al. 2017) However, HMT performed on rice starch of varying amylose content at 110 °C with 25% moisture has exhibited aggregated granules with irregular surface, and in the case of low amylose rice starch, signs of loss of physical integrity, characteristics of partial gelatinization, have been observed by Zavareze et al. (2010). Jiranuntakul et al. (2011) have also reported slight rough surface on some granules of the normal rice starch and obvious change in waxy-type granule. The formation of voids and the disappearance of birefringence at the granule center of potato starch (Kawabata et al. 1994; Vermeylen et al. 2006) and maize starch (Kawabata et al. 1994) have been observed at temperature exceeding 110 °C. However, granule periphery of both starches has remained highly birefringence even after HMT.

2.3.2 Impact of HMT on Starch Double-Helical Arrangement and Crystallinity

X-ray diffractometry has been extensively used to reveal the impact of HMT on the characteristics of crystalline structures of starch. HMT has been shown to change the wide-angle X-ray pattern from the B- to A-type (or A+B) for potato starch (Sair 1967; Hoover and Vasanthan 1994; Gunaratne and Hoover 2002; Vermeylen et al. 2006; Varatharajan et al. 2011; Ambigaipalan et al. 2014), yam starch (Hoover and Vasanthan 1994; Gunaratne and Hoover 2002), and breadfruit starch (Tan et al. 2017). A shift from C- to A-type on HMT has been observed for sweet potato starch by Shin et al. (2005). However, A-type of starch structure pattern was unaffected for cereal starches (Sair 1967; Hoover and Manuel 1996; Hoover and Vasanthan 1994) and cassava and yam starches (Gunaratne and Hoover 2002) after

HMT. B-polymorphic high-amylose maize starch structure has been found to be more susceptible to HMT than A-polymorphic regular maize starch resulting in more structural changes (Wang et al. 2016). X-ray intensities have been found to reduce for potato (Hoover and Vasanthan 1994), cassava (Abraham 1993), and barley (Lorenz and Kulp 1982) after HMT. However, cereal starches generally exhibit either increased or unchanged intensities after HMT. Temperature and the moisture content of HMT appear to be affected on the changes of X-ray pattern and intensities (Hoover and Vasanthan 1994; Vermeylen et al. 2006). Several theories have been suggested to explain the change of X-ray pattern, intensities, and crystallinity of starch on HMT:

1. Destruction of crystallites (decrease X-ray intensities). Hoover and Vasanthan (1994) explained that in B-type starch rupture of hydrated water bridges leads adjacent double helices to move apart and form less ordered crystalline array. Double-helical movement during heat-moisture treatment could disrupt starch crystallites and/or change the crystalline orientation (Gunaratne and Hoover 2002). The same authors found that in contrast to B-type (potato, true yam) starch, A-type tuber (new coco yam, taro, cassava) crystallinity was unaffected after HMT. However, HMT decreased relative crystallinity of A-type rice starch with differences in amylose content (Zavareze et al. 2010; Khunae et al. 2007).
2. Growth of new crystallites. Double helices that are shifted within the crystalline domain due to thermal energy and moisture during HMT could pack closely in more ordered crystalline array resulting in increased X-ray intensities mainly in A-type starches (Hoover and Vasanthan 1994). Vermeylen et al. (2006) observed increased crystallinity for potato starch heated at 130 °C, whereas, HMT between 90 and 120 decreased the crystallinity. These authors hypothesized based on debranching results of native and HMT amylopectin that at high temperature (130 °C) breaking of covalent linkages decouples the double helices from the amylopectin backbone and renders them sufficiently mobile to become organized in more perfect/larger crystallites. Interaction between amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin chains increases X-ray intensities due to formation of new crystallites (Hoover and Vasanthan 1994; Hoover and Manuel 1996).
3. Reorientation of the already existing crystallites may increase or decrease X-ray intensities (Lorenz and Kulp 1982; Hoover and Vasanthan 1994; Hoover and Manuel 1996).
4. Changes in the packing arrangement (B- to A-type crystallinity) of the double helices results change in the X-ray pattern. HMT has been shown to trigger the transformation of B-type packing arrangement to either pure A-type or a mixed A+B (Sair 1967; Vermeylen et al. 2006; Gunaratne and Hoover 2002; Hoover and Vasanthan 1994; Kawabata et al. 1994). The change in X-ray pattern (B to A+B) on HMT can be attributed to dehydration of water molecules occupied in the central channel of the B-unit cell and movement of pair of double helices into the central channel that was originally occupied by the vaporized water molecules (Gunaratne and Hoover 2002). From WAXD patterns, Vermeylen et al.

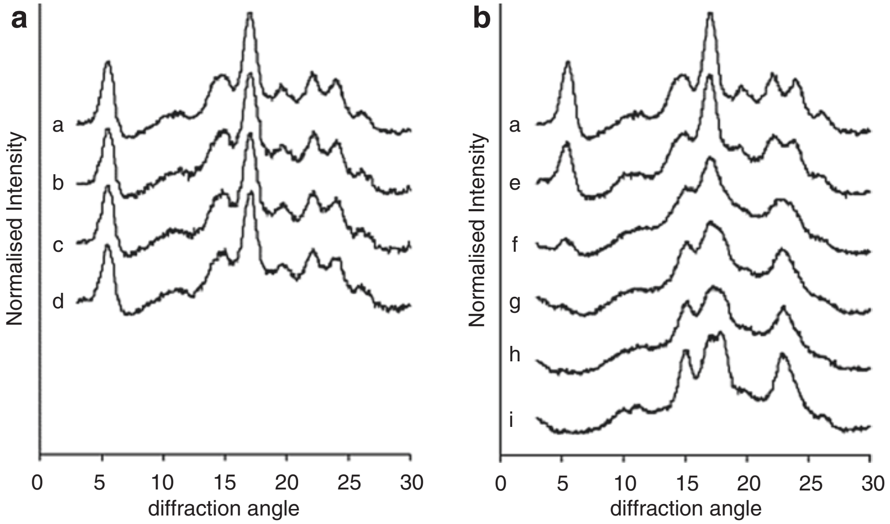

Fig. 2.1 Transformation of B-type starch structure of potato starch to A-type as the temperature of HMT (*b*) is increased (Vermeylen et al. 2006). Native potato starch (*a*), HMT-23-90 (*e*), HMT-23-100 (*f*), HMT-23-110 (*g*), HMT-23-120 (*h*), HMT-23-130 (*i*)

(2006) have confirmed the transition from B to A packing arrangement, and at higher temperature (HMT 130 °C, 23% mc, 24 h), a typical A-type diffraction resulted (Fig. 2.1)

5. Formation of crystalline amylose-lipid complexes increases X-ray intensities. Hoover and Vasanthan (1994), and Hoover and Manuel (1996) observed a decreased apparent amylose content on HMT of wheat and maize starches, indicating additional interaction between native starch lipid and amylose chains. A peak of crystalline V-amylose-lipid complexes has been clearly observed for HMT (100 °C, 16 h, 18–27% mc) rice starches, and the peak has been progressively increased with increase moisture content as a result of increase in mobility of V-amylose-lipid-complexed chains. This mobility facilitates the formation of more order large V polymorph (Khunae et al. 2007).

2.3.3 *Impact of HMT on Granular Swelling and Amylose Leaching*

HMT has been shown to reduce the granular swelling and amylose leaching of cereal (Kulp and Lorenz 1981; Hoover and Vasanthan 1994; Olayinka et al. 2008), tuber and root (Hoover and Vasanthan 1994; Gunaratne and Hoover 2002), and legume starches (Hoover and Vasanthan 1994; Hoover et al. 1994). The decrease in amylose leaching on HMT could attribute to the additional interactions between amylose-amylose and amylose-amylopectin chains (Gunaratne and Hoover 2002) and formation of amylose-lipid complex (Hoover and Manuel 1996) during HMT. This type of mechanism may also be partly responsible for the reduction for granular swelling in HMT starches along with decrease in granular stability due to unraveling of double helices and crystallite disruption, increase in crystallinity, and change in poly-starch structure from (B→A+B) (Hoover and Vasanthan 1994; Gunaratne and Hoover 2002; Shin et al. 2005).

2.3.4 Impact of HMT on Gelatinization Properties

Differential scanning calorimetry has been the most widely used technique to study the gelatinization characteristics of HMT starches. The impact of HMT on gelatinization properties is dependent on the source of starch, heating temperature, time, and level of moisture prevailing during the treatment. Generally, HMT increases the gelatinization transition temperatures, onset (To), peak (Tp), and conclusion (Tc) and broadens the gelatinization temperature range (Tc-To) (Sair 1967; Donovan et al. 1983; Stute 1992; Hoover and Vasanthan 1994; Hoover and Manuel 1996; Gunaratne and Hoover 2002; Ambigaipalan et al. 2014; Sun et al. 2014). Figure 2.2 shows the increased gelatinization transition temperatures of HMT corn, pea, and

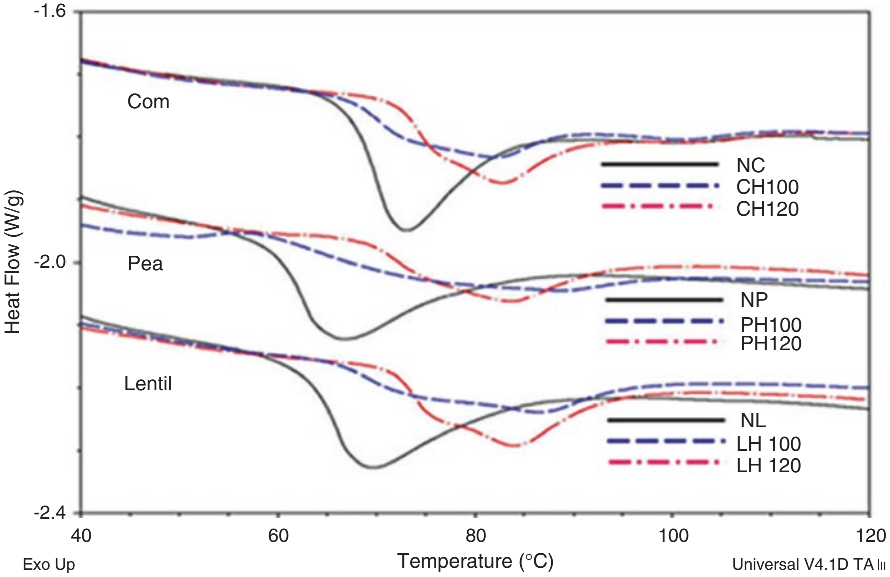

Fig. 2.2 DSC thermograms of native and HMT corn, pea, and lentil starches: *NC* native corn, *NP* native pea, *NL* native lentil, and CH100, PH100, LH100, and CH120, PH120, and LH120 represent HMT corn, pea, and lentil starches heat-moisture treated at 30% moisture for 2 h at 100 °C and 120 °C, respectively. (Chung et al. 2009)

lentil starches as measured by DSC. The melting temperatures of starch crystallites are controlled indirectly by the surrounding amorphous region. HMT triggers the interaction between amylose-amylose, amylose-amylopectin, and amylose-lipids (Hoover and Vasanthan 1994; Gunaratne and Hoover 2002; Ambigaipalan et al. 2014). These interactions suppress the mobility of starch chains in amorphous region. As a result of this, HMT starches require higher temperature to achieve the swelling that imparts the destabilizing effect on starch crystalline domain, leading to increase the transition temperatures (Hoover 2010; Gunaratne and Hoover 2002; Hoover and Vasanthan 1994; Zavareze and Dias 2011). In the gelatinization process, hydration and swelling of amorphous region of starch granules impart pressure on crystalline domain melting crystalline region and double helices (Adebowale et al. 2009). Some authors explained that the formation of more perfect crystallites upon HMT leads to melt them at high temperatures (Sun et al. 2014; Yadav et al. 2013). Tester (1997) has postulated that the extent of crystalline perfection is reflected in the gelatinization temperature whereas the ΔH reflects the overall crystallinity (quality and quantity). Ji et al. (2004) suggest that the onset of gelatinization would be a measure of the perfection of starch crystallites, and thus more perfection crystallites have high onset gelatinization temperatures. Pukkahuta and Varavinit (2007) noticed biphasic broadening of Tp for HMT sago starch. They explained an inhomogeneous heat transfer during HMT could be the possible reason for observed biphasic Tp. Varatharajan et al. (2010) found double endotherms in HMT waxy potato starch in contrast to normal potato starch and suggested that more heterogeneous crystallites, in terms of thickness and stability, may have been formed in HMT process in waxy potato starch. Structural transformation occurred in the crystalline micelles during HMT could increase the thermodynamic stability resulting in a newly developed high-temperature endotherm (Jiranuntakul et al. 2011). The gelatinization enthalpy has been shown to decrease (Kulp and Lorenz 1981; Hoover and Vasanthan 1994; Gunaratne and Hoover 2002; Ambigaipalan et al. 2014; Adebowale et al. 2009), unchange (Ambigaipalan et al. 2014; Hoover and Vasanthan 1994; Collado and Corke 1999), or increase (Sun et al. 2014) after HMT. The reduction of melting of enthalpy by HMT is much greater in tuber starches than that of cereal starches (Hoover and Vasanthan 1994; Donovan et al. 1983). Gunaratne and Hoover (2002) explained that the reduction of melting enthalpy of HMT starches is due to the disruption of some of the double helices present in crystalline and noncrystalline regions of the granules during HMT leaving fewer double helices to unravel and melt during the gelatinization of HMT starches. However, Hormdok and Noomhorm (2007) reported that partial gelatinization of less stable amylose and amylopectin molecules could reduce the melting enthalpy of HMT starches. Gunaratne and Hoover (2002) studied the effect of HMT on tuber and root starches and reported that the ΔH of B-type starches reduced to a greater extent than those of A-type starches. According to them, double-helical starch chains in B-type starches are more mobile than A-type starches due to more water molecules occupied in B-type unit cell and hence more prone to the disruption than those of A-type starches. Negatively charged phosphate groups on adjacent amylopectin chains of potato starch could have high impact on the disruption of double helices of potato starch because these negatively charged phosphate groups could hinder the strong interaction between double helices making them more susceptible for the disruption during HMT (Gunaratne and Hoover 2002).

2.3.5 Impact of HMT on Pasting and Gelling Properties

Starch heated in excess water undergoes various changes as a result of heat and moisture transfer. Gelatinization and pasting occur in the same system can be used to describe many changes that occur. Gelatinization may be used to refer to early changes, whereas pasting includes later changes. Pasting is defined as the phenomena following in the dissolution of starch, involving granular swelling exudation of molecular components from the granule and, eventually, total disintegration of the granules (Atwell et al. 1988). Properties of starch paste are highly correlated with the textural characteristics and storage ability of many food applications. HMT significantly alters the pasting profile of starches. Investigations on pasting behavior and properties of HMT starches have shown that HMT increases the pasting temperature and thermal shear stability of starch paste but decreases the peak viscosity and granular breakdown (Kulp and Lorenz 1981; Hoover and Vasanthan 1994; Lawal and Adebowale 2005; Gunaratne and Corke 2007; Shih et al. 2007; Varatharajan et al. 2010; Yadav et al. 2013; Sun et al. 2014). The setback which reflects the extent of retrogradation has been reported to either increase or decrease (Sun et al. 2013; Shih et al. 2007; Varatharajan et al. 2010; Gunaratne and Corke 2007).The extent of these changes have been found to depend on the source of starch, the HMT parameters (treatment conditions), and the instrument used to detect the pasting properties (Hoover 2010). Sun et al. (2014) found that pasting temperature of HMT sorghum starch and flour increased with the increase of moisture level of the HMT. Restricted swelling and amylose leaching, increased granular rigidity, interaction between starch chains, and changes in granular crystalline domain that resulted in HMT are believed to be associated with the changes of pasting properties of HMT starches (Hoover and Vasanthan 1994; Jiranuntakul et al. 2011). HMT promotes the intermolecular association of starch chains reinforcing the granular bonding, and thus high heat energy is required to disrupt the HMT granules in the formation of paste. In a typical pasting curve, rapid increase of viscosity is attributed to the granular swelling and starch leaching. The restricted swelling and amylose leaching in HMT starch restrict the viscosity development. Varatharajan et al. (2010) studied the pasting characteristics of normal and waxy potato starches and suggested that enhanced interactions between starch chains (amylose-amylose, amylose-amylopectin, amylopectin-amylopectin) in HMT starches reduce the peak viscosity and granular breakdown while increasing the pasting temperature. This effect is lower in waxy starch as the contribution of amylose for the above interaction is negligible. Jiranuntakul et al. (2011) also reported that the degree of granular strengthening after HMT was more pronounced in normal starches than waxy starches. Same authors, by studying the pasting and gel morphology of HMT normal and waxy rice, corn, and potato starches, have concluded that HMT had more impact on pasting properties of the B-type starch than those of A-type starches attributing to the greater mobility of starch chains in B-type starches during HMT process. In the final step (cooling step) of pasting, profile decrease of energy in the system and subsequent hydrogen bond formation between starch chains mainly in amylose increases the viscosity (setback) (Hoseney 1994). Varatharajan et al. (2010) reported that increased setback on HMT is attributed to the increase in the proportion of intact granule in the gel matrix. The extent of the setback (retrogradation) is governed by the amylose gelation and the presence of rigid granules embedded in leached amylose network (Jayakody et al. 2007). Figure 2.3 shows the pasting curves (RVA) of HMT normal and waxy potato starch showing that HMT has decreased peak viscosity and granular breakdown while increasing the pasting temperature (Varatharajan et al. 2010).

Gel hardness of potato and wheat starch (Gunaratne and Corke 2007) and sorghum starch (Singh et al. 2011) and rice flour (Sun et al. 2013) has been reported to increase after HMT. Gel hardness of HMT sorghum starch increased with the severity of HMT (Singh et al. 2011). Starch gel can be regarded as hydrated polymer composites where swollen amylopectin-rich granules are embedded in and reinforce continuous matrix of entangled amylose molecules (Ring 1985). Mechanical properties of a starch gel would depend on the rheological characteristics of the amylose matrix, the volume fraction and the rigidity (deformability) of the gelatinized granules, and the interactions between the dispersed and the con-

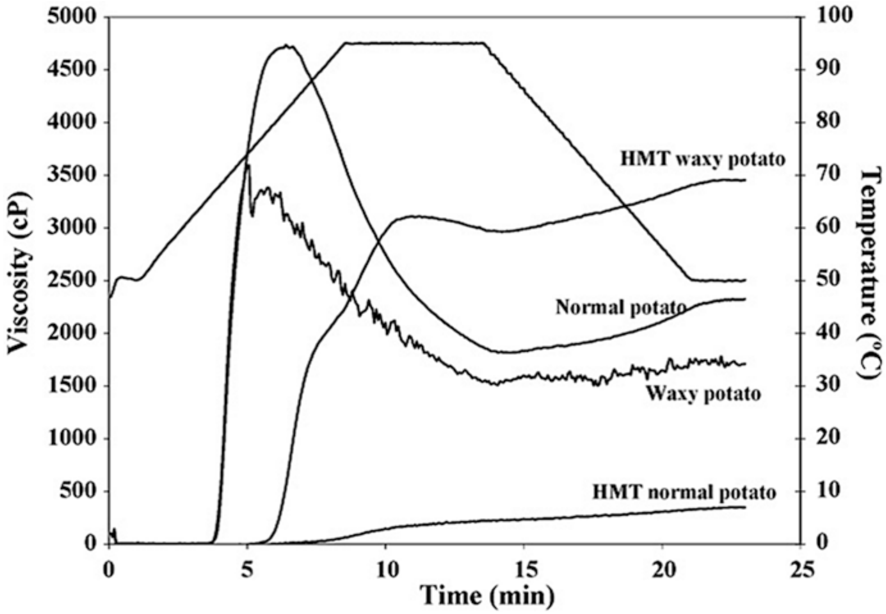

Fig. 2.3 RVA curves of native and HMT normal and waxy potato starches. (Varatharajan et al. 2010)

tinuous phases (Eliasson 1986). More intact and more orderly crystalline granules formed in HMT could form more rigid amylopectin-rich swollen granules embedded in the continuous phase of gel matrix resulting in harder gel. Hoover et al. (1994) reported that restriction of swelling by HMT favors amylose aggregation in the formation of gel matrix leading to firmer gel after HMT. During HMT, cross-linking between starch chains in the particular portion of amylose could form more junction zones in continuous phase of gel matrix forming firmer gels (Hormdok and Noomhorm 2007). Gunaratne and Corke (2007) concluded that the interplay of the following factors, amylose concentration and conformational ordering and intermolecular association of amylose chains, rigidity of the filler components, and interaction between filler components and gel matrix, affects the gel hardness of HMT starch.

2.3.6 Impact of HMT on Retrogradation

Reassociation of starch polymers via hydrogen bonding in gelatinized starch on cooling is generally termed as retrogradation and is time and temperature dependent. This association of starch molecules in starch gel results in precipitation, gelation, and changes in consistency flowed by the gradual formation of crystallites resulting in phase separation in polymer and solvent (Karim et al. 2000). Retrogradation is of great interest for food scientist since it has a profound effect on quality, shelf life, acceptability, and nutritional value of starch-based food products (Biliaderis 1991). Starch gel can be considered as composites containing gelatinized granules embedded in amylose matrix (Miles et al. 1985). Both amylose and amylopectin are involved in retrogradation. Miles et al. (1985) attributed the initial gel firmness is dominated by irreversible gelation and crystallization within the amylose matrix, and branched reversible amylopectin recrystallization is correlated with the long-term development of starch gel. The ordered retrograded starch crystallites show B-type X-ray diffraction pattern (Zobel 1988) containing both crystalline and amorphous region. Hoover and Vasanthan (1994) studied the retrogradation behavior of HMT (100 °C, 16 h, 30% moisture) wheat, potato, oat, and lentil starches by storing the starch gel at 25 °C for 20 days and postulated that the extent of retrogradation as measured by DSC is governed by the interplay of crystallinity changes and amylose-amylopectin (AM-AMP) interaction during HMT. Gunaratne and Hoover (2002) found that HMT decreased retrogradation in B-type starches but caused no significant effect on A-type starches. Crystallites are disrupted in B-type starches during HMT than those of A-type starches. The disruption of crystallites in B-type starch during HMT would enhance the degree of separation between the outer branches of adjacent amylopectin chains resulting in much slower association of amylopectin chains and formation of amylopectin double helices in starch gel.

2.3.7 The Impact of HMT on Enzyme Hydrolysis

The enzyme digestibility of starch has been shown to affect many factors such as starch source, granule size, amylose-amylopectin ratio, amylose-lipid complexes, crystalline structure, and granule surface organization (Zhang and Oates 1999; Ring et al. 1988; Holm et al. 1983; Snow and O'Dea 1981). The digestion of starch granule is a complex process that involves accessibility (diffusion and adsorption) and hydrolytic activity of enzyme toward substrate (Watcharatewinkul et al. 2010), and both morphological features and internal structural features affect the in vitro hydrolysis (Li et al. 2004). Depending on the botanical origin and HMT treatment conditions, increased (Kawabata et al. 1994; Hoover and Vasanthan 1994; Gunaratne and Hoover 2002,) or decreased (Kweon et al. 2000; Franco et al. 1995) α-amylase hydrolysis has been observed. Gunaratne and Hoover (2002) studied the enzyme hydrolysis of HMT (100 °C, 16 h, and 30% moisture level) on root and tuber starches and postulated that crystallite disruption near granule surface on HMT facilitates the rapid entry of enzyme into the granule surface which increases the extent of enzyme hydrolysis. The temperature, moisture content, duration of the treatment, and starch sources used in HMT have been reported to influenced on starch digestibility by α-amylase (Hoover 2010). The increased enzyme resistance of HMT starch could be attributed to the rearrangement of molecular chains and more compact granule structure (Tan et al. 2017). Studding on the impact of different temperatures of HMT on normal and waxy potato starches, Varatharajan et al. (2011) suggested that the interplay of the amount of A-type crystallites, starch chain interactions, and changes to double-helical conformation occurred in HMT is influenced by α-amylase hydrolysis of HMT starches. These authors further explained that the structural disorganization occurred near the granule surface as a result of HMT and transformation of B-type crystallite to A-type crystallites facilitates the α-amylase hydrolysis, whereas starch chain interactions (AM-AM, AM-AMP) hinder the susceptibility to α-amylase hydrolysis. The occurrence of these factors and subsequent influence on starch digestibility of HMT starches depend on the temperature used in HMT. According to Jane et al. (1997), inferior crystalline structure containing α-(1–6)-linked branch points and short double helices in A-type starch are more susceptible to enzyme hydrolysis compared to the B-type starch in which more branch points are clustered in the amorphous region and there are fewer short branch chains which make a superior less susceptible structure.

2.3.8 The Impact of HMT on Acid Hydrolysis

It is believed that acid hydrolysis occurred in a two-stage pattern in which acid molecules preferentially attack to more amorphous parts of the granules which have a relatively fast hydrolysis rate, whereas in the second stage, crystalline material is slowly degraded (Hoover 2000, 2010). To account for the slower hydrolysis rate of the crystalline parts of the starch granule, two hypotheses have been proposed (Kainuma and French 1971). First, dense packing of starch chains within the starch crystallites does not readily allow the penetration of H_3O^+ into the regions. Second, the acid hydrolysis of a glycosidic bond may require a change in conformation (chair → half chair) of D-glucopyranosyl unit. The mode of the distribution of the α-(1, 6) branch points is differed between A-type starches and B-types starches. In B-type starches, more branch points are clustered mainly in the amorphous region and thus more susceptible to acid hydrolysis than branch points located in crystalline region of A-type starches (Jane et al. 1997). The influence of HMT on acid hydrolysis varied among the starch sources. The susceptibility to acid hydrolysis decreased after HMT of maize (Hoover and Manuel 1996), potato (Hoover and Vasanthan 1994), and wheat, lentil, oat, and yam (Hoover and Vasanthan 1994), whereas Gunaratne and Hoover (2002) found increased acid hydrolysis for HMT (100 °C, 10 h, and 30% moisture) taro, cassava, and potato starches up to fourth, sixth, and fifth day of storage, respectively. From the investigations carried out on the influence of HMT on acid hydrolysis, four main influential factors have been proposed: crystallites disruption, starch chain interaction within the amorphous and crystalline domain, disruption of double helices in the amorphous region, and polymorphic transformation from B to (A+B). HMT increases the susceptibility toward acid hydrolysis through the crystallite disruption and the disruption of double helices in the amorphous region, but interaction between starch chains occurred in HMT reduces the extent of acid hydrolysis (Gunaratne and Hoover 2002). Interactions between starch chains reduce the chain flexibility and thereby hinder the conformational change (chair to half chair required for efficient protonation of glycosidic oxygen) (Gunaratne and Hoover 2002). Varatharajan et al. (2010) observed the reduction of acid hydrolysis for HMT normal and waxy potato starches and explained starch chain interaction (amylose and amylopectin), and the polymorphic transformation (B → A+B) could be the reasons for decreased acid hydrolysis of HMT potato starch. In A-type unit cell structure, amylopectin chains are closely packed in than those of B-type. Closely packed amylopectin chains hinder the accessibility of acid molecules.

2.4 Impact of HMT on the Formation of Slow Digestible and Resistant Starch

Based on the rate of starch hydrolysis by digestive enzymes, starch can be classified into rapidly digestible (RDS), slowly digestible (SDS), and resistant starch (RS) (Englyst et al. 1992). RDS is the starch fraction that rapidly and completely digested in the small intestine causing a sudden increase of blood glucose level and SDS slowly but completely digested in the small intestine. Starch fraction not hydrolyze in small intestine in healthy human is considered as resistant starch. Resistant starch can be subdivided into four groups: RS1 (type 1) represents physically inaccessible form of starch such as partly milled grains and seeds and in some very dense type of processed starch; RS2 (type 2) represent granular form of starch such as in raw potato and bananas; RS3, the most resistant type, is formed mainly from retrograded amylose in gelatinized starch; and RS4 is considered to be formed in chemically modified starch (Lehmann and Robin 2007). RS is believed to have health beneficial effects similar to those of some form of dietary fiber (Rabe 1999). RS have been reported to be beneficial on the colon health and protection of collateral cancers, hypoglycemic effects, inhibition of fat metabolism, lowering cholesterol, and growth of probiotic microorganisms (Walter et al. 2005; Sajilata et al. 2006; Lehmann and Robin 2007). With low to medium glycemic index, SDS reduces the glycemic load (Lehmann and Robin 2007), and thus RS and SDS can be considered as important nutritional components of foods. Many investigations have shown that HMT can modify the SDS and RS level without destroying the granular structure attributing that HMT can generate more highly ordered structure. The amount of RS and SDS produced in HMT starches appeared to be dependent on the level of moisture content, temperature, incubation period, and source of starch. Li et al. (2011) produced HMT mung bean starch with different moisture contents (15%, 20%, 25%, and 35%) heating at 120 °C for 12 h and found that RS content significantly increased at 20% moisture level. Sweet potato which was subjected to HMT with various combinations of moisture and temperature produced the highest content of granular slowly digestible starch with 50% moisture at 55 °C (Shin et al. 2005). The structure of SDS had very rigid amorphous regions and partially disrupted crystalline region. Chung et al. (2009) reported that enhanced interaction between starch chains and perfection of already existing starch crystallites resulted in HMT increase in RS and SDS content, and this is more pronounced in HMT than annealing. Further, they mentioned that amylose-amylose interaction occurred during treatment is not disrupted in gelatinization which reduces the accessibility of enzyme for digestion. In the strategies for the manufacture of resistant starch, partial acid hydrolysis prior to HMT can be used to enhance the RS yield (Brumovsky and Thompson 2001). The limited acid hydrolysis facilitates the mobility of the molecules which allows the formation of highly ordered structure resistant to α-amylase hydrolysis (Brumovsky and Thompson 2001; Thompson 2000). Further, Brumovsky and Thompson (2001) have shown that partial acid hydrolysis (78 h) followed by HMT at 120 °C can produce high content of boiling stable granular RS which should be stable to many subsequent thermal treatments. The amount as well as the quality of RS is important in terms of food applications. Jacobasch et al. (2006) reported that HMT of Novelose 330 produces high yield of RS3 with beneficial prebiotic properties, and thus HMT-Novelose with excellent prebiotic properties could be used to produce functional food ingredients.

2.5 Food Applications of HMT Starch

Thermal, pasting, and gelling properties are the key functionalities useful in food applications. HMT improves the stability for mechanical agitation and acid in pasting and thus could be applied in food as an alternative for chemically modified starch. HMT starch appears to be a suitable material for the production of retort foods, dressings, noodles, baked foods, batter products, confections, dairy products, creams, fat mimetics, and resistant starches (Kurahashi and Yoshino 2000). Baking quality and freeze-thaw stability of potato starch have been shown to improve by HMT (Collado and Corke 1999). Sweet potato starch has been modified by HMT and used as a substrate and composite with maize starch to produce bihon-type noodles. Acceptability values of raw starch noodles and plain boiled and sautéed noodles made from 100% HMT sweet potato starch and sweet potato composite with maize (50% HMT sweet potato with 50% maize starch) are found to be similar to that of commercial bihon (Collado et al. 2001). Incorporation of 50% of HMT (20 g/100 g moisture at 110 °C for 1.5 h) rice starch with rice flour resulted in remarkable effect on the cooking and textural quality of cooked noodles indicating the possibility of utilizing the HMT rice starch within composite with poor-quality rice flour (Hormdok and Noomhorm 2007). Chung et al. (2014) found that heat-moisture treated germinated brown rice could partially or completely replace the wheat starch in the preparation of cookies with improved nutrients and high consumer acceptability. Same authors (2012) reported that when heat-moisture-treated germinated brown rice is incorporated with wheat flour, the overall cooking and nutritive quality of noodles can be improved. Lorenz and Kulp (1981) evaluated the bread- and cake-baking potentials of HMT wheat and potato starches and found that bread quality and cake-making potential of HMT wheat starches were decreased with HMT, whereas HMT increased the backing potentials, grain texture and bread volume, and cake-making potentials of potato starch. However, compared to the native wheat starch, the overall bread- and cake-baking quality of HMT potato was lower. These authors believed that decreased baking potentials of HMT wheat starch could attribute to the starch damage occurred in HMT and improved baking potentials of HMT potato starch could be due to the changes of physicochemical properties as a result of structural changes that occurred in HMT. The effect of HMT maize starch on dough- and bread-making properties has been studied by incorporating 20% HMT maize or native maize starch with wheat starch (Miyazaki and Morita 2005). The results have shown that the HMT maize starch reduced the elasticity of dough compared to that of native maize starch or control (without any maize starch). However, by the addition of shortening, the specific volume of bread baked with HMT maize increased, and grain structure became finer, but bread crumb firmness baked with HMT was the same as at the presence or absence of shortening. These authors believed that HMT reduces the ability of maize starch to bind with gluten protein resulting in bread with lower quality and shortening improves the binding efficiency of HMT maize starch with gluten. Hoover (2010) suggested that starch chain interactions and amylose-lipid interactions during HMT may be the main causative factors responsible for decreased interaction of HMT maize starch with gluten.

2.6 Summary

Most of the studies on HMT have been focused on the impact of HMT on structure and physicochemical properties of starch. From these studies it is evident that starch chain interactions and disruption of starch crystallites that occurred within the amorphous and crystalline region of starch in HMT alter the thermal, pasting, gelling, and digestible properties of starch without destroying the starch granules. The functional properties of native starches that can be mainly improved by HMT are the acid stability and mechanical shear resistance in pasting. The extents of structural and subsequent changes of physicochemical properties have been shown to be affected by the amount of water, temperature, and time of heat treatment given in the treatment process. In case of type of starch structure, B-type starches are more susceptible to HMT. Though the structural and physicochemical changes occurred in HMT have been extensively studied, still little has done to study the influence of HMT on lamellar organization and molecular characteristics of amylopectin and amylose within the starch granule. Extensive researches are also required to broaden the applications of HMT starch in food product development.

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Chapter 3
Annealing

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Abstract Annealing is a physical modification of starch through heat treatment in the presence of water with controlled time. The heating temperature will be below the gelatinization temperature and above the glass transition temperature. It only uses water and heat energy without any chemical reagents and thus annealing could be regarded as an eco-friendly and cost-effective process. Compared to other technologies such as chemical and enzyme modification, property changes through annealing are relatively mild. Thus prepared starches maintain intact granule architecture but with substantial changes in physicochemical properties such as crystallinity, gelatinization, swelling factor, solubility, viscosity, and hydrolysis rate. In addition to heating time, temperature, and moisture, starch source influences the annealing properties. Overall, annealing is a cost-effective and simple technique to modify the starch functionality toward developing several value-added food products.

Keywords Annealing · Starch · Property · Application

3.1 Introduction

Starch is a natural botanical biomaterial from diverse plant sources such as cereals, roots, fruits, and beans. It is widely utilized in food and nonfood industries, e.g., textile, papermaking, feed, foundry, medicine, construction, and petroleum. Starch is composed of two biopolymers, amylose and amylopectin, that predominantly

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Table 3.1 Summary of industrial starch utilization

Industry requirements	Usage of functional starch
Adhesive	Glue, other adhesive products
Agriculture	Pesticide delivery, herbicide encapsulation, seed coating
Cosmetics	Makeup powder, bath cream
Detergent	Surfactants, builders, co-builders, bleaching agents, activators
Food	Major ingredients, viscosity modifier, glazing agents, fat replacer, emulsifier, encapsulation material, bulking agents
Medical	Plasma extender, transplant organ preservation materials, delivery materials
Oil drilling	Viscosity modifier
Paper	Binding, sizing, and coating
Pharmaceuticals	Diluent, binder, drug delivery
Plastics	Biodegradable fillers
Textile	Sizing, finishing, printing, fire resistance

Based on Ellis et al. (1998)

take account for its exceptional functional properties. Native starch, however, cannot completely meet the criteria for widespread industrial applications mainly due to its undesirable properties such as low gelatinization temperature and high swelling effect. In addition, higher amylopectin yields easier retrogradation and strong film formation, while elevated amylose results in soft gels. In this regard, modified starches are being engineered to gain required gelatinization temperature, viscosity, transparency, stability, and film-forming property, to name a few, and to meet the industry requirements (Table 3.1).

Generally, there are four starch modification approaches, namely, chemical, physical, enzymatic, and genetic modification. Among them, physical modification is nontoxic, cost-effective, and energy saving and stands out as a “clean label” technology (Jacobs and Delcour 1998). It could even support the burgeoning “green consumerism.” Annealing is a typical physical modification process that was originally applied in metal manufacturing to strengthen the blade and sword. It greatly improves strength of crystals, induces morphological changes in elastomer, raises hot carrier ability in glassy materials, and even affects the dielectric properties of materials (Van Bogart et al. 1981; Kizilyalli et al. 1997; Chatterjee et al. 2008). It is applied on biopolymers too, e.g., starch for modifying its semicrystalline structure to circumvent the undesirable properties. Annealing the starch modifies water solubility, thermal stability, and particle size and even enhances the viscosity profile without gelatinization, starch granule damage, and loss of birefringence (Stute 1992). The amount of treatment time, moisture, and temperature indeed influence the starch functionality. Annealing can only induce mild physicochemical changes compared to chemical modifications that usually involve harsh reactions leading to significant changes in the starch properties. As annealing of starch does not involve any toxic or harmful chemical reagents, it is preferred highly for food applications.

In recent years, there has been renewed interest on starch annealing, and several articles have appeared in the literature. This chapter is aimed at summarizing the newer developments coupled with the basic principles and concepts along with the influence of experimental parameters and starch sources with an emphasis on the future applications.

3.2 The Basic Principle and Concepts of Annealing

3.2.1 Definition

Annealing is generally defined as a process that combines water and heat with starch for a fixed period of time by controlling the temperature mainly above the glass transition and below the gelatinization temperature. This definition is somewhat vague to symbolize the actual annealing process. Findings about the heat and water effect on alternating the starch properties generate hydrothermal treatment, and thus the term "annealing" along with "heat-moisture treatment" (HMT) was coined to describe the hydrothermal process of starch. It certainly leads to a debate about the differentiation of annealing from HMT, as both are similar in the experimental processes and are associated with controlling the moisture level, temperature, and heating time (Jacobs and Delcour 1998). To some extent, there is no difference between both the protocols and the gelatinization temperature and viscosity increase as well as the shape, size, and optical birefringence in the starch granules, to name a few, as essentially the same. Products with higher temperature treatment, however, are found to be more altered than those at the low-temperature treatment, and hence in order to distinguish these two processes, the term annealing is being used for the low-temperature hydrothermal treatment while HMT for the high-temperature treatment. Variations between them (Table 3.2) are supported by viscosity, differential scanning calorimetry (DSC), and X-ray diffraction (XRD) (Stute 1992) analyses, to name a few. For example, annealing on potato starch does not alter the crystal structure even after prolonged durations of treatment. On the other hand, HMT changes significantly the B-type starch structure to the A type. Thus, annealing could be attributed as a lower-grade hydrothermal modification in contrast to HMT. Based on these observations, annealing could be defined as a process of physically treating starch by suspending in excess water (above 40% w/w) under mild

Table 3.2 Comparison between the annealing and heat-moisture treatment (HMT)

	Parameter	Annealing	HMT
Treatment	Moisture level (w/w)	Intermediate (40–80%)	Restrained (<35%)
	Temperature (°C)	Low (25–80)	High (> 80)
	Time period	Long (hours to days)	Short (1–24 h)
Property	Gelatinization temperature	Increase	Increase
	Retrogradation extent	High	Low
	Peak viscosity	Decrease	Decrease
	Crystal structure	Remain as the original	Change from B to A

Table 3.3 Summary of annealing parameters on popular starches from recent literature

Starch type	Temperature (°C)	Moisture (%)	Heating time (hr)	Reference
Banana	65	70	24	De la Rosa-Millan et al. (2014)
Cassava	55	80	3, 24	Vamadevan et al. (2013)
Common buckwheat	50	80	24	Liu et al. (2015)
Corn	45, 50	90	72	Yu et al. (2016)
Indian water chestnut	65	66.6	24	Yadav et al. (2013)
Normal barely	50	80	3, 24	Vamadevan et al. (2013)
Oat	45	80	3, 24	Vamadevan et al. (2013)
Pea	45	66.6	24, 72	Wang et al. (2013)
Potato	30, 40, 50	16.6	24	Wang et al. (2017)
Rice	58	80	3, 24	Vamadevan et al. (2013)
Rye	45	80	3, 24	Vamadevan et al. (2013)
Sorghum	50	80	24	Liu et al. (2016)
Sweet potato	55	90	72	Song et al. (2014)
Tartary buckwheat	50	80	24	Liu et al. (2016)
Wheat	30, 40, 50	16.6	24	Wang et al. (2017)
Yam	30, 40, 50	16.6	24	Wang et al. (2017)

temperature (<70 °C), above the glass transition temperature, and below the gelatinization temperature, conditions for longer durations (Table 3.3).

3.2.2 Mechanism of Annealing

Native starch granules possess semicrystalline organization made up of crystalline and amorphous regions (Oates 1997). Crystalline regions have tight and ordered helical structures that are predominantly composed of the branched amylopectin chains, while the amorphous regions have loose and randomly packed amylose chains. Due to tightly packed chains organization, there is no space in the crystalline regions, and hence free water cannot penetrate. Presence of heat, however, provides the required energy as well as melts the crystalline regions, and thus the water can sweep through and fill the space between the starch chains. This phenomenon is known as the gelatinization (Biliaderis et al. 1980). However, when the heat energy is not strong enough, crystalline regions cannot be thawed by the treatment, and consequently the initial organization will be retained. Thus, annealing can theoretically affect only the amorphous regions.

In general, there are two states of the amorphous regions, glass state and rubber state. The glass state has less mobility and the chains are highly stable; on the other hand, the rubber state contains higher energy, and consequently it could be modified easily. Transition between the glass state to rubber state could be modulated by the temperature and is known as the glass transition temperature. In the native starch, amorphous regions are in the glass state, and thus they are less feasible for modification.

The amount of heat and water are keys during annealing. Excess water penetrates the soft amorphous regions and hydrates them and thus provides the necessary chain mobility toward modification. Furthermore, annealing reduces the glass transition temperature making the starch more plastic, and thus the chains are susceptible to modification. The high temperature provides the required energy to transfer the glass state of amorphous starch to rubber state (Waigh et al. 2000). Consequently, starch chains gain freedom and the probability for their association leading to a steadier state increases significantly. Subsequent to annealing, when the temperature reverts to ambient conditions, the chains form thermally stable network arrangement and could eventually result in recrystallization of chains (Jayakody and Hoover 2008). Such intricate changes result in altered starch properties.

3.3 Effects of Annealing on Starch Property Changes

Although annealing is a low-degree physical modification, it indeed alters the starch structure and modulates the physicochemical properties. Thermal, pasting, swelling, hydrolysis, and digestive behavior are impacted most and are discussed in the following paragraphs.

3.3.1 Morphological Changes

The granule size, shape, and texture are important physical attributes in food and nonfood applications. During the annealing, temperature is controlled below the glass transition and granules retain their morphology. For example, retention of starch granules is evidenced in several cultivars such as wheat, corn, oats, potato, lentil, and rice (Stute 1992; Jacobs and Delcour 1998; Hoover and Vasanthan 1994; da Rosa Zavareze et al. 2010; Jayakody et al. 2009). In addition, annealed starch granules, for example, as in rice, are found to be aggregative with rough surface (da Rosa Zavareze et al. 2010). Porous surface structure as in high amylose rice, barley, and cassava starch could also be noticed (Nakazawa and Wang 2003; Waduge et al. 2006; Dias et al. 2010). These pores result in a more fragile starch granular structure and make it susceptible for erosion. This phenomenon could be attributed to the expanding effect. For example, due to the presence of excess water in the system, granules gain the ability to absorb excessive amounts of water that in turn expands the distance between clusters in the granule and results in pore-like channels on the surface.

3.3.2 *Influence on the Starch Crystallinity*

The native starches are semicrystalline materials. Their structural and network arrangements are assessed by the changes in the X-ray diffraction patterns that are composed of peaks. Starch type determines the overall crystallinity. In general, A-type starches possess more crystallinity, comparatively, than the B and C types (Sarko and Wu 1978), due to their tight network structures. Upon gelatinization, however, starch granules lose their intrinsic structural integrity and result in patterns deprived of profiles.

As the annealing treatment does not interfere with the granule shape and the heat energy is not enough to melt the crystalline regions, the semicrystalline structural arrangement is preserved. In addition, the diffraction pattern could be more defined with sharp peaks than the native one. For example, barely starch displays a typical A-starch diffraction, like other cereal starches but with an additional peak at 20° (Vasanthan and Bhatty 1996; Waduge et al. 2006). This peak suggests the presence of V-type crystallites that are likely to be due to the amylose and lipid complexes. After annealing, the A-type structure remains intact barring subtle peak intensities, but significant intensity changes could be evidenced in the 20° peak. This could be due to the reorientation of lipid molecules in the amorphous regions. The relative crystallinity also increases. In the case of cornstarch and cereal starches, low amylose cultivators display A-type diffraction pattern and B-type for the high amylose cultivators. After annealing, diffraction patterns remain the same, and the crystallinity does not change, which supports the notion that annealing does not significantly alter the crystalline regions in the granules (Liu et al. 2009; Tester et al. 2005).

The root starch behaviors are quite interesting. In the case of potato starch, annealing did not have meaningful influence; however, in starch from sweet potato, C-type, the ratio of A to B type changes leading to increase in the overall C-type crystallinity (Genkina et al. 2004). This interesting observation could presumably be due to the close proximity, 2–3 °C, of the annealing temperature used to the onset of gelatinization temperature, which is below the A-type starch melting temperature but above the B-type melting. Normally, the melting point of A starches is 20 °C higher than B starches (Whittam et al. 1990). In conclusion, annealing does not impart significant influence on the crystalline structure of starches.

3.3.3 *Influence on the Starch Gelatinization*

Gelatinization is one of the important attributes that determine the starch quality. In the presence of suitable amount of water and high temperature (above the melting temperature), semicrystalline arrangement in the starch granule gets converted to amorphous form. This unique property induces changes in the starch functional properties, mainly the viscosity and gel-forming ability, a couple of important attributes for industrial food applications. Since gelatinization is modulated by water and heat, annealing the starch granules will also have measureable influence. The differential scanning calorimetry (DSC) analysis is being used to study the impact of annealing on the starch gelatinization. Annealing increases the onset temperature (T_o) and peak temperature (T_p) and, however, decreases the temperature range of crystalline melting (T_c-T_o). As T_o represents the first melting of the starch crystalline regions, its increase suggests enhanced stability of the crystalline arrangement due to annealing. These changes indeed specify the narrow melting range and homogenized crystalline packing structure (Stute 1992; Jacobs and Delcour 1998; Tester and Debon 2000; Liu et al. 2009; Yadav et al. 2013; Zhang et al. 2015). More importantly, reestablishment of the amylose-amylose and amylose-amylopectin interactions in the amorphous regions is one of the reasons for an increase in the gelatinization temperature (Jacobs and Delcour 1998; Adebowalea et al. 2005).

There is a debate that the gelatinization enthalpy (ΔH) changes due to annealing. There are evidences for the significant increase in the ΔH despite the narrow temperature range indicating high endothermal peak (Jacobs and Delcour 1998; Alvani et al. 2014; Yadav et al. 2013) along with a few examples with no change in the ΔH (Stute 1992; Waduge et al. 2006). The higher the ΔH, extra energy to be absorbed during starch gelatinization that in turn results in more perfect crystalline starch structure. As annealing deems to form a tighter starch network leading to enhanced crystallinity, it is reasonable to associate annealing with higher ΔH. Changes in ΔH could be influenced by amylose content, amylose and amylopectin arrangement inside starch granules, and the chain length distribution (Jayakody and Hoover 2008).

3.3.4 Influence on Swelling Power and Solubility

The reduction of starch swelling power and solubility upon annealing has been widely reported especially for potato, corn, cassava, barely, wheat, oat, lentil, and pea starches (Tester and Debon 2000; Nakazawa and Wang 2004; Gomes et al. 2005; Waduge et al. 2006; Lan et al. 2008; Hoover and Vasanthan 1994; Hoover and Manuel 1996).

Swelling power relates to the water holding ability of starch and very well reflects the mouth feeling of starch-based foods and breakdown effect of medical tablets. Thus, greater swelling power is a better quality attribute for food and nonfood applications of starches. The swelling power of native starch is high as it could absorb significant amount of water. It is also related to starch gelatinization character. The higher the gelatinization temperature, the lesser the swelling power of starch. As annealing strengthens the starch internal structure, hence more energy is required to expand starch chains to trap water molecules. Furthermore, elevated amount of crystalline material increases the gelatinization temperature. Thus it is not surprising that annealing retards the starch swelling. Overall, the intricate amylose and amylopectin interactions coupled with the increased crystalline regions modulated by the amount of moisture and heat greatly influence the starch swelling (Hoover and Vasanthan 1994). The solubility is also reduced predominantly due to strong interactions between the amylose and amylopectin chains and the tight amylopectin-amylopectin organization that restrains the amylose leaching (Gomes et al. 2005).

3.3.5 Influence on Pasting and Viscosity Properties

Pasting is an important attribute that reflects the starch state in the presence of water and heat, which is an essential parameter for industrial applications. Interestingly, upon annealing, pasting alters significantly and shows dependence on the starch type and source. Increase in the pasting temperature and decrease of peak and final viscosity have been observed for the potato starch (Stute 1992; Jacobs et al. 1995). On the other hand, wheat and pea starch display higher peak and final viscosity (Jacobs et al. 1996). Annealing the starch renders better temperature resistance and stirring behavior mainly due to the intricate changes in crystalline regions. Crystallinity increase along with strong internal forces among the starch chains results in elevated pasting temperature, and the re-organized chains contribute to reduced viscosity. Viscosity differences between starches could be attributed to the amylose/amylopectin ratio, internal helix arrangement, and chain length distribution (Jayakody and Hoover 2008).

3.3.6 Influence on Chemical Hydrolysis

Starch granules can be hydrolyzed by acid to prepare products such as dextrin and resistant starch. Generally, amorphous regions in the starch are susceptible to hydrolysis due to their soft network structure and allow the acid to sweep through that in turn results in breaking the glucose linkages (Gallant et al. 1997). Impact of annealing on starch hydrolysis is quite interesting. Annealing the potato, cassava, and high amylose maize starches makes them susceptible to hydrolysis (Nakazawa and Wang 2003) but with decreased hydrolysis rate in wheat, lentil, and yam starches (Hoover and Vasanthan 1994; Jayakody et al. 2009) and subtle changes on the barely starch (Waduge et al. 2006). These results clearly indicate that merely the presence of crystalline regions cannot explain the acid hydrolysis. It can be influenced by several factors such as crystallinity, helical structure of free amylose chains, void space increase in the amorphous areas, interaction between amylose-lipid complexes, and increase of branch point in the crystalline regions, to name a few (Jayakody and Hoover 2008). In addition, acid type and concentration, reaction conditions, and the temperature are some of the factors that influence the starch hydrolysis.

3.3.7 Influence on Enzyme Hydrolysis

Enzyme hydrolysis is a function-related property of annealing starch and aids to predict the in vivo starch digestion. Annealing promotes changes in the amorphous areas of granules, making them more accessible to enzymatic activity. Staple starches such as wheat and rice could be easily hydrolyzed by α-amylase (Jayakody and Hoover 2008; Dias et al. 2010). Similarly, potato, lentil, and oat starches could be easily hydrolyzed upon annealing leading to increased starch digestion (Hoover and Vasanthan 1994). The reason for high digestive rate could be attributed to the pores forming on starch granules after annealing (Nakazawa and Wang 2003; O'Brien and Wang 2008). The porous structure could alter the enzymatic hydrolysis of starch depending on the type of starch and enzyme (O'Brien and Wang 2008). Furthermore, this phenomenon is more significant in starches with intrinsic porous structure such as cornstarch. These pores go through the whole granule and make them very easy for enzymes to penetrate into the internal soft part, which increases the hydrolysis rate. However, decrease in enzyme susceptibility is also noticed in some instances and has been attributed to perfection of crystallites and enhanced amylose-amylose and/or amylose-amylopectin interactions (Hoover and Vasanthan 1994). Annealing mainly induces two structural effects, increasing the porous structure on the granule and making perfect crystalline regions. The crystalline region is resistant to the enzyme because of their highly tight packing arrangement. Annealing increases the susceptibility of wheat starch to fungal and bacterial enzymes (Jayakody and Hoover 2008). Overall it appears that annealing the starches with porous structure is likely to increase the enzyme hydrolysis, while starches with higher crystallinity hydrolysis rate decrease. Changes in the hydrolysis rate of annealed starch alter rapidly digestive starch (RDS), slowly digestive starch (SDS), and resistant starch (RS) amounts. For example, elevated RDS and reduced SDS are noticed in corn and pea starches (Chung et al. 2009). The RDS increase could be due to the formation of porous structure induced by annealing that in turn influences the SDS content. Annealing also serves as an efficient method to prepare the RS (Chung et al. 2010).

3.4 Applications of Annealed Starches

Annealing the starches improves thermal stability, decreases viscosity and swelling, and modulates the digestion. Hence, a variety of functional foods such as frozen foods, rice noodles, and tablets could be developed. The viscosity change and low-degree swelling benefit products, namely, bread, cakes, and noodles, to name a few. The high RS and altered SDS amounts serve as new ingredients in the starch-based products toward developing biocompatible functional foods to address diabetic and obesity concerns. In addition, novel nonfood ingredients in papermaking and cosmetics (da Rosa Zavareze et al. 2010) are also made possible.

3.4.1 Applications in Breadmaking

Gelatinization and retrogradation are the important attributes to attain the bread quality. Annealed starches play a critical role in modifying the dough viscosity and texture (Miyazaki et al. 2006). The texture of annealing starch foods is tougher than with native starches with improved adhesiveness and chewiness (Hormdok and Noomhorm 2007). More importantly, unique bread texture can be obtained, controlled, as well as designed with suitable amount of annealing starch. The cost of annealed starch production is low and is quite economical. As a result, annealed starches have been gaining popularity in the breadmaking industry.

3.4.2 Applications in Frozen and Canned Foods

After annealing, starch granule structure is recrystallized and gets refined in obtaining a stable status that in turn reduces the retrogradation and increases the heat stability. Such improved thermal stability and shear resistance are helpful in food making. Frozen and canned foods are generally cooked foods that only need simple heating for consumption. However, cooling process is a major concern while retaining the food quality due to retrogradation at low temperature. As the annealed starches have much lower setback temperature than native starches, they are advantageous for applications in canned foods as well as frozen foods (Stute 1992).

3.4.3 Applications for Improving Noodle Quality

Annealing decreases starch swelling power and solubility, which are suitable in noodle processing. The overall noodle textural attributes such as chewiness and adhesiveness can be improved significantly by using annealed treated noodle flours. For example, RVA profile and gel formation of rice flour can be promoted through annealing leading to quality improvement (Hormdok and Noomhorm 2007). Overall, annealing results in a paradigm shift in utilizing fewer quality starches toward making quality noodles.

3.5 Summary

Annealing as a hydrothermal physical modification is an inexpensive and powerful tool in modifying the physicochemical and digestive properties of starches. It is defined as treating starch at intermediate and/or excessive water content and heat above T_g while below T_m. The physicochemical changes are mainly due to structural alternations induced by annealing. In the amorphous regions, free amylose chains could get reoriented as well as the amylopectin chains and lipids leading to more thermal stable areas in addition to enhancing the perfection among the crystalline regions. In the rearranged amorphous regions, some void spaces are created that in turn result in porous structure through the whole granule. These microstructural changes induce alternations in the starch macro-properties such as reduced swelling power, peak viscosity, higher gelatinization temperature, easily hydrolysis, and modulated RS properties, to name a few. All these changes are deemed to be helpful in developing novel food supplements, functional foods, and medicinal foods in the near future.

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Chapter 4
Pre-gelatinized Modification of Starch

Yan Hong and Xingxun Liu

Abstract A pre-gelatinized starch is one kind of physical modification of starches which are accomplished by heating and by mechanical shearing. Pre-gelatinized modification starch is produced by sufficient heat, followed by drying and grinding. The objective is to generate starch ingredients with instantaneous cold water solubility and thickening/gelling capabilities. Pre-gelatinized starch, sometimes called "instant" starches, can be dissolved in water at temperatures below gelatinization of the native starches (BeMiller, Reference module in food science. Elsevier, 2016). Pre-gelatinized starch particles exhibit a complete lack of birefringence and generally retain very little, if any, of the original native granule structure, although there are almost always some ungelatinized granules in any commercial preparation made on a hot roll, i.e., via drum drying (Fritze, Ind Eng Chem Process Des Dev 12:142–148, 1973).

Keywords Starch · Pre-gelatinization · Characterization · Application · Properties

4.1 Introduction

A pre-gelatinized starch is one kind of physical modification of starches which are accomplished by heating and by mechanical shearing. Pre-gelatinized modification starch is produced by sufficient heat, followed by drying and grinding. The objective is to generate starch ingredients with instantaneous cold water solubility and thickening/gelling capabilities. Pre-gelatinized starch, sometimes called "instant" starches, can be dissolved in water at temperatures below gelatinization of the native starches (BeMiller 2016). Pre-gelatinized starch particles exhibit a complete lack of

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birefringence and generally retain very little, if any, of the original native granule structure, although there are almost always some ungelatinized granules in any commercial preparation made on a hot roll, i.e., via drum drying (Fritze 1973).

4.2 Application of Pre-gelatinized Starch in Industry

4.2.1 Application of Pre-gelatinized Starch in Feed Industry

The feed industry consists primarily of livestock, poultry, and aquaculture subsectors. There are five major feed markets, namely, those for pig, chicken, duck, fish, and shrimp. Among the commercially important livestock, all are ruminants except for pig; however, the pig industry is therefore responsible for the bulk of the feeds consumed for livestock. Cattle and goats though with large populations are raised primarily on roughages. Poultry feed production consists mainly of chicken and duck feeds. Chickens are raised for meat (broiler) or for eggs (layer), while ducks are farmed for their eggs. Until recently, aquaculture feeds have been considered a minor sub-sector of the feed milling industry. However, today the production of fish feeds is the fastest growing feed market (Cruz 1997).

Pre-gelatinized starch can be used in feed industry to increase the adhesive and improve taste of plant meals. For the feed with powdered form, pre-gelatinized starch could act as the adhesive for the feed to have good viscoelasticity, maintain stability in water, and reduce the loss. On the other hand, pre-gelatinized starch could increase the digestion rate compared with native starch, which may help the livestock grow.

4.2.2 Pre-gelatinized Starch Products in Food Industry

Native-rich starches have unique properties. However, rice starches' limited versatility restricts their application in the full range of food industry. Therefore, starches are modified in order to enrich their functions in food manufacturing. Pre-gelatinization is one of the physical methods to modify starches. Pre-gelatinized starch has a wide range of application, including low-fat salad dressings, high-solid fillings, bakery fillings, and dry mixes. In processing, hot process is preferred against cold process where problems may arise if flour, fruit, spices, or other ingredients contain amylases. In a hot process, the enzymes will be inactivated before the swelling of the starch and their vulnerability to enzymes. In real practice, pre-gelatinized starches should first be mixed with other dry ingredients before addition to the aqueous phase, to slow hydration and reduce lumping. Regarding formulations with little sugar or other dry ingredients, starches are agglomerated to facilitate dispersion. One way to help desperation is a light coating of oil.

4.2.3 *Pre-gelatinized (Instant) Starch Products in Pharmaceutical Industry*

Recently, pre-gelatinized starch is also used in pharmaceutical industry as a versatile and multifunctional pharmaceutical excipient and acts as the tablet binder, disintegrant, and filler in pharmaceutical excipients (Elgorashi et al. 2016). Pharmaceutical excipients have substantial impact on manufacturability, quality, safety, efficacy, and stability of drug substances in a dosage form. Therefore, it is desired to employ the minimum number of excipients in efficient formulation design. As a result, the use of multifunctional excipients has increased.

Starches from different sources such as corn, potato, and wheat and other botanical source starches were used in pharmaceutical excipients. Compared with native starch, pre-gelatinized starches exhibited very good flow, low moisture uptake, improved weight uniformity, and excellent disintegration ability with no lubrication sensitivity. Pre-gelatinized starches also demonstrated good packing properties and displayed a higher degree of plastic deformation during compression indicating good binding properties of these excipients. Further, low elastic recovery values supported the good binding properties with less tendency for capping and lamination. The drug was released very rapidly from all the formulations, supporting robust excipient characteristics of these starches (Elgorashi 2016).

4.3 Methods to Prepare Pre-gelatinized Starch

Pre-gelatinized starches are cooked and then dried in one of several ways, including drum drying, spray drying, cooking in aqueous ethanol, and extrusion cooking; this section will discuss the commercial ways to prepare the pre-gelatinized starch.

4.3.1 *Drum Drying*

Drum drying is the traditional method to prepare pre-gelatinized starch by pouring a starch slurry onto a hot drum and scraping off the cooked sheet with a knife. Chemical modification, drum operation, and grinding of the dried sheets are the three methods to control the rate of rehydration and texture of the finished phase. The feed starch can be a chemically modified product to add more ultimate properties. To make different products, factors would be changed, such as solids concentration, drying time and temperature. The size of particles can be controlled. Drum-dried products have one shortcoming. In comparison with cook-up starches (as non-pre-gelatinized products are called), drum-dried products display slightly less viscosity and produce less glossy and less smooth pastes when dispersed in water. This deficiency is caused by the destruction of starch granule integrity in drum drying. Newer technologies have paid attention to this problem. Despite the shortness, drum drying is recommended for economy and for its ability to enable the usage of large particles in texturizing starches. Texturizing starches are typically obtained from highly cross-linked starches that are drum-dried. They are slow to hydrate and are applied in cookie fillings and toppings to control boil-out when subjected to high oven temperatures and offer a pulpy fruit texture.

Recently, the production of dry pre-gelatinized starch from maize starch and maize flour using four different drum drying processes is described (Fritze 1973). A comparison is made among the following items: the twin-drum sump dryer, the single-drum dryer with top applicator rolls and starch slurry feed ahead of the first roll only, the single-drum dryer with top applicator rolls and starch slurry feed ahead of each roll, and the single-drum dryer as described under the preceding item but preceded by a starch cooker. In particular the dryer capacity, water absorptivity, viscosity, cold water solubility, bulk weight, and degree of gelatinization were investigated as functions of the feed concentration of the starch slurry and partly also of the drum speed. It could be demonstrated that advantages are offered in particular by pre-gelatinization before drying and that as a result thereof, the physical properties could be varied (Fritze 1973).

4.3.2 Extrusion

Extrusion gelatinized (cooked) starch but damaged granules more than drum drying, thus reducing viscosity. Extrusion may even fragment amylopectin molecules. Drum-dried and extruded wheat starch both produced a continuous phase of melted starch. Drum-dried starch had higher average molecular weights in the amylose and amylopectin fractions than extruded starch. Davidson et al. demonstrated that both temperature and sheer stresses were responsible for this molecular fragmentation. By comparing the rheology of drum-dried and extruded starches, Loisel et al. found that extruded starches had lower cold water swelling power and greater solubility (Loisel et al. 2006). Starches extruded at lower temperatures and at higher moisture contents were more likely the drum-dried starches in these properties. Extrusion has been favored to reduce molecular weight and increase solubility for improved emulsification by octenyl succinylated starches.

Recently, the effects of pre-gelatinization, mild and severe parboiling processes on paddy rice, and the utilization of the corresponding flours (PGF, MPF, and SPF) for gluten-free (GF) pasta-making were investigated. Two pasta-making processes (extrusion cooking and conventional extrusion) were carried out. Compared to pre-gelatinization, both parboiling processes induced lower pasting viscosity at any temperature, enzymatic susceptibility, and hydration. The magnitude of these changes significantly increased with the severity of the parboiling treatment. The lowest value for cooking loss was detected for samples prepared by 100% SPF (extrusion cooking) or by mixture of SPF and PGF (50:50) (conventional extrusion).

Nevertheless, the extrusion cooking process promoted an extremely firm texture of cooked pasta when applied to parboiled flours (Marti et al. 2013).

4.3.3 Spray Drying

Starch slurry is injected through an atomization aperture in a nozzle assembly to form a fine spray. Steam is injected through another aperture in the nozzle assembly into the atomized starch spray to gelatinize the starch, the entire operation taking place in an enclosed chamber. The time for passage of the material through the chamber, i.e., from the atomization aperture through the vent aperture, defines the cooking or gelatinization time. The gelatinized starch is recovered essentially as granules. The technology is broadly applied to both native and chemically modified starches. For example, using this process, Katcher and Schara developed a pre-gelatinized, modified normal maize starch that is essentially flavor-free and which has a viscosity-building capacity equivalent to spray-dried and pre-gelatinized tapioca starch (Katcher 1994). In 1992, an improved process was reported. In it, starch is uniformly and simultaneously atomized and cooked in an aqueous medium by means of a single atomization step in an apparatus comprising a two-fluid, internal mix, spray-drying nozzle, coupled to a means for drying the cooked, atomized starch to produce a uniformly pre-gelatinized cold water swelling (CWS) starch with desirable textural, visual, and organoleptic properties.

4.3.4 Other Methods

Except for those three commercial methods, there are also new innovative and emerging technologies to prepare the pre-gelatinized starch, such as mechanical activation (Zhang et al. 2013) and microwave (González Parada and Pérez Sira 2003).

Mechanical activation (MA) using a customized stirring ball mill could be used to prepare partially pre-gelatinized cassava starch (PPCS) which has been studied recently. MA could significantly destroy the crystal structure of starch granules, contributing to the increase of cold water solubility, flowability, and flood ability, the variations of particle size and surface morphology, and the decrease in pasting temperature, viscosity of cooked PPCS paste, breakdown, and setback. It was also found that the PPCS with different degree of gelatinization could be prepared by controlling the milling time. With the unique properties induced by MA, the potential use of PPCS as excipient in pharmaceutical formulations is discussed (Zhang et al. 2013).

4.4 The Structure Change in Pre-gelatinization Processing

Native starch granules are widely regarded to be a multi-scale structure polymer which is from nanometer to micrometer scales, i.e., amylose and amylopectin chains (~nm) (Wu et al. 2013; Xie et al. 2012; Pérez and Bertoft 2010; Liao et al. 2014), crystalline and amorphous lamellae structure (9–10 nm), alternating amorphous and semicrystalline growth rings (100–400 nm), and starch granules (<1–100 μm). The two basic components in starch are near-linear amylose and highly multiple-branched amylopectin, which may affect higher-level structure of starch (aggregation structure) (Witt et al. 2012; Witt and Gilbert 2014; Chen et al. 2016). Generally, it is widely regarded that the amorphous zone is amylose and the branching points of amylopectin, while the short-branched chains in the amylopectin are the main crystalline component in granular starch (Liu et al. 2009). Recently, the techniques include fluorophore-assisted carbohydrate electrophoresis, high-performance anion-exchange chromatography, multiple-detector size-exclusion chromatography, and various scattering techniques (light, X-ray, and neutron), spectroscopy technology (FTIR and NMR), and microscopy technologies such as light and polarized microscopy, scanning electron microscopy, and confocal laser scanning microscopy were used to study starch structure and give the information of the relationship between structure and property.

The changes in starch molecular, aggregation structure, and granular structures, i.e., disruption of double helical crystallites and damage to starch granules, respectively, as the results of the grinding of cereal grains, will be discussed separately. Slurries of canna starch were heated at 60 °C to investigate the change of aggregation structure by Lan et al. (2016). For this purpose, solid-state ^{13}C CP/MAS NMR, X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS) were used to estimate the short- and long-range orders within the structure. Crystal stabilization was observed, and the critical time for the formation of double helical crystals was 3 h. With longer times, imperfect sub-crystal started to prevail (Lan et al. 2016).

DSC, XRD, and SEM were used to study the pre-gelatinized *Dioscorea dumetorum* (bitter yam) and *Dioscorea oppositifolia* (Chinese yam) starches (Okunlola et al. 2015). The pre-gelatinized starches had significantly larger structures that were gel-like, aggregated, and irregular. The DSC endotherms revealed that pre-gelatinized bitter and Chinese starches had higher gelatinization temperatures than the native forms, and XRD spectra showed that characteristic semicrystalline structures of the native starches (2θ between 13 and 23 °C) were disrupted by pre-gelatinization, forming amorphous structures.

Three rice starches with different amylose contents (glutinous, 1.4%; jasmine, 15.0%; and Chiang, 20.2%) were pre-gelatinized in a double drum dryer at 110, 117, and 123 °C. Starch granule and crystallinity were determined by SEM and XRD and FTIR, respectively (Nakorn et al. 2009). The disintegration of rice starch granules and the formation of holes were showed after pre-gelatinization. Pre-gelatinized glutinous-rich starch (PGS) and pre-gelatinized jasmine rice starch (PJS) had higher degree of disintegration of the granular and macromolecular structure. The increased release of soluble components during thermal treatment explained this phenomenon, which was proved by the completely amorphous X-ray diffractograms of PGS and PJS indicating a complete destruction of the granular order. On the contrary, the granular structure of high-amylose Chiang rice starch was less ruined. A V-type crystalline amylose-lipid complex structure formed in the pre-gelatinized Chiang rice starch (PCS), which was confirmed by XRD. FTIR spectroscopy was used to investigate the crystallinity change in the short-range order. This IR band appeared as a small peak for PCS, whereas the IR band at 1046 cm-1 disappeared for PGS and PJS, which was in accordance with XRD results (Nakorn et al. 2009).

4.5 The Physical-Chemical Properties During Pre-gelatinization

Pre-gelatinized (PG) starches are always processed at low temperature to increase viscosity and offer a desirable texture. The functional properties of PG starch can be influenced by other constituents used in food matrices. The functional properties such as gelatinization, pasting, solubility, swelling, and digestibility as well as other physical and chemical properties were discussed.

The functional properties of those three rice starches with different amylose contents (glutinous, 1.4%; jasmine, 15.0%; and Chiang, 20.2%) which were pre-gelatinized in a double drum dryer at 110, 117, and 123 °C(Nakorn et al. 2009) were also studied by Nakorn et al. The water absorption index (WAI) and water solubility index (WSI) indicate the mass of water absorbed by dry starch and the amount of soluble components that have leached out from the granules. The macromolecular disorganization and the degradation of starch during thermal treatment can result in higher WAI and WSI values of pre-gelatinized rich starches. Pre-gelatinized starches made from low-amylose rice exhibited a higher WAI and WSI. The rise in amylose content of the rice starches led to a less disrupted granule structure and accordingly a fall in the WAI and WSI values. Increased drum temperatures led to increased rupture of the granular structure and thus a decrease in WAI. Compared to PGS and PJS that displayed RVA cold peak viscosity and an amorphous structure, pre-gelatinized starch from high-amylose rice (Chiang) showed RVA hot peak viscosity and an amylose-lipid complex structure. This is because pre-gelatinization destroyed the granular structure of rice starch with lower amylose content more severely than that of rich starch with higher amylose content. Both PGS and PJS showed shear-thinning behavior at low temperature. The cold peak viscosity for the PGS and PJS decreased when increasing drum temperature. Nevertheless, apparent viscosity was only slightly affected by the rise of drum temperature.

Hedayati et al. have studied the effects of different levels of sucrose and glucose (0%, 10%, 20%, 30%, and 40% of dry starch weight basis) as two common sweeteners on drum-dried pre-gelatinized maize starch (Hedayati et al. 2016a). With the increase of sugar level, water absorption was increased due to the equatorial hydroxyl groups of sugars, formation of intermolecular hydrogen bonds, and cross-linking. The increased water uptake of pre-gelatinized starches resulted in higher viscosity and mechanical properties. Samples with sucrose have significantly higher water absorption and viscosity than those with glucose. Sucrose had more obvious effects on gel clarity and is more appropriate for products in which clarity is important. Freeze-thaw stability of starch pastes was also improved in the presence of sugars owing to their cryoprotective effects. Thus, pre-gelatinized starch has high potential to be used in frozen products which contain sugars (Hedayati et al. 2016a).

The effects of pre-gelatinization on the rheological properties of selected botanical starches as pharmaceutical excipients were evaluated. Pre-gelatinization of cassava starch and sweet potato was prepared.

Microscopic analysis indicated definitive alteration in the granular character of the modified starches. The native starches were susceptible to retrogradation, which was alleviated by pre-gelatinization. Pre-gelatinization modification increased resistance to retrogradation, solubility, swelling power, and water absorption capacity of the starches. The increases in solubility, swelling power, and water absorption capacity were directly related to decrease in amylose content (Lawal et al. 2015).

Rheological properties of native potato starch (NPS) and pre-gelatinized potato starch (PPS) were investigated under steady and dynamic shear conditions at 20 °C and 60 °C, respectively. The consistency index, apparent viscosity, and yield stress values of PPS were much lower than those of NPS. The flow behavior of PPS is more temperature-dependent. Dynamic moduli (G' and G'') and complex viscosity of PPS were much lower than those of NPS, while tan δ values of PPS were in the range of 2.30–3.50 (tan δ>1), indicating that PPS is more viscous than elastic. Rheological properties of NPS are strongly influenced by pre-gelatinization (Elgorashi 2016).

The influence of pH changes (3, 5, 7, and 9) on physical properties of pre-gelatinized (PG) and granular cold water swelling (GCWS) maize starches was also studied (Hedayati et al. 2016b). PG starches were fragmented in acidic pH; however, GCWS starches mainly reserved their granular integrity but were shriveled. For both modified starches, the water absorption, cold water viscosity, textural parameters, turbidity, and freeze-thaw stability of the samples decreased, whereas water solubility increased at pH 3 and 5. On the other hand, alkaline pH did not bring about evident changes on morphology of PG starch, but the surface of GCWS starch became smoother. Water absorption, solubility, rheological and mechanical properties, freeze-thaw stability, and turbidity of the starch pastes increased at high pH values. Overall, both starches were more stable at alkaline pH compared to acidic pH values, and GCWS starch was more resistant to pH changes than PG starch (Hedayati et al. 2016b).

The compression and mechanical properties of directly compressible pre-gelatinized sago starches at 65 °C with different pre-gelatinization times of 15, 30, 45, and 60 min were labeled as PS1, PS2, PS3, and PS4, respectively (Hedayati et al. 2016b). The compressibility of sago starch is found to be lower than that of its pre-gelatinized forms, and the compressibility increases with an increase in the pre-gelatinization time. The result of mechanical properties showed the same trends. This study confirms previous reports showing that pre-gelatinization is able to improve the compressibility and compatibility of a starch and therefore showing the potential of pre-gelatinized sago starch as a new directly compressible excipient in tablet formulations (Widodo and Hassan 2015).

Rheological properties of native potato starch (NPS) and pre-gelatinized potato starch (PPS) were investigated under steady and dynamic shear conditions at 20 °C and 60 °C. The consistency index, apparent viscosity, and yield stress values of PPS were much lower than those of NPS. The flow behavior of PPS is more temperature-dependent. Dynamic moduli (G' and G'') and complex viscosity of PPS were much lower than those of NPS, while tan δ values of PPS were in the range of 2.30–3.50 ($\tan \delta > 1$), indicating that PPS is more viscous than elastic. Rheological properties of NPS are strongly influenced by pre-gelatinization (Elgorashi 2016).

The changes of gelatinization, powder characteristics, and pasting properties of customized stirring ball mill treated partially pre-gelatinized cassava starch (PPCS) were studied. MA could significantly destroy the crystal structure of starch granules, contributing to the increase of cold water solubility, flowability, and flood ability, the variations of particle size and surface morphology, and the decrease in pasting temperature, viscosity of cooked PPCS paste, breakdown, and setback. With these unique properties induced by MA, PPCS was expected to be used as excipient in pharmaceutical formulations as it could exhibit dual functionality as both binder and disintegrant and improve the production efficiency and qualities of solid oral drugs (Zhang et al. 2013).

The effect of physical aging on the physicochemical properties of pre-gelatinized tapioca starch was investigated by Manchun et al. (2012). The tapioca starch was pre-gelatinized by either heating at 80 °C or using high-power (400 W) ultrasonic treatment. After pre-gelatinization, dextrose equivalent (DE), viscosity, turbidity, swelling power, and solubility were determined and compared with native tapioca starch. Compared to fresh tapioca starch, the aged starch exhibited an increase in DE, turbidity, and solubility. The viscosity and swelling power were decreased after storage. Similar results were found for both tapioca starches pre-gelatinized by heat and ultrasonic treatments. The results of the physicochemical properties of pre-gelatinized starches obtained from ultrasonic treatment related to the formation of low molecular weight components that aging starch is easily changed by disruption of molecular structure within the starch granule (Widodo and Hassan 2015).

4.6 Future Perspectives

Over the last decade, important industry application and fundamental science study have been made in the production of pre-gelatinized starch. As the most important physical modification starch, till now, pre-gelatinized starch has been widely used in feed, food, and pharmaceutical industry and also has a good most promising application in instant food and other high value fields.

Despite extremely interesting properties, such as solubility, thickening/gelling capabilities, and high digestion rate for pre-gelatinized starch, the applications of pre-gelatinized starch in the high value production area remain limited, mainly due to the extreme difficulty to control the physical modification extent and the starch molecular assembly. The applications in the instant food field change very promising but require more research and development to achieve significant results, such as exact control of starch molecular assembly, the interaction between starch and other components in food, and the new machine to prepare pre-gelatinized starch more economically. Summary, for the most important physical modification starch, more scientific fundament research, new preparation methods and related equipment development, and new field application, is still needed.

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Chapter 5
Gamma Irradiation of Starch

Xiangli Kong

Abstract As a physical treatment, gamma irradiation has many advantages, such as high efficiency, low-cost, eco-friendship, and no remarkable rise in temperature during the treatment process. The degradation changes of starch by radiation are reproducible and quantitative, without needing special appliances to control temperature and environment. The effects of irradiation on starch have attracted much more attention in the last decade. Gamma radiation may generate free radicals which can contribute to molecular changes and fragmentation of starch. Starch depolymerization leads to progressive reduction in molecular size of amylose and amylopectin by random cleavage of the glycosidic chains, and consequently changes the structural and physicochemical characteristics of starch. Visible or significant changes on starch granules upon irradiation were not found; however, some researchers found that Maltese cross became unclear and fissures or cracks developed on starch granules. To date, all researchers found that the C-type starches showed decrease in amylose content upon gamma irradiation, and most researchers reported that gamma irradiation treatment decreased amylose content in A-type starches but increased amylose content in B-type starches. The X-ray diffraction pattern of starches remained unchanged after gamma irradiation, but the relative crystallinity decreased upon irradiation in most cases; however, some A-type starches exhibited increase in relative crystallinity at low-dose irradiation and then decreased at higher doses. The Fourier transform-infrared spectral pattern of irradiated starch was not altered; however, most intensities increased indicating decreases in the ordered structure of starch upon irradiation. Gelatinization temperatures and enthalpy of gelatinization of A-type starches decreased upon irradiation in most cases. With regard to the B-type starches, the gelatinization parameters showed increase at lower dosage but decreased with irradiation dose increasing in some cases. For C-type starches, the gelatinization parameters were observed to increase by most researchers. The swelling power was observed to decrease under gamma irradiation treatment in most cases, water solubility index of irradiated starches increased with irradiation dosage elevated in all reports, and the syneresis of gels

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formed with irradiated treated starches decreased. Most pasting and rheological parameters of irradiated starches decreased continuously with irradiation dosage increasing. Gamma irradiation can be employed to elevate the resistant starch fraction, whereas some researchers observed that irradiation treatment could decrease resistant starch content. Radiation processing can promote cross-linking in the starch matrix under oxygen. Graft copolymerization of chemicals onto starch by a simultaneous irradiation technique can also be achieved to produce biodegradable film or superabsorbent hydrogel.

Keywords Gamma irradiation · Depolymerization · Structure · Physicochemical properties

5.1 Introduction

Most of the techniques currently employed for starch modification are usually complex, expensive, and time-consuming; however, radiation processing has been highlighted to provide a low-cost and environment-friendly alternative to alter the structural, physicochemical, and functional characteristics of starch. During the radiation processing, no pollutant agents are needed to be used, the toxic substances are not allowed to be penetrated in the treated products, and catalysts and laborious preparation of sample are not required (Bhat and Karim 2009; Wani et al. 2014). The degradation changes of starch by radiation are reproducible and quantitative, without needing special appliances to control temperature and environment. Based on the advantages mentioned above, irradiation was becoming an alternative technique to modify starch to replace common techniques of chemical and physical modifications. The modification of starch by irradiation technique is an impending development and the commonly used one is gamma irradiation (Reddy et al. 2015a; Atrous et al. 2017), which is an ionizing and nonthermal physical method. Gamma irradiation processing involves the use of a radioactive isotope, either in the form of cobalt-60 or cesium-137, which emits high-energy gamma rays or photons capable of intruding in-depth into the target product, up to several meters (Ocloo et al. 2014). The Unites States Food and Drug Administration (FDA) and international standards for food irradiation permit gamma rays from cobalt-60 or cesium-137, however, all industrial gamma irradiation facilities employ cobalt-60 rather than cesium-137 as the radiation source because of practical difficulties in handling the latter one. The radiation dose unit is a function of the energy of the radiation source and the time of exposure. Irradiation dosage, previously referred to as the rad, is currently expressed in kilograys (kGy). One kilogray is equal to 1 kJ of energy absorption per kilogram of a material and is equivalent to 100,000 rads. The unit gray can be used for any type of radiation, but it does not describe the biological effects of the different radiations (Mahapatra et al. 2005).

Gamma radiation may generate free radicals which can contribute to molecular changes and fragmentation of starch. Starch depolymerization lead to progressive reduction in molecular size of amylose and amylopectin by random cleavage of the glycosidic chains (Sujka et al. 2015), and consequently changes the structural and physicochemical characteristics of starch. Considering that the intensity of free radicals was observed to be dependent on starch water content, irradiation dose, temperature, and time of storage (Raffi and Agnel 1983), alterations of starch materials are dependent on irradiation conditions (e.g., dosage, dose rate, and temperature), starch moisture, and content starch types to a large degree. When water is irradiated, the following highly reactive entities are formed:

$$H_2O \rightarrow \cdot OH, e^{-}_{aq}, \cdot H, H_2, H_2O_2, H_3O^{+}.$$

where ·OH is a hydroxyl radical, e^{-}_{aq} is a hydrated electron, H is a hydrogen atom, H_2 is a hydrogen molecule, H_2O_2 is hydrogen peroxide, and H_3O^+ is a hydrated proton. The hydroxyl radical is a powerful oxidizing agent, whereas the hydrated electron is a strong reducing agent and the hydrogen atoms are slightly weaker reducing agents. Hydrogen (H_2) and hydrogen peroxide (H_2O_2) are the only stable end products of water radiolysis, being produced in a low yield even when the irradiation dosage is high. The presence of oxygen during irradiation can influence the course of radiolysis. Hydrogen atoms can reduce oxygen to the hydroperoxyl radical (·OOH), which is a mild oxidizing agent. Another oxidizing agent, the superoxide radical ($\cdot O_2$), is formed from the reaction of the solvated electron with oxygen. Both the hydroperoxyl radical and the superoxide radical can give rise to hydrogen peroxide. Oxygen can also add to other radicals produced when water is irradiated, giving rise to peroxy radicals ($\cdot RO_2$). Ozone (O_3), a powerful oxidant, can also be formed from oxygen during irradiation (Stewart 2001).

The general scheme of free radicals generation in starch molecules after exposure to radiation treatments is illustrated in Fig. 5.1. It is well known that radiation processing leads to the formation of radiolytic products or radiation degradation products (RDPs). Some of the major radiolytic products of carbohydrate molecules are formic acid, acetaldehyde, and formaldehyde (Bhat and Karim 2009; Zhu 2016). The major practical aim of high-level irradiation of starch is preparation of water soluble starch for food application, animal feed production, tablet preparation, or even as corrosion inhibitors for steel (Tomasik and Zaranyika 1995). Radiation processing can also promote cross-linking in the starch matrix under oxygen. This unique phenomenon is quite important as presently various methods employed for cross-linking purposes. Graft copolymerization of chemicals onto starch by a simultaneous irradiation technique can also be achieved to produce biodegradable film or superabsorbent hydrogel. In summary, gamma radiation can be employed as a convenient technique for modification of starch material by means of degradation, grafting, and cross-linking.

5.2 Starch Change Under Gamma Irradiation

5.2.1 Granule Morphology

The morphological properties of native and irradiated starch granules can be observed by regular or polarized light microscope and scanning or transmission electron microscope to analyze damages at granular level. Most researchers did not

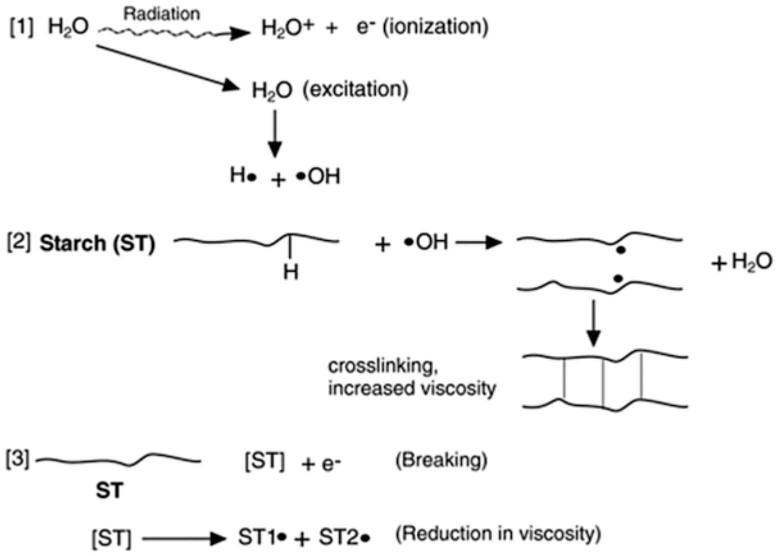

Fig. 5.1 Possible degradation and cross-linking of starch chains influenced by gamma irradiation. (Bhat and Karim 2009)

find visible or significant changes on starch granules upon irradiation, whereas some researchers found that Maltese cross became unclear and fissures or cracks developed on starch granules; furthermore, granule size decreased in some studies (Table 5.1). The appearance of cracks on the granule surface, caused by highly energetic and penetrating radiations, is dependent of the starch source, irradiation dosage, dose rate, and water content. Essential changes in the potato granular appearance were not found after irradiation even with 600 kGy; however, deformed shape and rough surface observed on granules were attributed to the mechanical treatment (Cieśla and Eliasson 2002). Chung and Liu (2010) observed that B-type starch granules were more resistant than C-type under gamma irradiation and concluded that B-type starches might have more resistance than A-type starch to gamma irradiation treatment based on the results of thermal treatment. Low-dosage irradiation promoted aggregation of potato starch granules, which was attributed to the starch-starch interactions; actually gamma irradiation could cause degradation or cross-linking of starch. Low-dosage irradiation might mainly cause cross-linking instead of degradation, which can be verified by the phenomenon that low dosage caused increase in final viscosity (Singh et al. 2011). With increasing irradiation dose, increases in surface cracking and the amount of small-sized granules were observed by some researchers. These changes were caused by free radicals generated by gamma irradiation cleaving large starch molecules, and some starch granules were fractured along the cleaved molecules, and this kind of breakage resulted

Table 5.1 Granular change of starches under gamma irradiation

Starch samples		Irradiation treatment conditions		Results	
		Material status			
Source/type	Amylose content	Dosage/ dose rate	Water content	Granular change	Literatures
Rice^A	~20%	Starch powder 1, 2, 5 kGy at 0.4 kGy/h	~9%	No change in granule morphology, the larger granules increased or decreased	Polesi et al. (2016)
Rice^A	~20%	Starch powder 2, 5, 10 kGy at 0.4 kGy/h	~12%	No visible changes in granule morphology; however, a few granules were deformed at dosage of 10 kGy; particle diameter of starch granules decreased upon irradiation	Gul et al. (2016)
Rice^A	~26%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~12%	Surface cracking of starch granules and the amount of small-sized granules were observed to increase with increasing irradiation dose	Ashwar et al. (2014)
Rice^A	~19%	Grain 2, 5, 8, 10 kGy at 1 kGy/h	~30%	The amount of small-sized granules increased	Yu and Wang (2007)
Rice^A	~1–26%	Grain 0.2, 0.4, 0.6, 0.8, 1 kGy at 1 kGy/h	ND	The shape of starch granules was deformed	Wu et al. (2002)
Wheat^A	~34%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~13%	Unaffected by irradiation	Atrous et al. (2017)
Wheat^A	~35%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~13%	Maltese cross in some starch granules irradiated at 50 kGy has become somewhat unclear, but the granules surfaces were unaffected by irradiation	Atrous et al. (2015)
Arrowhead^A	~31%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	Unaffected by irradiation	Wani et al. (2015)

(continued)

Table 5.1 (continued)

Starch samples		Irradiation treatment conditions		Results	
Source/type	Amylose content	Material status Dosage/dose rate	Water content	Granular change	Literatures
Indian horse Chestnut^{A}	~27%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~12%	No significant differences between native and irradiated starches	Wani et al. (2014)
Sorghum^{A}	ND	Flour powder 10, 10 + 25 kGy	ND	External structure of sorghum starch granules was unaffected by irradiation	Mukisa et al. (2012)
Maize^{A}	ND	Starch powder 1, 2, 5, 10, 20, 50, 100, 200, 500 kGy at 5 kGy/h	ND	Unaffected by irradiation	Liu et al. (2012)
Corn^{A}	ND	Starch powder 3, 5, 10, 20, 50 kGy at 1.14 Gy/h	ND	No notable changes on the shapes and sizes of starch granules under irradiation	Ben Bettaïeb et al. (2014)
Corn^{A}	~29%	Starch powder 2, 10, 50 kGy at 2 kGy/h and 0.40, 0.67, 2 kGy/h to a total dose of 10 kGy	~9%	Granule structure and birefringence remain unchanged up to 10 kGy; however, some starch granules became fractured at 50 kGy. Polarization cross in some starch granules has become unclear at 50 kGy	Chung and Liu (2009)
Corn$^{A\text{ or }B}$	2–72%	Starch powder 5, 10, 25 and 50 kGy at 1 kGy/h	~12%	Only marginal pin holes were observed on the surface of few granules, no significant change in starch granule surfaces	Lee et al. (2013)
Corn$^{A\text{ or }B}$	4–70%	Starch powder 1, 5, 10, 25, 50 kGy at 1 kGy/h	ND	Intact and visually unchanged	Chung et al. (2015)
Maize^{B}	~58%	Starch powder 30, 60 kGy at 1.2 kG/h	~10%	Unaffected by irradiation	Ocloo et al. (2014)

(continued)

Table 5.1 (continued)

Starch samples		Irradiation treatment conditions		Results	
Source/type	Amylose content	Material status Dosage/dose rate	Water content	Granular change	Literatures
Potato^B	~30%	Starch powder 5, 10, 20, 30 kGy at 3.6 kGy/h	~12%	Granules were covered with a layer of probably products of starch depolymerization above 10 kGy	Sujka et al. (2015)
Potato^B	~30%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~18%	Unaffected by irradiation	Atrous et al. (2017)
Potato^B	ND	Starch powder 5, 10, 20, 30 kGy at 3.6 kGy/h	~14%	Defective structures are present in large granules, and the number of small granules increased at dosage of 30 kGy	Cieśla et al. (2015)
Potato^B	~32%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~10%	The number of fractured granules increased with increasing irradiation dosage	Gani et al. (2014)
Potato^B	~15%	Starch powder 0.01, 0.05, 0.1, 0.5 kGy	ND	Presence of aggregated starch granules	Singh et al. (2011)
Potato^B	~32%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	Granule surface unaffected by irradiation, maltese cross in some starch granules of irradiated starches became unclear	Chung and Liu (2010)
Potato^B	~17%	Tuber 0.1, 0.5 kGy	NA	The proportion of small-sized granules was increased	Ezekiel et al. (2007)
Potato^B	ND	Starch powder 20 kGy at 1.66 kGy/h, 600 kGy at 2.02 kGy/h, 446 kGy at 3.1 kGy/h	~20%	Essential changes in the granular appearance were not found after irradiation even with 600 kGy. The granules with a deformed shape and rough surface were present in the amorphized sample due to the mechanical treatment. A large fraction of the needle-shaped long granules was noticed	Cieśla and Eliasson (2002)

(continued)

Table 5.1 (continued)

Starch samples		Irradiation treatment conditions		Results	
		Material status			
Source/type	Amylose content	Dosage/ dose rate	Water content	Granular change	Literatures
Elephant foot yam^B	~28%	Starch powder 5, 10, 15, 20, 25 kGy at 2 kGy/h	~11%	No visual changes in granule morphology	Reddy et al. (2015a)
Chickpea^C	~30%	Flour powder 0.5, 1, 2.5, 5, 10 kGy at 0.5 kGy/h	ND	Slight surface fissures in irradiated starch granules treated with 5 and 10 kGy	Bashir and Aggarwal (2017)
Chickpea^C	~33%	Starch powder 4, 8, 12 kGy at 2 kGy/h	~12%	Fissures developed on surfaces, granule width reduced significant irradiated at 12 kGy	Bashir and Haripriya (2016)
Chickpea^C	ND	Grain 2, 5, 10, 20, 30, 50 kGy at 3.6 kGy/h	ND	No significant changes in size distribution and structure of starch granules	Graham et al. (2002)
Cowpea^C	ND	Flour powder and paste 2, 10, 50 kGy	ND	Unaffected by irradiation	Abu et al. (2006)
Broad bean^C	~52%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	Fissures developed on starch granules, but mean granule length, mean granule width, and width range of native and modified starches did not vary significantly	Sofi et al. (2013)
Kidney beans^C	36–41%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~13%	Surface fracturing of granules increased with increasing irradiation dose	Gani et al. (2012)
Bean^C	~36%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	Cracks observed after irradiation with 10 kGy and increased with 50 kGy	Chung and Liu (2010)
Bean^C	ND	Starch powder 2.5, 5, 10, 20 kGy	~12%	Gamma irradiation increased the susceptibility to central fissures	Duarte and Rupnow (1993)

(continued)

Table 5.1 (continued)

Starch samples		Irradiation treatment conditions		Results	
Source/type	Amylose content	Material status Dosage/dose rate	Water content	Granular change	Literatures
Sago^{C}	~27%	Starch powder 6, 10, 25 kGy at 8.3 kGy/h	~13%	No changes in granule size, shape, distribution, and surface	Othman et al. (2015)

in increased number of small-sized starch granules (Ashwar et al. 2014). Some researchers also observed that granules seem to be the starch granules which were covered with a layer of probably products of starch depolymerization, making granules "fused." Gamma irradiation damage to some starch granules might exist only in the form of changes to the structure of the starch molecules when starch granules remained intact and visually unchanged. Considering that the researchers performed their studies under various conditions, so it is necessary to remain other factors unchanged in order to explore the effects of one factor.

5.2.2 Chemical Change

Chemical changes of starch under gamma irradiation included reducing sugar content, carboxyl content, acidity, pH value, amylose content, and starch molecules degradation. Gamma irradiation increased the reducing power of amylose and amylopectin continuously with increasing dose (Kertesz et al. 1959; Samec 1960; El Saadany et al. 1974, 1976; Nene et al. 1975; Sokhey and Hanna 1993; Ezekiel et al. 2007). Glucose, maltose, and small dextrins were found in the irradiated starch specimen by chromatographical analysis (Mishina and Nikuni 1959). The carboxyl content and acidity was observed to increase, and pH value decreased by all the researchers who measured these indices (Table 5.2); formic, acetic, pyruvic, and glucuronic acids were identified in irradiated starch (Ghali et al. 1979). So the main radiolytic products of starch were carboxylic acids, which resulted in an increase in carboxyl content and a decrease in pH value in all studies. Increased carboxyl content of irradiated starch was attributed to the breakdown of starch molecules by the action of free radicals; the slower irradiation dose rates produced much lower carboxyl content than a high-dose rate (Chung and Liu 2009, 2010).

Greenwood and Mackenzie (1963) reported gross molecular degradation of amylose and amylopectin isolated from irradiated starch. Chaudhry and Glew (1973) observed that the iodine binding capacity, the β-amylolysis limit and the average chain length of the starch amyloses were decreased by radiation treatment which

Table 5.2 Chemical change of starches under gamma irradiation

Starch samples		Irradiation treatment conditions		Results		Literatures
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Carboxyl content, acidity, and pH	Amylose content and molecular changes	
Rice^A	~27%	Grain 1, 2, 5 kGy at 0.4 kGy/h	~10%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓	Polesi et al. (2017)
Rice^A	~19%	Grain 2, 5, 8, 20 kGy at 1 kGy/h	~30%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓	Yu and Wang (2007)
Rice^A	~20%	Starch powder 1, 2, 5 kGy at 0.4 kGy/h	~9%	Carboxyl: ↑, Acidity: ↑, pH: ↓	Amylose: ↑ Amylose/amylopectin degraded; however, debranched short chains varied because of cleavage or cross-linking	Polesi et al. (2016)
Rice^A	~20%	Starch powder 1, 5, 10 kGy at 0.4 kGy/h	~13%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓	Gul et al. (2016)
Rice^A	~26%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~12%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓	Ashwar et al. (2014)
Rice^A	27–40%	Flour powder 0.5, 1, 2, 3, 4, 5 kGy at 1.0 kGy/h	NA	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓ Maximum wavelength and blue value of starch-iodine complex decreased which indicated that the degree of polymerization and average chain length of amylose and amylopectin reduced	Shu et al. (2013)

Rice^{A}	ND	Grain	~12%	Carboxyl: ND,	Amylose: ND	Bao et al. (2005)
		0.5, 1, 3, 5, 7, 9 kGy at 0.5 kGy/h		Acidity: ND, pH: ND	Amylopectin molecules degraded, molecular weight of amylopectin and amylose decreased with the increase in irradiation dosage, gamma irradiation had no significant effect on amylopectin chain-length profiles	
Rice^{A}	~1–26%	Grain	ND	Carboxyl: ND,	Amylose: ↓ more for low amylose samples	Wu et al. (2002)
		0.2, 0.4, 0.6, 0.8, 1 kGy at 1 kGy/h		Acidity: ND, pH: ND		
Wheat^{A}	~25%	Flour powder	~11%	Carboxyl: ND,	Amylose: ↑	Bashir and Aggarwal (2017)
		0.5, 1, 2.5, 5, 10 kGy		Acidity: ND, pH: ND		
Wheat^{A}	~34%	Starch powder	~13%	Carboxyl: ND,	Amylose: ↓	Atrous et al. (2017)
		3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h		Acidity: ND, pH: ND		
Wheat^{A}	~35%	Starch powder	~13%	Carboxyl: ND,	Amylose: ↓	Atrous et al. (2015)
		3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h		Acidity: ND, pH: ND	Free radicals were detected by electron paramagnetic resonance (EPR) spectrometry and increased with dosage	
Indian horse Chestnut^{A}	~27%	Starch powder	~12%	Carboxyl: ↑,	Amylose: ↓	Wani et al. (2014)
		5, 10, 15 kGy at 5 kGy/h		Acidity: ND, pH: ↓		
Arrowhead^{A}	~31%	Starch powder	~8%	Carboxyl: ND,	Amylose: ↓	Wani et al. (2015)
		5, 10, 15 kGy at 5 kGy/h		Acidity: ND, pH: ↓		

(continued)

Table 5.2 (continued)

Starch samples		Irradiation treatment conditions		Results		
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Carboxyl content, acidity, and pH	Amylose content and molecular changes	Literatures
Corn^A	Waxy and normal	Starch powder at various pH and salt Concentrations 5, 10, 20 kGy at 10 kGy/h	6%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ND Reduction in the molar mass, size, and specific volume was observed; adjustments of pH had little influence on the average molar mass and size of irradiated starch, whereas incorporation of salt greatly reduced the molar mass and size of irradiated waxy and normal maize starches	Baik et al. (2010)
Corn^A	Waxy and normal	Starch powder 5, 10, 20 kGy at 10 kGy/h	5%, 12%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ND Molecular weight of starch decreased, starch molecules became smaller and denser, structural changes were more significant when the moisture content of the irradiated starch was 5% than the changes at 12%. The chain degradation appeared more significant for waxy corn starch than for normal corn starch	Yoon et al. (2010)
Corn^A	~29%	Starch powder 2, 10, 50 kGy at 2 kGy/h and 0.40, 0.67, 2 kGy/h to a total dose of 10 kGy.	~9%	Carboxyl: ↑, Acidity: ND, pH: ND	Amylose: ↓ Short A chains (DP 6–12) increased, while the longer chains (DP ≥37) decreased, resulting in a significant decrease in average chain length. The extent of this change was more pronounced at higher dosage	Chung and Liu (2009)
Corn^A	ND	Starch powder 5, 10, 20, 30, 40 at 1 kGy/h	~12%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ND Number-average degree of polymerization decreased with dosage increasing; amylopectin degradation resulted in increase of low molecular weight molecules	Lee et al. (2006)

Maize^{A}	~25%	Maize flour 5, 10, 20, 40 kGy at 0.5 kGy/h	~14%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ND The proportion of β(1–3)- and β(1–4)-bonded starch increased; higher irradiation doses led to a reduction in the molecular size of amylopectin involved debranching and an increase in the production of short, straight-chain molecules	Rombo et al. (2004)
Corn$^{A\text{ or }B}$	4–70%	Starch powder 1, 5, 10, 25, 50 kGy at 1 kGy/h	ND	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↑ for waxy at 10 kGy, slight decrease for all samples <10 kGy and ↓ significantly for all samples under 25, 50 kGy treatment Starch-iodine complex absorption spectrum analysis indicated that the reduction of the molecular size of the samples has taken place	Chung et al. (2015)
Corn$^{A\text{ or }B}$	2–72%	Starch powder 5, 10, 25 and 50 kGy at 1 kGy/h	~12%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↑ with lower doses then ↓ with higher doses	Lee et al. (2013)
Maize^{B}	~58%	30, 60 kGy at 1.2 kGy/h	~10%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↑ Weight-average MW values of amylose and amylopectin decreased with irradiation dosage increase	Ocloo et al. (2014)
Potato^{B}	~30%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~18%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓	Atrous et al. (2017)
Potato^{B}	~30%	5, 10, 20, and 30 kGy at 3.6 kGy/h	~12%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓ Long linear chains degraded and showed lower iodine binding ability	Sujka et al. (2015)
Potato^{B}	~32%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~10%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓	Gani et al. (2014)

(continued)

Table 5.2 (continued)

Starch samples		Irradiation treatment conditions		Results		
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Carboxyl content, acidity, and pH	Amylose content and molecular changes	Literatures
Potato^{B}	~31%	Tuber	~75%	Carboxyl: ND,	Amylose: ↑	Lu et al. (2012a, b)
		0.1 kGy at 32.4 kGy/h		Acidity: ND, pH: ND	No significant difference was observed in chain-length profile of amylopectin upon irradiation	
Potato^{B}	~15%	Starch powder	ND	Carboxyl: Remain constant, ↑ at 0.5 kGy. Acidity: ND, pH: ↓	Amylose: ↑	Singh et al. (2011)
		0.01, 0.05, 0.1, 0.5 kGy				
Potato^{B}	~32%	Starch powder	~10%	Carboxyl: ↑,	Amylose: ↓	Chung and Liu (2010)
		10, 50 kGy at 2 kGy/h		Acidity: ND, pH: ↓	The proportions of short chain (DP 6–12) and long chain (DP ≥37) increased, whereas the proportion of DP 13–24 decreased with increasing irradiation dose	
Potato^{B}	~18%	Tuber	ND	Carboxyl: ND,	Amylose: ↑	Ezekiel et al. (2007)
		0.1 kGy, 0.5 kGy		Acidity: ND, pH: ND	Reducing sugars increased	
Cassava^{B}	ND	Starch powder	~10%	Carboxyl: ND,	Free radicals formed	Bertolini et al. (2001)
		1 kGy at 8.1 kGy/h		Acidity: ND, pH: ND		
Elephant foot yam^{B}	~28%	Starch powder	~11%	Carboxyl: ↑,	Amylose: ↓	Reddy et al. (2015a)
		5, 10, 15, 20, 25 kGy at 2 kGy/h		Acidity: ND, pH: ↓		
Banana^{B}	~25%	5, 10, 15, 20, 25 kGy at 2 kGy/h	ND	Carboxyl: ↑,	Amylose: ↓	Reddy et al. (2015b)
				Acidity: ND, pH: ↓		

Chickpea[C]	~33%	Starch powder 4, 8, 12 kGy at 2 kGy/h	~12%	Carboxyl: ND, Acidity: ND, pH: ↓	Amylose: ↓	Bashir and Haripriya (2016)
Bean[C]	~36%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓ The proportions of short chain (DP 6–12) and long chain (DP ≥37) increased, whereas the proportion of DP 13–24 decreased with increasing irradiation dose	Chung and Liu (2010)
Bean[C]	~35%	Maize flour 5, 10, 20, 40 kGy at 0.5 kGy/h	~9.8%	Carboxyl: ND, Acidity: ND, pH: ND	The proportion of β(1–3)- and β(1–4)-bonded starch increased; higher irradiation doses led to a reduction in the molecular size of amylopectin involved debranching and an increase in the production of short, straight-chain molecules	Rombo et al. (2004)
Bean[C]	ND	Starch powder 2.5, 5, 10, 20 kGy	~12%	Carboxyl: ND, Acidity: ↑, pH: ↓	Amylose: ND Reducing value increased with increasing irradiation dosage; radicals was observed by ESR	Duarte and Rupnow (1994)
Bean[C]	ND	Starch powder 2.5, 5, 10, 20 kGy	~12%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ND Irradiation changed molecular weight distribution of amylose and amylopectin, produced more amylose-like fraction	Duarte and Rupnow (1993)
Broad bean[C]	~52%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓	Sofi et al. (2013)
Kidney beans[C]	36%–41%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~13%	Carboxyl: ↑, Acidity: ND, pH: ↓	Amylose: ↓	Gani et al. (2012)
Sago[C]	~27%	Starch powder 6, 10, 25 kGy at 8.3 kGy/h	~13%	Carboxyl: ND, Acidity: ND, pH: ND	Amylose: ↓ at lower doses, ↑ at higher doses. Reducing sugars content increased	Othman et al. (2015)

suggested that degradation of the molecule had taken place; however, the iodine binding capacity and the β-amylolysis limit of the starch amylopectins were increased as a result of radiation treatment. A significant decrease of the amylopectin peak and a concomitant increase of the amylose-like peak area were observed by using gel permeation chromatography when starch was irradiated (Rayas-Duarte and Rupnow 1993; Polesi et al. 2016). Ionizing radiation caused a greater fragmentation of the amylopectin fraction of starch; the fragments became smaller in molecular weight and merged with the amylose in gel permeation chromatography (Sokhey and Hanna 1993). The increased proportion of β(1–3)- and β(1–4)- bonded starch as a result of transglucosidation was observed with increasing irradiation dose, which could in part explain the reduction in digestibility of some irradiated starches (Rombo et al. 2004). The number-average degree of polymerization (DP) decreased with the increase in gamma irradiation intensity; the degradation of amylopectin leading to increases in low molecular weight molecules was also observed (Lee et al. 2006). The proportion of short A chains increased; meanwhile, the longer chains decreased, resulting in a significant decrease in average chain length of amylopectin (Chung and Liu 2009). When amylopectin contained very long branch chains, this fraction could be degraded into long chains and resulted that the proportions of short chains and long chains increased (Chung and Liu 2010). However, Polesi et al. (2016) reported that increasing doses of gamma radiation promoted an increase or decrease in the number of short chains and long chains for different starch samples upon irradiation; the authors attributed this to cleavage or cross-linking under irradiation. Gamma irradiation reduced the molar mass, size, and specific volume considerably and consistently (Baik et al. 2010), since starch depolymerization by gamma irradiation caused decrease in amylopectin molecular weight.

To date, all researchers found that the C-type starches showed decrease in amylose content upon gamma irradiation, and most researchers reported that gamma irradiation treatment decreased amylose content in A-type starches but increased amylose content in B-type starches (Table 5.2). Chung and Liu (2010) found that B-type starch granules had more resistance under gamma irradiation than C-type base on morphological observations. The increase in amylose content might be attributed to the degradation of the amylopectin branches (Bashir and Aggarwal 2017). The degradation of amylopectin upon irradiation could release more linear chains of amylose, which were capable of complexing with iodine and increased the apparent amylose content (Othman et al. 2015). So waxy starch samples showed increase in apparent amylose content under irradiation (Chung et al. 2015). However, irradiation could cause breakdown of both amylopectin and amylose chains, and produced short chains, which might not complex with iodine and diminish its iodine binding capacity; hence the amylose content of some irradiated starches became lower. It is proposed that low irradiation dose produced short and amylose-like straight-chain molecules from amylopectin degradation (Rombo et al. 2004; Singh et al. 2011), which can better bind iodine. In contrast, high irradiation doses degraded amylose and amylopectin into fragments that are too short to bind iodine effectively, so the apparent amylose content of the irradiated samples reduced. When the amylose content was determined by separation of amylopectin precipitated based on its high molecular weight; as irradiation breaks the starch chains, the amylopectin fragments generated by irradiation were not eliminated during the step of precipitation of amylopectin, and they were still quantified as amylose (Polesi et al. 2016). In summary, the change in amylose content of irradiated starches was dependent on starch type, amylose content, irradiation treatment conditions, and methods employed for amylose determination.

5.2.3 Crystalline Structure and Thermal Properties

Two major crystal types are identified by using wide angle X-ray diffraction for native starches. Most cereal starches have A-type crystals, while tuber and amylose rich starches have B-type crystals, there is also C-type that is a combination of A-type and B-type. Reddy et al. (2015a) reported the pattern of elephant foot yam starch changed from B- to C-type, but the result can be challenged since the native starch showed strange X-ray diffraction curve compared with those irradiated starches; except this case, gamma irradiation did not change the X-ray diffraction pattern of starches in all studies reported, but the relative crystallinity decreased upon irradiation in most cases; however, some A-type starches exhibited increase in relative crystallinity at low-dose irradiation and then decreased at higher doses (Table 5.3). Gamma irradiation treatments degraded both crystalline and amorphous regions in starch granules, which could increase or decrease relative crystallinity, and this depended on which region was most affected by various irradiation doses (Chung and Liu 2010). The reduction in crystallinity with increasing irradiation is attributed to the breakage of the crystalline regions of starch granules. However, the packing of double helices within the A-type crystalline structure is relatively compact and less sensitive to irradiation than B-type and C-type polymorphs (Gul et al. 2016), resulting that the relative crystallinity increased slightly at lower dosages possibly.

Short-range order structure of starch can be probed by Fourier transform-infrared spectroscopy (FT-IR) to analyze the breakdown of various bonds and decrease of the double helices. The FTIR spectral pattern of irradiated starch did not change; however, most intensities showed increases indicating decreases in the ordered structure of starch upon irradiation (Table 5.3). Because the bands at 1047 and 1022 cm^{-1} are sensitive to changes in the crystalline and amorphous regions, respectively, the ratio of 1047/1022 was employed by some researcher to analyze the degree of order at the surface of starch granules and observed that the degree of starch granule surface order decreased with increase in irradiation dose (Chung and Liu 2009, 2010; Kong et al. 2016).

Gelatinization temperatures (onset, T_o; peak, T_p; conclusion, T_c) and enthalpy of gelatinization (ΔH) of A-type starches decreased upon irradiation in most cases. With regard to the B-type starches, the gelatinization parameters showed increase at lower dosage but decreased with irradiation dose increasing in some cases. For C-type starches, the gelatinization parameters were observed to increase by most researchers (Table 5.3). The effects of gamma irradiation on gelatinization parameters were complicated. Gamma irradiation could cause defective crystalline struc-

Table 5.3 Crystalline structure and thermal properties change of starches under gamma irradiation

Starch samples		Irradiation treatment conditions		Results		Literatures
		Material status Dosage/dose rate	Water content			
Starch/type	Amylose content			Crystalline structure	Thermal properties	
Rice^A	~20%	Starch powder 1, 2, 5 kGy at 0.4 kGy/h	~9%	No change in XRD pattern, relative crystallinity increased with 1 kGy, then decreased with higher doses	T_o, T_p, T_c, ΔH remained unaffected; however, gelatinization temperature increased at 5 kGy for some sample	Polesi et al. (2016)
Rice^A	~20%	Starch powder 2, 5, 10 kGy at 0.4 kGy/h	~12%	No change in XRD pattern, relative crystallinity decreased with increasing doses. The spectral patterns did not change except for an increase in intensities at 995 cm^{-1} indicating a decrease in the ordered structure	T_o, T_p, T_c, ΔH showed slight decrease initially and significant decrease at 10 kGy. The retrogradation enthalpy decreased with increase in irradiation dose	Gul et al. (2016)
Rice^A	~26%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~12%	No significant change in XRD pattern, relative crystallinity decreased significantly	ND	Ashwar et al. (2014)
Rice^A	27–40%	Flour powder 0.5, 1, 2, 3, 4, 5 kGy at 1.0 kGy/h	NA	No significant change in XRD pattern and relative crystallinity	T_o, T_p, T_c, ΔH decreased more significantly for high amylose starches	Shu et al. (2013)
Rice^A	ND	Grain 0.5, 1, 3, 5, 7, 9 kGy at 0.5 kGy/h	~12%	Relative crystallinity increased at 1 kGy, then decreased with more irradiation dosages	T_o remained unchanged; T_p, T_c, ΔH decreased slightly	Bao et al. (2005)
Wheat^A	~25%	Flour powder 0.5, 1, 2.5, 5, 10 kGy	~11%	FTIR spectra pattern did not change with irradiation; intensities in the bands at 1001.84 cm^{-1} increased with increasing irradiation dosage	ND	Bashir and Aggarwal (2017)

Wheat^{A}	ND	Starch powder 1, 3, 5, 7, 9 kGy at 1 kGy/h	~12%	The relative crystallinity showed slight increase with irradiation dose increasing up to 7 kGy and decrease at 9 kGy. No significant differences on FTIR spectra patterns were observed; gamma irradiation treatment increased the absorbance of wheat starch at band of 1018 cm^{-1}	T_o, T_p, T_c, ΔH showed slight decrease but not statistically significant. Transition temperatures of retrograded wheat starches increased slightly with irradiation dose up to 5 kGy, then decreased with higher irradiation dose	Kong et al. (2016)
Wheat^{A}	~35%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~13%	No change in XRD pattern and relative crystallinity, intensity decreased dramatically with increasing irradiation doses by FTIR	T_o, T_p, T_c, ΔH remained unaffected until 50 kGy	Atrous et al. (2015)
Amaranth^{A}	6–10%	2, 4, 6, 8, and 10 kGy at 1 kGy/h	~10%	Slight decrease in relative crystallinity,	T_o, T_p, T_c, ΔH showed slight decrease; ΔH exhibited a certain level of fluctuation	Kong et al. (2009)
Indian horse Chestnut^{A}	~27%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~12%	No change in XRD pattern; however, the intensity of characteristic peaks decreased. FTIR spectra pattern did not change; there was increase in intensities of the band at 1018 cm^{-1} at high irradiation dose indicating a decrease in the ordered structure	ND	Wani et al. (2014)
Arrow-head^{A}	~31%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	No change in XRD pattern; intensity of the characteristic peaks reduced. The intensity of absorption band at 1047 cm^{-1} gets reduced referring decrease of the crystalline order due to irradiation	T_o, T_p, T_c, ΔH showed slight decrease upon irradiation and steep decrease at 15 kGy	Wani et al. (2015)
Corn^{A}	ND	Starch powder 3, 5, 10, 20, 50 kGy at 1.14 kGy/h	ND	No change in XRD pattern, intensity decreased dramatically	T_o, T_p, T_c showed slight decrease upon irradiation	Ben Bettaïeb et al. (2014)

(continued)

Table 5.3 (continued)

Starch samples		Irradiation treatment conditions		Results		
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Crystalline structure	Thermal properties	Literatures
Maize^A	ND	Starch powder 1, 2, 5, 10, 20, 50, 100, 200, 500 kGy at 5 kGy/h	ND	No change in XRD pattern; relative crystallinity decreased; the ordered structure decreased as indicated by the increase in intensities of the band at 1018 cm^{-1} by FTIR	Decreases in T_o, T_p, T_c, ΔH were not statistically significant from up to 20 kGy; however, significant decreases at higher than 50 kGy	Liu et al. (2012)
Corn^A	~29%	Starch powder 2, 10, 50 kGy at 2 kGy/h and 0.40, 0.67, 2 kGy/h to a total dose of 10 kGy	~9%	No change in XRD pattern; the relative crystallinity decreased; the degree of order analyzed by FTIR at starch granule surface decreased. High-dose rate disrupted the crystalline structure more significantly	T_o, T_p, T_c decreased slightly up to 10 kGy, and significantly at 50 kGy, but ΔH remained unaffected	Chung and Liu (2009)
Corn^A	ND	Starch powder 5, 10, 20, 30, 40 at 1 kGy/h	~12%	No significant change in XRD pattern and relative crystallinity; the basic structure of anhydrous glucose was affected by FTIR	T_o, T_p, T_c, ΔH showed continuous decrease with irradiation dosage increasing	Lee et al. (2006)
Maize^A	~25%	Maize flour 5, 10, 20, 40 kGy at 0.5 kGy/h	~14%	ND	Remained unaffected	Rombo et al. (2004)
Corn$^{A \text{ or } B}$	4–70%	Starch powder 1, 5, 10, 25, 50 kGy at 1 kGy/h	ND	No change in XRD pattern, relative crystallinity decreased and more significantly with low amylose content samples	T_o, T_p, T_c decreased significantly; however, ΔH fluctuated	Chung et al. (2015)
Maize^B	~58%	30, 60 kGy at 1.2 kGy/h	~10%	ND	T_o, T_p, T_c, ΔH decreased significantly	Ocloo et al. (2014)
Banana^B	~25%	5, 10, 15, 20, 25 kGy at 2 kGy/h	ND	No change in XRD pattern; relative crystallinity decreased slightly	T_o, T_p, T_c, ΔH showed slight decrease upon irradiation	Reddy et al. (2015b)

Elephant foot yam^B	~28%	Starch powder 5, 10, 15, 20, 25 kGy at 2 kGy/h	~11%	XRD pattern changed from B to C-type upon irradiation; relative crystallinity decreased slightly; intensities of the band at 1155 cm^{-1} increased by FTIR; crystalline and amorphous regions were destructed by irradiation	T_o, T_p, T_c, ΔH showed increase at lower dosage and decrease with dose increasing	Reddy et al. (2015a)
Potato^B	~30%	Starch powder 5, 10, 20, 30 kGy at 3.6 kGy/h	~12%	ND	T_o, T_p, T_c, ΔH showed slight decrease upon irradiation	Sujka et al. (2015)
Potato^B	~31%	Tuber 0.1 kGy at 32.4 kGy/h	~75%	Decrease in relative crystallinity was observed	T_o, T_p, T_c, ΔH showed slight decrease upon irradiation	Lu et al. (2012a, b)
Potato^B	~15%	Starch powder 0.01, 0.05, 0.1, 0.5 kGy	ND	The intensity of peaks decreased; starches irradiated at 0.5 kGy did not show presence of any peaks	T_o, T_p, T_c, ΔH showed slight increase	Singh et al. (2011)
Potato^B	~32%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	No change in XRD pattern; the relative crystallinity decreased; the degree of order analyzed by FTIR at starch granule surface decreased	T_o, T_p, T_c increased at 10 kGy but decreased at 50 kGy; ΔH decreased as irradiation dose increased	Chung and Liu (2010)
Potato^B	~32%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~10%	No change in XRD pattern; relative crystallinity decreased	ND	Gani et al. (2014)
Chickpea^C	~30%	Flour powder 0.5, 1, 2.5, 5, 10 kGy at 0.5 kGy/h	ND	No change in FTIR spectra pattern; the ordered structure of starch decreased. The intensities of the peaks and relative crystallinity by XRD decreased	T_o, T_p, T_c, ΔH : decreased with dose	Bashir and Aggarwal (2017)
Chickpea^C	~33%	Starch powder 4, 8, 12 kGy at 2 kGy/h	~12%	Relative crystallinity showed decrease at 4 kGy and 8 kGy doses, but a steep increase at 12 kGy dose. Decrease in absorbance intensity of the band was observed by FTIR at higher doses of irradiation	ND	Bashir and Haripriya (2016)

(continued)

Table 5.3 (continued)

Starch samples		Irradiation treatment conditions		Results		
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Crystalline structure	Thermal properties	Literatures
Cowpea^C	ND	Flour powder and paste 2, 10, 50 kGy	ND	No change in FTIR spectra pattern and the ordered structure of starch granule surface	Peak temperature of gelatinization increased, however, enthalpy of gelatinization fluctuated	Abu et al. (2006)
Broad bean^C	~52%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	No change in XRD pattern; relative crystallinity decreased. FTIR spectral patterns did not change, but there was increase in intensities of the band at 1018 cm^{-1} at high irradiation dose, indicated a decrease in the ordered structure	ND	Sofi et al. (2013)
Kidney beans^C	36–41%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~13%	No significant change in XRD pattern; relative crystallinity decreased	ND	Gani et al. (2012)
Bean^C	~36%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	No change in XRD pattern; the relative crystallinity decreased; the degree of order at starch granule surface decreased	T_o, T_p, T_c increased at 10 kGy but decreased at 50 kGy; ΔH decreased as irradiation dose increased	Chung and Liu (2010)
Bean^C	~35%	Maize flour 5, 10, 20, 40 kGy at 0.5 kGy/h	~9.8%	ND	T_o, T_p, ΔH increased	Rombo et al. (2004)
Bean^C	ND	Starch powder 2.5, 5, 10, 20 kGy	~12%	No notable change in XRD pattern	Enthalpy and temperature of gelatinization increased	Duarte and Rupnow (1993), (1994)
Sago^C	~27%	Starch powder 6, 10, 25 kGy at 8.3 kGy/h	~13%	No change in crystal type by XRD, but irradiation induced a decrease in degree of granule crystallinity	T_o and T_p showed slight increase; T_c and ΔH were not altered significantly	Othman et al. (2015)

ture and amylopectin short chains increasing, which resulted in decrease in gelatinization temperatures. However, irradiation could also destroy weaker crystal structure making the remaining structures more stable, which would result in increase in gelatinization temperatures. The differences in gelatinization parameters induced by gamma irradiation at the same dose might also be attributed to dose rate of treatment, ratio of amylose/amylopectin, and native starch structure (Kong et al. 2016).

5.2.4 Physical and Digestion Properties

Physical properties discussed here included swelling power, water solubility, syneresis, freeze-thaw stability, transmittance, oil and water absorption, pasting properties, and starch gel textural properties. Starch swelling power represents its capacity to trap and hold water in starch granules and primarily resulted from amylopectin fraction, which can be measured at various temperatures, and normally from 50 to 95 °C. The swelling power was observed to decrease under gamma irradiation treatment in most reports (Table 5.4); the decrease in swelling power could be attributed to fragmentation of amylopectin, and this is beneficial to improve the textural quality upon cooking as the bursting of starch could be prevented (Gani et al. 2012; Ashwar et al. 2014). Whereas some researcher reported that the swelling power increased at lower doses (Table 5.4). It was well known that the presence of amylose and lipids inhibited starch swelling, and gamma irradiation could fragment both amylose and lipid, which would promote starch swelling. Water solubility index of irradiated starches increased with irradiation dosage elevated in all works (Table 5.4); the increase in the solubility index is attributed to the radiation-induced depolymerization of the starch molecules resulting from breakage of glucosidic bonds and production of lower molecular weight fractions that can be dissolved by neighboring water molecules more easily, contributing to increases in both solubility index and light transmittance of irradiated starches. Syneresis refers to expulsion of liquid from the starch gel during storage; it is an index of gel stability. The syneresis of gels formed with irradiated treated starches decreased in all previous reports (Table 5.4); the decrease in the syneresis values was attributed to the production of lower molecular weight fractions that have higher tendency for water and also resulting from reduction in the magnitude of hydrogen bonding forces, interaction between amylose-amylose and amylose-amylopectin chains, in starch molecules upon irradiation (Bashir and Aggarwal 2017).

Pasting and rheological properties of starches could be characterized by Rapid Visco Analyzer (RVA) or rheometer; most pasting and rheological parameters of irradiated starches decreased continuously with irradiation dosage increasing (Table 5.4). The reduction in the pasting properties can be attributed to starch degradation resulted from irradiation induced. Pasting parameters can be easily correlated with the texture profile and quality of the product (Bashir and Aggarwal 2017). It was supposed that the degradation of amylopectin and amylose in starch

Table 5.4 Physical and digestion properties change of starches under gamma irradiation

Starch samples		Irradiation treatment conditions		Results	
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Physical and digestion properties	Literatures
Rice^{A}	~27%	Grain 1, 2, 5 kGy at 0.4 kGy/h	~10%	Values of viscosity parameters decreased with exception of breakdown and pasting temperature. Resistant starch of cooked samples reached the highest at 1 kGy	Polesi et al. (2017)
Rice^{A}	~20%	Starch powder 2, 5, 10 kGy at 0.4 kGy/h	~12%	Values of pasting parameters and swelling power decreased significantly; the solubility increased	Gul et al. (2016)
Rice^{A}	~26%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~12%	Swelling power, syneresis, and pasting properties decreased, whereas water absorption capacity and transmittance increased	Ashwar et al. (2014)
Rice^{A}	27–40%	Flour powder 0.5, 1, 2, 3, 4, 5 kGy at 1.0 kGy/h	NA	Starch digestibility decreased upon irradiation	Shu et al. (2013)
Rice^{A}	~19%	Grain 2, 5, 8, 10 kGy at 1 kGy/h	~30%	Pasting properties decreased significantly	Yu and Wang (2007)
Rice^{A}	ND	Grain 0.5, 1, 3, 5, 7, 9 kGy at 0.5 kGy/h	~12%	Pasting properties decreased	Bao et al. (2005)

Rice^{A}	~1–26%	Grain 0.2, 0.4, 0.6, 0.8, 1 kGy at 1 kGy/h	ND	Peak, hot pasting, cool pasting, and setback viscosities decreased considerably	Wu et al. (2002)
Wheat^{A}	~25%	Flour powder 0.5, 1, 2.5, 5, 10 kGy	~11%	Values of viscosity parameters decreased; swelling, solubility, syneresis, and freeze-thaw stability were improved with dosage	Bashir and Aggarwal (2017)
Wheat^{A}	ND	Starch powder 1, 3, 5, 7, 9 kGy at 1 kGy/h	~12%	Values of viscosity parameters decreased with exception of breakdown; gel hardness and gumminess decreased	Kong et al. (2016)
Wheat^{A}	~34%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~13%	Viscosity, rheological, and textural parameters decreased, water solubility increased, and swelling power showed maximum at 20 kGy	Atrous et al. (2017)
Wheat^{A}	~35%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~13%	Solubility increased; swelling power increased to the maximum at 20 kGy and then decreased significantly. Rheological properties decreased	Atrous et al. (2015)
Amaranth^{A}	6–10%	2, 4, 6, 8, and 10 kGy at 1 kGy/h	~10%	Pasting and rheological properties decreased	Kong et al. (2009)
Arrow-head^{A}	~31%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	Peak, trough, final, and setback viscosities were significantly reduced, whereas the breakdown viscosity increased. Solubility, water absorption capacity, and transmittance increased, whereas swelling power, bulk density, and syneresis decreased	Wani et al. (2015)
Indian horse chestnut^{A}	~27%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~12%	Water absorption capacity, oil absorption capacity, solubility, and freeze-thaw stability increased, whereas syneresis, swelling power, and pasting properties decreased	Wani et al. (2014)

(continued)

Table 5.4 (continued)

Starch samples		Irradiation treatment conditions		Results	
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Physical and digestion properties	Literatures
Corn^A	ND	Starch powder 3, 5, 10, 20, 50 kGy at 1.14 kGy/h	ND	Maximal consistency of the starch paste decreased determined by Brabender Visco-Amylo-Graph test	Ben Bettaïeb et al. (2014)
Maize^A	ND	Starch powder 1, 2, 5, 10, 20, 50, 100, 200, 500 kGy at 5 kGy/h	ND	Peak, trough, final, and setback viscosities decreased, whereas solubility increased	Liu et al. (2012)
Corn^A	Waxy and normal	Starch powder 5, 10, 20 kGy at 10 kGy/h	5%, 12%	Resistant starch content increased; slowly digestible starch content decreased	Yoon et al. (2010)
Corn^A	Waxy and normal	Starch powder at various pH and salt Concentrations 5, 10, 20 kGy at 10 kGy/h	6%	Pasting viscosities and rheological properties decreased	Baik et al. (2010)
Corn^A	~29%	Starch powder 2, 10, 50 kGy at 2 kGy/h and 0.40, 0.67, 2 kGy/h to a total dose of 10 kGy	~9%	Pasting viscosities decreased, and rapidly digestible starch (RDS) content slightly decreased up to 10 kGy but increased at 50 kGy; resistant starch (RS) content slightly decreased at 2 kGy and then increased up to 50 kGy. The slowly digestible starch (SDS) content showed the opposite trend to RS content	Chung and Liu (2009)

Corn$^{A\text{ or }B}$	4–70%	Starch powder 1, 5, 10, 25, 50 kGy at 1 kGy/h	ND	Peak, final, and setback viscosities decreased; however, peak and final viscosities increased for high amylose samples	Chung et al. (2015)
Corn$^{A\text{ or }B}$	2–72%	Starch powder 5, 10, 25 and 50 kGy at 1 kGy/h	~12%	Resistant starch content increased	Lee et al. (2013)
Maize^{B}	~62%	Starch powder 30, 60 kGy at 1.2 kG/h	ND	Pasting viscosity reduced	Ocloo et al. (2016)
Maize^{B}	~58%	Starch powder 30, 60 kGy at 1.2 kG/h	~10%	Swelling power decreased; solubility increased. Oil and water absorption capacities increased at 30 kGy but remained stable when irradiation dosage increased to 60 kGy	Ocloo et al. (2014)
Potato^{B}	~30%	Starch powder 3, 5, 10, 20, 35, 50 kGy at 0.83 kGy/h	~18%	Viscosity and rheological and textural parameters decreased, water solubility increased, and swelling power showed maximum at 20 kGy	Atrous et al. (2017)
Potato^{B}	~30%	Starch powder 5, 10, 20, 30 kGy at 3.6 kGy/h	~12%	Water absorption, least gelling concentration, solubility, paste clarity, and susceptibility to a-amylolysis increased, whereas fat absorption and viscosity decreased	Sujka et al. (2015)
Potato^{B}	ND	Starch powder 5, 10, 20, 30 kGy at 3.6 kGy/h	~14%	The gel structure became smooth rather than honey-comb like, swelling power decreased	Cieśla et al. (2015)
Potato^{B}	~32%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~10%	Pasting properties, swelling power and syneresis decreased, whereas water absorption capacity and solubility increased	Gani et al. (2014)

(continued)

Table 5.4 (continued)

Starch samples		Irradiation treatment conditions		Results	
Starch/type	Amylose content	Material status Dosage/dose rate	Water content	Physical and digestion properties	Literatures
Potato^{B}	~31%	Tuber 0.1 kGy at 32.4 kGy/h	~75%	Rheological properties, pasting viscosities decreased, resistant starch content decreased	Lu et al. (2012a, b)
Potato^{B}	~15%	Starch powder 0.01, 0.05, 0.1, 0.5 kGy	ND	Peak, trough, breakdown, final viscosities, and gel hardness decreased, whereas gel cohesiveness increased	Singh et al. (2011)
Potato^{B}	~32%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	Pasting viscosity decreased; resistant starch contents (determined with uncooked starch) increased	Chung and Liu (2010)
Elephant foot yam^{B}	~28%	Starch powder 5, 10, 15, 20, 25 kGy at 2 kGy/h	~11%	Pasting parameters, swelling power, and syneresis decreased; solubility, light transmittance, and water absorption capacity increased	Reddy et al. (2015a)
Banana^{B}	~25%	5, 10, 15, 20, 25 kGy at 2 kGy/h	ND	Peak, hold, final and setback viscosities, swelling power, and syneresis decreased, whereas in vitro digestibility, solubility, and water absorption capacity increased	Reddy et al. (2015b)
Broad bean^{C}	~52%	Starch powder 5, 10, 15 kGy at 5 kGy/h	~8%	Water absorption capacity, freeze-thaw stability, and solubility increased, whereas pasting properties and syneresis decreased	Sofi et al. (2013)
Kidney beans^{C}	36–41%	Starch powder 5, 10, 20 kGy at 2 kGy/h	~13%	Solubility, water absorption capacity, and transmittance increased, whereas swelling power, syneresis, and pasting properties decreased	Gani et al. (2012)

Bean^C	~36%	Starch powder 10, 50 kGy at 2 kGy/h	~10%	Pasting viscosity decreased; resistant starch contents (determined with uncooked starch) increased	Chung and Liu (2010)
Bean^C	ND	Starch powder 2.5, 5, 10, 20 kGy	~12%	Swelling power decreased; solubility increased	Duarte and Rupnow (1994)
Chickpea^C	~30%	Flour powder 0.5, 1, 2.5, 5, 10 kGy at 0.5 kGy/h	ND	Pasting properties showed a significant decrease in peak viscosity, final viscosity, setback viscosity, trough viscosity, and pasting temperature in dose-dependent manner. Swelling, solubility index, oil absorption capacity, and water absorption capacity increased significantly with dose, while as syneresis decreased with dose	Bashir and Aggarwal (2017)
Chickpea^C	~33%	Starch powder 4, 8, 12 kGy at 2 kGy/h	~12%	Swelling power, turbidity, syneresis, and pasting parameters reduced, whereas solubility increased	Bashir and Haripriya (2016)
Chickpea^C	ND	Grain 2, 5, 10, 20, 30, 50 kGy at 3.6 kGy/h	ND	Peak viscosity decreased significantly	Graham et al. (2002)
Cowpea^C	ND	Flour powder and paste 2, 10, 50 kGy	ND	Pasting and swelling properties decreased significantly	Abu et al. (2006)

induced by gamma irradiation treatment might cause a considerable decrease in water binding capacity and then reduced the swelling degree of starch granules, which resulted in a significant decrease in peak viscosity. The setback and cool paste viscosities are mainly attributed to reordering or polymerization of leached amylose and long linear amylopectin; accordingly, degradation or shortening of amylose and longer amylopectin branch chains after irradiation contributed to the decrease in setback and cool paste viscosities (Chung and Liu 2009).

Gamma irradiation can be employed to elevate the resistant starch fraction; however, some researchers observed that irradiation treatment could decrease resistant starch content (Table 5.4). The cleavage of anhydrous glycosidic linkages increases the accessibility of the digestive enzymes and thus decreases resistant starch content. The increase of resistant starch thus indicates that there were structural changes besides the chain cleavage; some authors attributed this to the increase in the proportion of β-bonded starch after irradiation as a result of transglucosidation (Rombo et al. 2004) or the increase in carboxyl groups which would result in inhibition of enzyme attack (Chung and Liu 2010).

5.3 Grafting and Cross-Linking Synthesis of Starch with Chemicals

Radiation-induced graft polymerization is a powerful method for preparation of polymeric materials with new properties (Suwanmala et al. 2012), such as superabsorbent polymer, biomaterials, and drug delivery systems. Radiation processing has many advantages over other conventional methods. In radiation processing, no catalysts or additives are needed to initiate the reaction, so that this process does not cause any further contamination associated with chemical initiators. They are relatively simple and of high efficiency, and the degree of cross-linking and grafting can be controlled easily by varying the absorbed dose (Eid 2008). Zhang and Xu (2017) compared potassium persulfate and irradiation as initiator to graft acrylic acid onto starch and concluded that irradiation was more time-saving, energy-saving, and efficient. This kind of work has been done by many researchers (Ali and Abdel Ghaffar 2017; Abdel Ghaffar et al. 2016; Mahmoud et al. 2014; Sheikh et al. 2013; Lv et al. 2013; Abd El-Rehim et al. 2013; Suwanmala et al. 2012).

5.4 Conclusions

From literatures we listed in the tables, we could find that the research about starch irradiation boomed in the last decade, partly because this method is safe, inexpensive, and time-saving and has an enormous potential in various applications. Several review articles about the subject of current chapter are available for the readers (Zhu

2016; Bhat and Karim 2009; Sokhey and Hanna 1993). Combination irradiation treatment with other modification was performed to widen applications of modified starch products and will attract more and more attention in future.

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Chapter 6
Microwave Treatment

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Abstract Microwave technology has been widely used in food processing and consumption industries for various purposes and can also be used for physical modification of starch. Unlike conventional heating methods, microwave heating has characteristics such as low cost, short start-up time, high heating rate and efficiency. The modification effects of microwave treatment (MWT) on starch are influenced by many factors, like starch properties (starch type, moisture content, density, dielectric properties, temperature, etc.) and microwave processing conditions (frequency, power, radiation time, oven type and geometry). This chapter gives detailed information about starch physical properties changes after MWT such as composition, pasting properties, gelation, micromorphology, swelling and gelatinization, and in vitro digestibility.

Keywords Microwave treatment · Starch composition · Starch pasting properties · Gelation

Abbreviations

ANN	Annealing treatment
BD	Breakdown viscosity
CHT	Conventional heat treatment
CPV	Cold paste viscosity
FTIR	Fourier transform infrared spectroscopy
HMT	Heat-moisture treatment
HPV	Hot paste viscosity
IMC	Initial moisture content

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MWT	Microwave treatment
PT	Peak temperature
PV	Peak viscosity
RHT	Rapid conventional heat treatment
SB	Setback viscosity
T_c	Conclusion temperature
T_o	Onset temperature
T_p	Peak temperature
XRD	X-ray diffraction

6.1 Introduction

Microwaves are defined as the electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz, corresponding to wavelengths from 1 m to 1 mm (Banik et al. 2003). Under microwave radiation, polar molecules (e.g., water molecules) absorb microwave energy, orient themselves rapidly with respect to the electric field, and quickly generate bulk heat by molecular friction (Román et al. 2015), quite different from conventional heating methods, which include three forms: conduction, convection, and radiation. Microwave technology has been widely used in food processing and consumption industries for various purposes (e.g., baking, dehydration, tempering, thawing, cooking, pasteurization, drying, and expansion) since the last century, and a frequency of 2450 MHz is most commonly used in food industry (Ma et al. 2015). The dielectric property of food is largely determined by the salt and moisture content (Mudgett 1986) and affects microwave heating through influencing the microwave response characteristics and penetration depth (Piyasena et al. 2003). Compared with conventional heating, microwave heating offers many advantages such as lower cost, less start-up time, high heating rate and efficiency, and convenient process control (Lewandowicz et al. 1997; Sumnu 2001). Though certain drawbacks in microwave heating such as the nonuniform heat distribution and high equipment costs exist, they do not hinder the high potentials of microwave heat treatment for the processing of agricultural products, as equipment costs can change with time and developing technology (Vadivambal and Jayas 2007).

As dry food components are thought to be electrically inert, starch-microwave radiation interaction has to be investigated at certain moisture content (Lewandowicz et al. 1997). Microwave irradiation has been reported to assist preparations of extruded starch pellets (Lee et al. 2000), cross-linked starch microsphere (Lin et al. 2013), and starch-based porous materials for drug delivery (Malafaya et al. 2001) and can benefit glucose extraction from starch-based wastes (Villière et al. 2015). It can also be used to reduce the cooking time by producing partial gelatinized noodles (Xue et al. 2008). On the other hand, microwave heating can be an effective drying method and will cause some morphological and physicochemical property changes (Chen et al. 2016), as a result of starch modification. At present, the microwave modification effects on starch are reported to be influenced by starch properties (starch type, moisture content, density, dielectric properties, temperature, etc.) and microwave processing conditions (frequency, power, radiation time, oven type, and geometry) (Braşoveanu and Nemţanu 2014).

6.2 Temperature-Time Curve During Microwave Treatment

Moisture and heating temperature are the key conditions for starch modifications based on hydrothermal methods and are mostly restricted to proper combinations for traditional methods. For examples, heat-moisture treatment (HMT) usually restricts the moisture content in a range of 10–30% with relatively high temperature (90–120 °C) to avoid starch gelatinization, and annealing treatment (ANN) adopts high water content (50–60%) and relatively low temperatures (<gelatinization point) (Lewandowicz et al. 2000b; Maache-Rezzoug et al. 2008). However, studies about microwave treatment (MWT) on starches are not restricted by these rules (Table 6.1). For example, microwave irradiation with both high initial moisture content (IMC) (>90%) and high heating temperature (80 °C) were performed on rice starch, and a following freeze-drying method was adopted to obtain the irradiated samples (Fan et al. 2012b). Another particular characteristic of MWT is the extremely high heating rate. For example, an oil bath with quite high temperature (200 °C) was reported to be able to reach the same heating speed with microwave irradiation power (1.2 kW) only before 65 °C, but afterward, the heating rate of oil bath began to fall behind significantly (Fan et al. 2013b). Unlike hours or days for most HMT and ANN, the treatment time of MWT has to be limited in a range (often in minutes), in order to prevent the irradiated starch to become a hard gel due to excess water loss (Palav and Seetharaman 2007). It is also reported that a long irradiation time at low power may not be suggested due to occurrence of starch clumps and peeled skins as for cornstarch (Stevenson et al. 2005).

The temperature-time curve of microwave-irradiated starch depends on the moisture content, starch type, microwave irradiation power, and temperature measuring methods (Braşoveanu and Nemţanu 2014). Generally higher microwave power leads to higher heating temperatures. However, the temperature-time curve in MWT is often nonlinear though under constant power, e.g., tuber starch (Lewandowicz et al. 1997), and higher moisture content often contributes to higher heating rate (Stevenson et al. 2005; Zhang et al. 2009). Therefore, water friction determines the elevation of the temperature, and samples with abundant amounts of polarized water have a rapid increase in heating rates (Lee et al. 2007). Microwave heating of a material depends on its dielectric constant which determines how a material couples with microwaves and on the dielectric loss factor which expresses the ability of the material to absorb microwave energy and transform it into heat (Mudgett 1986). Bilbao-Sáinz et al. (2007) reported both dielectric constant and dielectric loss factor were affected by the moisture content during treatment, while dielectric loss factor can also be influenced by the degree of degree of starch gelatinization.

Table 6.1 Starch-microwave related studies

Starch type	Initial moisture content	Microwave power and irradiation time	Heat attributes	Major findings	References
Barley	42.1–45.1%	330–713 W, 150–180 min	90 °C	Increased starch digestibility, lower melting enthalpy, and higher gelatinization temperature	Emami et al. (2012)
				Changes on pasting attributes varied with amylose content	
Canna edulis Ker	20%	1000 W, 30 min		Double higher resistant starch, increased molecular order and crystallinity during enzyme digestion	Zhang et al. (2010)
	20–45%	400–1000 W, 0–30 min	60 °C for 35–45% moisture	Moisture content, irradiation power, and heating time had different impacts on heating rate, amylose leaching, enzymatic digestibility, crystallinity, and thermal stability	Zhang et al. (2009)
			110 °C for 20–30% moisture		
Cassava	20%	650 W, 3–15 min		Significant changes on pasting properties	Abraham (1993)
				Lower swelling power, water-binding capacity, paste translucency, enzyme susceptibility	
Lentil	25%	Half power of 650 W	85 °C, 6 min	Lower amylograph viscosities and limited retrogradation	Gonzalez and Perez (2002)
				Boat-shaped granule surface appeared roughened	
Indian horse chestnut	22%	15–45 s		Improved physicochemical, functional, and antioxidant properties	Shah et al. (2016)

(continued)

Table 6.1 (continued)

Starch type	Initial moisture content	Microwave power and irradiation time	Heat attributes	Major findings	References
Maize/ corn		605 ± 17.5 W	30–80 °C, 4.52–5.29 °C/min	No differences in swelling behavior of common and modified maize starches between microwave and conventional heating	Casasnovas and Anantheswaran (2016)
	6.8%	450 W, 15 min		Deformed particles, decreased crystallinity	Szepes et al. (2005)
	10–35%	650 W, 3 min		Partial disruption of crystalline structure Significant changes on pasting properties	Lee et al. (2007)
	15–40%	0.17 and 0.50 W/g, 1 h	48–65 °C for 0.17 W/g, 91–115 °C for 0.50 W/g	Irradiated power and IMC had significant impacts on gelatinization and pasting properties	Stevenson et al. (2005)
	30%	1 W/g, 20 min		Granule surface became porous with cavities in the center Increased gelatinization temperature and Tc–To and decreased melting enthalpy Modification changes varied with amylose content	Luo et al. (2006)
	30%	0.5 W/g	60 min	Reduced crystallinity, solubility and swelling characteristics, melting enthalpy and increased gelatinization temperature Modification changes depended on amylose content	Lewandowicz et al. (2000)
Lotus seed native	70%	2.4–8.0 W/g	Until fully gelatinized	Increased starch-water interaction and crystalline region; decreased swelling power, amylose leaching, and molecular properties; and decreased digestibility	Zeng et al. (2016)

(continued)

Table 6.1 (continued)

Starch type	Initial moisture content	Microwave power and irradiation time	Heat attributes	Major findings	References
Potato	2–35%	10% output power of 800 W, 0–160 min	20–170 °C	Higher gelatinization temperature and less solubility Pasting properties changing from tuber starch to typical cereal starch	Lewandowicz et al. (1997)
	9.6%	450 W, 15 min		Increased crystallinity, crystal structure changed from B to A	Szepes et al. (2005)
	10–90%	1.3 kW, 0–150 s		Proportion of damaged granules depended on moisture content rather than heating methods	Collison and Chilton (1974)
	97%	Modified power to simulate RHT	20 to over 80 °C, 27.2 °C/min	The microwave-specific effects occurred mainly at initially irradiation stage, and thermal effects began to dominate during and after gelatinization	Ma et al. (2015)
Rice	20%	270–1350 W, ≈2–17 min	Melting temperature	Waxy and non-waxy had different pasting property changes after MWT Slight digestibility changes	Anderson and Guraya (2006), Anderson et al. (2002)
	33.3%	800 W, 125 s	Completely gelatinized	Less damage to starch granules by MWT for non-waxy starch gels, compared with CHT Lower retrogradation rate and gel firmness and hydrolysis rate in non-waxy gel, compared with CHT	Jiang et al. (2011)
	94%	Modified power to simulate RHT	20 to over 80 °C, 1.12–1.5 °C/s	Rapid heating accounted for the major property changes Microwave effects occurred mainly in the early stage of MWT	Fan et al. (2012a, b), (2013a, b, c), (2014)
Tapioca	1–35%	10% output power of 800 W, 0–160 min	20–170 °C	Higher gelatinization temperature and less solubility Crystal structure changed	Lewandowicz et al. (1997)

(continued)

Table 6.1 (continued)

Starch type	Initial moisture content	Microwave power and irradiation time	Heat attributes	Major findings	References
Wheat	30%	0.5 W/g	60 min	Reduced crystallinity, solubility and swelling characteristics Increased gelatinization temperature, a drop in solubility and crystallinity for all starches, and the extent and type of these changes depended on variety of starches	Lewandowicz et al. (2000)
	50–67%	4300 W (absorbed: 1140 W), 10–30 s	94–98 °C	Lack of granular swelling and softer gel properties Mechanism of MWT may be different with CHT	Palav and Seetharaman (2007)
	91%	2000 W, ≈5–80 s	40–100 °C	No differences in gelatinization mechanism between MWT and CHT Crystallinity disappeared at higher rate after MWT	Bilbao-Sáinz et al. (2007)
	92–99%	1.3 kW	55–95 °C, 90–350 °C/min	Granule swelling and leaching of polymers occurred only after complete loss of granule birefringence presenting evidence of an asynchronous process of gelatinization	Palav and Seetharaman (2006)

MWT microwave treatment, *RHT* rapid conventional heat treatment, *CHT* conventional heat treatment

However, the contrary results were also reported in Lewandowicz et al. (1997) who found tuber starch samples with lower moisture content (1–5%) had much faster temperature rise than samples with high moisture content (7–15%), at microwave power 800 W with up to 200 min. They also reported a plateau in the curve (around 80 °C judged visually on the curve) with moisture content 17–35%, and the plateau length tended to grow with increased moisture content. For starch in sealed beakers, the plateau was observed to be higher. The authors considered some isothermal transformation occurred in the samples. Similarly, a temperature plateau emerged at 70 °C was observed for rice starch during MWT, accrediting to swelling and hydration in a gelatinization process slowing down the heating rate (Fan et al. 2013b; Fan et al. 2012c). In addition, plateau phenomena were also observed in *Canna edulis* Ker starch (microwave power: 400–1000 W, 10 min, maximum temperature 60 °C, MC = 40%) by Zhang et al. (2009), but the plateaus were not obvious with MC 20–30%. However, Stevenson et al. (2005) did not find any temperature plateaus on microwaved cornstarches and explained this phenomenon with four reasons. First, the plateaus may be caused by imprecisely control of microwave conditions due to domestic microwave oven they used, unlike sophisticated microwave oven in their study. Second, a constant wattage without any oscillation was adopted in their study and may be more stable than oscillating wattage in domestic microwave ovens. Third, they put temperature probe inside reaction vessels, while other researchers took the samples outside for temperature measurement and may not be accurate. Finally, the starch type may also have an impact on the temperature curve. For examples, Lewandowicz et al. (2000b) reported cereal starch was less affected by microwave irradiation compared with tuber starches. Anderson and Guraya (2006) found the heat transfer in waxy rice starch was higher than in non-waxy rice starch (microwave power: 270–1350 W, MC = 20%), and this was explained by the more bulky structure of amylopectin molecules in waxy starch facilitated rapid heat penetration. With moisture content 91%, Bilbao-Sáinz et al. (2007) found the temperature on irradiated wheat starch was gradually increased with time and no plateaus were found. These differences on time-temperature curve need further investigations.

6.3 Changes on Starch Composition and Functional Properties Under Microwave Irradiation

6.3.1 Composition

After MWT, only the minor impurities in the starches have some changes. It has been found that the chemical bonds, chemical groups, skeleton, and the way that they connect with each other was not destroyed, indicating no occurrence of chemical reaction (Fan et al. 2012c). A decrease of crude protein and crude fiber and an increase of ash, reducing sugars, and absolute density were found by Gonzalez and Perez (2002) for microwaved lentil starch (IMC = 25%, half power of 650 W, 6 min at 85 °C). Shah et al. (2016) found the amylose content showed no significant changes before and after MWT, but the phenolic content increased with antioxidant activity improvement. It is also reported some radicals are generated in microwaved starch (Dyrek et al. 2007) and can be influenced by the microwave power level and water content (Fan et al. 2016). However, the quite small concentration of these radicals and their rapid annihilation in water make them inoffensive (Braşoveanu and Nemţanu 2014).

6.3.2 Pasting Properties

Starch pasting properties are one of most important properties not only for direct industrial application but also for structure analysis. Starch type, amylose content (waxy or non-waxy), IMC, and irradiation dose can all have an impact on viscosity properties of microwave-modified starches in addition to irradiation dose. For examples, under irradiation condition of 10% output power of 800 W at IMC 20%, Lewandowicz et al. (1997) found the viscosity curves during heating in microwave-irradiated potato and tapioca starches were almost the same with their untreated starches and the greater the IMC deviated from 20%, the lower the viscosity curves. After MWT, the pasting characteristics of tuber starches are widely found to be changed to like cereal starches (Lewandowicz et al. 1997), while for wheat and cornstarches, the viscosity pattern remained the same as cereal starch (Lewandowicz et al. 2000b). After MWT (IMC = 20%, heated to melting temperature), the peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown viscosity (BD), and setback viscosity (SB) had significant increase in non-waxy rice starches, whereas for waxy rice starches under the same treatment condition, all of these attributes decreased except SB increased (Anderson and Guraya 2006; Anderson et al. 2002), which were explained as reaggregation of amylopectin branches in waxy rice starches were much higher than non-waxy rice starches after MWT. The pasting properties of waxy barley starch were more likely to be influenced by microwave irradiation than high-amylose and normal barley starches (Emami et al. 2012). The impact of MWT on Brabender viscosity curves appeared to be less in waxy cornstarch than in normal cornstarches (Lewandowicz et al. 2000b). The viscosity patterns of amylomaize V starch was changed after MWT, while waxy and normal maize starch did not change (Luo et al. 2006). Luo et al. (2006) found under greater irradiation doses generally led to greater changes on pasting properties (PV, HPV, BD, CPV, SB), but for peak temperature (PT), it was decreased after irritated at 0.17 W/g for 1 h with IMC 20–40% whereas increased after irradiation at 0.50 W/g for 1 h with IMC 25–40%. With increased treatment time, PV, HPV, FV, and SB were all significantly decreased in Indian horse chestnut starch (Shah et al. 2016).

However, though the impact of MWT on Brabender viscograph can be influenced by these factors, an increase in PT and/or a decrease in PV is mostly reported, e.g., wheat and cornstarches (Lewandowicz et al. 2000b; Stevenson et al. 2005), lentil starch (Gonzalez and Perez 2002), cassava starch (Abraham 1993), maize starches (Luo et al. 2006), and non-waxy rice starches (Anderson and Guraya 2006; Anderson et al. 2002). But there are also some exceptions, e.g., cornstarches were found to have higher PT but lower PV after MWT (Luo et al. 2006), and Palav and Seetharaman (2007) reported a lower PT in microwave-modified wheat starch. Though heating methods were reported to have no influence on starch viscosity values (at 60 °C, 200 s^{-1}) measured immediately after MWT and conventional heat treatment (CHT) (Bilbao-Sáinz et al. 2007), the pasting properties of starches modified by the two methods (MWT and CHT) can still have significant differences in most recent studies. For example, a significant lower PT and FV, but higher PV was found in microwave-modified wheat starch sample than conduction-heated sample, and this difference was considered to be incomplete disruption of granular integrity and less amylose leaching into the extragranular matrix, resulting in weaker amylose network formation (Palav and Seetharaman 2007). Therefore some internal structure changes may occur after MWT and can be supported by light microphotographs of wheat starches that showed that MWT can postpone the temperature point for symptoms of solubilization from 75 to 95 °C (Lewandowicz et al. 2000b). Moreover, an increase on X-ray diffraction (XRD) intensity is found in many microwave-irradiated starch, indicating more ordered crystalline array and increased inter- and intramolecular hydrogen bonding (Luo et al. 2006), which may also contribute to pasting property changes.

6.3.3 Gelation

With heating temperature above gelatinization temperature and adequate high moisture content, the starch formed a paste during MWT, and this paste turns to a gel once cooled. However, most studies show that this gel is much weaker and has significantly lower firmness than that formed after CHT, though they have lower moisture content, e.g., wheat starch (Palav and Seetharaman 2007). Even the paste did not form a gel at IMC 8% upon cooling, while other starches form a gel at 6% concentration, which was explained by that amylose did not contribute to the continuous network needed for gel formation following microwave heating (Palav and Seetharaman 2006). Compared with CHT, starch samples after MWT had lower amount of reducing sugars produced by the action of a-amylase, suggesting greater granular disruption during conduction heating (Palav and Seetharaman 2007). This is in agreement with Luo et al. (2006) who suggested less separated amylose chain in irradiated starch than normal starch. Therefore this could contribute to the absence of a continuous network formation through the leaching of amylose after MWT (Palav and Seetharaman 2007), resulting in weaker gel formation. The tendency of retrogradation in lentil starch was reduced after MWT (Gonzalez and Perez 2002), but the impacts vary in different starches and irradiation doses. For example, Palav and Seetharaman (2007) reported that the enthalpy of amylopectin recrystallization in microwave-irradiated sample was initially higher than conduction-heated sample (stored for 2 h), indicating a closer proximity of polymers in the gel causing a more rapid and greater crystal formation, but it was later significantly lower, indicating less retrogradation. Increasing microwave irradiation time and starch concentration led to increased gel firmness, and this may be explained as the rapid heating rate led to lack of granule swelling and less amount of leached amylose into extragranular matrix and a weaker amylose network formation, resulting in softer gel texture (Palav and Seetharaman 2007). It is also reported that compared with CHT, microwave irradiation could change the water distribution and result in a certain level of free water shifting to immobile water in starch gel, indicating improved starch-water interaction (Zeng et al. 2016). By investigating the freeze-thaw stabilities of three maize starches after MWT, Luo et al. (2006) found the decrease of syneresis was significant in normal and amylomaize V starch, while it was only marginal in waxy starches, suggesting that interaction between amylopectin chains did not occur to a significant extent during microwave irradiation. Therefore, the rapid heating rate during microwave heating likely results in lesser amount of leached amylose into the extragranular matrix and also a weaker amylose network formation (Palav and Seetharaman 2007), and its impact on waxy starches will not be significant.

6.3.4 Micromorphology

Generally with appropriate irradiation dose and moisture to avoid gelatinization (low moisture content or heating temperature), the morphology of starch granule will have minor changes after MWT. For example, both granule morphology of waxy and non-waxy rice (IMC = 20%, heated to Tm) did not appear to be influenced by MWT except only if little more aggregation was found (Anderson and Guraya 2006). No obvious changes in the molecular structure after MWT were observed in lotus seed starch (Zeng et al. 2016). Potato starch had no significant micromorphology changes, while maize starch particles had some deformations (Szepes et al. 2005), indicating the granular morphology change may vary for different starch types. The granule size and shape of normal maize, waxy, maize, and amylomaize V starches had no changes after MWT (IMC = 30%, 1 W/g), but the granule surface became porous with cavities in the center, indicating rearrangement of molecular structure (Luo et al. 2006). After MWT (IMC = 25%, half power of 650 W, 85 °C), the boated-shape surface of lentil starch appeared to be roughened (Gonzalez and Perez 2002). Lewandowicz et al. (1997) found the microimages of conventional heated potato starch (IMC = 35%) heated at 68 °C were similar to microwaved heated at 90 °C, indicating starch-starch bonds were stronger after MWT. The microwave-induced micromorphology changes during gelatinization are included in the following swelling and gelatinization section.

6.3.5 Swelling and Gelatinization

Swelling and gelatinization are important properties of starches, and the detailed process may help explaining above modification changes. After microwave irradiation, most starches exhibit decreased starch swelling properties and solubility and increased gelatinization temperature. However, as MWT has been conducted with broad moisture range, these changes may have some differences. It is reported that gelatinization cannot occur with less than IMC 30%, but can partially and fully occur with IMC 30–55% and over 55%, respectively (Collison and Chilton 1974).

Therefore the impact of microwave irradiation will be demonstrated in two sections as follows.

6.3.5.1 Crystalline and Thermal Property Changes at Low Moisture Content (<50%)

With relatively low moisture content, the microwave impact on starch are found to be similar to HMT, e.g., reduced swelling, increased gelatinization temperature, and crystalline rearrangement existence. During MWT, imperfect or weak crystallites may melt while the strong crystalline be reinforced, and this impact was more significant in type B starch than type A starch (Luo et al. 2006). The XRD pattern of microwaved type B starch shift to type A has been generally observed, e.g., potato starches (Lewandowicz et al. 1997; Szepes et al. 2005), amylomaize V starch (Luo et al. 2006), and canna edulis Ker starch (Zhang et al. 2009), similar to the effect of HMT on type B starches like sweet potato starch (Genkina et al. 2004) and tuber and root starches (Gunaratne and Hoover 2002), and is explained similarly based on crystalline structure. As double helices of type A and B starches are packed in a pseudohexagonal array, type B starch has a large void in which 36 water molecules can be accommodated, while type A starch contains a helix in the center rather than a column of water. Thus the changes in X-ray pattern can be explained as dehydration (vaporization of the 36 water molecules in the central channel of the B-unit cell) and movement of a pair of double helices into central channel, which was originally occupied by vaporized water molecules. The pattern changes may also bring a higher increase on T_c–T_o (T_c, conclusion temperature; T_o, onset temperature) after MWT (Luo et al. 2006). Type A starch is found to have no changes on XRD pattern after MWT, e.g., wheat and cornstarch (Lewandowicz et al. 2000b), but crystalline rearrangements also occur and can be reflected by some changes on XRD peak intensities and thermal properties (Luo et al. 2006; Zhang et al. 2009).

An increase on gelatinization temperature and decrease on melting enthalpy have been mostly observed in microwave-irradiated starch, such as potato and tapioca starch (Lewandowicz et al. 1997), wheat starch (Lewandowicz et al. 2000b), cornstarch (Lewandowicz et al. 2000b; Luo et al. 2006; Stevenson et al. 2005), canna edulis Ker starch (Zhang et al. 2009), and waxy and normal barley starch (Emami et al. 2012). But lower values of T_o, T_p (peak temperature), and melting enthalpy after MWT have also been reported, e.g., Indian horse chestnut starch (Shah et al. 2016). A dropped solubility has been observed due to limited amylose leakage (Gonzalez and Perez 2002; Lewandowicz et al. 1997; Luo et al. 2006), and thus the increase on gelatinization temperature may be caused by the reduced destabilization of the amorphous areas induced by reduced granular swelling, and the reduction on gelatinization melting enthalpy may be explained as some of the double helices present in crystalline and in noncrystalline regions of the granule have been disrupted under the conditions prevailing during MWT (Luo et al. 2006). However, the extent of changes may be influenced by starch type and amylose content. For example, Lewandowicz et al. (2000b) found the decreasing extent of melting enthalpy followed the order wheat (significantly decreased) > corn (significantly decreased) > waxy corn (slightly decrease), and these results were consistent with the changes on crystallinities. Luo et al. (2006) reported that amylomaize V (type B starch) had the greatest reduction extent on swelling power, solubility, and melting enthalpy and greatest extent of increase on gelatinization temperature, compared with other waxy and normal starches. On the other hand, an increase on crystallinity has been observed on wheat (Lewandowicz et al. 2000b), normal cornstarch (Lewandowicz et al. 2000b; Luo et al. 2006), amylomaize V starches (Luo et al. 2006), potato starch (Szepes et al. 2005), and canna edulis Ker starch (Zhang et al. 2009). It had been postulated that MWT produced double helix chains with the starch crystallites shift and led to a crystalline array that was more randomly distributed and ordered than that in native starch, and the rearrangement of molecules in sections of starch that are part of the crystalline region and that irradiation had a more pronounced effect on amylose than on amylopectin (Luo et al. 2006). The crystallinity was increased in potato starch, while decreased in maize starch after MWT, indicating crystalline changes may also be affected by starch origin (Szepes et al. 2005).

The irradiation power and IMC are found to have significant impacts on changes on crystallinity and thermal properties. Stevenson et al. (2005) reported higher irradiation power and higher IMC led to higher gelatinization temperature and lower melting enthalpy on cornstarch, but this impact was relatively minimal with less than 30% IMC. Zhang et al. (2009) investigated the impact of microwave irradiation on *Canna edulis* Ker starch (IMC = 20–45%, 400–1000 W, 0–30 min), and the maximum temperature was set as 60 °C for IMC 35–45%, while it was 110 °C for IMC 20–30%. Interestingly, at IMC 40%, the increased irradiation time led to the XRD pattern remained unchanged as half-A/half-B type. The authors found increased IMC (20–40%) led to increased crystallinity but started to decrease at IMC 45%, and this explained this as surplus water molecules preventing perfection of the small-crystalline region and formation of additional crystallites. Increased IMC and decreased maximum temperature could lead to decreased amylose leaching. The impact of treatment time was rather complicated, leading to a first decrease but later increase on crystallinity and a first increase followed by decrease on amylose leaching. The author explained this as the structure of treated starch became strengthened with prolonged MWT due to leached amylose recombining with starch molecules. Besides, a two-phase transition containing one exothermic peak and one endothermic peak was observed in most of their samples.

6.3.5.2 Gelatinization at High Moisture Content (>50%)

Recent studies tend to support that some crystal disruption and formation occurs during MWT before or in the early gelatinization process. A proposed gelatinization process for MWT has been established by Palav and Seetharaman (2006), which is different compared to conventional heating. By using polarized microscopy, the authors found with increasing temperatures (55–95 °C, heating rate 90–350 °C/min) at IMC 92–99%, half of wheat starch granules after MWT exhibited birefringence though granule size appeared unchanged at 55 °C and melting enthalpies decreased by tenfold compared with raw starch and then at 60 °C only small B-type starch granule had birefringence with little swelling, in agreement with higher T_o. At 65 °C, all granules had size increases and no birefringence was observed. From 65 to 95 °C, increasing amount of leachate was observed, and finally all granules were completely ruptured. Thus it was considered that the polar molecule vibration during MWT impacted the amylopectin crystalline lamella and crystalline arrangement was destroyed before glass transition of the amorphous region of the granule, unlike CHT, in which loss of birefringence and granule swelling typically occur semi-cooperatively. In addition, Palav and Seetharaman (2006) also pointed that the rupture of granules should be mainly attributed to the vibration motion. Moreover, the initial starch concentration (1–8%) was also found to greatly affect polymer leaching during MWT. The same authors (Palav and Seetharaman 2007) further investigated and characterized the changes at macroscopic level with higher starch concentrations (33–50%) after MWT and considered that the MWT-induced water molecule vibration in the crystalline regions destroyed the lamellar arrangement of the amylopectin crystals, even before the system reached gelatinization temperature. The rapid temperature rising and water molecular vibration caused that granule hydration fails to keep pace with granule expansion, and resultant stress generated caused granule collapse and rupture, forming film polymers coating the granule surface observed by SEM. These have been supported in a study on wheat starches (IMC = 91%) (Bilbao-Sáinz et al. 2007). The authors found intragranular population was significantly increased before gelatinization peak temperature, which came from mobilized starch protons, indicating partial gelatinization occurred at short heating time during MWT. Besides, an increase in melting enthalpy before swelling and starch granule hydration occurred during MWT, and the author confirmed that no annealing effects occurred by conducting experiments under similar condition using CHT. Therefore this was explained by that higher extent of hydration led to smaller exothermic portion of the gelatinization process, allowing more of the endothermic events to be recorded. Accordingly MWT may lead to more completed gelatinization, and this was supported by the higher rate of loss of crystallinity after MWT. However, these impacts seem to be rather little when heated to high temperature, as the viscosity of wheat starch samples after MWT and CHT at 85 °C, 90 °C, 95 °C was the same (at shear rate 200 s^{-1} at 60 °C), indicating the gelatinization process is not generally affected by the heating methods and also no unique structure differences during gelatinization were found between MWT and CHT. Both MWT and CHT exhibited similar changes to the double helix, V-type single helix, and amorphous structures with rising temperature (Fan et al. 2013b), and at controlled low and the same heating rate (≈5 °C/min), the swelling process was found to be the same for the three kinds of cornstarch suspensions after MWT and CHT (Casasnovas and Anantheswaran 2016).

A more specific and extensive gelatinization process under MWT at high IMC (>50%) has been established based on a series of studies on rice starches (IMC = 94%) by comparing MWT and rapid conventional heat treatment (RHT) at similar high heating rate, together with CHT (Fan et al. 2012b, c, 2013a, b, c, 2014), and a freeze-drying method was applied immediately to the microwaved starches. By changing the microwave power at appropriate time, the authors successfully got MWT to have almost the same heating curve with RHT (heating rate ≈60–90 °C/min). At the very beginning of MWT (e.g., <50 °C), the water molecules in the suspension absorb the microwave electromagnetic energy and became to vibrate fiercely with increased temperature. An initial increase on melting enthalpy at around 50 °C has been on observed on rice (Fan et al. 2012b, 2013c) and wheat starch (Bilbao-Sáinz et al. 2007), indicating structure changes. MWT and RHT had similar thermal results, and the activation energy and melting enthalpy were both higher than CHT; therefore, rapid heating had an enhanced effect on the stability of starch molecules in this initial heating stage (Fan et al. 2013c). In addition, Fan et al. (2013b) found the heating rate determined the differences in the proportions of amorphous starch, double helices, and V-type single helices, while the electromagnetic effects of microwave heating did not have a significant impact on the ordered structures in starch granules. Therefore this impact on initial treatment stage has been generally thought to be caused by the rapid heating. Bilbao-Sáinz et al. (2007) suggested the rapid heating rate led to a more complete swelling on wheat starch at this stage, resulting in smaller exothermic portion of the gelatinization process and more of the endothermic events to be recorded with higher melting enthalpy. By investigating rice starch with MWT, RHT, and CHT, Fan et al. (2014) considered the loose double helices through the fast heating might not be realistic though the crystalline lamellae exhibited increased thickness and the rapid heating seems to be the major factor accounting for the double helices of amylopectin densely packed, causing crystalline lamellae to become slightly ordered with strengthened H-bond in the initial heating of microwave (Fan et al. 2013c). This agrees with NMR and FTIR study in Fan et al. (2012c, 2013b), who suggested that microwave heating did not significantly change the ordered and disordered structures compared with RHT. Therefore these changes in the amorphous and double and single helix structures in starch granules are primarily related to the rapid increase in heat rather than electromagnetic effects of microwave heating (Fan et al. 2013b). However, starch with different types may have different structure changes. For example, the gelatinization enthalpy decreased rapidly for potato starch when heated to only 45 °C in all MWT, RHT, and CHT (Ma et al. 2015) and was explained as the starch polymorphs had become relatively loose by this point and the energy required for further destruction of the crystalline regions was diminished. This was also explained as type B starch (potato) has lowered density and stability at original status. Besides, RHT led to the largest melting enthalpy, indicating that fast heating led to insufficient expansion of the crystalline regions and therefore total heat required for destruction of this part of the granules was relatively large, while microwave could have some vibration impact, leading to a loose crystalline regions to some extent (Ma et al. 2015).

With further heating below onset gelatinization temperature (e.g., 50–60 °C), crystalline starts to be melted, and a progressive shift of the endotherm to higher temperatures and decrease on melting enthalpies was observed once the onset of the endothermic transition was reached in both microwaved and conduction-heated sample, but the former had higher gelatinization peak and melting enthalpy like around 50 °C, e.g., potato starch (Ma et al. 2015), rice starch (Fan et al. 2013c), and wheat starch (Bilbao-Sáinz et al. 2007). The decrease on gelatinization melting enthalpy may be explained as the rapid heating can destroy the ordered lamellar arrangements within starch semicrystalline region before T_o and molecular vibration of the microwaves could accelerate this impact (Fan et al. 2014). The higher gelatinization enthalpy in microwaved sample than conventional heated sample could be due to the more perfect structure of the remaining crystals (Bilbao-Sáinz et al. 2007). On the other hand, the starch-water interactions at this stage are quite different between RHT and MWT. Based on starch-water interaction analysis by using H-1 NMR, Fan et al. (2013a) reported that water absorption was the major process that occurred before 60 °C for samples under RHT and CHT, and before 55 °C for samples under MWT. Thus, the water-binding capability was lower when reaching the gelatinization temperature in microwaved sample. Heating rate directly affects the strength of the hydrogen bonds in amylopectin with respect to their molecular and submicroscopic lamellar structure (Fan et al. 2013c). The starch slurry started to from hydrocolloid gels at 55 °C for microwaved sample and at 60 °C for convention heating and rapid conventional heating, according to Fan et al. (2013a). The authors also found the glass transition temperature followed a descending order RHT, CHT, and MWT. They suggested the rapid heating inhibited the disruption of hydrogen bonds and thus possessed the stronger hydrogen bonds and lowest water mobility, while the microwave effect of vibration contributed to the hydrogen bonds disruption, but its impact was significantly stronger than former, leading to the weakest hydrogen bonds and highest water mobility. Zeng et al. (2016) found higher irradiation power led to increased extent on reducing swelling power of lotus starch. Besides, the authors also found unlike CHT, the granule surface of microwave treated lotus seed starch granules was collapsed and wrinkled before the beginning of gelatinization, suggesting the mobility of the starch protons may occur at the beginning of gelatinization. Similarly Bilbao-Sáinz et al. (2007) found the mobilization of the wheat starch protons was slightly greater for microwaves heated samples before any swelling and hydration of the starch granules occurred through NMR.

With further heating approaching or above gelatinization temperature, the ordered structure of starch granules disrupts and gelatinizes. It has been confirmed the vibrational motion of polar molecules did not impact the gelatinization of rice starch (Fan et al. 2012b). The high thermal impact becomes predominant, and all treatments gradually reached the same gelatinization status. However, a lower amorphous content in microwaved starch was observed, compared with traditional and rapid heated starches at the range of 65–70 °C (Fan et al. 2013b). Zeng et al. (2016) reported the amylose leaching was significantly lower in microwaved lotus seed starches than conventional heating from 50 to 90 °C, and the higher the irradiation power, the more extent of the restricting impact. The authors explained this as the increased amylose-amylose interaction, and reduced branching degree in amylopectin as a result of partially degraded dextrins, as the molar weight was significantly decreased. In addition, the authors also found the proportion of crystalline region in microwaved starch was higher than that of conventional heating, indicating that the existence of more efficient packing of double helices within the crystalline lamella and the intensive interaction between amylose-amylose interaction occur in microwave heating.

6.3.6 In Vitro Digestibility

Starch is the major carbohydrate source as daily energy source, and thus its digestibility is important. Usually native starch belongs to the high glycemic index (GI) food and has low resistant starch content. The starch digestibility is mostly reduced after MWT. For example, the resistant starch content of *Canna edulis* Ker starch increased from 27% to 55% after MWT (IMC, 20%, irradiated at 1000 W for 30 min and freeze-dried) (Zhang et al. 2010). After MWT, the enzyme susceptibility of cassava starch lowered from 30.00% to 27.50% (Abraham 1993). The extent of reduction on digestibility is found to vary with different irradiation doses, amylose content, and moisture. For example, Zeng et al. (2016) found the digestibility of lotus seed starch had higher resistant starch and slowly digestible starch with greater microwave power. Zhang et al. (2009) found IMC and maximum heating temperature, irradiation time, and power all could influence the enzymatic hydrolysis on canna edulis Ker starch, and an appropriate combination led to a lowest digestibility. The enzyme susceptibility of wheat starch after MWT decreased with increased irradiation time and decreased solids concentration (Palav and Seetharaman 2007). There are also a few exceptions, e.g., both Anderson et al. (2002) and Anderson and Guraya (2006) found the digestibility of waxy and non-waxy rice starch had slight increases after MWT. The digestibility of barley starch was increased after MWT, and the higher the irradiation power, the greater the digestion rate (Emami et al. 2012). The digestibility of microwave cooked rice had initially higher digestibility than conductive cooked rice, while after certain storage time, it became lower (Li et al. 2014).

As molecular arrangement, degree of crystallinity, and retrogradation of starch influence the enzymatic availability and rate of digestion (Lopez-Rubio et al. 2008), the explanations for the digestibility changes relate to previous described internal structure changes caused by MWT. Zeng et al. (2016) suggested decreased branching degree after MWT contributed to amylose-amylose interaction and the retrogradation of lotus seed starch, promoting the formation of resistant starch during cooling. A predicted two-stage in vitro digestion mechanism for microwaved starch has been drawn by Zhang et al. (2010). The authors considered the enzymes initially eroded selected zones of granule surface, rapidly forming pits which became canals as observed by SEM. Then the enzyme would hydrolyze the whole granule through the canals. The author found the crystalline structure of treated starch was not destroyed in the process of digestion. Besides, the analysis on Fourier transform infrared spectroscopy (FTIR) and XRD results suggested that during digestion, the hydrogen bonds were strengthened and ordered content and crystallinity were increased within the starch granule, indicating the enzymatic resistance of microwaved *Canna edulis* starches may be mainly caused by the specific structures formed during digestion.

6.4 Conclusion and Application Perspectives

The main advantages of microwave processing are the high heating speed, short time cost, and simple operation steps. Generally microwave irradiation causes internal molecular rearrangements inside starch granules, resulting in property changes such as pasting, swelling, and gelatinization properties, and the rapid heating speed may be the most important factor accounting for the changes rather than polar molecular vibration. The modification effects depend on the starch type (amylose content), initial moisture content, heating temperature, heating rate, and irradiation time. Its effects may also be influenced by the sample storing conditions before and/or after MWT (Emami et al. 2012). The common uneven heating caused by microwave heating should also be noticed (Fan et al. 2012a). Therefore, the comparison between different literatures is difficult to some extent due to different starches used and treatment conditions adopted, and systematic research on microwave modification are in still need to reach full understandings on the modification mechanisms. MWT can improve molecule manipulation and modification (Zhongdong et al. 2005), and recently it is reported to assist other treatment/modification methods with synergistic effects to further change starch properties, e.g., vacuum treatment (Mollekopf et al. 2011), ultrasonic treatment (Jiang et al. 2011), and conventional heat-moisture treatment (Deka and Sit 2016). It can help some chemical modifications (Rivero et al. 2009) and significantly reduce the reaction time for starch esterification (Lewandowicz et al. 2000a; Lukasiewicz and Kowalski 2012). Microwave treatment does have high potential for the processing of agricultural products (Vadivambal and Jayas 2007), but some other potential application areas of microwave modification products has been reported, e.g., microwave-modified rice starch can be used to control drug release in the simulated gastric fluid (Luu et al. 2015). However, generally it has not yet been implemented for industrially purpose (Braşoveanu and Nemţanu 2014).

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Chapter 7
Ultrahigh Pressure Treatment

Junrong Huang, Huayin Pu, and Qi Yang

Abstract Ultrahigh pressure, also called high hydrostatic pressure, is an important physical process to modify starch. In this chapter, the effects of ultrahigh pressure on physicochemical properties (including gelatinization, rheological and digestibility properties) and structures (including granular, crystalline and molecular structures) of starches are reviewed. Many studies show that ultrahigh pressure can realize starch gelatinization at room temperature. However, the pressure-induced and heat-induced gelatinization have different characteristics. In present, the potential applications mainly include the preparation of pregelatinized starch and cold water-swelling starch, as well as chemical modified starch. The future research can focus on the structural recombination of starch treated at lower pressure (lower than gelatinization pressure) and the performance of dry starch in ultrahigh pressure treatment.

Keywords Ultrahigh pressure · Gelatinization · Crystalline structure

7.1 Introduction

Ultrahigh pressure (UHP), also called high hydrostatic pressure (HHP), is often defined as pressure exceeding 100 MPa. The implementation of UHP technology depends on the UHP equipment. A typical laboratory-scale UHP equipment includes a pressure vessel, closures for sealing the vessel, pumps to intensify the high pressure, and a controlling system, in general with cavity volume of 10 mL to 5 L. A commercial UHP equipment has a product handling system to transfer the product without stirring apparatus and difficult to realize the continuous monitoring of structure and properties changes (Bolumar et al. 2015) (Fig. 7.1). Depending on the equipment, the pressure settings vary from 100 to 900 MPa but frequently in the

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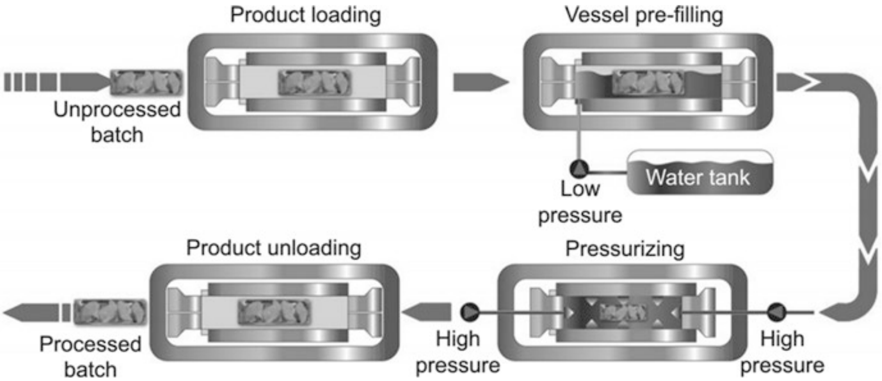

Fig. 7.1 Scheme of high pressure processing. (Source: Courtesy of Francisco Purroy (Hiperbaric, Spain)) (Bolumar et al. 2015)

range of 400–600 MPa in an industrial environment (Bolumar et al. 2015). Pressure transmits through a specific medium, which in most cases is water but is replaced by oil at a higher pressure (usually exceeds 600 MPa).

UHP is traditionally applied in ceramics, synthetic materials, steel, and superalloy production (Mota et al. 2013). The original application of UHP in food industry was reported in increasing shelf life of milk in 1899. At present, the application of UHP mainly involves in food nonthermal sterilization, inactivation of enzyme, macromolecular modification, and quality improvement for end-use products such as meats and wines. Since 1981, as the gelatinization of starch at room temperature is reported by Thevelein and his co-workers, the UHP treatment of starch attracts more and more attention (Thevelein et al. 1981).

Most often, starches are subjected to UHP treatments as suspensions in water. In contrast, less information is available for dry (lower moisture content) starch. Without adequate moisture, starch granules show high-pressure resistance. Only extreme UHP (>600 MPa) treatment can alter the shape and surface appearance of dry starch granules, as well as destroy the crystalline structure (Liu et al. 2008; Slominska et al. 2015; Kudla and Tomasik 1992a, b).

Earlier reports were about pressure-induced gelatinization process and comparison with heat-induced gelatinization. In recent years, more investigations were conducted on the structure-properties relationship of starch and the potential application of UHP. Heat-induced gelatinization can be represented directly by using hot-stage polarized light microscope (HS-PLM), rapid visco analyzer (RVA), and differential scanning calorimeter (DSC). However, for pressure-induced gelatinization, it is difficult to carry out the pressure treatment and properties determination simultaneously due to instrumental limitation. The diamond anvil cell (DAC) combined with synchrotron radiation technology realizes the online analysis for lamellar structure change during pressure-induced gelatinization process but fails to obtain macroscopic properties because of the smaller sample capacity for this device. Almost all studies on pressure-induced gelatinization must prepare UHP-treated samples first. The gelatinization process is commonly evaluated by the degree of gelatinization, calculated by gelatinization enthalpy in DSC results. Besides, Bauer and Knorr characterized the gelatinization according to the electrical conductivity of UHP-treated starch and found the electrical conductivity correlated well with the degree of gelatinization (Bauer and Knorr 2004). This is applicable for the quick and simple determination of pressure-induced starch gelatinization.

Botanical source and pressure are the most important factors in pressure-induced gelatinization. Besides, concentration, holding time, temperature, and pH also influence the gelatinization of starch. Starches with different botanical sources vary in gelatinization pressure, usually evaluated by the gelatinization pressure, which is defined to be the initial pressure (or a pressure range) to induce starch gelatinization and generally determined by using polarizing microscope (PLM) or DSC. In general, without heating or addition of other components, a complete gelatinization usually needs 600 MPa (Liu et al. 2010). Potato starch (with B-type crystal) exceeds 600 MPa and is considered to have a higher-pressure resistance (Kawai et al. 2007). At present, it is still controversial whether or not UHP treatment at the pressure lower than gelatinization pressure can affect starch structure. Thus, study on the effects of UHP on starch structure at a lower pressure (lower than gelatinization pressure) is worth to carry out and will facilitate the comprehensive understanding of starch performance during UHP treatment processing.

7.2 The Effects of UHP on Starch Physicochemical Properties

7.2.1 Gelatinization Properties of Starch

The gelatinization properties are mainly reflected in the change of gelatinization enthalpy/temperature and viscosity. In general, UHP treatment lowers the gelatinization enthalpy in a certain pressure range, while gelatinization temperature decreases with increasing pressure (Table 7.1). However, Thevelein and Muhr reported that a treatment of potato starch in dilute (0.4%) suspension with pressures up to a relatively low pressure (<150 MPa) increased its gelatinization temperature (Thevelein et al. 1981; Muhr and Blanshard 1982). Rice, waxy maize, high-amylose maize, sorghum, and buckwheat starches also increase in gelatinization temperature (onset temperature) after UHP treatment (Table 7.1). This may be related to the preferential gelatinization of starch granules with low-pressure resistance or formation of new starch crystal with higher gelatinization temperature due to the retrogradation of starch molecules, while Kweon and his co-workers propose that the reason is the annealing of amylopectin (Kweon et al. 2008a).

Table 7.1 The effects of ultrahigh pressure (UHP) treatment on gelatinization enthalpy (△H) and onset gelatinization temperature (To) of various starches

Starch	Pressure (gelatinization pressure) /MPa	Starch content/%	Time/ min	△H	To	References
Potato	51–253	0.4	4	Decline	Rise	Thevelein et al. (1981)
Wheat, potato, smooth pea	58–401	0.4	–	Decline	Rise and decline	Muhr and Blanshard (1982)
Barley	450–600	10, 25	15, 30	Decline	–	Stolt et al. (2001)
Maize, waxy maize, tapioca, rice, potato, high-amylose maize	690	1:1, 1:2 (w/V)	5, 60	Decline	Decline (rise for waxy maize, rice, and high-amylose maize)	Katopo et al. (2002)
Potato	600	10	2, 3	Decline	Decline	Błaszczak et al. (2005a)
Potato	600–1000	10–70	60–3960	Decline	–	Kawai et al. (2007)
Sorghum	200–600 (600)	25	10	Decline	Rise	Vallons and Arendt (2009a)
Buckwheat	200–600 (600)	25	10	Decline	Rise	Vallons and Arendt (2009b)
Mung bean	120–600 (600)	20	30	Decline	Decline	Li et al. (2011a)
Rice	120–600 (600)	20	30	Decline (120–480 MPa)	Decline	Li et al. (2011b)
Lotus seed	100–600 (600)	15	30	Decline (100–500 Mpa)	–	Guo et al. (2015a)

As a kind of nonthermal processing technology, UHP is mainly applied at room temperature. However, in some case, it is interesting to discuss the gelatinization induced by pressure-heat combinations. For pressure-induced gelatinization at a constant holding time, either increasing temperature or pressure can promote starch gelatinization. In other words, the higher the temperature, the lower pressure to realize the complete gelatinization of starch (Bauer and Knorr 2005; Tan et al. 2009). On the other hand, at a constant temperature and pressure, the degree of gelatinization increases with increasing holding time. However, if the temperature and/or pressure is unable to induce starch gelatinization, it is invalid to prolong holding time (Stolt et al. 2001; Bauer and Knorr 2005). In order to further understand the heat-pressure combination effect, the phase diagrams of various starches have been provided and used to estimate the degree of gelatinization after applying a certain pressure and temperature on a starch-water mixture with starch concentrations in the range of 5% and 60% w/w (Baks et al. 2008).

Just as heat-induced gelatinization, pressure-induced gelatinization is also influenced by solutes in the starch suspensions. The addition of sugar (20%) reduced gelatinization pressure (wheat starch/350 MPa tapioca starch/530 MPa, potato starch/700 MPa, 5% suspension, 15 min at 29 °C), whereas the degree of gelatinization is linearly correlated with the number of equatorial hydroxyl groups for different sugars (fructose, glucose, sucrose, trehalose) (Rumpold and Knorr 2005). UHP-induced gelatinization can also be affected by salt. The presence of salt significantly protected glass and crystalline transitions of wheat starch during the UHP treatment (Kweon et al. 2008b). Additionally, the influence of salts on the gelatinization pressure varies, and the extent of effect on the gelatinization pressure depends not only on the solute added but also on the source of starch (700 MPa, 15% suspension, 15 min at 29 °C) (Rumpold and Knorr 2005). At high chloride concentrations (>2 M), the impact of the salts on starch gelatinization augmentation followed the order $Na^+<K^+<Li^+<Ca^{2+}$, which corresponds to the order of the lyotropic series. At concentrations above 1 M, the effect of potassium salts on starch gelatinization upon pressurization also followed the order of the Hofmeister series ($Cl^-<Br^-<I^-<SCN^-$). This conclusion is helpful in the practical application of UHP-treated starch (Rumpold and Knorr 2005).

The change of viscosity in gelatinization process is mainly measured by RVA or the rheometer after UHP treatment. If the UHP-treated starch sample still appears a drastic increase in viscosity during heating, it indicates the treatment pressure is lower than the gelatinization pressure of the starch. In contrast, the treatment pressure is higher than gelatinization pressure. Thus, the gelatinization pressure can be obtained by comparing the RVA curves of samples treated at different pressures. Oh and his co-workers determined the gelatinization pressures (10% suspension, 30 min at 20 °C) of normal rice, waxy rice, normal corn, waxy corn, tapioca, and potato starches by using this method (Oh et al. 2008). More information can also be obtained by using RVA. The pasting properties of mung bean (20% suspension, 30 min at room temperature), rice (20% suspension, 30 min at room temperature), red adzuki bean (20% suspension, 15 min at 25 °C), and lotus seed starches (15% suspension, 30 min at room temperature) were reported (Li et al. 2011a, b, 2015; Guo et al. 2015a). Gelatinized starch (treated at 600 MPa) exhibits the lowest peak viscosity (PV), breakdown (BD), and setback (SB) (except for mung bean starch). PV is an indicator of early and rapid swelling of starch granules, and BD represents the stability and resistance of starch granules to shear stress, while SB represents the rapid retrogradation of leached amylose in starch. Therefore, UHP-gelatinized starch has generally a stronger starch aggregation, more stable hot paste, and lower retrogradation tendency compared with native starch, although some starches exist a varying trend. This could be due to some structural factors such as granular swelling, amylose leaching, and starch-water and amylose-lipid interaction.

7.2.2 Rheological Properties of Starch Paste and Gel

Starch is mainly used in the food industry in the form of gelatinized starch. Therefore, the properties of starch paste and starch gel are widely studied. In steady-state rheological behavior, the consistency coefficient (*K*) value is an approximate measurement of the viscosity of the starch paste at rest. The elevating *K* value reflects the granular swelling and the increasing in degree of gelatinization. After UHP treatment for starch suspension, the *K* of starch paste increased with increasing pressure or holding time however existing a limit *K* value during the increasing of holding time (Stolt et al. 1999, 2001; Guo et al. 2015b; Jiang et al. 2015). Furthermore, increasing temperature could further increase the *K* value in a constant pressure (Tan et al. 2009).

The dynamic rheological behavior and textural parameters reflect the properties of gels, which are related to the retrogradation of starch molecules. The dynamic rheological test is generally carried out according to strain sweep measurement. The storage modulus G' is a measure of the energy stored in the sample. For a gel, it reflects the cross-link density of the network (Stolt et al. 1999). In most reports, G' value increases with increasing pressure or holding time; however, continuous increasing pressure or holding time could show an opposite effect for starch gels, indicating that excessive pressurization can produce weaker gel (Stolt et al. 1999; 2001; Tan et al. 2009; Guo et al. 2015b).

The gel prepared in a higher concentration (related to the source of starch) is usually measured by textural analyzer. The properties of pressure-induced gels differ from that of the heat-induced gels. Stute and his co-workers reported a rapid retrogradation peak in DSC curve for UHP-treated (wheat, corn, pea, waxy rice) starches (450–500 MPa, 25%, 15 min at 20 °C) (Stute et al. 1996), suggesting that amylose significantly retrogrades and mainly occurs within the granules because of the limited swelling of starch granules and a limited releasing of amylose during UHP gelatinization. Due to rapid retrogradation, UHP-induced gel is harder than heat-induced gels for tapioca starch (Vittadini et al. 2008). However, the contradictory results were reported for wheat starch (Douzals et al. 1998). Pressure-induced gel was softer but dense compared with heat-induced gel, indicating that starch gels obtained under pressure would be less sensitive to retrogradation. The retrogradation of pressure-gelatinized starches was slower than that of heat-gelatinized starches as observed with enzyme digestibility and starch-iodine reaction (Stolt et al. 2001). These results do not mean that all pressure-induced gels behave in a similar way.

The retrogradation properties of tapioca starch gels illustrate that UHP (600 MPa, 25% suspension, 10 min at 30–80 °C/20, 30 min at 30 °C) resulted in the formation of harder gel than thermal processing (25% suspension, 20 min at 90 °C) (Vittadini et al. 2008). The increased hardness induced by UHP (600 MPa) was found to be more significant in the samples processed at 30 °C compared with treatment at higher temperature (50 or 80 °C) (Vittadini et al. 2008). Longer UHP treatments (600 MPa, 25% suspension, 10–30 min at 30 °C) caused only a slight decrease in hardness and were significant only at longer processing times (30 min). These can be explained by the different water-starch and/or starch-starch molecular interactions due to partial preservation of the granular structure in gel after UHP-induced gelatinization (Vittadini et al. 2008).

7.2.3 *Starch Digestibility*

The amylase digestibility of pressure-treated starch was first discussed in 1989 by Hayashi and Hayashida (1989). The author indicates that the amylase digestibility increases with increasing pressure because of the starch gelatinization. However the formation of new structure during long-period pressure treatment decreases the digestibility. The relationship between starch structure and the content of resistant starch (RS) or slowly digestible starch (SDS) after UHP treatment was studied (Mu et al. 2015). General, more SDS and RS were observed in UHP-gelatinized starches than in heat-gelatinized starches (Bauer et al. 2005; Tian et al. 2014). Linsberger-Martin and his co-workers reported that increasing pressure, holding time, or temperature led to increases in RS (Linsberger-Martin et al. 2012). However, Deng and his co-workers (20% suspension, 30 min at 25 °C) proposed that excessive pressurization (600 MPa) and cycle UHP treatment (15 + 15 min) decreased the RS but increased the SDS content of rice starch (Deng et al. 2014). Additionally, UHP treatment could further induce increasing RS in starch paste (Bauer et al. 2005). In comparison, resistant (RS3, retrograded starch) and waxy corn starches treated by UHP are characterized by the lower levels of released glucose after enzymatic digestion, compared with that for wheat, potato, tapioca, and corn starches (Papathanasiou et al. 2015). Besides, initial rate of glucose production obtained from heat-induced gelatinization is faster than that obtained from the UHP treatment, in spite of the equilibrium yield of glucose found to be similar (Papathanasiou et al. 2015).

The gels prepared by UHP treatment have the potential application in drug release. The drug release rate depends on the starch source. Gel-forming polymer containing potato starch exhibits faster drug dissolution, while the pressurization of maize starch results in a gel exhibiting sustained drug release (Szepes et al. 2008). Overall amylose content, pressure, and starch source are important factors in affecting the digestibility of starch treated with UHP (Dupuis et al. 2014).

7.3 The Effects of UHP on Starch Structure

7.3.1 *Granular Micrograph Structure*

Granular micrograph variation can intuitively reflect the effects of UHP on various starches. Light microscope (LM) and scanning electron microscope (SEM) are the main tools to observe starch granules. Atomic force microscope (AFM) and confocal laser scanning microscopy (CLSM) are also utilized to observe the surface and internal structure in detail.

Starch granules in pressure-induced gelatinization are inclined to show a restricted swelling and a lower release of amylose in UHP treatment, differed from heat-induced gelatinization (Stute et al. 1996). This is possibly caused by the absence of shear forces, and no hot paste is formed in UHP treatment (BeMiller and Huber 2015). Another explanation could be that amylose somehow stabilizes the starch granule structure under pressure (Stolt et al. 2001; Douzals et al. 1998).

Corn (300–600 MPa, 30% suspension, 15 min at room temperature) and red adzuki bean (150–600 MPa, 20% suspension, 15 min at 25 °C) starch show a granular maintaining with rough surface followed by complete disintegration (Li et al. 2015, 2016; Stute et al. 1996). Rice starch (120–600 MPa, 20% suspension, 30 min at 25 °C) presents an angular destruction (Li et al. 2011b). Mung bean (120–600 MPa, 20% suspension, 30 min at room temperature), lotus seed (100–600 MPa, 15% suspension, 30 min at room temperature), buckwheat (200–600 MPa, 25% suspension, 10 min at 20 °C), and sorghum starches (200–600 MPa, 25% suspension, 10 min at 20 °C) are inclined to form a doughnut-shaped structure (Fig. 7.2a–c) (Vallons and Arendt 2009a, b; Li et al. 2011a; Guo et al. 2015a).

The inner structure destruction (gel-like network formation) along with maintaining of external structure for potato starch granules during UHP treatment (600 MPa, 10% suspension, 3 min at 20 ± 2 °C) was observed by Błaszczak and his co-workers, indicating the special granular structure of potato starch, which may be related to the characteristic surface organization of potato starch (Fig. 7.2d) (Błaszczak et al. 2005a). The results of Gebhardt and his co-workers obtained by micro small-angle and wide-angle X-ray scattering (SAXS/WAXS) also support this conclusion (Gebhardt et al. 2007). On the basis of AFM results, the number of surface blocklets of rice starch granules increases, and the diameter decreases after treatment at a relatively low pressure (200 MPa, 20% suspension, 30 min at 25 °C). When the pressure reaches 600 MPa, starch granules show totally different structures with more fine and flat surfaces (Deng et al. 2014).

7.3.2 Order and Disorder Structure

As a kind of semicrystalline polymer, the spherocrystal structure of starch induces the polarization cross under polarizing microscope. The crystalline structure is destroyed, and polarization cross disappears, as well as gelatinization enthalpy decreases during common heat gelatinization, indicating an order-disorder transformation. Polarizing microscope (PLM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) are frequently applied to study on order and disorder structure change of starch after UHP treatment.

Starch crystal exists in four different forms and shows different XRD patterns. In general, cereal starches generate A-type XRD patterns, B-type patterns exist in tuber and high-amylose starches, and legume, root, and some fruit and stem starches show C-type patterns. V-type patterns are also present in high-amylose starch or retrograded starch and are in the form of the amylose single helices co-crystallized with compounds such as iodine, dimethyl sulfoxide (DMSO), alcohols, or fatty

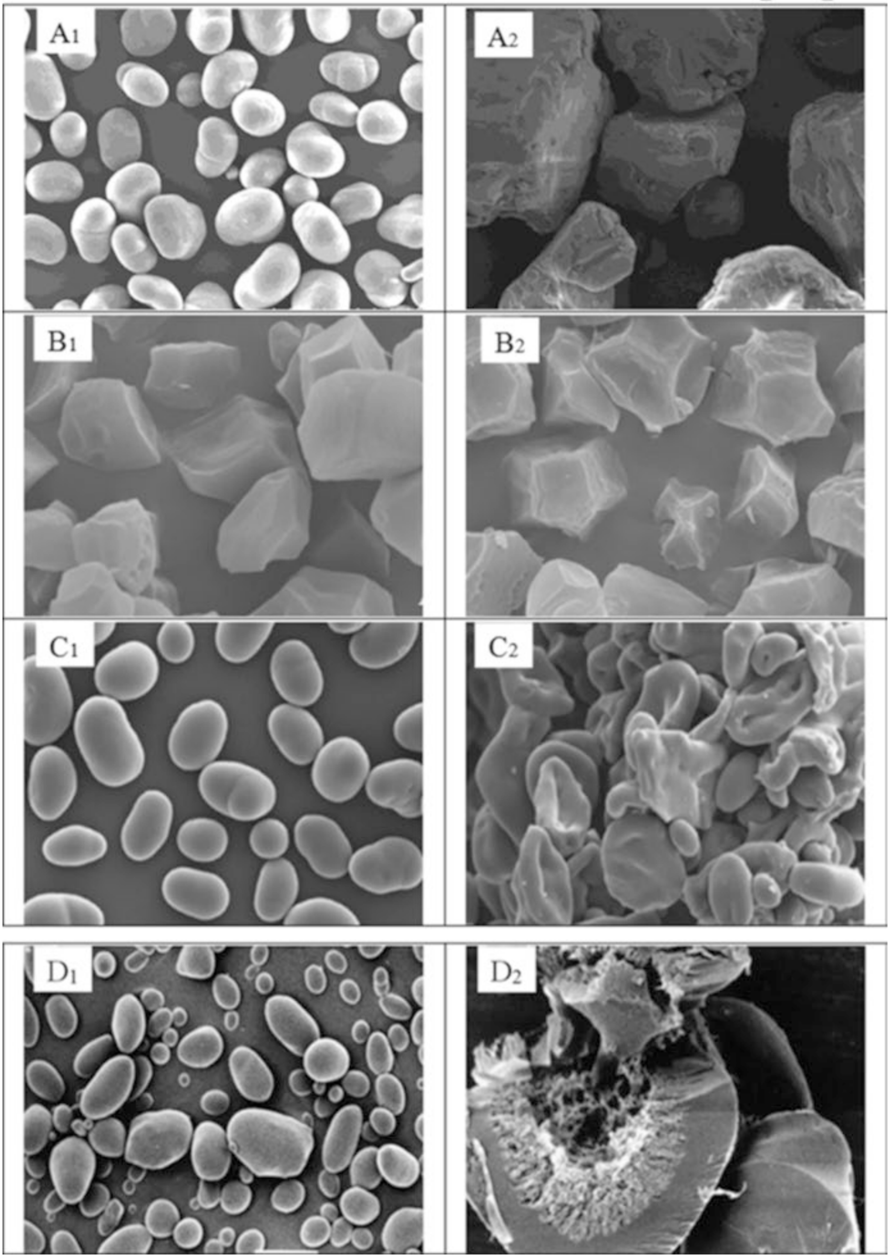

Fig. 7.2 Scanning electron micrographs of typical native (**A_1** red adzuki bean starch, **B_1** rice starch, **C_1** mung bean starch, **D_1** potato starch) and UHP-treated starch granules (**A_2** 600 MPa, 20% suspension, 15 min at 25 °C; **B_2** 480 MPa, 20% suspension, 30 min at room temperature; **C_2** 600 MPa, 10% suspension, 30 min at room temperature; **D_2** 600 MPa, 10% suspension, 3 min at 20 °C) (Błaszczak et al. 2005a; Li et al. 2011a, b, 2015)

acids (Buléon et al. 1998). Most A-type and C-type starches can be completely gelatinized at 600 MPa except in some rare starches such as taro, wrinkled pea, and babassu starches (5% suspension, 15 min at 20 °C). This pressure cannot induce the gelatinization of starch with B-type pattern (potato starch, 5% suspension, 15 min at 20 °C) (Oh et al. 2008; Stute et al. 1996; Yang et al. 2016; Rubens et al. 1999), suggesting a better pressure resistance of B-type starches. Potato starch can just be gelatinized completely when the pressure reaches 800 MPa at low starch concentration (10–20%, 1 h at 40 °C) and the required pressure to realize complete gelatinization increases with increasing starch concentration (Kawai et al. 2007). A- and C-type patterns could be converted into B-type patterns during UHP treatment, which is attributed to water being introduced into the crystalline packing unit under UHP (Liu et al. 2010). Nevertheless, there are still some exceptions (unchanged), as shown in Table 7.2.

Studies on the lamellar and double helix structure for starch granules after UHP treatment provide further information on the order and disorder structures. The influence of UHP treatment (waxy corn and Hylon VII starches, 650 MPa, 30% suspension, 9 min at 20 °C; rice starch, 20% at 25 °C, 200 MPa, 30 min/200 MPa, 15 + 15 min/600 MPa, 30 min/600 MPa, 15 + 15 min) on C1 and C4 peaks is obvious as determined by using solid-state ^{13}C CP/MAS NMR, indicating the decrease of double helix and the increase of single helix (Deng et al. 2014; Błaszczak et al. 2005b). This is attributed to the unwinding of double helix during UHP treatment. The synchrotron SAXS results illustrated the pressure-induced compression for waxy corn and potato starches. The average thickness of long period (≈9 nm) and amorphous layers decreased with increasing pressure, while the thickness of the crystalline layer first increased and then decreased (Yang et al. 2016). The compression effect is identified as the “shock absorbers” of amorphous layer and acting as a protection for crystalline layer during compressive forces. On the other hand, the initial increase of the thickness of the crystalline layer is likely to indicate the annealing of starch (Yang et al. 2016). Additionally, compared with waxy corn starch, the decrease of long period with pressure (up to 750 MPa) is less for waxy potato starch, indicating the B-type starch (waxy potato starch) is much less compressible compared to A-type starch (waxy corn starch), which is identified to be caused by the different amylopectin structures. These conclusions are benefit to the understanding of the high-pressure resistance of B-type crystal starches (Yang et al. 2016).

7.3.3 Molecular Structure

Błaszczak and his co-workers found that corn amylopectin formed a polydispersed product after UHP treatment (690 MPa, 30% suspension, 3 min at 20 °C), measured by using HPLC, indicating molecular degradation (Błaszczak et al. 2005b). However, it is not valid for high-amylose corn starch (Hylon VII). Guo and his co-workers utilized high-performance size-exclusion chromatography and multiangle laser-light scattering and refractive index detectors (HPSEC–MALLS-RI) to study the influence of UHP (15% suspension, 30 min at room temperature) on

Table 7.2 The effects of ultrahigh pressure (UHP) treatment on of starches

Starch	Pressure (gelatinization pressure)/MPa	Starch content/%	Time/ min	PLM	XRD	References
				Polarization cross	Crystal form	
A-type						
Maize, waxy maize, tapioca, rice	690	1:1,1:2	5,60	–	A→B	Katopo et al. (2002)
Waxy corn	650	30	3–9	Disappeared (9 min)	Unchanged	Błaszczak et al. (2005b)
Sorghum	200–600 (600)	25	10	Disappeared (500 MPa)	–	Vallons and Arendt (2009a)
Buckwheat	200–600 (600)	25	10	Disappeared (400 MPa)	–	Vallons and Arendt (2009b)
Rice	120–600 (600)	20	30	–	A→B	Li et al. (2011b)
Rice	200, 600	20	30	–	A→B	Deng et al. (2014)
Waxy corn, corn	100–600	40	30	Partially disappeared (600 MPa)	A→B	Yang et al. (2016)
B-type						
Potato, high-amylose maize	690	1:1,1:2	5		Unchanged	Katopo et al. (2002)
B+V-type						
*Hylon VII	650	30	3–9	Unchanged (9 min)	Unchanged	Błaszczak et al. (2005b)
*G50, G80	100–600	40	30	Unchanged (600 MPa)	Unchanged	Yang et al. (2016)
C-type						
Mung bean	120–600 (600)	20	30	–	C→B	Li et al. (2011a)
Lotus seed	100–600 (600)	15	30	–	C→B	Guo et al. (2015a)
Red adzuki bean	150–600 (600)	20	15	Disappeared (600 MPa)	Unchanged	Li et al. (2015)

*Hylon VII is high-amylose (70%) corn starch
G50 and G80 are high-amylose corn starches, containing 50% and 80% amylose, respectively

molecular weight distribution of lotus seed starch and suggested that the *Mw* and *Mn* values decreased with increase of pressure, indicating that lotus seed starch was slightly degraded during UHP treatment and formed molecular chains with a low degree of polymerization (Guo et al. 2015a). More studies in molecular structure of pressure-treated starch need to be carried out.

7.4 The Potential Applications of UHP

The potential application of UHP is necessarily related to the superiority of UHP treatment and modified starch. Generally, UHP treatment can induce starch gelatinization at room temperature, providing a method for the preparation of pregelatinized starch and cold water-swelling (CWS) starch. However, considering the requirement of special equipment and the discontinuous product preparation process, UHP treatment shows no advantages as compared to the thermal process. Nevertheless, application of UHP treatment is feasible in starch-containing high value-added or heat-sensitive system. On the other hand, compared with heat-gelatinized starch, UHP-gelatinized starch shows a diverse interior structure organization and has better granular maintaining. This is very important because many potential applications are based on this characteristic, including preparation of resistant starch (*RS*). Additionally, some reports indicate that UHP-modified starch can be applied in the binding of aroma compounds and textural improvement (Błaszczak et al. 2007; Zhang et al. 2014).

Recently, the utilization of UHP in preparation of chemical modified starch was introduced. Combining chemical modification with UHP technology has been applied in acid hydrolysis (Lee et al. 2006; Choi et al. 2009a), hydroxylpropylation (Chotipratoom et al. 2015), acetylation (Choi et al. 2009b; Colussi et al. 2014; Kim et al. 2010), cationization (Chang et al. 2014), and cross-linking (Hwang et al. 2009; Kim et al. 2012) of starches. The maintenance of granular structures along with the improvement of reaction efficiency by UHP-assisted modification facilitates the industry application, although the structure-properties relationship needs to be further studied.

In general, many factors such as starch source, pressure, temperature, concentration, and holding time can affect the starch properties; therefore, the application of UHP depends on the reasonable selection of these parameters and further illustrating the structure-properties relationship. Investigations on the structural recombination of starch treated at lower pressure (lower than gelatinization pressure) and the performance of dry starch in UHP treatment will be helpful to broaden the application of UHP-treated starch.

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Chapter 8
Ultrasonic Treatment

Zhaofeng Li

Abstract Ultrasound defines the mechanical waves at a frequency above the upper value of normal human hearing range (>16 kHz). It can be divided into three frequency ranges including power ultrasound (6–100 kHz), high-frequency ultrasound (100 kHz–1 MHz), and diagnostic ultrasound (1–10 MHz) (Patist and Bates, Innovative Food Sci Emerg Technol 9:147–154, 2008). Ultrasonic equipment is environmentally friendly, easy to operate and control, and also simple to realize automation (Bartsch and Schmidt-Naake, Macromol Chem Phys 207:209–215, 2006). What's more, ultrasonic treatment exhibited positive impacts in food processing and preservation, such as to improve the product yields, cut down the processing times and costs, raise the product ranks and safety, reduce the pathogens, and help to create novel products with desired properties. As a promising new technology, it is supposed to be full of potentialities in future development of food processing (Awad et al., Food Res Int 48:410–427, 2012; Knorr et al., Trends Food Sci Technol 15:261–266, 2004; Patist and Bates, Innovative Food Sci Emerg Technol 9:147–154, 2008).

Keywords Ultrasonic treatment · Starch system · Granular structure of starch · Physicochemical properties of starch

8.1 Overview of Ultrasonic Treatment in Starch System

Ultrasound defines the mechanical waves at a frequency above the upper value of normal human hearing range (>16 kHz). It can be divided into three frequency ranges including power ultrasound (6–100 kHz), high-frequency ultrasound (100 kHz–1 MHz), and diagnostic ultrasound (1–10 MHz) (Patist and Bates 2008). Ultrasonic equipment is environmentally friendly, easy to operate and control, and also simple to realize automation (Bartsch and Schmidt-Naake 2006). What's more, ultrasonic treatment exhibited positive impacts in food processing and preservation,

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such as to improve the product yields, cut down the processing times and costs, raise the product ranks and safety, reduce the pathogens, and help to create novel products with desired properties. As a promising new technology, it is supposed to be full of potentialities in future development of food processing (Awad et al. 2012; Knorr et al. 2004; Patist and Bates 2008).

Most of the ultrasonic application in starch is in a starch-water system. When the sinusoidal ultrasound waves pass through the liquid, the acoustic energy of ultrasound cannot be absorbed by molecules, and thus propagates via a series of compression and rarefaction waves induced in the medium molecules, and then it is transformed to a chemically usable form via the cavitation phenomenon (Chan et al. 2010; Knorr et al. 2004). This phenomenon is caused by ultrasonic treatment when the amplitude is high enough, leading to the formation of bubbles in the system. The pressure from the wave motion make the bubbles grow during the expansion cycle and shrink during the compression cycle. The bubbles keep growing over a lot number of cycles, and when they reach the point that the oscillation frequency of the ultrasound waves equals that of the bubble wall, the bubbles explode during the compression cycle (Chan et al. 2010; Patist and Bates 2008). The explosion of bubbles produces extremely high shearing force and turbulence with large energy waves and results in drastic temperature rise locally; consequently the physical and chemical conditions of the system are changed. Bubble collapsing causes a water jet shooting onto the granule surface. These “micro-jets”, as well as the “shear forces” induced by cavitation, can availably damage the starch granules (Zuo et al. 2012). Besides, the cavitation dissociates the water molecules, leading to the release of free radicals such as hydroxide (OH) and hydrogen (H) radicals. These radicals may chemically modify the system in turn (Czechowska-Biskup et al. 2005; Riesz and Kondo 1992).

Early in 1933, Szent-Györgyi (1933) firstly reported the action of ultrasound on starch, which decreased viscosity and cut off the starch chains. During the past decades, a large number of efforts have been devoted to further investigate the impacts of ultrasonic treatment on different aspects of starches, which are expounding in this chapter, and many factors have been found to influence the effects of ultrasound on starch granules, such as the frequency and power of ultrasonic treatment, temperature and time of the treatment, and the properties of starch dispersion systems including concentration and botanical origin of starch. Although it is difficult to compare the experimental results from different research directly because their methods and materials varied greatly, this chapter describes the trends of effect caused by ultrasonic treatment on starch.

8.2 Effect of Ultrasonic Treatment on the Starch Yield and Composition

8.2.1 Starch Yield

Cereals, tubers, and roots are major materials to produce starch. Starch granules, especially starch granules present in the tubers and roots, are usually embedded in cellulosic fibres and combined by pectin substrates. Hence, the raw materials need to be grated firstly, breaking the cells and releasing the starch (Daiuto et al. 2005). The yield of starch is decreased, however, since it's impossible to grate the plant cell walls completely by mechanical disintegration. Enzymatic methods have been used to increase the recovery of starch from roots and tubers, but the methods are ineluctably time-consuming and costly, because long incubation periods and pure enzyme are required (Dzogbefia et al. 2008).

It has been reported that ultrasonication can increase the yield of starch. In one research, an increased recovery of starch from corn and sorghum starch was achieved by using ultrasonic treatment method compared to conventional method (Benmoussa and Hamaker 2011). As both cycle and amplitude were constant, the longer treatment time caused higher breakdown of plant cells, thus releasing more starch and increasing the starch yield. Wang and Wang (2004b) reported a higher yield of rice starch at lower amplitude rather than 100% amplitude, the reason might be that high amplitude, which provided more energy, not only disintegrated the cellulosic materials but also broke the starch molecules, causing the dissolution of partial starch in water, and it was difficult to recover the dissolved starch by centrifugation in the later process. Sit et al. carried out a study on the effect of sonication parameters on yield of taro (a tropical tuber crop) starch, and similar results were observed: the starch yield significantly increased under the control of all ultrasonic treatment combinations (Sit et al. 2014).

Ultrasonic treatment has been combined with other additives such as sodium dodecyl sulphate (SDS) (Park et al. 2006; Wang and Wang 2004a) and protease (Cameron and Wang 2006; Wang and Wang 2004b) for the improvement in the efficiency of starch extraction from various cereals. When coupled with SDS, both the starch recovery and purity from different cereals (such as rice, sorghum, barley) were enhanced by ultrasonic treatment without the use of alkaline solution (Park et al. 2006; Wang and Wang 2004a). With the aid of protease, ultrasonic treatment reduced the steeping time during wet-milling process of degermed corn flour without the use of SO_2 (Cameron and Wang 2006), and evidently increased the starch recovery from rice flour, while the morphology and molecular structure of the granules were not influenced (Wang and Wang 2004b). Ultrasonic treatment has also been coupled with sucrose density separation for better extraction of starch from a small amount of flour. This strategy could be significantly useful in cases when plenty of raw materials are difficult to get, for example, genetic breeders and crop molecular biologists (Benmoussa and Hamaker 2011). There is no doubt that the conditions of ultrasonic treatment should be carefully controlled in order to avoid the damage to granules. And there is still a series of complex processes to apply the lab-scale results to the industrial scale.

8.2.2 Starch Composition

Amylose content is a decisive factor affecting the properties and applications of starch (Srichuwong and Jane 2007). Researchers used iodine complexation to determine the amylose content of native and sonicated corn starches. The result showed an increase in the amylose content after ultrasonic treatment, implying that partial amylose may depolymerize during the ultrasonication process (Li et al. 2016). Ultrasound may also scissor the starch chains and produce more linear molecules, as reported by Chan et al., focusing on the increase in amylose content of corn, potato, mung bean, and sago starches after ultrasonic treatment (Chan et al. 2010).

Minor components such as protein and lipid in starch granules can influence the functionality of starch. Besides, the residual protein is combined with the starch granules tightly and may inhibit the enzymolysis of starch (Srichuwong and Jane 2007). It was revealed that ultrasonic treatment in a bath improved the enzyme susceptibility of mung bean and corn starches because the protein content of starch was decreased by ultrasonic treatment (Chan et al. 2010). Ultrasonic treatment has also been employed in wet-milling of corn flour and hominy feed (Zhang et al. 2005a, b). Compared to starch extracted by single wet-milling treatment, the starch recovered with the involvement of ultrasonic treatment had fewer residual impurities such as proteins and lipids (Zhang et al. 2005a, b).

8.3 Effect of Ultrasonic Treatment on the Structure of Starch

8.3.1 Effect of Ultrasonic Treatment on the Granular Structure of Starch

Ultrasonic treatment often resulted in the morphological changes of starch granules by forming cracks and pores, and damaging the granules, as Fig. 8.1 shows. Various techniques have been used to observe the morphology of starch granules caused by ultrasonic treatment, such as light microscopy (LM), polarized light microscopy (PLM), scanning electron microscopy (SEM), transmission electron microscopy

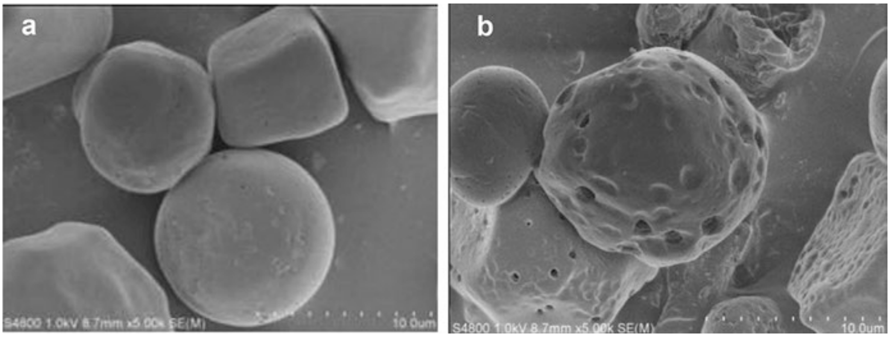

Fig. 8.1 SEM figures of native (**a**) and sonicated (**b**) corn starches (Li et al. 2016)

(TEM), and laser light scattering (LLS) technique (Sujka and Jamroz 2013; Zhu et al. 2012; Zuo et al. 2009, 2012).

Plenty of factors could impact the effect of ultrasonic treatment on the morphology of starch granules: the temperature (Zuo et al. 2009). (1) The starch type and structure, as well as the concentration of starch slurry. They are closely related to results of ultrasonic treatment because they determine the susceptibility of starch to ultrasonication. For example, after ultrasonication treatment, pores formed on the surface of normal and waxy corn starches, while amylomaize V starch became cracked (Luo et al. 2008). Treated with the same ultrasonic action, fractures and depressions on the surface of granules were better seen in the case of potato and wheat starches than corn and rice ones (Sujka and Jamroz 2013). Besides, the damage of granules decreased with increasing starch concentration (Gallant et al. 1972). (2) The parameters of ultrasonication settings, including the power, frequency, and duration of treatment. The granules tended to agglomerate when increasing the power input (Jambrak et al. 2010), and increasing duration caused more damage on starch granules (Huang et al. 2007). Dual-frequency ultrasound (25 and 80 kHz) caused more dents and pores on granules' surface than single-frequency ultrasound (25 kHz or 80 kHz) (Zheng et al. 2013). (3) Other conditions such as temperature, the type of ultrasonication equipment (probe or bath), and the gas type of the atmosphere. Heating made it more easier for ultrasonication to damage the granules (Zuo et al. 2009). Ultrasonication bath and probe led to different outcomes for the same kind of starch (Jambrak et al. 2010). The gas type affected the extent of damage to granules. The hydrogen atmosphere resulted in the most damage followed by air and oxygen, carbon dioxide, and vacuum (Gallant et al. 1972), and the solubility of atmosphere gas had negative effect on the pit size (Degrois et al. 1974).

Since the ultrasonication treatment change the morphology of starch granules, the crystallinity of starch is consequently altered. The conditions of ultrasonication are one of decisive factors to change the crystallinity degree of the granules. Li et al. found that ultrasonic treatment (starch concentration 40%, 20 kHz, 800 W, 4 h) did not change the crystalline structural type of the corn starch (Fig. 8.2) but caused the destruction of approximately 25.1% of the crystalline structure of the starch

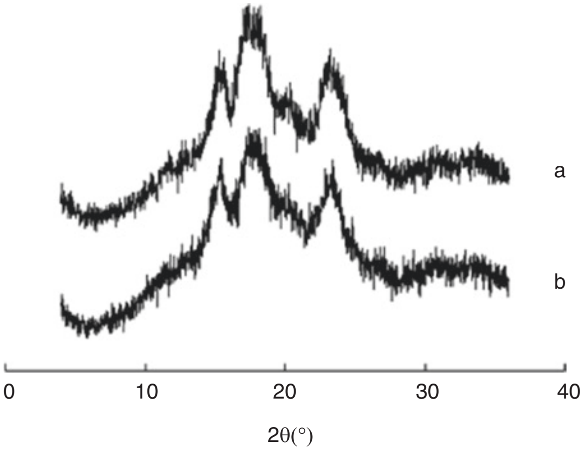

Fig. 8.2 X-ray diffraction patterns of native (**a**) and sonicated (**b**) corn starch (Li et al. 2016)

granules, which could be attributed to excessively small crystallites or a decreased degree of crystalline arrangement (Li et al. 2016). Similar results could be seen in another study where ultrasonic treatment was applied to isolate starches from brown rice grains (Park and Han 2016). Huang et al. reported that ultrasonication (starch concentration 30%, 500 W, frequency unknown) up to 3 min increased the crystallinity degree, but further treatment (15 min) decreased it (Huang et al. 2007). It could be inferred that in the initial process, ultrasonication disrupted the amorphous parts in the granules, causing the increased crystallinity degree, and the later decrease may be attributed to the damage of crystals in the granules by further ultrasonication (Huang et al. 2007).

Small-angle X-ray scattering (SAXS) analysis showed that the repeated lamellae thickness was unaffected, while the background material (electron density as ρ_u) was more affected than the amorphous material (electron density as ρ_a) (Zhu et al. 2012). It seems that the amorphous region of the granules is more susceptible to ultrasonication than the crystalline part. Thus starches with a higher content of amylose (most amorphous in the granules) were more easier to be influenced in structure and properties by ultrasonication (Luo et al. 2008; Zhu et al. 2012). Fourier transform infrared spectroscopy (FT-IR) analysis revealed that ultrasonication affected the crystal structure of sweet potato starch but did not change the functional chemical groups, and the dual-frequency treatment led to more obvious outcome than single ones (Zheng et al. 2013). To get systematic and comprehensive data, it is advantageous to combine various methods such as FT-IR, solid-state nuclear magnetic resonance (NMR) spectroscopy, WAXS, as well as SAXS.

8.3.2 Effect of Ultrasonication on the Molecular Structure of Starch

The influence of ultrasonication on molecular structure of starch chains has been examined by different methods (Iida et al. 2008; Isono et al. 1994; Zheng et al. 2013). Starch chains of amylose/amylopectin can form inclusion complex with iodine and exhibit different colours, reflecting the length and branching pattern of starch. It has been reported that ultrasonication converted the colour of starch-iodine complex from blue to red (Szent-Györgyi 1933) and reduced the blue value, λ_{max}, and A_{680}/A_{545} ratio (A_{680} and A_{545} represent the absorbance of the starch solution at the wavelengths of 680 nm and 545 nm, respectively) of starches from different origins (e.g. potato, wheat, corn, and rice) (Sujka and Jamroz 2013). These phenomena indicated that the ultrasonic treatment induced the chain scission and weakened the ability of starch to form complex with iodine.

The effect of ultrasonication on molecular structure of starch chains has been studied in more details by diverse methods. Chains of starches from various sources were disrupted by ultrasonication. The sonicated starch showed smaller molecular size, lower weight average molar mass, and narrower molecule weight with the use of chromatography (Iida et al. 2008; Isono et al. 1994; Li et al. 2016). The ^{1}H and ^{13}C NMR spectrogram of sonicated starch showed increased portion of highly mobile fraction (Iida et al. 2008). Once the molecular weight of sonicated starch got closer to a certain limit (e.g. this limit for rice starch was 1.1×10^4 (number-average molecular weight), using pullulan as standards), the ultrasonication became much less effective (Isono et al. 1994). As mentioned before, ultrasonication can decrease the polydispersity of polymers through the competing degradation process and recombination process (Lorimer and Mason 1987). During the degradation process, the cavitation induces high pressure, dramatically elevated temperature, and shear force which causes the scission of the molecular chains. Besides, ultrasonication also produces free radicals that may break the chains (Kardos and Luche 2001).

Further study remains to be carried out for better understanding about the fine structure of starch as treated with ultrasound, such as the cluster and internal molecular structure of amylopectin, in the light that amylopectin is the main component of amorphous part, which is more susceptible to ultrasonication than the crystalline region in the granules. In some other researches, it appears that ultrasonication hardly affected the molecular size of chains of starches from various origins (Chung et al. 2002; Jackson et al. 1988; Zuo et al. 2009). It is thus clearly that the extent of degradation of the starch chains is dominated by experimental conditions and parameters of ultrasonication. Hence, by setting appropriate parameters, ultrasonication could be used to promote the dissolution of starch samples for HPSEC analysis without any molecular degradation and involvement of alkaline or DMSO which may either result in starch degradation or environmental pollution (Jackson et al. 1988).

8.4 Effect of Ultrasonication on the Physicochemical Properties of Starch

8.4.1 Solubility and Swelling

Ultrasonication has been reported to increase the swelling power of starches from diverse sources including potato, wheat, rice, and corn with different amylose contents (Jambrak et al. 2010; Luo et al. 2008; Sujka and Jamroz 2013). Ultrasonication also enhanced the solubility of starches in water (Chan et al. 2010; Jambrak et al. 2010; Luo et al. 2008; Sujka and Jamroz 2013; Zheng et al. 2013), because of the promoted water penetration and starch hydration since the starch granules were damaged both physically and chemically. Recently, a kind of granular cold-water-swelling starch was prepared from corn starch by using ultrasound-assisted alcoholic-alkaline treatment. The maximum cold-water solubility reached the maximum of 93.33% when the process was optimized (Zhu et al. 2016).

The type and composition of the starch could influence the change in swellability and solubility of granules as affected by ultrasonication. For example, corn starches varying in amylose content (waxy, normal, and high-amylose genotypes) exhibited varying extent of change in swelling power and solubility after ultrasonication (Luo et al. 2008). As results showed, the most significant increase in swelling and solubility appeared in high-amylose genotypes, which followed by normal and waxy corn starches (Luo et al. 2008), confirming that amylose in the starch granules is more susceptible to ultrasonication. Apart from the internal factors of granules, varying ultrasonication parameters also led to different outcomes. For example, the increased ultrasound power and intensity caused an increase in the swelling power of corn starch (Jambrak et al. 2010); and the ultrasonication with dual frequency (25 kHz and 80 kHz) is more efficient than that of single frequency (25 kHz or 80 kHz) to improve the solubility of sweet potato starch (Zheng et al. 2013).

8.4.2 Gelatinization

Differential scanning calorimetry (DSC) is the most typical technique to measure the gelatinization properties of starch as affected by ultrasonication. And enthalpy change (ΔH) and the gelatinization temperatures, including onset (T_o), peak (T_p), and conclusion (T_c) temperatures, are common parameters to reflect the gelatinization. The ΔH indicates the loss of molecular order, and the T_p represents the crystallinity related to double-helix length (Sang et al. 2008). However, it seems that various studies showed paradoxical results of ultrasonic effect on the gelatinization of starch. Ultrasonication has been reported to decrease the ΔH of rice starch (Yu et al. 2013) and increase/decrease that of corn starches with different amylose content (Huang et al. 2007; Jambrak et al. 2010; Luo et al. 2008). And it was also observed to decrease the gelatinization temperatures of rice starch (Yu et al. 2013), increase or hardly increase that of corn starch (Huang et al. 2007; Jambrak et al. 2010), or reduce the gelatinization temperature range of corn starches containing different amounts of amylose (Luo et al. 2008). These discrepancies from various reports may be due to the different type and composition of starch and the discrepant operational conditions of ultrasonication. The initial erosion of the amorphous part in the granules caused the increase in the crystallinity of starch, resulting in the raise of gelatinization temperatures and ΔH of corn starch (Huang et al. 2007). The further ultrasonication treatment gradually damaged the crystallinity, and relatively the ΔH and gelatinization temperatures of starch were reduced (Jambrak et al. 2010; Luo et al. 2008; Yu et al. 2013). In some researches, the ultrasonication conditions were so intensive that the whole granules were damaged quickly and consequently the initial increases in ΔH and gelatinization temperatures may be ignored. Moreover, in some studies, during the ultrasonication process without thermostat, the temperature of starch slurry raised, leading to the partial gelatinization of starch granules which thus had decreased ΔH and gelatinization temperatures (Yu et al. 2013).

8.4.3 Properties of the Paste

8.4.3.1 Pasting

The effect of ultrasonication on pasting properties of starch have been commonly determined by Rapid Visco Analyser (RVA) (Chan et al. 2010; Zuo et al. 2009), Brabender Viscograph (Herceg et al. 2010; Huang et al. 2007; Isono et al. 1994; Li et al. 2016; Luo et al. 2008; Zheng et al. 2013), and other viscosity analysers (Azhar and Hamdy 1979; Chung et al. 2002; Sujka and Jamroz 2013). Figure 8.3 showed the amylograms of native and sonicated corn starches measured by the Brabender Viscograph. During the pasting process, the starch slurry is stirred under a fixed shearing force, and the granules are heated and cooled in a set procedure. The recorded viscosity development revealed that ultrasonication caused the decrease in viscosity of starch-water system during pasting. Similar outcomes has been reported by different studies using starches from diverse origins (Herceg et al. 2010; Isono et al. 1994; Li et al. 2016; Luo et al. 2008; Zheng et al. 2013; Zuo et al. 2009). Ultrasonication damaged granules, resulting in worse swellability, and these disrupted granules were further permeated by water thus facilitating the hydration, which cause the lower pasting viscosity of starch. By controlling the ultrasonication conditions, a lower viscosity can be achieved through the physical disruption of the starch granules without scission of molecular chains (Zuo et al. 2009). However, contrary results were observed in another study where the pasting temperature, peak viscosity, hold viscosity, final viscosity, and setback viscosity of the taro starches extracted by ultrasound pretreatment were significantly higher than those of control (Sit et al. 2014). Chan et al. also reported that ultrasonication increased the peak viscosity during pasting of potato starch (Chan et al. 2010). These contradictories may result from the different extent of damage in the amorphous and crystalline

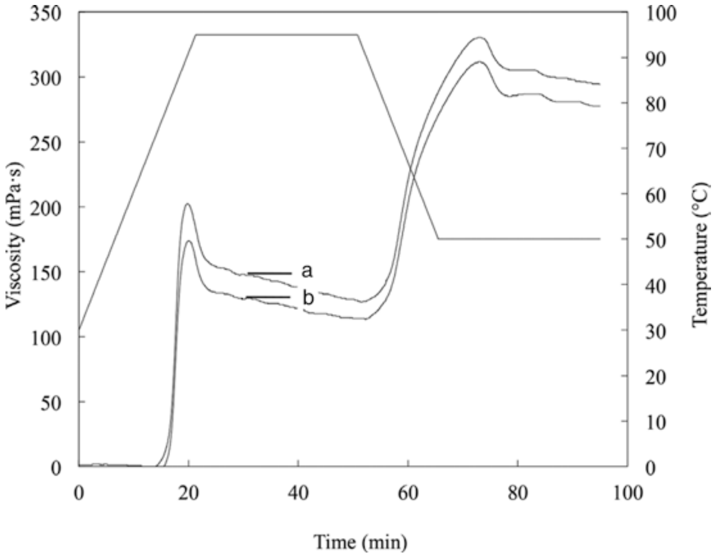

Fig. 8.3 Brabender viscosity curves of native (**a**) and sonicated (**b**) corn starch at 6% (w/w) (Li et al. 2016)

regions of the granules due to varying ultrasonication conditions, as mentioned in the previous sections.

Obviously the ultrasonication conditions influence the ultrasound effect on pasting properties of starch. The dual-frequency ultrasonication showed more effective than a single frequency one (Zheng et al. 2013), and the extent of changes was expanded by the increasing temperature and duration (Park and Han 2016; Zuo et al. 2009). Apart from the experimental conditions, the starch composition also influenced the extent of changes in pasting behaviours. In a study, the pasting properties of corn starches (native/sonicated) with varying amylose content were measured. Under the same ultrasonication conditions, pasting viscosity of high-amylose starch was much more influenced by ultrasound than waxy starch, indicating that the amylose in the granules is more sensitive (Luo et al. 2008). However, it is notable that when starches were imposed of high-power ultrasound which depolymerised the starch pastes, the apparent viscosity was decreased by molecular scission occurred at the C–O–C bond of α-1,6 glycosidic linkage as the FT-IR showed, and the extent of molecular scission was inversely correlated with amylose content (Kang et al. 2016). The better resistance to ultrasonication of high-amylose starch pastes could be attributed to the aggregation of amylose. The effect on other rheological properties including dynamic oscillation and small deformation rheology of starch remains to be investigated.

8.4.3.2 Gel Transparency

When using the gelatinized starch paste for many industrial applications, the transparency is one of important qualities that should be considered. It has been reported that ultrasonication can help to improve the transparency of the starch paste/gel from various sources including potato, sweet potato, mung bean, and rice (Chung et al. 2002; Sujka and Jamroz 2013). The reason of the enhancement in transparency may be that ultrasonication increases the solubility of starch in water and facilitates the hydration of starch chains, thus improve the light transmittance. However, in another study using taro starch, the decrease in transparency was found to be consistent with increased viscosity values in pasting profile as mentioned before. It could be speculated that in the experimental conditions, ultrasonication allowed more water to be absorbed, making the granules swelled more, and thus the starch paste was more viscous and the transmittance decreased (Sit et al. 2014).

8.4.3.3 Flow Behaviour

It has been reported that the flow behaviour of starch gels as treated with ultrasonication could be described by the power law equation. The consistency coefficient which is dependent on ultrasound power was decreased by ultrasonication acting corn starch, and the flow index was higher than 1 (Jambrak et al. 2010). It was indicated that the stronger ultrasound resulted in shorter starch chains, and the minimum chain length was obtained when the ultrasound couldn't degrade the chains anymore (Czechowska-Biskup et al. 2005; Jambrak et al. 2010).

8.4.4 Retrogradation and Freeze-Thaw Stability

When the gelatinized starch paste is cooled down gradually, the crystallinity, gel firmness, and turbidity of the starch gel begin to increase, and B-type polymorph appears in the system, accompanied by other changes. These changes are characteristics of the phenomenon which is defined as the retrogradation of starch (Hoover 1995). Short-term retrogradation is mainly attributed to the recombination of amylose, while the long-term one is much related to the recrystallization of amylopectin (Hoover 1995; Miles et al. 1985). The difference in retrogradation of the gels from sonicated or non-sonicated starches had been reported. Results showed that the former (stored at 4 °C for 24 h after gelatinization) exhibited higher hardness, cohesiveness, and adhesiveness than control (Herceg et al. 2010). Ultrasonication (before the gelatinization of starch) caused the increase in onset melting temperature and decrease in ΔH of the retrograded rice starch, and the increasing power input affected more (Yu et al. 2013). As for freeze-thaw stability, ultrasonication increased the syneresis of gel of high-amylose corn starch (amylose content 50%) while reducing that of waxy corn starch during freeze-thaw cycle (Luo et al. 2008), so it can be concluded that the effect of ultrasonication is influenced by the type and composition of starch, although the direct comparison of data from various studies is difficult. Better freeze-thaw stability of was also obtained in another study where the taro starch was the ultrasonically extracted starches, making the starch more acceptable for application in frozen foods (Sit et al. 2014).

8.5 Effect of Ultrasonication on the Modification of Starch

As the concept of "green chemistry and technology" is emerging, nonpolluting processes and products have become more and more popular in synthetic chemistry, and ultrasonication has been widely employed in order to optimize the use of materials (especially renewable biologic resources) and decrease the wastes and pollutions (Kardos and Luche 2001). As for starch modification, native starches are generally modified by physical, chemical, and enzymatical methods, creating novel starch with new properties for various applications. Ultrasonication is used not only as a kind of physical treatment but also as an auxiliary method to promote the reactivity and efficiency of other kinds of modifications, which will be reviewed later.

8.5.1 Physical Modification

Comparing with starches which are modified chemically and enzymatically, physically modified products are more popular because they are considered healthy and green. Ultrasonication has been employed to improve the melting process of high-amylose corn starch (70% amylose content) using glycerol as the plasticizer. Ultrasonication reduced the viscosity of melt and increases the water solubility of melt-processed high-amylose corn starch, thus greatly enhancing the melt-processing efficiency (Lima and Andrade 2010).

It remains to be studied about the influence of ultrasonication on other kinds of physical modification of starch including extrusion and hydrothermal treatments.

8.5.2 Chemical Modification

By controlling the experimental conditions, ultrasonication could shorten the modification time and improve the degree of substitution (e.g. acetylation, hydroxypropylation, octenyl succinylation, and carboxymethylation) of starches from various origin, such as corn (Chen et al. 2014; Huang et al. 2007), potato (Čížová et al.

2008), cassava (Gao et al. 2011), and yam (*Dioscorea zingiberensis*) (Zhang et al. 2012). Here comes some examples: Simultaneous ultrasonication enhanced reaction efficiency and increased the contents of carbonyl and carboxyl groups of corn starch due to the expedited oxidation process (Chong et al. 2013). Ultrasonication applied to carboxymethylated potato starch reduced the time of octenyl succinylation to a few minutes comparing with conventionally spent 24 h and also made the modification free of p-toluenesulphonic acid (a kind of potential pollutant to environment) (Čížová et al. 2008). During the carboxymethylation of corn starch, a degree of substitution up to 38.7% could be achieved when the ultrasonication was employed before alkalization process (Shi and Hu 2013). It is obviously significant to study the effect of ultrasonication on other kinds of chemical modifications or their combinations.

Two factors may account for the effect of ultrasonication on these modifications: As mentioned in anterior sections, ultrasonication can bring about pores, cracks, and holes on starch granules and improvement in swelling power and water solubility of starch. These changes make the structure of granules more open for the chemical agents and catalysts to permeate into the granules, thus increasing the probabilities for chemical reactions (Zhang et al. 2012). Besides, the cavitation and sonolysis can produce free radicals (e.g. hydroxide radicals (OH) and hydrogen (H)) from water, also facilitating the chemical modifications (Chong et al. 2013), and the detailed reaction mechanism needs further exploration. Obviously, in order to obtain the desired results, the optimization of ultrasonication conditions is necessary since the conditions of ultrasonic treatment determined the extent of enhancement in the degree of substitution (Shi and Hu 2013).

8.5.3 *Enzymatic Modification*

Ultrasonication has been used to increase the efficiency of enzymatic modification of starch from diverse sources such as corn (Apar et al. 2006; Wu et al. 2011), mung bean (Hu et al. 2013), rice, and wheat (Apar et al. 2006). For example, ultrasonication facilitated the hydrolysis of mung bean starch by α-amylase, and ultrasonication with dual frequency (25 kHz and 40 kHz) affected more than that with single frequency (25 kHz or 40 kHz) (Hu et al. 2013). Using the glucoamylase as a catalyser to prepare microporous corn starch, the production efficiency was greatly enhanced by ultrasonication (Wu et al. 2011).

The increased efficiency of enzymatic modification of starch could be attributed to the enhanced enzyme susceptibility of starch as affected by ultrasonication. As mentioned before, ultrasonication created pores and cracks on the granules, making it easier for enzymes to permeate into the granules and thus increasing the interfacial area of enzyme substrate as well as the chance for modification. It is necessary to optimize the experimental conditions to avoid excessive disruption of granules and negative effects on the activity and stability of some enzymes (Özbek and Ülgen

2000) while maximizing the efficiency of ultrasonication on the enzymatic modifications of starch at the meanwhile.

8.6 Effect of Ultrasonication on the Application of Starch

Ultrasonication has been widely employed in different industries, and it has proved to be a success to commercialize ultrasound techniques for various food and other industrial applications such as defoaming and extrusion (Awad et al. 2012; Knorr et al. 2004; Patist and Bates 2008). So it shows great potentials to commercialize the ultrasonication for starch applications.

8.6.1 Food Application

Among diverse uses of ultrasonication in starch-related industries, the most reported application has been the improvement of starch extraction from various botanical sources, which was mentioned in the starch yield section. Recently, ultrasonication was employed to assist the production of glutinous rice flour from broken rice by extracting amylose. By utilizing ultrasonication in alkaline solution, amylose could be extracted by washing at lower temperature within shorter time compared to the traditional aqueous leaching technique. Amylose content of the resulting starch decreased to lower than 2% with a yield of more than 80% (Setyawati et al. 2016).

Ultrasonication has been used in rough rice parboiling due to its facilitation in gelatinization of native starch (Wambura et al. 2008). Aided with ultrasound treatment, a better reservation of the micronutrients in the rice could be achieved because of the lower temperature, and one-step combined soaking and gelatinization for rice parboiling was greatly enhanced, while the energy consumption and duration of the whole processes were decreased (Wambura et al. 2008).

Some micronutrients are faced with poor water solubility that has great influence in their bioavailability. And nanoemulsion is a feasible technique to solve this problem (Abbas et al. 2014). During the preparation of food-grade oil-water nanoemulsion of curcumin which was stabilized by OSA-modified starch (corn starch octenyl succinate), the ultrasonication treatment was successfully applied not only to aid the formation of this nanoemulsion but also to effectively reduce the energy consumption through the whole process (Abbas et al. 2014). The Nile red fluorescent probe dyed oil droplets of PGU-stabilized emulsions were observed by confocal laser scanning microscopy (CLSM), as shown in Fig. 8.4. It is thus expected to employ ultrasonication for nanoemulsification of other nutrients.

As substitutes for fossil oil-based materials, biodegradable packaging biomaterials appeal to many researchers and entrepreneurs due to their great potentials for sustainable development. Starch-based edible films are typical representatives of these developing environmental biomaterials (Cheng et al. 2010). When treated the

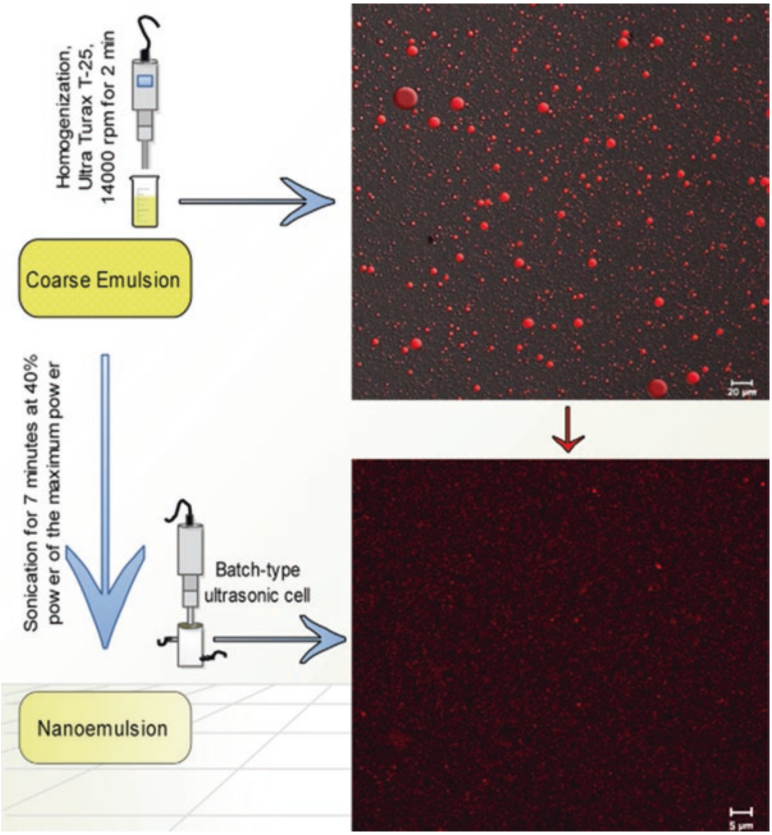

Fig. 8.4 Confocal laser scanning microscopy (CLSM) of conventional emulsions and ultrasound-assisted nanoemulsion (Abbas et al. 2014)

gelatinized normal corn starch (amylose content 28%) solution with ultrasound, the resulting films had better transparency, enhanced moisture resistance, and tougher structure (Cheng et al. 2010). However, plasticizers such as glycerol may be needed to overcome the decrease in strain at break, which was caused by ultrasonication at the meantime.

The preparation of V-type amylose inclusion complex with small bioactive compounds is commonly used in encapsulation and sustained releasing products (Tian et al. 2013). For example, cinnamaldehyde (a type of antimicrobial agent) was complexed successfully using high-amylose corn starch when treated with ultrasound, and the controlled releasing of cinnamaldehyde in food is beneficial for food preservation (Tian et al. 2013). Ultrasonication is also expected to improve the encapsulation efficiency and load of other small hydrophobic bioactive molecules for sustained releasing applications.

8.6.2 Industrial Applications

8.6.2.1 Preparation of Functional Nanoparticles

Nanoparticles with special properties have been applied in many aspects, and creating them from biomacromolecules including cellulose and starch has been a focus appealing to both manufacturers and scholars (Bel Haaj et al. 2013; Konwarh et al. 2011). With the aid of ultrasonication, nanoparticles can be produced from diverse starches and have different sizes (around a few nm to hundreds nm).

Nanoparticles made from pinhão (*A. angustifolia*) seeds had a size around 453 nm, and they showed great potentials to serve as the materials for coating and film formation (Gonçalves et al. 2014). Smaller starch nanoparticles was produced from waxy and normal corn starches (30–100 nm) without the involvement of chemicals, while both the efficiency and yield were enhanced by the assistance of ultrasonication (Bel Haaj et al. 2013). Antimicrobial nanoparticles were produced by the ultrasonication of the mixture of starch and aqueous extract of leaves of *Mesua ferrea Linn*, and they had a less size of up to 5.4 nm (Konwarh et al. 2011). The ultrasonication can be used to produce nanoparticles mainly because of its capacity of damaging the starch granules and scissoring the molecular chains in the amorphous region which has been mentioned before.

Recently, retrograded starch (RS III) and resistant starch type IV nanoparticles (chemically modified starch, RS IV) were prepared from a novel and convenient synthesis route via employing ultrasonication combined with water-in-oil miniemulsion cross-linking technique, with a size around 600–700 nm (Ding and Kan 2016; Ding et al. 2016). It appeared that ultrasonication increased the amylose content and decreased the RS contents, but the resulting nanoscale RS III and RS IV had high adsorption capacities and retained good anti-digestibility, so they would show great potentials in biomedical applications and in the development of new medical materials such as the drug carrier material. In another study, ultrasonic treatment was utilized to prepare amylose nanoparticles (ANPs) by nanoprecipitation. The ANPs obtained with ultrasonic treatments were smaller and more uniform than those prepared without ultrasonic treatment, indicating a higher efficiency and lower cost (Chang et al. 2017).

8.6.2.2 Production of Starch Sugar and Bioethanol

It has been reported that ultrasonication can be employed in liquefaction and saccharification. For example, ultrasonic pretreatment was used to improve the high-temperature liquefaction of corn starch at high concentrations. The results showed the lower viscosity of sonicated starch paste and the higher reducing sugar content than those of control, indicating more efficient liquefaction of starch (Li et al. 2016). It could be mainly attributed to a rough and holey surface, looser granule structure, lower crystallinity, and higher amylose content which were caused by ultrasonication, thus enhancing the enzymatic reaction. Ultrasonication that was used during the enzymatic hydrolysis could also improve the releasing rate of glucose, but the experimental conditions should be optimized in order to avoid the loss of enzyme activity (Nikolić et al. 2010).

Bioethanol has been considered as a promising alternative of the major energy resources especially the fossil fuels which are becoming in short supply and not friendly to the environment. Among various substrates for bioethanol production, starch-based feedstocks are most common in industries because they are easy to obtain and inexpensive (Nikolić et al. 2010). Ultrasonication has been reported to expedite the saccharification and conversion to ethanol from diverse sources. Usually, the feedstocks containing starch were treated with ultrasound in advance, and then they were liquefied and saccharified for fermentation-derived ethanol production (Montalbo-Lomboy et al. 2010; Nikolić et al. 2010; Nitayavardhana et al. 2010; Pejin et al. 2012). It was found that the pretreatment with optimized ultrasonication conditions not only improved the conversion rate and ethanol yield but also decreased the cost of the whole processes (Pejin et al. 2012).

8.6.2.3 Waste Recycling

Ultrasonication combined with microwaving was employed in a complex facility to recycle the starch-based industrial waste in sulphuric acid solution (Hernoux-Villière et al. 2013). During the composite treatment, microwaving expedited the heat transfer, while ultrasonication enforced the mass transfer. Thus the granules in starch-based industrial waste was disrupted and converted into sugars with a conversion rate of 46% (Hernoux-Villière et al. 2013).

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Chapter 9
Milling Process of Starch

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Abstract Milling of cereal grains is a very important process for cereal and feed industry. It is accompanied with starch granules damage, starch crystalline structure disruption, and starch molecules change, and therefore performance of the finished products is subject to milling process. This chapter reviews the development of commercial and laboratory mills system, discusses the latest discovery on starch multi-scale structure, and gives a review of starch structure damage at granule, crystalline, and molecular level. One case of study is related to effect of wheat starch damage in bread baking and importance of starch damage to wheat flour milling industry. Quality control and test of starch damange in flour milling are introduced.

Keywords Milling · Starch · Multi-scale Structure · Physical · Chemical Properties · Quality Control

9.1 Importance of Milling in Starch Industry

Milling is a gradual mechanical process to produce flour from grain. Dry milling is commonly found in producing flour from grains such as wheat, rice, millet, buckwheat, and legume. By applying one or two mechanical forces such as impact, compression, shear, and attritions, the milling equipment can reach milling capacity from several kilograms in a lab to hundred tones in a commercial mill in 1 h, with

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particle from ultrafine (20 µm) to coarse (100 µm) sizes. During the dry milling process, flour streams containing endosperm, bran, and germ may be separated, milled, and reconstituted differently to fit needs for different product applications.

Starch is the main component in cereal grains and a major glycemic carbohydrate in the human diet. Starch is commonly extracted from corn, potato, and cassava (tapioca); and wet-milling process is more common than dry milling to extract starch. The grains are steeped, pulped, milled, separated, centrifuged, sieved, dried, and ground to form starch powder. During the process, fiber and protein are mostly isolated earlier than starch, and some acid or alkali may be applied to facilitate separation of the components.

Milling is important because different milling equipment and process lead to products of different particle size profiles and possibly change of physical structure in starch, protein, fiber, and others. Especially for starch that has over 60% content of most grains, structure changes from milling process can largely affect the functional properties of the finished product, either flour or starch. These include pasting profile, thermal properties, swelling properties, solubility, and digestibility. This chapter covers some recent discoveries in how milling technology changes starch profiles in terms of structure and physical properties and how differently milled products impact food application and the importance of quality control in flour milling.

9.2 Milling Equipment

9.2.1 Commercial Mill System

Modern commercial flour milling is a complicated process involving many mill units; and each mill unit setting is depended on different stage or function of milling process. While roller mill is the principle and basic grinding machine in commercial flour mills, supplementary mills, such as impact and debranning systems, would help reduce the cost due to wear out and high maintenance of roller mill. In general, the grinding process is composed of four systems: break, sizing, reducing, and retailing. Break system opens up the wheat kernel, which contains endosperm, bran, and germ. Out from break rolls that are mostly corrugated, there is a distribution of large middlings with small amount of refined flour and middling too fine to be purified before reduction into flour. Sizing system separates small bran pieces on large pieces of endosperm in order to obtain clean middling. Rolls from sizing system can be either finely corrugated or smooth. Unlike corrugated rolls, smooth rolls produce more flour or fine sizing, while corrugated rolls help detach the bran and clean sizing that contains middlings and bran particles. Both are easily separated in a purifier. Wheat germ usually is separated from sizing stream, in which the germ is attached to large particles of bran. Reduction system reduces the endosperm to flour. After purification, middlings pass through a series of smooth rolls. The rolls are spaced such that each successive reduction produces finer particles. Flour is sifted out after each reduction milling. Most fine bran is removed from the germ in this step. Tailing system recovers small portion of endosperm by reducing their size with mostly smooth rolls or corrugated rolls with low milling pressure. Impact rolls may also be found to reduce the endosperm and to break up the flakes.

9.2.2 Laboratory Mills System

Laboratory setting allows mills to operate under limited space and capacity. The mills deliver less streams and by-product than commercial mills, yet they are convenient to be adjusted by grinding rolls, sieve selection, and flow to materials. Direct impacts of mills at different settings are the degree of starch damage in the flour and variations in flour color from bran contamination. During milling process, flour yield and corresponding ash content of flour are mainly evaluated. There are more types of laboratory mills than commercial mills because milling efficiency, space design, and energy loss are not concerns. The principle forces of grinding are compression, shear, friction/abrasion, and impact. The most common grinding machines are roller mills, attrition mills, impact mills, ball mills, and disk mills. Their applications are mostly found in grain grinding for food or animal feeds.

9.2.2.1 Stone Mill

There are two stones in a stone mill: one is stationary and the other one is rotated by a pulley and a shaft. The force of compression, shear, and abrasion is used in the milling during which wheat is fed into the stationary stone. The grain is ground between the two stones as it is propelled radially to the circumference by furrow on the surface of the stone. The milled flour is discharged by the rotating plate and outlet.

9.2.2.2 Roller Mill

Roll mill is the principal grinding equipment in commercial wheat flour mills. Flour is produced by cutting or squeezing the grain through a series of rollers. The most popular one are the four-roll or eight-roll roller mills which divide half rolls on either side of the stand. The mills always work in pairs, and the grain material is subject to shear and compressive forces due to corrugations on the roll surfaces and pressure exerted by the rolls when sending particle toward the nip. If the rolls rotate at the same speed, compression is the primary force used. If the rolls rotate at different speeds, shearing and compression are the primary forces used. If the rolls are grooved, a tearing or grinding component is introduced. In commercial mill environment, the rolls that make up a pair are 9–2 in. (23–30.5 cm) in diameter, and their ratio of length to diameter can be as great as 4:1 (Posner 2005). Each pair of rolls is counter rotating. For improved size reduction, one roll rotates faster than the other. This results in a differential in speed between the roll pair. Typical differentials range from 1.2:1 to 2:1 (Glossary: Roller mill 2018) (fast to slow). Milling force/stress on the grain varies to the rate and uniformity of flow of stock to rolls, the roll velocities, ratio of speeds between the fast and slow rolls, the gap between the rolls, the type of the roll surfaces, and hardness of the grain kernels. Advantage of roller mills includes energy efficiency: for coarse reduction of grain, a roller mill may have as high as 85% over a hammer mill in terms of throughput/kwh of energy (Glossary: Roller mill 2018), uniform particle size distribution, little noise, and dust; the disadvantage of roller mills is little or no effect on fiber, particles tend to be irregular in shape, and, when required, maintenance can be expensive. Some common brand names for roller mills, such as Buhler, Brabender, and Chopin, can be found in a lab or production scale.

9.2.2.3 Pin Mill

Pin mill is a type of disk grinder, also known as centrifugal impact mills. It consists of a feed inlet, a set of two disks with concentric rings of pins (one stationary at the door and one rotating connected to the motor), a narrow grinding chamber, and a product outlet. The finished product out a pin mill can be as fine as less than 40 μm and with a uniform product size. The main force of grinding is shearing and impact. The material is impacted by a series of hardened steel pins in rotation at high speed, and therefore the grinding action is controlled by the air flow, feed rate, and the speed of the motor (the differential speed of the outer two rows of pin).

In the pill mill, the pins are located symmetrically and concentrically. The product particles are shattered/impacted into fragment and progressed toward the outlet, smaller in size as they approach periphery. To avoid temperature increase, cooled inert gas is blasted during grinding. This also prevents accumulation of particles in between the pins and on the disks. The fineness of final product depends on distribution of pins, circumferential speed of the rotors, feed rate, and physical properties of the material. No screen is used in pin mill to control top particle size. The advantage of pin mill is that very fine grinding at relatively low energy consumption, little floor space required, and easy cleaning ensures high hygiene standards. Materials that tend to be sticky and clog the hammer mill screen work fine in pin mills. Under cryogenic processing much lower particle sizes can be achieved. The disadvantage includes low capacity, narrow range of size reduction, and internal cooling may be required.

9.2.2.4 Hammer Mill

Hammer mill works under the principle that most materials crush, shatter, or pulverize upon impact. Inside of the mill, there are free-swinging hammers that are suspended from rods running parallel to the shaft and through the rotor disks. The material is crushed or shattered by a combination of repeated hammer impacts, collisions with the walls of the grinding chamber, and particle on particle impacts. Perforated metal screens or bar grates covering the discharge opening of the mill retain coarse material for further grinding while allowing properly sized materials to pass. There are both laboratory scale hammer mill and large high production industrial hammer mills. Fast rotor speed, small screen, large hammer gives fine finished particle size and vice versa. Hammer mill is highly effective as well as nonstop continuous pulverizing process with particle size of a wide range, and most of time it is designed to achieve medium to fine particle sizes (50–70 μm) (Hosakawa 2018). It has compact size and is dust-free. However, it requires high energy comparing to a roller mill (top speed for motor of the hammer can be over 100 m per second), generates excessive dust, produces greater particle size variability (less uniform), and is considered as a hazardous operation.

9.2.2.5 Ball Mill

Ball mill is a tumbling mill using spherical balls to reduce the materials to flour inside a cylindrical rotating shell. The material size is decreased by impact and compression when the balls tumble on it in a rotation cylinder. It lost certain popularity because of concerns of high starch damage, low capacity, and need for high maintenance.

9.2.2.6 Cutting/Knife Mill

In a knife mill, there are knife blades inside of the steel cylindrical cage; and particle size is reduced by shearing forces. It can also be considered as a type of hammer mill except that it is a knife instead of a heavy duty hammer, yet it may share the same milling chamber as the hammer mill. It is considered as a coarse grinder for milling of biomass such as grass, straw, bran, and corn stover. When material is fed into the cylinder, it is cut by the knife until its size is small enough to pass through the screen. The granulation is controlled by the spacing of the knives on the motor and the liner and the screen applied. It is more often seen as pre-grinding device for substances with a high water, oil, or fat content as well as for grinding dry, soft, and medium-hard products.

9.2.3 Other Mills

In many cases, starch production is based on wet milling. Using corn milling as an example, corn starch production usually includes cleaning, steeping, milling/separating (obtaining germ), milling/sieving (obtaining fiber and starch), centrifugation (obtaining gluten), cleaning, and drying (obtaining more starch). The purpose of corn cleaning is to remove impurities by pre-cleaner and magnet separator. Clean corn is pumped into steeping system and steeped with H_2SO_3. The purpose of steeping is to soften the corn kernels for milling purpose and restrain microorganism growing (germination and fermentation). Corn is transferred into disk mills and

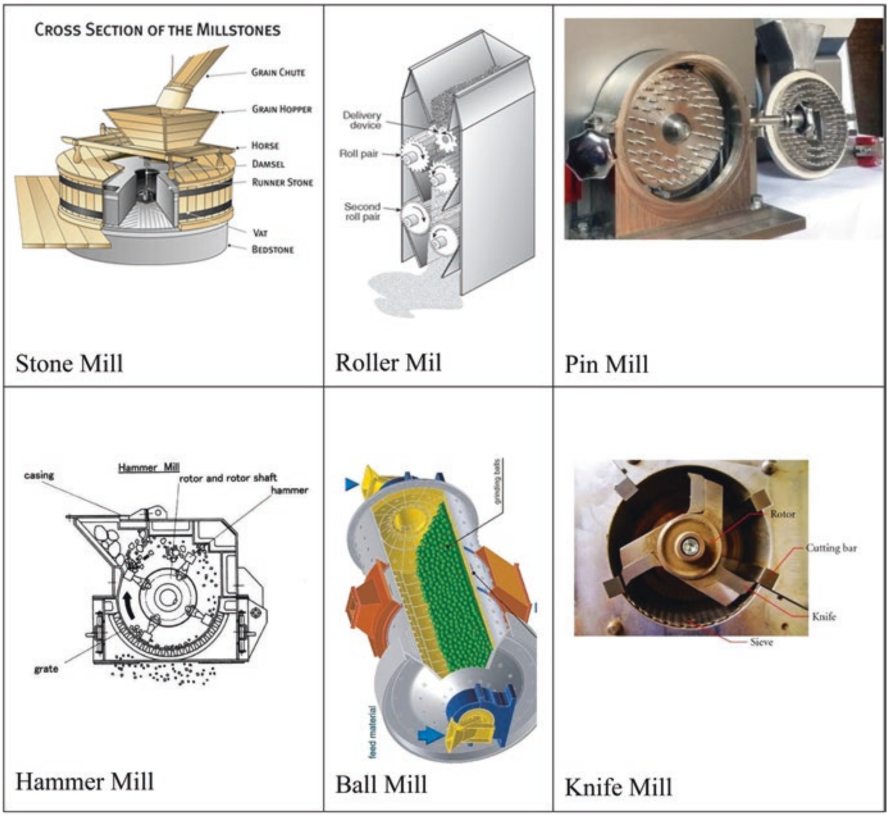

Fig. 9.1 Different types of mills

broken into four to six pieces, where most germ can be separated by germ cyclone separator. A disk mill is a type of crusher, similar as stone mill. It consists of two irons or steel disks/plates. One disk is stationary and the other one rotates (there are mills with two rotating disks, too). Grain feed between the plates is crushed and sheared. Type and spacing of plates determine fineness of the feed. Impact mill is later used for fine milling to remove bound starch from the fiber, breaking starch free from the fiber and reducing the particle size of starch grits. Slurry materials after fine grinding are transferred into pressure arc sieve, and coarse starch solution is obtained from this stage. Wet starch went through dehydrating by vacuum filter machine, hydro-cyclone, and drying machine.

The above mills described are commonly found in grain milling industry. The principles and operation of the mills can be extended to other manufacture industry, such as fine chemicals, pharmaceuticals, and food ingredients other than grain, in which some other mills may also be found, such as air classified mills and fluidized bed jet mills (Fig. 9.1).

9.3 The Multi-scale Structure Change in Milling Process

Native starch granule is a multi-scale structured polymer from nanometer to micron: amylose and amylopectin chains (~nm), crystalline and amorphous lamellar structure (9–10 nm), alternating amorphous and semicrystalline growth rings (100–400 nm), and starch granules (<1–100 mm). Amylose and amylopectin are the two basic components in starch granule. Generally, the amylose molecules in native starch granules are mostly (if not all) in linear amorphous conformation, while amylopectin molecules are in double helical conformation forming alternating crystalline and amorphous lamellae, which are further arranged into growth rings in native starch granules. One single starch granule contains several growth rings positioned radially from the hilum or nucleus of the granule to the periphery.

9.3.1 Starch Granule Change: Grain and Process Conditions

Damaged starch is starch of which granule structure is broken into smaller fragments, sometimes with starch hila exposed during milling (Dhital et al. 2010; Hasjim et al. 2009). Higher degree of damage to starch granules is related to greater mechanical force and longer grinding time and increases with the severity of grinding process (Nowakowski et al. 1986; Han et al. 2002). It has been reported that milling of cereal grains with higher grain hardness, especially those with higher protein content, results in greater damage to starch granules than the milling of softer grains, due to the greater amount of mechanical energy required to break the structure of harder grains (Hasjim et al. 2009; Williams et al. 1987). The surface of severely damaged starch granules sometimes appears rougher and more porous compared with that of intact native starch granules (Evers et al. 1984; Craig and Stark 1984; Tamaki et al. 1998). The size of the damaged starch granules, however, does not always decrease with high degree of damage to starch granules. This is due to the agglomeration of damaged starch granules, especially when they are severely damaged.

Grinding conditions including moisture content, temperature, and grinding force also affect the degree of damage to starch granules. Grinding of cereal grains in excess water (also named wet milling) commercially isolates starch granules with minimal damage (Syahariza et al. 2010; Singh et al. 1997), since water molecules can act as a plasticizer increasing elasticity and fracture toughness of the starch granules, minimizing the damage to the starch granules. Even so, the damage (<5%) is still present in both commercially and laboratory-isolated starch granules (Dhital et al. 2010; Hasjim et al. 2009). In the case of dry milling, the damage mostly forms pinholes on granule surface, and channels inside of the granule are attributed to hydrolysis by endogenous enzymes in grains instead of by mechanical force. Significantly low starch damage was found on the isolated starch granules which were cryogenically ground with 60% moisture (Dhital et al. 2010), probably because of the ability of water molecules to absorb and to reduce the mechanical energy experienced by the starch granules. Most milling processes are performed at atmospheric dry condition (~15% moisture content), and the temperature of grinder or mill does not exceed 100 °C, keeping the starch granules from gelatinization and heat-induced damage. Compared with milling at ambient temperature, cryogenic milling and pin milling of cryogenically frozen sample produce less damage to starch granules due to the low grinding temperature (Nowakowski et al. 1986; Tran et al. 2011). In contrast, wet milling is the only technique that allows starch gelatinization during milling, yet relatively higher temperature (>80 °C) may be needed to gelatinize starch with limited moisture content, although some starches can be gelatinized at 50 °C in excess water (Jang and Pyun 1996; Burt and Russell 1983). In fact, extrusion, a common method to gelatinize starch or to cook flour at low moisture condition using the combination of shear and heat, requires external energy to keep the heating barrels above 100 °C in addition to the heat generated by the shearing of starch granules or flour (Hasjim and Jane 2009; Liu et al. 2010).

9.3.2 Starch Crystalline Structure

The loss of starch crystalline structure by milling was widely reported for isolated starch granules (Liu et al. 2011; Dhital et al. 2010; Morrison et al. 1994; Tamaki et al. 1998; Chen et al. 2003). At prolonged grinding, the crystalline structure of starch can be completely destroyed, which is confirmed by the absence of defined peaks in the X-ray diffractogram. The loss of crystalline structure of starch granules by milling is accompanied by the loss of double helices (Dhital et al. 2010; Liu et al. 2011; Morrison et al. 1994), implying that the loss of crystallinity is more likely related to the splitting of double helices.

The loss of starch crystalline structure by milling is different from thermal starch gelatinization (Jang and Pyun 1996; Burt and Russell 1983), since most milling treatments (except wet milling) are performed at atmospheric dry condition (~15% moisture content) and the temperature of grinders or mills during grinding is usually below starch gelatinization temperature at limited moisture condition. Isolated starch granules with lower amylose contents experienced greater loss in the degree of crystallinity than those with higher amylose contents or, equivalently, lower amylopectin contents under the same grinding condition (Dhital et al. 2010). It reveals that glycosidic linkages in the double helices of amylose are susceptible to the cleavage by grinding force, as anhydroglucose units in the flexible and amorphous conformation are less rigid than that of those in the double helices. This is in accordance with the lower susceptibility of amylose molecules to degradation by milling than amylopectin molecules, which will be discussed in the next section.

9.3.3 Starch Molecular Structure

Starch molecules comprise mainly amylopectin that has a high number of short branches, amylose that has a few long branches, and minor percentage of intermediate components in forms of α-glucan and phytoglycogen. The number of intermediate components can be abundant in some mutant starches, such as high-amylose maize starch (Li et al. 2008) and sugary-1 maize starch (Wong et al. 2003).

Amylose and amylopectin molecules can be degraded during the milling of cereal grains and isolated starch granules. Morrison and Tester (Morrison et al. 1994) reported that the degree of molecular degradation increased with grinding time; and they found that 41% of native amylopectin molecules in isolated wheat starch granules were converted to low-molecular-weight amylopectin when the starch granules were ball-milled for 24 h. Similarly, pin milling also decreased the molecular weight of amylopectin in oat grains from 8.37×10^8 to 4.32×10^8 (Stevenson et al. 2007). Furthermore, Tran and Shelat (Tran et al. 2011) and Dhital and Shrestha (Dhital et al. 2010) observed that the amylopectin molecules in hammer-milled or cryogenically milled rice grains were both degraded to the size similar to amylose molecules. Analysis results of size exclusion chromatography (SEC) showed the cleavage happened at the inner chains of amylopectin molecules by shearing: if the cleavage occurred at or near the outer branch chains, molecular size of degraded amylopectin would be smaller than that of amylose as amylopectin branches are much smaller than amylose branches (degree of polymerization of 6~200 vs. 200 ~50,000, respectively) (Vilaplana and Gilbert 2010).

Degradation of starch molecules by shearing occurs at α-(1→4) glycosidic linkages in double helical crystallites and may also happen at α-(1→6) glycosidic linkages/branching points in the amorphous lamellae of starch granule. Breakdown of α-(1→4) glycosidic linkages in double helical crystallites is indicated by disappearing of starch crystallinity after milling. Also because of the susceptibility of α-(1→4) glycosidic linkages, longer amylopectin branches of potato starch were evidently cleaved during cryogenic milling, showing an apparent increase amount of shorter amylopectin branches (Dhital et al. 2010). The α-(1→6) glycosidic linkage breakage is evidenced by no apparent change of branch-chain length distribution before and after milling from many isolated cereal starches, measured by SEC, high-performance anion-exchange chromatography (HPAEC), and fluorophore-assisted capillary electrophoresis (FACE) with enzymatic debranching treatment (Tran et al. 2011; Dhital et al. 2010; Morrison et al. 1994; Stevenson et al. 2007). This is also explained by likely very small amount of cleaved branch in the amylopectin molecules.

In general, amylose molecule is less susceptible to milling degradation compared with amylopectin molecules, because of the amorphous conformation of amylose molecules in native starch granules and/or the smaller size of amylose molecules. Molecules in amorphous conformation are more flexible than the molecules in double helical crystalline conformation, helping reduce the impact from the mechanical shear during milling. Furthermore, there may be a size range of most stabled polymer, which may be close to the size of amylose molecules, leading to least damage by shear during extrusion, milling, and SEC separation. This is proved by the fact that long amylose molecules can also be cleaved by shear during milling in hammer-milled rice grain and the finding that amylopectin can also be sheared to the size close to amylose molecules during extrusion (Lelievre 1974) and SEC separation (Vandeputte et al. 2003).

For finished product with similar particle size, cryogenic milling is found to cause less degree of starch damage than hammer-milled grain (Chen et al. 1999). Also milling grain into flour gives less starch damage than milling isolated starch, indicating that the non-starch components in flour, such as protein and certain polysaccharides in flours, may provide structural protection to starch granules during milling.

9.4 Change of Physical Rheological Properties During Milling

9.4.1 Gelatinization Properties

Starch gelatinization is the transition of native semicrystalline structure in granules into amorphous structure. Differential scanning calorimetry (DSC) heats starch in the presence of water to obtain the enthalpy of gelatinization (ΔH) and the gelatinization temperature. It is a common method to assess the gelatinization property of starch. The gelatinization temperature tells heat stability of the crystallites, which is associated with the heat transfer from the surface of granules to hilum. The gelatinization temperature distribution is normally reported as onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c). Due to the heterogeneity of starch granule size and/or shape, the range of starch gelatinization temperature (ΔT), which is the difference between T_o and T_c, can be used to indicate the heterogeneity of starch granules within a sample.

The gelatinization temperature (T_o, T_p, and T_c) of isolated starch granules is decreased after milling, especially after prolonged grinding (Morrison et al. 1994; Tamaki et al. 1998; Chen et al. 2003), without much change in the ΔT. This indicates that the thickness of the remaining crystalline lamellae or the length of remaining crystallites is modified by milling. The similar ΔT after milling also indicates that every starch granule is subjected to similar grinding force.

Gelatinization profile of flour is different than that of isolated starch. No obvious milling effects on the T_o of flour that is milled from rice and sorghum grains can be observed, although the T_p, T_c, and ΔT are somewhat decreased with increasing severity of milling treatments (Mahasukhonthachat et al. 2010; Marshall 1992). However, for the starch granules isolated from milled rice flours, there was a slight decrease in the T_o but no significantly altered T_p and T_c (Hasjim et al. 2013). The differences between flour and starch gelatinization profiles indicated that the gelatinization temperature of milled flour is not fully related to starch crystalline structure. Rice flour with larger particle size has a greater barrier for heat transfer. This also indicates that the damage or disruption to starch structures is more heterogenous for the starch granules in coarse-milled flour than fine-milled flour and that non-starch components in flour can affect the starch gelatinization temperature.

ΔH is related to the amount of crystallites melted during heating. The reduction of ΔH of isolated starch granules is associated with the increasing severity of milling treatments, such as longer grinding time. The ΔH of starch was found to decrease with the reduction of flour particle size, which is similar to the isolated starch granules (Mahasukhonthachat et al. 2010; Hasjim et al. 2013; Marshall 1992), possibly because of the greater disruption of starch crystalline structure with increasing severity of milling treatments.

9.4.2 Pasting Properties

Pasting properties, commonly measured using Rapid Visco Analyzer (RVA) and Brabender Viscoamylograph, demonstrate apparent viscosity of starch or flour during cooking in excess water. The standard procedure includes heating a starch or flour suspension to 95 °C, holding at 95 °C for a period of time, cooling to 50 °C, and then holding at 50 °C for a period of time. Pasting temperature is the temperature at which apparent viscosity starts to develop exponentially. Maximum viscosity during heating and holding at 95 °C is called peak viscosity. After reaching to peak viscosity, the gel becomes thinner, and therefore the difference between peak and trough viscosities is called breakdown. With external temperature going up, the gel then becomes thicker, and the viscosity starts to pick up. The difference between final and trough viscosities is called setback indicating the degree of starch retrogradation. The peak viscosity represents the swelling of starch granules. It is known that amylose-lipid complex can inhibit granule swelling and amylopection starts pasting earlies than amylose.

Milling is important for the pasting properties of starch as the pasting viscosity (peak, trough, and final viscosities) decreases with increasing severity of milling treatments, such as increasing grinding time, on isolated starch granules from normal rice, normal maize, normal potato, and high-AM maize (Chen et al. 2003; Devi et al. 2009). The pasting temperature is also negatively related to the grinding time. (Chen et al. 2003; Devi et al. 2009).

The pasting viscosity of flour from rice, sorghum, and maize is reduced greatly by the increasing severity in the milling of cereal grains, similar to the milling of isolated starch granules (Mahasukhonthachat et al. 2010; Hasjim et al. 2013; Becker et al. 2001). In a recent study, the pasting temperature of rice flour was found to be significantly correlated with flour particle size, and the final viscosity was significantly correlated with flour particle size and degree of damage to starch granules (Hasjim et al. 2013). It was suggested that the pasting properties of rice flour are less affected by the degradation of starch molecule structure by milling, but rather they by flour particle size and damage to starch granules. Larger flour particles have the greater physical barrier for heat transfer and water diffusion; therefore, it takes time to paste the flour of large particle size. The viscosity of cold starch paste (final viscosity) can attribute to the presence of swollen starch granules due to high amount of damaged starch.

The presence of non-starch components, such as protein and polysaccharide as cell-wall matrices, plays important roles in the pasting profile of flour. First it may stabilize the starch paste and prevent the rupture of swollen starch granules in flour by shearing during heating. Direct evidence is the absence of peak viscosity in RVA curve for large flour particle, in which the non-starch components exist as functional whole parts. Also, a more defined peak viscosity during holding at 95 °C can be obtained under a treatment with cellulase on the flour from aged rice grains (Zhou et al. 2003). Lower pasting viscosity of rice flour is produced by the chemical and enzymatic degradation of proteins, but the pasting properties of isolated starch are not affected by the same treatments (Hamaker and Griffin 1990; Fitzgerald et al. 2003). The native protein and cell-wall structures can be degraded by severe milling treatment, therefore high possibility of weakened pasting viscosity of flour.

9.4.3 Cold-Water Solubility and Swelling

In food application, starch solubility affects the amount of solid mass loss during cooking. Milling of cereal grains (Hasjim et al. 2012; Mahasukhonthachat et al. 2010) and isolated starch granules (Stark and Yin 1986; Dhital et al. 2010; Devi et al. 2009; Tester 1997) mostly lead to high cold-water starch solubility caused by damaged starch. The cold-water-soluble starch molecules after milling are mostly highly branched similar to amylopectin molecules but with smaller molecular size similar to amylose molecules (Stark and Yin 1986; Hasjim et al. 2012). The cold-water extract normally contains no or only a small amount of amylose.

Degradation of starch in molecular level may not be the precondition of increased cold-water starch solubility by milling. A recent study showed that using cryogenically milled rice flour (Hasjim et al. 2012), the cold-water starch solubility of flour at 30 °C increased with increasing degree of damage to starch granules although the degradation of starch molecules was not evident, and the cold-water-soluble starch was essentially a low-molecular-weight amylopectin. Not all highly soluble, low-molecular-weight amylopectin molecules are the products of the degradation of amylopectin molecules; some might be originally present in the native, undamaged starch granules, such as intermediate components. It is possible that increased relative surface area of starch granules due to fragmentation allows the leaching out of more molecules, and exposure of the inner part of starch granules allows the leaching out of highly soluble molecules located near the loosely packed hilum.

Swelling power is the ability of insoluble starch or flour particles to retain water molecules by forming hydrogen bond between hydroxyl groups in starch and water molecules. In general, the severe milling treatments can increase swelling of cold-water-isolated starch granules. Milling causes reduction of the rigidity of amorphous growth rings in the native starch granules and allowing larger space for the amorphous growth rings in the inner part of starch granules to expand to form hydrogen bonds with water. Increased surface area in starch molecule by milling also contributes to more swelling. Exception may happen when there is excess degradation of starch molecules, increasing their solubility in water and reducing the amount of swollen starch granules (Tester 1997; Tester and Morrison 1994).

Swelling of flour particles is different than that of isolated starch granules due to the presence of non-starch components, such as protein and cell-wall matrices. Besides degree of damage to starch, particle size is another factor to consider because it affects how non-starch components function. For example, decreasing flour particle size increased the cold-water swelling of both hammer-milled and cryogenically milled rice flours (Hasjim et al. 2012) although the two gave different degree of damaged starch.

9.4.4 Digestibility

The degree of damage to starch granules is commonly measured as the susceptibility of starch granules to rapid enzyme hydrolysis, normally fungal α-amylase, since damaged starch granules in isolated starch granules and grain flour have greater enzyme digestibility than intact native starch granules.

Due to fragmentation, relative surface area for enzyme hydrolysis of damaged starch granules is larger than intact native starch granules. Furthermore, the exposure of the inner part of the starch granules, which is normally more susceptible to enzyme hydrolysis than the surface of the granules, is increased by breakage of starch granules, even for intact native starch granules which have smooth surface structure (lack of the pinholes and channels) and high resistance to enzyme hydrolysis, such as normal potato and high-amylose maize starches (Dhital et al. 2010).

The decrease in flour particle size also increases the in vitro starch digestibility of flour from the milling of cereal grains, which can be explained by the postulation that the starch digestibility of flour is controlled by the diffusion of enzymes into the flour particles (Mahasukhonthachat et al. 2010; Al-Rabadi et al. 2009). The starch digestion rates were, however, different between barley and sorghum flours with similar particle sizes (Al-Rabadi et al. 2009) and between the sorghum flours from cryogenic milling and hammer milling with similar particle sizes (Mahasukhonthachat et al. 2010). In addition, finer particle size improved the in vivo starch digestibility of wheat grains fed to pig, and the starch digestibility of large particles was higher with the supplementation of enzymes degrading cell-wall polysaccharides (Kim et al. 2005). Therefore, the structures of non-starch components in flour, alterations of these structures by milling, and plant sources can greatly affect starch digestibility.

It is not clear which is the more important factor for the starch digestibility, whether it is damage to starch granules or flour particle size. Furthermore, considering that most foods are consumed after cooking, the main nutrition implication for the digestibility of ungelatinized starch granules and uncooked flour is only animal feed. It has not extensively explored the relations between starch digestibility after cooking and the structures of milled flour/starch. Cooking process easily disrupts starch crystalline structures and grain flour structure because of starch gelatinization and the solubilization of starch molecules, proteins, and cell-wall materials. The starch or flour structure is highly swollen and can be easily ruptured even they still exist after cooking, inducing difficulty in analyzing its size and structures. The dominant factors for starch digestibility are the molecular structures of starch and non-starch components if present or, say, whether the starch granule or flour structure disappears after cooking.

9.5 Case Study: Effect of Wheat Starch Damage in Bread Baking

Wheat starch makes up 67–68% of whole wheat flour content and 78–82% of the refined wheat flour. In yeast leavened bread, wheat starch plays the following roles: (1) dilutes wheat gluten and provides a surface for strong bonding with wheat gluten, (2) produces maltose for fermentation via enzyme hydrolysis, (3) provides flexibility for loaf expansion during partial gelatinization while baking, (4) sets loaf structure by providing a rigid network to prevent loaf from collapsing on cooling, (5) gives structural and textural properties to baked products, and (6) holds/losses water and contributes to staling (Maningat et al. 2009). Farrand recognized early in his work that to make a loaf of good volume and texture, gluten must spread far enough to cover the total surface of the starch, and therefore the potential of using damage starch to maximize water absorption is limited by protein/gluten content (Acklin 1997).

The damaged starch granules are left with cracks and fissures and therefore are ready for water penetration. When placed in excess water, intact starch granules absorb about 30% of its weight; but damaged starch takes up more water and swells more: water absorption of damaged starch on average is reported slightly differently, ranging from 2% to 4%, probably due to the different degree of damage, wheat hardness, and milling severity (Rakszegi et al. 2010). Besides high water absorption, the damaged starch is highly susceptible to enzyme attack, degrading itself into maltose and dextrins under a combination of α- and β-amylase.

Damaged starch affects many properties of flour and bread process, such as water absorption of flour, dough mixing properties, dough power to produce gas, dough handling properties (stickiness), bread loaf volume, softness of bread crumb, and color of bread crust. Table 9.1 is a summary of influences of damaged starch on bread baking.

Great starch damage increases flour absorption and, in most cases, bake absorption, too. It is known that for breadmaking, there is a range of bake absorption for

Table 9.1 Effect of DS on common flour and bread-baking behaviors (Dhotel 2010)

	Too low DS	Optimal DS	Excessive DS
Water absorption	Low	High	Very high
Gelatinization temperature	High	Low	Low
Bread volume	Low	High	Low (bread collapse)
Crust color	Pale	Good	Too red (visible blemishes)
Bread crumb	Dense	High	Open, gummy, fast crumb hardening

certain flour to reach optimum loaf volume and flour with high starch damage is reported to impair tolerance to variations in absorption. For example, for flour with high starch damage, bread loaf volume decreased more rapidly at lower than optimum absorption and less rapidly at higher than optimum absorption (Farrand 1972).

Relatively high starch damage positively affects the water absorption capacity of flour and may lead to a better dough yield. Farrand derived a relationship between optimum water absorption, protein, starch damage, and moisture content (Farrand 1968).

Water absorption = $1.4P + 0.38D - [1.6M + 0.004D(M + P)] + 57.3$ + correction factor

D: damage starch level in Farrand unit
P: protein content (12% moisture basis)
M: moisture of flour

In general, gas power was significantly higher in flour with higher starch damage (60 Farrand unit), compared to flour of lower starch damage (34 Farrand units) (Dexter et al. 1985). The degree of this effect may vary from one situation to another, depending on when and what supplementary sugar source is added to the fermentation process. For example, in sponge and dough method, the initial sponge fermentation is mainly dominated by maltose consumption via breakdowning of damaged starch, and the final dough has a large amount of glucose and fructose produced by sugar inversion after remixing; however, for straight dough system, the fermentation is dominated by consumption of all three sugars, glucose and fructose first and then maltose (Tang et al. 1972). As a result, damaged starch promotes fermentation more readily under sponge and dough process than straight dough process.

However, excessive starch damage deteriorates bread quality. Early works by Tipple and Farrand suggest that in order to make stable dough and a loaf of good volume and texture, the gluten must spread far enough to contain the total surface of starch; failure of gas retention happens when there is insufficient gluten to cover increase surface area caused by increased amount of damaged starch (Tipple 1969; Farrand 1972). Study of flour baking with severe damaged starch levels (ranges from 33 to 79 Farrand units) showed dramatic decrease in specific volume. Meantime, too much starch damage indicates very little starch and very much dextrin left after fermentation. In this case, after being utilized for starch gelatinization, water is left for protein hydration and dextrin-water binding and leads to gumminess texture. There is limited amount of starch forming a gel that sets loaf structure by providing a rigid network.

Optimum starch damage for breadmaking has been studied for years, mostly from the original Farrand's theory, and it evolves with changing baking process and analytical tests. Below are commonly found equations for calculation of optimum starch damage:

$$S.D.\left(\text{in Farrand Unit}\right) = \text{Protein}^2 / 6\left(\text{Farrand 1968}\right) \tag{9.1}$$

$$S.D.\left(\text{in Farrand Unit}\right) = \text{Protein}^2 / 5.2, \text{for no} - \text{time dough}\left(\text{Acklin 1997}\right) \tag{9.2}$$

Application of Equation 9.2 applies to no-time dough process. For example, Farrand's study for optimum starch damage used long fermentation process. But in fast bread processes, with short resting time, the effect of starch damage in providing substrate is minimal.

Early study by Farrand (1972) stated that satisfactory bread could be made from pin-milled flour over a range of 18–30 Farrand units using a straight dough method. The flour protein is 12.2–12.3% and was with lean formulation. A range of 4.5–8.0% (flour dry weight) was recommended for bread baking by Pyler (Pyler and Gorton 2000). According to Chopin Technologies, with appropriate alpha-amylase use and flour protein, it is the end products that determine the range of starch damage, for example, French type (Baguette), 16–20 UCD; pan bread, 19–23 UCD; and biscuit/cookie, 14–16 UCD (Chopin 2018).

Specification of starch damage content is developed in flour milling industry. Below is a chart that serves as database for relationship between damage starch content (in UCD unit created by Chopin) in wheat flour and baked products (Fig. 9.2).

9.6 Quality Control in Flour Milling

The quality for starch or flour is very important for both manufacturer and end users. Traditionally, flour yield, color, and ash are considered as main parameters in the milling industry. However, starch granules in cereal grains are damaged during milling. This review provides a better understanding of the effects of milling on starch structure and corresponding changes in physical and chemical properties of starch and flour, demonstrating why the damaged starch content should be developed as an important parameter for industry user.

Different methods were used to measure damaged starch, including extraction procedures ("blue value"), dye-staining procedures, NIR procedures, and enzyme digestion procedures. Of these, the enzyme digestion procedures are generally preferred for its accuracy. Starch damage assay kit from Megazyme is a method adjusted from AACC Method 76-31.01. Cereal and fungal α-amylase preparations

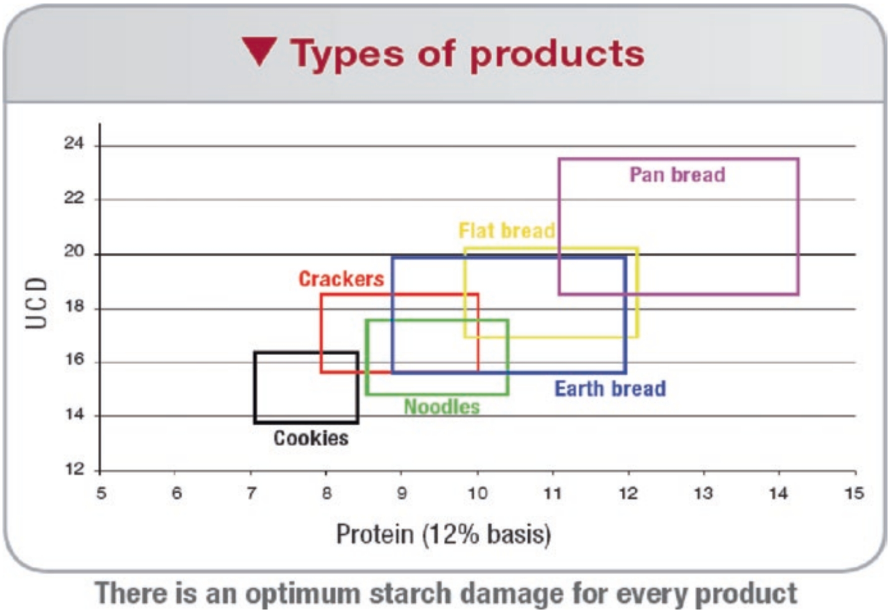

Fig. 9.2 Optimum starch damage for baked products

have been employed as crude malt extracts or crude fermentation broths. The degree of hydrolysis has traditionally been measured using nonspecific reducing-sugar methods such as ferricyanide titration or reaction with dinitrosalicylic acid (DNS). This method is accurate in determining the damaged starch content, because it is a direct method, while blue value and others may be dependent on the max wavelength absorbance of amylose, which varies in plant sources and intermediate components in starch.

9.7 Conclusions

This chapter describes common milling process of starch and flour from grains, the multi-scale change ranging from starch granules to molecular structure during grain or starch milling, and the milling effects on physical and rheological properties of finished products. Using wheat flour milling as an example, this chapter also advocates starch damage as specification for quality control in flour milling industry.

Milling of cereal grains causes damage to starch granules or even disruption of starch crystalline structure and degradation of starch molecules. Amylose is mostly in amorphous conformation in native starch granules. It is flexible and thus less affected by milling, comparing to amylopectin double helices with rigid crystallinities. The grinding of isolated starch granules, however, does not replicate the milling of cereal grains, because the effects on starch structure are more heterogeneous in flour than isolated starch granules. Non-starch components in flour particles may protect starch from grinding forces. Among all milling techniques, cryogenic milling of cereal grains produces the least damage to starch granules and least degradation of starch molecules. Starch gelatinization properties are highly related to starch crystalline structure; however, non-starch components in flour particles can affect starch gelatinization profiles. The pasting properties of flour are highly governed by flour particle size and by the degree of damage to starch granules.

The starch solubility of flour is more strongly related to the damage to starch granules than flour particle size and the degradation of starch molecules, indicating that molecular degradation is not the precondition of increased starch solubility by milling. The cold-water swelling of flour shows high correlations with the damage to starch granules and flour particle size and weak correlations with starch molecular structures. The starch digestibility of raw flour is greatly affected by flour particle size and damage to starch granules; however, it is not well understood if the same applies to the digestibility of gelatinized starch in cooked flour or flour applications.

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