Carbohydrate Polymers 83 (2011) 317–328

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

Impact of heat-moisture treatment and annealing in starches: A review

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ARTICLE INFO

Article history:
Received 5 July 2010
Received in revised form 15 August 2010
Accepted 25 August 2010
Available online 19 September 2010

Keywords:
Annealing
Heat-moisture treatment
Physical modification
Safe food
Starch

ABSTRACT

Heat-moisture treatment (HMT) and annealing (ANN) are physical modifications that change the physicochemical properties of starch without destroying its granular structure. These hydrothermal treatments are processes in which the starch-to-moisture ratio, temperature, and heating time are critical parameters that need to be controlled. In HMT, starch is heated to temperatures above the gelatinisation temperatures but with insufficient moisture to gelatinise. In ANN, starch is exposed to excess water for an extended period of time at a temperature above the glass transition but below the gelatinisation temperature. The impact of such hydrothermal treatments on starch pasting, morphological, crystalline, thermal, and physicochemical properties, as well as on the enzymatic and acid susceptibility of starch will be discussed. The paper also highlights some applications of hydrothermally treated starch. This review is of significance not only for the development of novel starches for food and non-food applications, but also for understanding the impact of HMT and ANN on starch and its functionality.

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doi:10.1016/j.carbpol.2010.08.064

1. Introduction

Starch is a semi-crystalline biopolymer that serves as a carbohydrate reserve in many plants, including cereals, roots, tubers, seeds, and fruits. Starch granules can vary in shape, size, structure, and chemical composition, depending on the origin of the starch (Smith, 2001). Starch granules are composed of amylose and amylopectin macromolecules. The structure of the starch granule depends on the way in which amylose and amylopectin are associated and distributed throughout the starch granule. Several studies have been conducted to elucidate the location of amylose within the granule (Gerard, Colonna, Buleon, & Planchot, 2002; Jane, 2006; Jenkins & Donald, 1995; Jane & Shen, 1993; Tatge, Marshall, Martin, Edwards, & Smith, 1999). Saibene and Seetharaman (2010) most recently also investigated the location and role of amylose within the granule. These authors reported that the molecular size distribution, iodine binding and X-ray diffraction analysis of the potato and corn starches and the respective lintners elucidated differences in the location of amylose within the amorphous or crystalline regions. For potato starch, they concluded that there was a partial involvement of amylose in the B-type crystallites. For corn starch, the amylose would be located within the amorphous regions of the granule, independent of the amylopectin crystallites, free to complex with iodine without disruption of the A-type crystallinity.

Starch, in its native form, does not always have the physical and chemical properties appropriate for certain types of processing. However, modification can increase the use of starch in various industries, such as the food, paper, and textile industries. Starches are often modified by physical, chemical, and enzymatic processes to promote specific functional properties. The physical modification of starch by moisture, heat, shear, or radiation has been gaining wider acceptance because no by-products of chemical reagents are present in the modified starch. Modification can achieve functional properties not found in native starches, which have specific applications in various industries. Chemical modification is widely implemented, but there is also a growing interest in the physical modification of starch, especially in food applications. A major advantage of physical modification is that starch is considered to be a natural material and a highly safe ingredient, so its presence and quantity in food is not limited by legislation (Bemiller, 1997).

Heat-moisture treatment (HMT) and annealing (ANN) are physical modifications that alter the physicochemical properties of starch without destroying its granular structure (Adebowale, Afolabi, & Olu-Owolabi, 2005; Hormdok & Noomhorm, 2007; Jacobs & Delcour, 1998; Maache-Rezzoug, Zarguili, Loisel, Queveau, & Buléon, 2008). These two related processes both require that the starch-to-moisture ratio, temperature, and heating time are controlled (Chung, Liu, & Hoover, 2009b). However, these treatments differ in the amount of water and in the temperature used. HMT is carried out under restricted moisture content (10–30%) and higher temperatures (90–120 °C), while ANN involves a large excess of water (50–60%) and relatively low temperatures that fall below the gelatinisation point (Maache-Rezzoug et al., 2008).

Regardless of the starch's origin, HMT promotes an increase in the gelatinisation transition temperature, a widening of the gelatinisation temperature range, a decrease in granular swelling and amylose leaching, and an increase in thermal stability. However, depending on the botanical origin of the starch and the treatment conditions, changes in the X-ray pattern, the formation of amylose–lipid complexes, the disruption of crystallinity, and either increases or decreases in enzymatic susceptibility may occur due to HMT (Chung et al., 2009b). In addition, ANN changes the physicochemical properties of starches by improving crystalline perfection and facilitating interactions between starch chains (Jayakody & Hoover, 2008). More specifically, ANN leads to a reorganisation of starch molecules, and amylopectin double helices acquire a more organised configuration (Gomes, Silva, & Ricardo, 2005).

There is currently great interest in using physical modification techniques, such as HMT and ANN, to alter the physicochemical properties of starches. The extent of modification is influenced by the starch composition, source, and the ratio of amylose to amylopectin, as well as by the arrangement of the starch chains within the amorphous and crystalline domains of the native starch granules. Heat-moisture-treated and annealed starches have important applications in the food industry, especially due to their improved thermal stability and decreased extent of retrogradation (Adebowale et al., 2005). These properties make hydrothermally treated starches suitable for utilisation in the canned and frozen food industries. The decrease in granular swelling and amylose leaching and the increase in heat and shear stability that result from HMT and ANN are also desirable properties for noodle manufacture (Hormdok & Noomhorm, 2007). Additionally, these treatments have been used to enhance resistant starch levels while maintaining granule structure (Brumovsky & Thompson, 2001).

The physical modification by hydrothermal treatments such as HMT and ANN is consistent with societal trends towards natural products and offers the potential to change starch functionality at a low cost and in an environmentally friendly way. In this review, the impact of hydrothermal treatments on starch pasting, morphological, crystalline, thermal, and physicochemical properties, as well as on the enzymatic and acid susceptibility of starch, will be examined. Furthermore, the applications of hydrothermally treated starches in products that require specific properties are also summarised.

2. Structure and organisation of starch granules

Starch is formed of granules of variable size and is composed of amylose and amylopectin macromolecules. The amylose and amylopectin in starch are not free in nature, but compose a semi-crystalline aggregate organised in the form of granules. The size, form and structure of starch granules vary with the botanical source. The diameter of the granules ranges from 1 to 100 μm and their shape can be regular or irregular. Amylose is a linear molecule composed of D-glucose units linked by α-1,4 glucosidic bonds with a small number of branches (Liu, 2005). According to You, Stevenson, Izydorczyk, and Preston (2002), the molecular weight of amylose varies from 1×10^5 to 1×10^6 g/mol. Amylose has a helical structure where the interior of the helix contains hydrogen atoms, while the hydroxyl groups remain on the outside (Buléon, Colonna, Planchot, & Ball, 1998). The presence of hydrogen atoms in the interior of the helix makes amylose hydrophobic and enables it to form complexes with free fatty acids, component glycerides of fatty acids, iodine and some alcohols. Amylose complexes with fats and emulsifiers in foods such as mono- and di-glycerides can alter the temperature of gelatinisation and the texture and viscosity profile of the paste and can limit retrogradation (Thomas & Atwell, 1999).

Amylose has the ability to form paste after the gelatinisation of the starch granules; this behaviour is evident in certain starches that contain higher levels of amylose, such as corn, wheat, rice and in particular high-amylose corn starch. The paste is mainly formed due to the reassociation (retrogradation) of starch polymers solubilised after gelatinisation (Thomas & Atwell, 1999). The amylose content presented in scientific papers is usually expressed as apparent amylose content; this is due to the ability of some external branched amylopectin chains to interact with iodine, thereby overestimating the actual amylose content. However, many authors refer to the apparent amylose content as that obtained from starches that have not previously been defatted because the presence of lipids in starch interferes with iodine affinity (Morrison, 1995).

Amylopectin is a highly branched macromolecule with linear chains of shorter linked by α-1,4 glucosidic bonds containing 10–60 glucose units and side chains with 15–45 glucose units with an average of 5% of links α(1–6) in branched points (Van der Maarel, Van der Veen, Uitdehaag, Leemhuis, & Dijkhuizen, 2002). The molecular weight of amylopectin is about 1000 times the molecular weight of amylose and ranges from 1×10^7 to 5×10^8 g/mol (You et al., 2002). Amylopectin chains are arranged radially within the granule with their non-reducing terminal ends oriented towards the surface, and these are arranged with alternating crystalline areas (as a double helix) and amorphous areas (with regions of branching points).

The functionality of starch is due to the ratio of these macromolecules as well as the physical organisation within the granular structure. Starch granules present crystalline and amorphous regions. The crystalline regions are formed by branched chains of amylopectin molecules and are alternated with amorphous layers (Liu, 2005). The semi-crystalline structure of starch granules is composed of linear and branched macromolecules arranged in the radial direction; the macromolecules form hydrogen bonds because they are associated in parallel, which results in the appearance of crystalline regions (Gallant, Bouchet, & Baldwin, 1997). Starch granules are birefringent; however, this birefringence does not necessarily imply a crystalline form, but rather a high degree of molecular organisation of the granules (Zobel, 1988). According to Billiaderis (1991), the crystalline areas of starch maintain the structure of the granule, control its behaviour in the presence of water and make it more or less resistant to chemical and enzymatic attack. The amorphous zone of starch granules is the least dense, is more susceptible to enzymatic attacks and absorbs more water at temperatures below the gelatinisation temperature.

The different degrees of structural ordering of the granules are responsible for the properties of birefringence and crystallinity. The optical birefringence and X-ray diffraction properties provide ample evidence of an ordered structure of the starch granule. This structure consists of concentric layers, which can be observed in electron microscope images of granules treated with acid or partially digested by amylases. The crystallinity of the granules is mainly described as a function of the double helix formed by the branches of amylopectin (Hoover, 2001), which ranges between 15 and 45% of relative crystallinity. The crystalline structure is categorised according to its profile from a diffractogram using X-ray diffraction. Patterns known as types A, B and C represent specific diffraction angles caused by the double helix packing of the amylopectin branched chains (Parker & Ring, 2001). The pattern of crystallinity is defined on the basis of interplanar spaces and the relative intensity of the diffraction lines of the X-ray. The polymorphic form of type C is considered an arrangement intermediate between the types A and B (Fuentes-Zaragoza, Riquelme-Navarrete, Sánchez-Zapata, & Pérez-Álvarez, 2010). Billiaderis (1991) reported that pattern A is characteristic of cereal starches, pattern B is characteristic of starches from tubers, fruits, and high-amylose corn starch, and pattern C is characteristic of starches of legumes. Amylose, when complexed with organic compounds, water or iodine, may appear as the standard type V.

3. Properties of starches

An important property of partially crystalline materials, such as starch granules, is the glass transition of amorphous regions at a certain temperature. The glass transition temperature (T_g) is obtained from differential scanning calorimetry (DSC) curves. During heating, the amorphous regions are transformed from a rigid glassy state to a mobile rubbery state (Jacobs & Delcour, 1998). Below the T_g, the polymer has sufficient internal energy to allow the displacement of the chains by conformational changes, presenting a glassy state. Above the T_g, rotational and diffusional movements of the polymer chains occur. In general, T_g depends on the thermal history of the material, the molecular weight of the polymer chains, the degree of crystallinity and the composition of the sample. This is a reversible transition and occurs prior to gelatinisation.

Intact starch granules are not soluble in cold water but can retain small amounts of water, causing a small amount of swelling that is reversible by drying. At certain concentrations, starch granules in solution becomes a dilatant fluid where the flow is inversely proportional to the pressure that is exerted; the greater the pressure, the lower the fluidity. The insolubility of starch granules is due to strong hydrogen bonds holding the starch chains together. However, when starch is heated in excess water above the paste temperature, the crystalline structure is disrupted due to the relaxation of hydrogen bonds, and the water molecules interact with the hydroxyl groups of amylose and amylopectin, causing an increase in granule size and partial solubilisation of starch (Hoover, 2001).

The heating of starch suspensions in excess water and above a certain temperature causes an irreversible transition called gelatinisation, which can be characterised by an endotherm obtained by differential scanning calorimetry, the loss of birefringence observed through polarised light microscopy, and the disappearance of crystallinity as evidenced by X-ray diffraction (Garcia, Colonna, Bouchet, & Gallant, 1997). The gelatinisation of starch results in the collapse of its molecular arrangement and irreversible changes to its properties, including the loss of crystallinity, water absorption, the swelling of the granules and the leaching of some components, mainly amylose (Zhong et al., 2009). Retrogradation is a phenomenon whereby solubilised amylose molecules and linear fractions of amylopectin form reassociations by hydrogen bonds. This process has been used to describe the changes that occur in starch after gelatinisation, from an initially amorphous state to a more ordered or crystalline state (Liu & Thompson, 1998). The process is accompanied by the loss of water from the gel and is called syneresis.

The changes that occur in starch granules during gelatinisation and retrogradation are the main determinants of the behaviours of starch paste, which have been quantified mainly by measuring changes in viscosity during the heating and cooling of starch dispersions using a Viscoamylograph. In viscoamylographic analysis, an increase in viscosity is recorded when the granules begin to swell during the initial phase of heating a slurry of starch. At this point, low molecular weight polymers, particularly amylose molecules, begin to be leached from the granules. Peak viscosity is achieved during the formation of paste, when the granules are the most swollen (Tsai, Li, & Lii, 1997). Factors such as temperature, granule size and concentration and the presence of lipids can influence the behaviour of the starch paste (Jane et al., 1999).

Apparent viscosity curves provide information about the paste temperature, the peak viscosity, the resistance of the swollen granules to mechanical action, as well as the influence of cooling on viscosity (retrogradation). Amylose molecules reassociate more easily due to their linear structure, and are primarily responsible for the occurrence of retrogradation. However, amylose is not the only component that is involved in starch retrogradation. Studies by Jaillais, Ottenhof, Farhat, and Rutledge (2006) showed that under certain experimental conditions, the retrogradation of amylopectin cannot be excluded from the total fraction of retrograded starch.

Differential scanning calorimetry, when applied to starch, provides quantitative measurements of heat flow associated with gelatinisation, where the endothermic peaks are indicative of melting. To detect the transition phase in starch, DSC methods have the advantage of being independent of the birefringence of the granules. This is an important difference when birefringence is present due to molecular orientation in amorphous regions, or is absent due to the crystals being small or randomly oriented. The changes in enthalpy observed in DSC are usually related to the transition between ordered and disordered crystals presented in the form of ordered internal arrangements and in regions of low order crystalline regions of the granule (Karlsson & Eliasson, 2003). Lopez-Rubio, Flanagan, Gilbert, and Gidley (2008) proposed that the enthalpy associated with granule gelatinisation is due to melting of imperfect amylopectin-based crystals, with potential contributions from both crystal packing and helix melting enthalpies. The temperature required for the gelatinisation of starches verified by thermal analysis is important because it defines the proportion of required energy for cooking. On an industrial scale, the energy cost of the process must be carefully controlled. Thermoanalytical techniques are commonly used in the analysis of transitions that occur when synthetic polymers are heated. However, these techniques are also widely used in the study of starch gelatinisation (Leliévre & Liu, 1994).

4. Hydrothermal modifications

4.1. Heat-moisture treatment (HMT)

HMT is a physical modification that involves low moisture levels, usually in a restricted range of 10–30%, and heating at high temperatures (90–120 °C) for a period of time ranging from 15 min to 16 h (Chung et al., 2009b; Maache-Rezzoug et al., 2008). HMT allows control of molecular mobility at high temperatures by limiting the amount of water. HMT-induced changes in starch structure and properties have been found to vary with starch source and amylose content. For instance, tuber starches are more sensitive to HMT than legume or cereal starches (Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994; Jacobs & Delcour, 1998). Significant progress in HMT research has been made over the few last years, as reflected by numerous publications on this subject. The HMT conditions for starches of different botanical origin are summarised in Table 1.

According to Gunaratne and Hoover (2002), HMT promotes the interaction of polymer chains by disrupting the crystalline structure and dissociating the double helical structure in the amorphous region, followed by the rearrangement of the disrupted crystals. Crystalline disruption near the granule's surface can facilitate the attack of α-amylase within it. When the crystals are not disrupted by HMT, increased enzymatic susceptibility results due to the disruption of the double helices by treatment in amorphous regions. This disruption facilitates enzymatic access to the sites of interaction between the amylose chains during the rearrangement of the polymer chains.

4.1.1. Impact of HMT on starch swelling power and solubility

Several researchers have studied the effect of HMT on the swelling power of potato, cassava (Gunaratne & Hoover, 2002), rice (Hormdok & Noomhorm, 2007), sorghum (Olayinka, Adebowale, & Olu-Owolabi, 2008), and corn starches (Chung et al., 2009b). In all of these studies, the authors observed a reduction in the swelling power of HMT starches. This reduction in swelling power has also been attributed to increased crystallinity, reduced hydration (Waduge, Hoover, Vasanthan, Gao, & Li, 2006), increased interactions between amylose and amylopectin molecules, strengthened intramolecular bonds (Jacobs, Eerlingen, Clauwaert, & Delcour, 1995), the formation of amylose–lipid complexes (Waduge et al., 2006) and changes in the arrangements of the crystalline regions of starch (Hoover & Vasanthan, 1994).

Starch solubility results from the leaching of amylose, which dissociates from and diffuses out of granules during swelling. This leaching represents a transition from order to disorder within the starch granules that occurs when starch is heated with water (Tester & Morrison, 1990). Adebowale and Lawal (2002), who studied the effect of HMT on the solubility of bambarra groundnut starch at 60, 70, 80, and 90 °C, observed a reduction in solubility at all temperatures. Olayinka et al. (2008) also noted a decrease in the solubility of hydrothermally treated white sorghum starch compared to native starch. This solubility decrease was enhanced by

Table 1
Heat-moisture treatment conditions for starches and references.

Starch source	Temperature (°C)	Time	Water content (%)	Reference
Cassava	110	3–16 h	18–24	Abraham (1993)
	100	10 h	30	Gunaratne and Hoover (2002)
Canna	100	16 h	18–25	Watcharatewinkul et al. (2009)
	110	5–30 min	20–30	Zhang, Wang, and Shi (2009)
Corn	100–120	2 h	30	Chung et al. (2009b)
	120	15–60 min	20	Pukkahuta et al. (2008)
	120–130	–	13.5	Miyazaki and Morita (2005)
	110	16 h	15–27	Kweon et al. (2000)
	100	16 h	18–27	Franco et al. (1995)
Pea	120	2 h	30	Chung et al. (2009b)
Lentil	120	2 h	30	Chung et al. (2009b)
	100	16 h	10–30	Hoover and Vasanthan (1994)
Rice	110	1 h	15–25	Zavareze et al. (2010)
	100–110	0.5–1.5 h	15–25	Hormdok and Noomhorm (2007)
	100	16 h	18–27	Khunae et al. (2007)
Potato	100	16 h	24	Varatharajan et al. (2010)
	90–130	24 h	17–26	Vermeylen et al. (2006)
	100	10 h	30	Gunaratne and Hoover (2002)
	100	16 h	10–30	Hoover and Vasanthan (1994)
White sorghum	110	16 h	18–27	Olayinka et al. (2008)
Sweet potato	100	16 h	27	Vieira and Sarmento (2008)
	110	4–16 h	25	Collado and Corke (1999)
Sago	100–120	1 h	20	Pukkahuta and Varavinit (2007)
Finger millet	100	16 h	20–30	Adebowale et al. (2005)
Wheat and yam	100	16 h	10–30	Hoover and Vasanthan (1994)
Peruvian carrot	100	16 h	27	Vieira and Sarmento (2008)
Ginger	100	16 h	27	Vieira and Sarmento (2008)
Borlotti bean	100	16 h	22	Güzel and Sayar (2010)
Chickpea	100	16 h	22	Güzel and Sayar (2010)
Chestnut	110	3 h	25–28	Singh et al. (2009)

increasing the moisture content of the treated starches from 18 to 27%. In contrast, Hormdok and Noomhorm (2007) observed no significant difference in the solubilities of hydrothermally treated rice and native rice starch.

The reduction in swelling power and solubility following HMT has been attributed to the internal rearrangement of the starch granules, which causes further interactions between the starch's functional groups (Hoover & Manuel, 1996), the formation of more ordered double helical amylopectin side-chain clusters and the formation of amylose–lipid complexes within the granules (Olayinka et al., 2008; Tester & Morrison, 1990).

4.1.2. Impact of HMT on starch pasting properties

HMT promotes intense changes in starches, significantly altering their pasting profile. Several studies have been conducted to investigate the effect of HMT on bambarra groundnut (Adebowale & Lawal, 2002), white sorghum (Olayinka et al., 2008), rice (Hormdok & Noomhorm, 2007; Zavareze, Storck, Castro, Schirmer, & Dias, 2010), corn (Chung et al., 2009b), and canna starches (Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009). According to the latter group, HMT (15, 18, 20, 22, and 25% moisture/100 °C/16 h) of canna starch altered its pasting profile, resulting in increased paste temperature and decreased peak viscosity, final viscosity, and breakdown. These authors explained that changes in treated starch's pasting properties are due to associations between the chains in the amorphous region of the granule as well to changes in crystallinity during hydrothermal treatment. This behaviour intensified as the moisture content of the HMT increased.

Olayinka et al. (2008) studied the effect of HMT on white sorghum starch and reported that the intensity of its effects on starch's pasting properties depends on the treatment conditions. As the moisture level increased, paste temperature increased and peak viscosity declined. There was also a significant reduction in breakdown and retrogradation after HMT. As the forces of the intragranular bonds are strengthened, the starch requires more heat for structural disintegration and paste formation. A high paste temperature thus indicates that more forces and cross-links are present within the starch granules.

The HMT-induced reduction in breakdown demonstrates that starches are more stable during continuous heating and agitation, which is supported by Adebowale et al. (2005), Hormdok and Noomhorm (2007), Olayinka et al. (2008) and Watcharatewinkul et al. (2009). Lan et al. (2008) have shown that retrogradation is influenced by the amount of leached amylose, granule size, and the presence of rigid, non-fragmented swollen granules. Meanwhile, Chung et al. (2009b) found that HMT reduces amylose leaching from starch granules and that this reduction is more significant in starches containing high levels of amylose. They also reported that HMT promotes additional amylose–amylose and/or amylopectin–amylopectin chain interactions, which reduce amylose leaching and decrease retrogradation.

4.1.3. Impact of HMT on gel texture

The textural properties of gels depend on the constituents of starch and amylose, the volume and deformation of the granules and the interaction between the continuous and dispersed phases (Choi & Kerr, 2003). Gel strength has been reported to be dependent on the binding capacity of starch molecules to water by hydrogen bonding (Lee & Osman, 1991). The hydrogen bonds that stabilise the double helical structure are broken during gelatinisation and replaced by hydrogen bonds with water, where the degree of swelling is controlled by the crystallinity of the molecule (Tester & Karkalas, 1996).

HMT affects the textural properties of starch gels. Hormdok and Noomhorm (2007) studied the effect of HMT on rice starch (27% amylose) and concluded that this treatment increased the gel hardness of starch treated with 15 and 20% moisture. For treatments under 25% moisture, they found no difference with native starch and attributed this fact to a possible partial gelatinisation, resulting in a less rigid gel due to the partial collapse of the structure of the granules. During HMT, increase in gel hardness has been attributed to the increased cross-linking between starch chains in the particular amylose portion. These allowed the formation of more junction zone in the continuous phase of the gel, resulting in the increased gel hardness (Liu, Corke, & Ramsden, 2000). Collado and Corke (1999) treated sweet potato starch with HMT and found that the starch paste became short and stable to shear and showed a significant increase in gel hardness and adhesiveness.

Temperature and moisture content were the dominant factors affecting starch granules (Cham & Suwannaporn, 2010). Liu et al. (2000) reported that the higher the temperature and moisture content, the more perfect the crystalline starch granules. These findings suggest that starch granule swelling is restricted by hydrothermal treatment. During HMT, the increase in rheological properties was attributed to the increase in cross-linking between starch chains. This allowed the formation of more junction zones in the continuous phase of the gel, resulting in an increase in gel hardness (Hoover & Manuel, 1996).

4.1.4. Impact of HMT on granule morphology

Granule morphology, granule size distribution, and surface characteristics play an important role in many food and non-food applications of starch. HMT did not alter the size or shape of the potato, taro, new cocoyam, true yam, and cassava (Gunaratne & Hoover, 2002), maize (Hoover & Manuel, 1996), wheat (Hoover & Vasanthan, 1994), finger millet (Adebowale et al., 2005), rice (Khunae, Tran, & Sirivongpaisal, 2007) and canna (Watcharatewinkul et al., 2009) starch granules. However, Kawabata et al. (1994) observed a formation of cracks on the surface of treated maize and potato starches, together with a hollow inside the granule. Zavareze et al. (2010) also investigated the effect of HMT on granule morphology of rice starches with different amylose contents. These authors reported that the HMT (25% moisture) of the high- and medium-amylose rice starch granules slightly affected the format and degree of agglomeration, making the granules more aggregated and the surface of the granules more irregular, as compared with the native starches. However for HMT (25% moisture) low-amylose rice starch there was signs of the loss of physical integrity with distension of the granular surface. This change in granular morphology of low-amylose rice starch by HMT is probably due to high moisture content of hydrothermal treatment, because this condition is more susceptible to the occurrence of partial gelatinisation and morphological changes.

4.1.5. Impact of HMT on starch crystallinity

According to Miao, Zhang, and Jiang (2009), crystallinity differences between starches may be attributed to the following: (1) crystal size; (2) the number of crystalline regions that are influenced by amylopectin content and chain length; (3) the orientation of the double helices within the crystalline area; and (4) the extent of interaction between the double helices. The effect of HMT on crystallinity depends on the starch's source and treatment conditions. Changes in the X-ray diffraction pattern from B- to A-type has been noted in heat-moisture-treated potato (Gunaratne & Hoover, 2002; Vermeylen, Goderis, & Delcour, 2006) and yam starches (Gunaratne & Hoover, 2002). However, according to Jacobs and Delcour (1998), not all temperature and moisture conditions induce a change from B- to A-type crystallinity in potato starch. In contrast, other types of starches did not have an altered X-ray diffraction pattern after HMT, including taro, cassava

(Gunaratne & Hoover, 2002), and cereal starches (Jacobs & Delcour, 1998).

As stated by Genkina, Wasserman, Noda, Tester, and Yuryeva (2004), HMT often results in the transformation of the less thermodynamically stable B-polymorphic structure (with hexagonal packing of double helices and about 36 water molecules inside each cell) into a more stable monoclinic structure of A-type polymorphs (with about six water molecules inside the helices). The HMT-induced changes in the diffraction pattern of starches can be attributed to dehydration as well as to movement of a pair of double helices into the central channel. This movement during HMT could disrupt starch crystallites and/or change the crystalline orientation (Gunaratne & Hoover, 2002).

Some authors have reported an increase in the intensity of the X-ray diffraction of corn (Hoover & Manuel, 1996) and sweet potato starches (Vieira & Sarmento, 2008) after HMT. An increase in the X-ray intensity of heat-moisture-treated starches is due to the displacement of the double helical chains within the starch crystals, resulting in a crystalline matrix that is more orderly than in native starch. However, others have identified a reduction in the relative crystallinity of potato (Vermeylen et al., 2006), cassava, true yam (Gunaratne & Hoover, 2002), corn (Franco, Ciacco, & Tavares, 1995), and Peruvian carrot starches (Vieira & Sarmento, 2008). This reduction in X-ray intensity due to hydrothermal treatment results from either reduced crystallinity or increased amorphous area in the semi-crystalline lamella.

4.1.6. *Impact of HMT on starch gelatinisation characteristics*

HMT influences the onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and gelatinisation enthalpy (ΔH) of starch. This effect is dependent on the moisture level of the treatment, the starch source, and the amylose content. The onset, peak, and conclusion gelatinisation temperatures generally rise as the heat and moisture intensity increase. This increase has been noted for potato, cassava, true yam (Gunaratne & Hoover, 2002), corn (Chung et al., 2009b; Hoover & Manuel, 1996; Maache-Rezzoug et al., 2008), pea, lentil (Chung et al., 2009b), and canna starches (Watcharatewinkul et al., 2009). Increased T_o, T_p, and T_c have been attributed to structural changes within the starch granules, which involve amylose–amylose and amylose–lipid interactions (Hoover & Vasanthan, 1994). Adebowale, Henle, Schwarzenbolz, and Doert (2009) found that the process of gelatinisation, which involves the melting of crystalline regions and double helices, is determined by the hydration and swelling of the amorphous regions of starch granules. When the amorphous region swells, it imparts a stress on the crystalline regions and polymer chains are stripped from the surface of starch crystallites. After HMT, the amylose–amylose and amylose–lipid interactions reduce the mobility of the amorphous region. As a result, heat-moisture-treated starches require a higher temperature in order for swelling and disruption of the crystalline regions to occur, leading to increased T_o, T_p, and T_c.

The reduction in ΔH promoted by HMT has been reported in potato, cassava (Gunaratne & Hoover, 2002), jackbean (Lawal & Adebowale, 2005), corn (Chung et al., 2009b; Pukkahuta, Suwannawat, Shobsngob, & Varavinit, 2008), pea, and lentil starches (Chung et al., 2009b). However, Hoover and Manuel (1996) found no reduction in the ΔH of heat-moisture-treated corn starch at 100 °C. Gunaratne and Hoover (2002) reported that decreased ΔH due to HMT is a result of the disruption of double helices present in the crystalline and non-crystalline regions of the granules. In addition, Hormdok and Noomhorm (2007) argued that the reduction in ΔH after hydrothermal treatment may be due to the partial gelatinisation of amylose and amylopectin molecules that are less stable during heating.

4.1.7. *Impact of HMT on the susceptibility of starch to enzymatic hydrolysis*

Zhang and Oates (1999) reported that the enzymatic susceptibility of starch is influenced by several factors, including the ratio of amylose to amylopectin, the crystalline structure, and the size of the particles. Among these factors, the crystalline granular structure is perhaps the most important.

HMT-induced changes probably occur in the amorphous regions of the starch granules, which are more accessible to hydrolysis. These amorphous areas are more rapidly degraded by α-amylases than the crystalline areas. According to Gunaratne and Hoover (2002), HMT specifically promotes crystalline disruption and the dissociation of double helical structures in the amorphous region, which can facilitate the attack of α-amylase within the granules. Based on the hydrothermal treatment (30% moisture/100 °C/10 h) of taro, cassava, and potato starches, these authors concluded that the enzymatic susceptibility of starch increases with HMT. Therefore, the structural rearrangement of starch caused by HMT facilitates enzymatic accessibility to the amorphous areas. Vieira and Sarmento (2008) studied the effect of HMT in Peruvian carrot, sweet potato and ginger starches and reported that the percentages of hydrolysis after 24 h with α-amylase of the heat-moisture-treated sample (27% moisture/100 °C/16 h) were 29%, 5% and 22%, respectively; these levels were higher than in native starches.

Augmented starch digestibility with increased HMT moisture content was observed by Kweon, Haynes, Slade, and Levine (2000). Franco et al. (1995) also found that HMT (18% moisture/100 °C/16 h) enhanced the crystallinity of corn and cassava starches, resulting in a significant increase in enzymatic susceptibility. According to these authors, the results suggested a rearrangement of starch molecules with the strengthening of bonds within the granules. Moreover, HMT at a moisture level of 27% led to the disruption and subsequent rearrangement of bonds within the granules, causing starch degradation and thus increasing the number of regions accessible to enzymatic hydrolysis.

4.1.8. *Impact of HMT on the susceptibility of starch to acid hydrolysis*

The influence of HMT on acid hydrolysis has been shown to vary widely among starch sources. In cereal starches, susceptibility towards acid hydrolysis after HMT decreases in wheat (Hoover & Vasanthan, 1994) and maize (Hoover & Manuel, 1996) starches, whereas tuber starches (potato, cassava, and taro) show increased hydrolysis during the first 5 days of hydrolysis on HMT (Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994). According to Varatharajan, Hoover, Liu, and Seetharaman (2010), the acid hydrolysis of potato starch decreased with HMT and this decrease could be explained on the basis of changes in crystalline polymorphism ($B \rightarrow A + B$) and starch chain interactions (amylose and amylopectin). The unit cells of A-type starches are more densely packed than those of B-type starches. This structure suggests that closely packed A-type amylopectin chains could hinder the accessibility of H_3O+ towards the α-1,4 and α-1,6 glycosidic bonds. These authors reported that the extent of the decrease in acid susceptibility with HMT is mainly influenced by the extent of polymorphic transformation.

According to Gunaratne and Hoover (2002) the changes in the extent of acid hydrolysis with HMT can be explained through the interplay of the following factors: (1) crystallite disruption (increases acid hydrolysis by making more amorphous regions available); (2) interactions between starch chains (decreases hydrolysis by reducing chain flexibility and thereby hindering the conformational change); and (3) disruption of double helices in the amorphous region (increases hydrolysis by making glycosidic oxygen more accessible to protonation).

4.1.9. Impact of HMT on slowly digestible starch and resistant starch

Englyst, Kingman, and Cummings (1992) classified starch into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) based on the rate of glucose released during starch hydrolysis by digestive enzymes. RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion and SDS is a starch fraction that is digested completely in the small intestine at a lower rate as compared to RDS. RS is represented by the fraction of starch not digested in the small intestine of healthy individuals. SDS is the portion of starch converted to glucose between 20 and 120 min of in vitro enzyme hydrolysis and this type of starch predominates in most raw cereal products. Starch not hydrolysed after 120 min of in vitro enzyme hydrolysis is termed RS. SDS and RS are the starch fractions that have different positive impacts on human health. The main potential health benefits of SDS are linked to a stable glucose metabolism. According to Lehmann and Robin (2007) the SDS has a medium to low glycemic index and thus reduces the glycemic load of a food product compared to RDS with a high glycemic index. Therefore the production of SDS can have a positive effect in preventing diabetes and cardiovascular disease, because it stabilises the rate of glucose in the blood.

Shin, Kim, Ha, Lee, and Moon (2005) investigated the formation and structural characteristics of SDS in sweet potato starch under various hydrothermal treatments. They reported that depending on the temperature and the moisture content of the hydrothermal treatment, the SDS content could be doubled compared to the native starch. According to Chung et al. (2009b), when the starch was heat-moisture treated at 120 °C, the RDS decreased by 10.2%, 14.0%, and 15.1%, the SDS content increased by 2.5%, 2.8% and 4.7%, and the RS content increased by 7.7%, 11.2% and 10.4% for corn, pea, and lentil starches, respectively, as compared to gelatinised unmodified starches. These authors also reported that the increase in thermo-stable SDS and RS suggests that some interactions formed during hydrothermal treatments may have survived after gelatinisation, thereby partly restricting accessibility of starch chains to the hydrolysing enzymes. Niba (2003) also investigated the effect of heat treatment, storage temperature and time on digestibility of maize, potato, cocoyam, yam, plantain, and rice flours. This author reported that the SDS content for all flours were increased compared to the native flours.

RS is fermented in the large intestine and its properties are similar to those of dietary fibre; it has a prebiotic effect, acts on lipid metabolism, reduces cholesterol and reduces the risk of ulcerative colitis and colon cancer (Walter, Silva, & Denardin, 2005). The formation of resistant starch usually involves partial acid hydrolysis and hydrothermal treatments, heating, retrogradation, extrusion cooking, and chemical modification. Resistant starch has been classified into four general subtypes called RS 1–4. The four distinct classes of RS in foods are (1) RS 1: physically inaccessible starch, which is entrapped within whole or partly milled grains or seeds; (2) RS 2: some types of raw starch granules such as banana, potato and high-amylose corn starch; (3) RS 3: retrograded starch either processed from unmodified starch or resulting from food processing applications; and (4) RS 4: starches that are chemically modified to obtain resistance to enzymatic digestion, such as some starch ethers, starch esters, and cross-linked starches (Fuentes-Zaragoza et al., 2010; Ratnayake & Jackson, 2008; Sanz, Salvador, Baixauli, & Fiszman, 2009).

Physical methods to raise resistant starch content include hydrothermal treatments such as heat-moisture treatment and annealing (Jacobs & Delcour, 1998; Kurakake, Tachibana, Masaki, & Komaki, 1996). HMT may be used to increase resistant starch content in starch without the disruption of granular structure. According to Chung et al. (2009b), pea and lentil starches, which have higher amylose contents, showed higher levels of resistant starch than corn starch. These authors studied the effect of HMT (30% moisture/100 °C/24 h) on these starches and found that native and heat-moisture-treated corn starch had 4.6% and 10.5% resistant starch, respectively. Brumovsky and Thompson (2001) found that heat-moisture-treated high-amylose corn starch had 43.9% resistant starch compared to 18.4% in native starch.

4.2. Annealing (ANN)

ANN is the hydrothermal treatment of starch in the presence of excess water for an extended period of time. This treatment is performed at a temperature above the glass transition but below the gelatinisation temperature of starch (Gomes et al., 2005; Jayakody & Hoover, 2008). ANN specifically changes the physicochemical properties of starch by improving its crystalline perfection and facilitating interactions between the starch chains. The ANN process leads to a reorganisation of starch molecules and amylopectin double helices such that the structure acquires a more organised configuration (Gomes et al., 2005). The extent of starch chain mobility and the realignment of double helices on annealing may differ between cereal and tuber starches and also among cultivars. The ANN conditions for starches differ by botanical origin (Table 2).

It has been difficult to define what happens to the internal structure of starch granules in response to hydrothermal treatment. The main changes in annealed starches are as follows: (1) a reorganisation of the granular structure (Gomes et al., 2005; Waduge et al., 2006); (2) an increase in granular stability; (3) an increase in crystallinity (Waduge et al., 2006; Lan et al., 2008); (4) an increase in the interactions between starch chains in the amorphous and crystalline regions of the granules; (5) the formation of double helices (Chung et al., 2009b); (6) an elevation in the starch gelatinisation temperature and a sharpening of the gelatinisation range (Waduge et al., 2006; Lan et al., 2008); (7) a reduction in granular swelling and a change in the potential for and extent of amylose leaching (Gomes, Silva, Ricardo, Sasaki, & Germani, 2004; Gomes et al., 2005; Lan et al., 2008; Waduge et al., 2006); (8) a reduction in peak viscosity and retrogradation (Gomes et al., 2004, 2005); (9) an increase in enzymatic susceptibility (Serrano & Franco, 2005; Wang, Powel, & Oates, 1997); and (10) the formation of resistant starch (Chung et al., 2009b). However, the presence and degree of these changes depend on the source of the starch (Chung et al., 2009b).

Jayakody and Hoover (2008) referred to the two main models of the ANN process in semi-crystalline polymers as "sliding diffusion," in which complete molecular sequences move within a crystalline lattice (a mechanism that is favoured by the high mobility of the chains in the crystals) and/or "complete or partial fusion" of the crystals and a subsequent re-crystallisation of the melted materials at the ANN temperature.

4.2.1. Impact of ANN on starch swelling power and solubility

ANN generally reduces the swelling power of starch. This reduction is largely influenced by the interplay between the extent of crystalline perfection and the amylose–amylose and/or amylose–amylopectin interactions. Both crystalline perfection and amylose-chain interactions decrease the hydration of the amorphous regions of starch, thereby decreasing granular swelling. This reduced granular swelling due to ANN has specifically been observed in potato starch (Hoover & Vasanthan, 1994).

Gomes et al. (2005) explained that an increase in molecular organisation is responsible for the reduction in the swelling power and solubility of starch. ANN has also been reported to reduce swelling power in barley (Waduge et al., 2006), fermented cassava (Gomes et al., 2005), unfermented cassava (Gomes et al., 2004), bambarra groundnut (Adebowale & Lawal, 2002), and wheat (Lan et al., 2008) starches. Specifically, swelling power has been shown to be influenced by amylopectin structure (Sasaki & Matsuki, 1998),

Table 2
Annealing conditions for starches and references.

Starch source	Temperature (°C)	Time	Water content[a]	Reference
Potato	50	24 h	1:2 (w/w)	Jacobs et al. (1995)
	20 and 50	72 h	1:10 (w/w)	Kohyama and Sasaki (2006)
	48 and 53	24 h	1:2 (w/w)	Jacobs et al. (1998a)
Bambarra groundnut	50	24 h	1:2 (w/v)	Adebowale and Lawal (2002)
Corn	30–50	72 h	Excess	Liu et al. (2009)
	10 and 15	24 h	Excess	Chung et al. (2009a, 2009b)
	25–65	72 h	Excess	Tester et al. (2000)
	20 and 50	72 h	1:10 (w/w)	Kohyama and Sasaki (2006)
Waxy maize	55	168 h	Excess	Qi, Tester, Snape, and Ansell (2005)
Fermented cassava	50	72–240 h	1:5 (w/w)	Gomes et al. (2005)
Unfermented cassava	50	24–192 h	1:5 (w/w)	Gomes et al. (2004)
	50–60	48 h	1:2 (w/v)	Serrano and Franco (2005)
Barley	29–31	0.5–4 h	Excess	Kiseleva et al. (2004)
	50	72 h	Excess	Waduge et al. (2006)
Pea	10 and 15	24 h	Excess	Chung et al. (2009b)
	50	24 h	1:2 (w/w)	Jacobs et al. (1995)
Lentil	10 and 15	24 h	Excess	Chung et al. (2009b)
Rice	45–55	16 h	1:3 (w/w)	Dias et al. (2010)
	45–55	8–24 h	1:3 (w/w)	Hormdok and Noomhorm (2007)
	55	24 h	1:2 (w/w)	Jacobs et al. (1995)
Wheat	45	24 h	1:2 (w/w)	Jacobs et al. (1995)
	20 and 50	72 h	1:10 (w/w)	Kohyama and Sasaki (2006)
	48 and 53	24 h	1:2 (w/w)	Jacobs et al. (1998a)
Navy bean	50	24 h	Excess	Chung et al. (2010)
Yam bean	50	24 h	1:2 (w/v)	Adebowale et al. (2009)
Black bean	50	24 h	1:3 (w/w)	Hoover and Manuel (1996)
Sago	60	5 h	1:5 (w/w)	Wang et al. (1997)

[a] w/w: starch:water.

amylose content, and the extent of amylose–amylose- and/or amylopectin–amylopectin-chain interactions (Tester, Debon, & Sommerville, 2000). The reduced solubility of annealed starch is due to a strengthening of the bonds between amylose and amylopectin or between amylopectin molecules, preventing leaching out of the granules (Gomes et al., 2005).

According to Waduge et al. (2006), the swelling power of annealed barley starches was lower than their native counterparts. These authors reported that the extent of this reduction depended on the amylose content of barley starches and followed the order: normal > waxy > high amylose. The reduction in swelling power in the waxy starches on annealing is mainly due to the perfection of starch crystallites because crystallite perfection reduces the extent of hydration of the amorphous regions. In contrast, in the normal and high-amylose starches, the interplay of crystallite perfection and amylose–amylose interactions on annealing may have been responsible for the reduction in swelling power.

4.2.2. *Impact of ANN on starch pasting properties*

The impact of ANN on the pasting properties of starch is very controversial. According to Stute (1992) and Jacobs et al. (1995), ANN increases the paste temperature and final viscosity of potato starch and decreases its peak viscosity. Meanwhile, others (Jacobs, Eerlingen, & Delcour, 1996) have found that ANN increases the peak and final viscosities of wheat, pea, and rice starches. Taken together, published results suggest that the effect of ANN on starch pasting properties mainly depends on the structural characteristics of the starch and the analysis conditions. According to Jacobs et al. (1996), the influence of ANN on the pasting profile of starch varies with the heating and cooling rates applied during analysis. Depending on the rate of heating, annealed starches can better resist heat and mechanical stirring than native starches (Serrano & Franco, 2005).

Based on the work of Gomes et al. (2004), the bond strengthening promoted by ANN indicates that a higher temperature will be required to gelatinise starch granules. Adebowale et al. (2009) also reported that the increase in pasting temperature after hydrothermal treatments supports the fact that the modification process tends to increase the region of crystallinity as a result of the reorientation of the starch granules. The strengthening of intragranular bonded forces results in starch requiring more heat before structural disintegration and paste formation occurs. Along these lines, a reduction in retrogradation due to ANN was noted by Gomes et al. (2004), although Hormdok and Noomhorm (2007) found that retrogradation actually increased in annealed rice starch. In any case, ANN promotes a reorganisation of starch molecules, causing them to occupy a more stable conformation and decreasing amylose leaching.

4.2.3. *Impact of ANN on the gel texture*

Using ANN, temperature and time are the dominant factors affecting gel hardness. According to Cham and Suwannaporn (2010), the increase in crystalline perfection of granules by the ANN technique affected starch gel properties. Crystalline perfection resulted from an increase in mobility of the amorphous part, which facilitated the ordering of double helices and probably greater ordering in the amorphous regions (Lin, Wang, & Chang, 2008).

Chung, Moon, and Chun (2000) reported that ANN causes a rearrangement of starch molecules, resulting in the reduction of swelling power and solubility; this reduction in the volume of gel promotes an increase in gel hardness. Hormdok and Noomhorm (2007) also found an increase in gel hardness of rice starch subjected to annealing.

4.2.4. *Impact of ANN on granule morphology*

Several authors (Adebowale et al., 2005; Hoover & Vasanthan, 1994; Jacobs, Eerlingen, Spaepen, Grobert, & Delcour, 1998b; Jayakody, Hoover, Liu, & Donner, 2009; Stute, 1992) have found no changes to granule morphology on annealing of wheat, oat, lentil, potato, finger millet, and yam starches. However, Kiseleva et al. (2005) observed that the granules of high amylose and waxy wheat starches were slightly deformed on annealing and the extent of this deformation was greater in the waxy starch. According to Dias, Zavareze, Spier, Castro, and Gutkoski (2010), the annealed high-amylose rice starch granules presented pores on the surface, as compared with the native high-amylose starch granules. These authors also reported that the annealing slightly affected the morphology of medium- and low-amylose rice starches; the granules were more agglomerated compared to the native starches.

Liu, Yu, Simon, Dean, and Chen (2009) reported that all samples of corn starches annealed at 30 °C showed a similar thermal behavior as their corresponding native samples, indicating that this temperature was not high enough to affect the microstructures. However, the annealing treatment at 50 °C increased the granule sizes in all samples of corn starches with different amylose content, and the average rate of size change was increased with increasing amylopectin content. According to Waduge et al. (2006), the pore size of some barley cultivars also have been shown to increase slightly on annealing. The increase in granule size can be explained by the ingress of moisture through the amorphous regions of the starches during annealing.

4.2.5. *Impact of ANN on starch crystallinity*

The effects of ANN on crystallinity and X-ray diffraction patterns are dependent on the type of starch. The diffraction patterns of starch granules result from the parallel packing of left-handed, co-axial double helices in extended regular arrays (Lan et al., 2008). ANN is a condition in which granules assume a more stable configuration due to realignment of the polymer chains within the non-crystalline and crystalline regions of the granule, enhancing crystallinity. Lan et al. (2008) observed an increase in wheat starch crystallinity, while Waduge et al. (2006) demonstrated a similar increase in high-amylose barley starch after ANN treatment. Augmented crystallinity due to ANN may arise from the interplay of several factors, such as increased crystalline perfection, the generation of new crystallites formed by interactions between starch chains, and increased crystalline size and reorientation. However, Jayakody and Hoover (2008) found that a slight reduction in potato starch crystallinity due to ANN may be a reflection of crystalline disruption or reorientation, as reported by Vermeylen et al. (2006). According to Gomes et al. (2004), all annealed starches exhibit a reduced intensity of the crystallinity peak. These authors reported that the increase in helical order is not induced by the formation of amylose–lipid complexes, but rather by interactions between amylose and amylopectin chains. Reduced intercrystalline spacing may indicate that helical packing becomes more compact and organised.

Small-angle X-ray scattering peak positions after ANN of wheat and potato starches were unchanged, indicating that the repeat distance of crystalline and amorphous lamellae was not altered by the treatment (Jacobs et al., 1998a). According Jacobs and Delcour (1998), ANN may affect the individual lamellar sizes and the more pronounced peaks for the annealed starches, indicated by higher electron-density contrast between the amorphous and crystalline regions. Jenkins and Donald (1995) have also shown that amylose disrupts the packing of amylopectin crystallites by small-angle X-ray scattering of normal, waxy, and high-amylose corn and barley starches. These data suggest that because structural changes due to ANN occur within starch crystallites, the extent of these changes may be influenced by the number of crystalline defects (high amylose > normal > waxy) in native starches.

4.2.6. *Impact of ANN on starch gelatinisation characteristics*

Stute (1992) suggested that changes in DSC curves are sensitive indicators of the type of hydrothermal treatment that a starch underwent. He emphasised that narrower peaks after ANN indicate greater homogeneity during melting of the crystallites and swelling and hydration of the starch granules.

The effect of annealing on gelatinisation characteristics is well established, particularly using DSC, where there tends to be an increase in T_o and T_p, a decrease in the gelatinisation range (T_c–T_o) and either no change or an increase in gelatinisation enthalpy. The increase in gelatinisation temperatures is associated with a decrease in swelling power, provided that some granular structure is retained. This is reflected in a higher temperature for the onset of swelling and reduced swollen volume (Tester & Debon, 2000).

Adebowale et al. (2005) reported that an increase in T_o, T_p, and T_c reflects the melting of crystallites that are formed as a result of amylose–amylose and amylose–amylopectin interactions along the chains. These interactions suppress the swelling of the granule, leading to delayed gelatinisation and higher T_o, T_p, and T_c values. According to Kohyama and Sasaki (2006), the DSC endotherm associated with the gelatinisation of amylopectin shifted to a higher temperature and became narrower after ANN at 50 °C. These authors reported that the treatment increased the T_o and T_p values of gelatinisation, while the T_c and ΔH values were not changed by ANN.

Waduge et al. (2006) studied the effect of ANN on barley starches and reported that the treatment increased T_o, T_p, and T_c and decreased the temperature range (T_c–T_o). They also attributed such changes to the perfection of the crystalline structure and amylose–amylose and/or amylose–amylopectin interactions, leading to the formation of new double helices.

4.2.7. *Impact of ANN on the susceptibility of starch to enzymatic hydrolysis*

Some studies have indicated that annealed wheat, sago and rice starches are more easily hydrolysed by α-amylases than native starches (Dias et al., 2010; Jayakody & Hoover, 2008; Wang et al., 1997). These findings have been contradicted by other research on wheat, lentil and potato starches, although small starch granules (oat) have been reported to be much more easily hydrolysed post-annealing (Hoover & Vasanthan, 1994). The increase in hydrolysis with ANN has been attributed to an increase in granule porosity (O'Brien & Wang, 2008). A decrease in enzyme susceptibility with ANN has been attributed to crystallite perfection and amylose–amylose and/or amylose–amylopectin interactions (Hoover & Vasanthan, 1994; Hoover & Zhou, 2003).

ANN promotes changes in the amorphous areas of granules, making them more accessible to enzymatic activity. Jayakody and Hoover (2008) reported that ANN increased the susceptibility of wheat starch to fungal and bacterial enzymes. Meanwhile, Nakazawa and Wang (2003) observed that ANN promotes the formation of pores on the surface of starch granules. This porous structure could alter the enzymatic hydrolysis of starch depending on the type of starch and enzyme (O'Brien & Wang, 2008). For example, the enzymatic susceptibility of waxy, normal, and high-amylose corn starches specifically increases after ANN.

Because ANN promotes the formation of pores or fissures on the granular surface, the hydrolysis profile of the starch changes and α-amylase enters the granules more easily (Wang et al., 1997). According to Serrano and Franco (2005), despite the fact that the amorphous and crystalline lamellae of the granules become more ordered with ANN, the enzyme makes the amorphous areas more accessible. They also reported that although ANN increased the crystallinity of cassava starch, when evaluated by X-ray diffraction the annealed starch was found to be more susceptible to the action of α-amylase than the native starch.

4.2.8. *Impact of ANN on the susceptibility of starch to acid hydrolysis*

When a starch granule is treated with acid, the amorphous regions of the granule are preferentially hydrolysed, leaving intact the more resistant crystalline regions (Gallant et al., 1997). The amorphous regions of starch granules are less dense and therefore more susceptible to modifications than the more highly organised crystalline regions. The susceptibility of starch to acid hydrolysis depends of reaction time and the degree of hydrolysis.

The impact of ANN on the susceptibility of starch to acid hydrolysis has been shown to be influenced by the method used for annealing (single step, double step, or multistep), the starch source, and the ANN temperature (Hoover & Vasanthan, 1994; Nakazawa & Wang, 2003). According to Hoover and Vasanthan (1994), annealing in a single step has been reported to decrease the acid susceptibility of wheat, potato and lentil starches. However, Nakazawa and Wang (2003) showed that multistep ANN of wheat, tapioca, potato, maize, waxy maize and high amylomaize increased acid susceptibility during both phases of acid hydrolysis.

According to Jayakody et al. (2009), ANN reduced susceptibility to acid hydrolysis in yam starch. They also reported that variation in the extent of reduction in hydrolysis among the starches may reflect differences in the size and/or number of crystallites. These authors also reported that the perfection of starch crystallites during annealing cannot be considered as a factor influencing hydrolysis of the annealed starches.

Various theories have been advanced to explain the susceptibility of annealed starches to acid hydrolysis. The decrease in acid hydrolysis with ANN has been attributed to the perfection of starch crystallites, the formation of double helical structures between amylose chains, and the formation of V-amylose–lipid complexes (Hoover & Vasanthan, 1994; Jacobs et al., 1998a).

4.2.9. Impact of ANN on slowly digestible starch and resistant starch

According to Guraya, James, and Champagne (2001), the slowly digestible starch (SDS) can be produced by physical, chemical and enzymatic treatments. These authors reported that each produced SDS in different level and form depends upon the treatment condition. The annealing is hydrothermal method that has been used to modify starch digestibility. Chung et al. (2009b) investigated the effect of ANN on digestibility of corn, pea, and lentil starches and reported that the ANN increased the RDS and decreased SDS levels in all native granular starches. O'Brien and Wang (2008) explained that the increase in RDS levels on ANN is probably due to the formation of a more porous structure and the formation of a porous structure would allow greater accessibility of hydrolytic enzyme into the granular interior. Chung, Hoover, & Liu (2009a), in study with corn starch ANN at 50 °C, also found an increase in the RDS level and a decrease in SDS level.

Annealing has been used to enhance resistant starch (sum of starch and starch-containing products not absorbed in the small intestine) levels while maintaining granule structure (Brumovsky & Thompson, 2001). The initial temperature of gelatinisation in ANN should not be exceeded; therefore, there is no change in molecular structure due to the gelatinisation process. This modification makes the starch granule more organised and more stable, strengthening the links between the molecules of amylose and amylopectin. Brumovsky and Thompson (2001) studied the effect of ANN on high-amylose corn starch and reported that there is an increase of 53% in resistant starch compared to native starch. High-amylose maize starch has been used for enhancing resistant starch because it is digested very slowly. Chung, Liu, and Hoover (2010) found a reduction in the resistant starch content of annealed pea, lentil and navy bean starches compared to native starches, and they reported that the crystalline perfection and amylose–amylose and/or amylose–amylopectin interactions should have theoretically increased the resistant starch level. However, increased granule porosity caused by ANN may negate the effect of crystalline perfection and starch chain interactions on enzyme susceptibility. These authors studied the effect of dual modification (ANN–HMT and HMT–ANN) in gelatinised samples, which resulted in further increases in resistant starch levels.

Pomeranz (1992) and Kutos, Golob, Kac, and Plestenjak (2003) reported that the resistant starch content is related to gelatinisation and retrogradation, although its content in food depends of the type of processing, the amylose/amylopectin ratio, the storage time and the temperature and the amount of water used in processing. However, the change in resistant starch content promoted by ANN is not related to gelatinisation and retrogradation because the annealed starch does not gelatinise. The changes in resistant starch content are therefore related to structural changes, such as molecular reorganisation and changes in the crystallinity of starch.

5. Applications of hydrothermally treated starches

Hydrothermal modifications (HMT and ANN) of starches promote increased thermal stability and reduced retrogradation (Adebowale et al., 2005). Therefore, hydrothermally treated starches could be utilised in the canned and frozen food industries due to these respective advantages (Jayakody & Hoover, 2008). Collado and Corke (1999) studied some industrial applications of hydrothermally treated starches, including in their use in infant food, the processing of potato starch to replace corn starch in times of shortage, the production of starches with excellent freeze–thaw stability, and the improvement of the baking quality of potato starch.

The decrease in swelling power and amylose leaching and the elevation in heat and shear stability that result from HMT and ANN are all desirable properties for noodle manufacture. Hormdok and Noomhorm (2007) evaluated the quality of noodles when rice flour was substituted for rice starch modified by HMT and ANN. This study showed an improvement in the texture (adhesiveness, chewiness, and tensile strength) of the noodles prepared with hydrothermally modified rice starch. Miyazaki and Morita (2005) also investigated the properties of dough and bread made from wheat flour partially replaced by heat-moisture-treated corn starch to improve bread quality. Suzuki and Sekiya (1994a, 1994b) studied functional properties of industrialised HMT maize starch in search of an application for processed foods, such as pouch-packed food, canned food and for fillings.

Brumovsky and Thompson (2001) and Chung et al. (2009b) found that HMT and ANN may be used to enhance resistant starch levels while maintaining granular structure. According to Brumovsky and Thompson (2001), high-amylose corn starch treated by HMT or ANN was composed of 43.9% or 28.1% resistant starch, respectively, compared to 18.4% in native starch. These authors also demonstrated that partial starch hydrolysis with hydrochloric acid followed by hydrothermal treatment intensified the increase in resistant starch content. Acid hydrolysis may thus increase the mobility of starch chains. Finally, Jayakody and Hoover (2008) reported that resistant starch can be incorporated into foods without altering their appearance and texture, partly due to its bland taste and white colour, allowing it to be used as a fat mimetic or to increase the dietary fibre content of food.

HMT also has been used to prepare biodegradable films. Singh, Bawa, Riar, and Saxena (2009) characterised biodegradable films from native and HMT chestnut starches. The film elaborated with HMT starch presented higher peak force, puncture energy and tensile strength and lower solubility as compared to the native starch. These authors reported that the film forming ability of native and heat-moisture-treated starches showed a promising future for exploration as packaging material.

6. Conclusion

Among the known starch modifications, hydrothermal treatments are highly promising for generating food additives or ingredients that require specific properties. In the literature, there is a broad description of the physicochemical changes in starches of different botanical origins that result from hydrothermal treatments. The extent of these changes is influenced by the starch composition and source, the ratio of amylose to amylopectin, and treatment conditions (temperature, time, and moisture levels). However, the exact molecular mechanisms of these treatments remain poorly characterised. Therefore, it would be interesting to have more studies to investigate the effects of hydrothermal treatments on molecular structure of starches from different sources, such as location of amylose, amorphous zone size, amylose and amylopectin conformation and their interactions, as well as the interactions with water molecules intra and intermolecular before and after hydrothermal treatments. The study of hydrothermal treatment for starch modification is of interest due to its possible applications in the food industry, either for use alone or in combination with other types of starch modifications. There are studies that show that acid modifications in combination with hydrothermal modifications (HMT and ANN) have important properties such as the formation of RS. Furthermore, the combination of HMT with ANN can also change the SDS and RS contents. Therefore it would be interesting to study the effects of HMT and ANN with other physical and chemical modifications.

References

Abraham, T. E. (1993). Stabilization of paste viscosity of cassava starch by heat-moisture treatment. *Starch/Stärke*, *45*, 131–135.

Adebowale, K. O., Afolabi, T. A., & Olu-Owolabi, B. I. (2005). Hydrothermal treatments of Finger millet (Eleusine coracana) starch. *Food Hydrocolloids*, *19*, 974–983.

Adebowale, K. O., Henle, T., Schwarzenbolz, U., & Doert, T. (2009). Modification and properties of African yam bean (*Sphenostylis stenocarpa Hochst. Ex. A. Rich.*) Harms starch. I: Heat moisture treatments and annealing. *Food Hydrocolloids*, *23*, 1947–1957.

Adebowale, K. O., & Lawal, O. S. (2002). Effect of annealing and heat moisture conditioning on the physicochemical characteristics of bambarra groundnut (Voandzeia subterranea) starch. *Nahrung-Food*, *46*, 311–316.

Bemiller, J. N. (1997). Starch modification: Challenges and prospects. *Starch/Stärke*, *49*, 127–131.

Billiaderis, C. G. (1991). The structure and interactions of starch with food constituents. *Canadian Journal of Physiology and Pharmacology*, *69*, 60–78.

Brumovsky, J. O., & Thompson, D. B. (2001). Production of boiling-stable granular resistant starch by partial acid hydrolysis and hydrothermal treatments of high-amylose maize starch. *Cereal Chemistry*, *78*, 680–689.

Buléon, A., Colonna, P., Planchot, V., & Ball, S. (1998). Starch granules: Structure and biosynthesis. *International Journal of Biological Macromolecules*, *23*, 85–112.

Cham, S., & Suwannaporn, P. (2010). Effect of hydrothermal treatment of rice flour on various rice noodles quality. *Journal of Cereal Science*, *51*, 284–291.

Choi, S. G., & Kerr, W. L. (2003). Water mobility and textural properties of native and hydroxypropylated wheat starch gels. *Carbohydrate Polymers*, *51*, 1–8.

Chung, H. J., Hoover, R., & Liu, Q. (2009a). The impact of single and dual hydrothermal modifications on the molecular structure and physicochemical properties of normal corn starch. *International Journal of Biological Macromolecules*, *44*, 203–210.

Chung, H. J., Liu, Q., & Hoover, R. (2009b). Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches. *Carbohydrate Polymers*, *75*, 436–447.

Chung, H. J., Liu, Q., & Hoover, R. (2010). Effect of single and dual hydrothermal treatments on the crystalline structure, thermal properties, and nutritional fractions of pea, lentil, and navy bean starches. *Food Research International*, *43*, 501–508.

Chung, K. M., Moon, T. W., & Chun, L. K. (2000). Influence of annealing on gel properties of mung bean starch. *Cereal Chemistry*, *77*, 567–571.

Collado, L. S., & Corke, H. (1999). Heat-moisture treatment effects on sweet potato starches differing in amylose content. *Food Chemistry*, *65*, 339–346.

Dias, A. R. G., Zavareze, E. R., Spier, F., Castro, L. A. S., & Gutkoski, L. C. (2010). Effects of annealing on the physicochemical properties and enzymatic susceptibility of rice starches with different amylose contents. *Food Chemistry*, *123*, 711–719.

Englyst, H. N., Kingman, S. M., & Cummings, J. H. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition*, *46*, S33–S50.

Franco, C. M. L., Ciacco, C. F., & Tavares, D. Q. (1995). Effect of the heat-moisture treatment on the enzymatic susceptibility of corn starch granules. *Starch/Stärke*, *47*, 223–228.

Fuentes-Zaragoza, E., Riquelme-Navarrete, M. J., Sánchez-Zapata, E., & Pérez-Álvarez, J. A. (2010). Resistant starch as functional ingredient: A review. *Food Research International*, *43*, 931–942.

Gallant, D. J., Bouchet, B., & Baldwin, P. M. (1997). Microscopy of starch: Evidence of a new level of granule organization. *Carbohydrate Polymers*, *32*, 177–191.

Garcia, V., Colonna, P., Bouchet, B., & Gallant, D. J. (1997). Structural changes of cassava starch granules after heating at intermediate water contents. *Starch/Stärke*, *49*, 171–179.

Genkina, N. K., Wasserman, L. A., Noda, T., Tester, R. F., & Yuryeva, V. P. (2004). Effects of annealing on the polymorphic structure of starches from sweet potatoes (Ayamurasaki and Sunnyred cultivars) grown at various soil temperatures. *Carbohydrate Research*, *339*, 1093–1098.

Gerard, C., Colonna, P., Buleon, A., & Planchot, V. (2002). Order in maize mutant starches revealed by mild acid hydrolysis. *Carbohydrate Polymers*, *48*, 131–141.

Gomes, A. M. M., Silva, C. E. M., & Ricardo, N. M. P. S. (2005). Effects of annealing on the physicochemical properties of fermented cassava starch (polvilho azedo). *Carbohydrate Polymers*, *60*, 1–6.

Gomes, A. M. M., Silva, C. E. M., Ricardo, N. M. P. S., Sasaki, J. M., & Germani, R. (2004). Impact of annealing on the physicochemical properties of unfermented cassava starch (polvilho doce). *Starch/Stärke*, *56*, 419–423.

Gunaratne, A., & Hoover, R. (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydrate Polymers*, *49*, 425–437.

Guraya, H. S., James, C., & Champagne, E. T. (2001). Effect of enzyme concentration and storage temperature on the formation of slowly digestible starch from cooked debranched rice starch. *Starch/Stärke*, *53*, 131–139.

Güzel, D., & Sayar, S. (2010). Digestion profiles and some physicochemical properties of native and modified borlotti bean, chickpea and white kidney bean starches. *Food Research International*, doi:10.1016/j.foodres.2010.07.025

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers*, *45*, 253–267.

Hoover, R., & Manuel, H. (1996). Effect of heat-moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylomaize V starches. *Journal of Cereal Science*, *23*, 153–162.

Hoover, R., & Vasanthan, T. (1994). The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. *Journal of Food Biochemistry*, *17*, 303–325.

Hoover, R., & Zhou, Y. (2003). In vitro and in vivo hydrolysis of legume starches by a-amylase and resistant starch formation in legumes—A review. *Carbohydrate Polymers*, *54*, 401–417.

Hormdok, R., & Noomhorm, A. (2007). Hydrothermal treatments of rice starch for improvement of rice noodle quality. *LWT-Food Science and Technology*, *40*, 1723–1731.

Jacobs, H., & Delcour, J. A. (1998). Hydrothermal modifications of granular starch, with retention of the granular structure: A review. *Journal of Agricultural and Food Chemistry*, *46*, 2895–2905.

Jacobs, H., Eerlingen, R. C., Clauwaert, W., & Delcour, J. A. (1995). Influence of annealing on the pasting properties of starches from varying botanical sources. *Cereal Chemistry*, *72*, 480–487.

Jacobs, H., Eerlingen, R. C., & Delcour, J. A. (1996). Factors affecting the viscoamylograph and rapid visco-analyser evaluation of the impact of annealing on starch pasting properties. *Starch/Stärke*, *48*, 266–270.

Jacobs, H., Eerlingen, R. C., Spaepen, H., Grobert, P. J., & Delcour, J. A. (1998). Impact of annealing on the susceptibility of wheat, potato and pea starches to hydrolysis with pancreatin. *Carbohydrate Research*, *305*, 193–207.

Jacobs, H., Mischenko, N., Koch, M. H. J., Eerlingen, R. C., Delcour, J. A., & Reynaers, H. (1998). Evaluation of the impact of annealing on gelatinisation at intermediate water content of wheat and potato starches: A differential scanning calorimetry and small-angle X-ray scattering study. *Carbohydrate Research*, *306*, 1–10.

Jaillais, B., Ottenhof, M. A., Farhat, I. A., & Rutledge, D. N. (2006). Outer-product analysis (OPA) using PLS regression to study the retrogradation of starch. *Vibrational Spectroscopy*, *40*, 10–19.

Jane, J. (2006). Current understanding on starch granule structures. *Journal of Applied Glycoscience*, *53*, 205–213.

Jane, J., Chen, Y. Y., Lee, L. F., Mcpherson, A. E., Wong, K. S., Radosavljevic, M., et al. (1999). Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. *Cereal Chemistry*, *76*, 629–637.

Jane, J., & Shen, J. J. (1993). Internal structure of the potato starch granule revealed by chemical gelatinization. *Carbohydrate Research*, *247*, 279–290.

Jayakody, L., & Hoover, R. (2008). Effect of annealing on the molecular structure and physicochemical properties of starches from different botanical origins—A review. *Carbohydrate Polymers*, *74*, 691–703.

Jayakody, L., Hoover, R., Liu, Q., & Donner, E. (2009). Studies on tuber starches III. Impact of annealing on the molecular structure, composition and physicochemical properties of yam (Dioscorea sp.) starches grown in Sri Lanka. *Carbohydrate Polymers*, *76*, 145–153.

Jenkins, P. J., & Donald, A. M. (1995). The influence of amylose on starch granule structure. *International Journal of Biological Macromolecules*, *17*, 315–321.

Karlsson, M. E., & Eliasson, A. C. (2003). Gelatinization and retrogradation of potato (*Solanum tuberosum*) starch in situ as assessed by differential scanning calorimetry (DSC). *LWT-Food Science and Technology*, *36*, 735–741.

Kawabata, A., Takase, N., Miyoshi, E., Sawayama, W., Kimura, T., & Kudo, K. (1994). Microscopic observation and X-ray diffractometry of heat/moisture-treated starch granules. *Starch/Stärke*, *46*, 463–469.

Khunae, P., Tran, T., & Sirivongpaisal, P. (2007). Effect of heat-moisture treatment on structural and thermal properties of rice starches differing in amylose content. *Starch/Stärke*, *59*, 593–599.

Kiseleva, V. I., Genkina, N. K., Tester, R., Wasserman, L. A., Popov, A. A., & Yuryev, V. P. (2004). Annealing of normal, low and high amylose starches extracted from barley cultivars grown under different environmental conditions. *Carbohydrate Polymers*, *56*, 157–168.

Kiseleva, V. I., Krivandin, A. V., Fornal, J., Blaszczack, W., Jelinsk, T., & Yuryev, V. P. (2005). Annealing of normal and mutant wheat starches. LM, SEM, DSC and SAXS studies. *Carbohydrate Research*, *340*, 75–83.

Kohyama, K., & Sasaki, T. (2006). Differential scanning calorimetry and a model calculation of starches annealed at 20 and 50 °C. *Carbohydrate Polymers*, *63*, 82–88.

Kurakake, M., Tachibana, Y., Masaki, K., & Komaki, T. (1996). Adsorption of α-amylase on heat-moisture treated starch. *Journal of Cereal Science*, *23*, 163–168.

Kutos, T., Golob, T., Kac, M., & Plestenjak, A. (2003). Dietary fiber content of dry and processed beans. *Food Chemistry*, *80*, 231–235.

Kweon, M., Haynes, L., Slade, L., & Levine, H. (2000). The effect of heat and moisture treatments on enzyme digestibility of AeWx, Aewx and aeWx corn starches. *Journal of Thermal Analytical Calorimetry*, *59*, 571–586.

Lan, H., Hoover, R., Jayakody, L., Liu, Q., Donner, E., Baga, M., et al. (2008). Impact of annealing on the molecular structure and physicochemical properties of normal, waxy and high amylose bread wheat starches. *Food Chemistry*, *111*, 663–675.

Lawal, O. S., & Adebowale, K. O. (2005). An assessment of changes in thermal and physicochemical parameters of jack bean (*Canavalia ensiformis*) starch following hydrothermal modifications. *European Food Research Technology*, *221*, 631–638.

Lee, Y. E., & Osman, E. M. (1991). Correlation of morphological changes of rice starch granules with rheological properties during heating in excess water. *Journal of Korean Agricultural Chemical Society*, *34*, 379–385.

Lehmann, U., & Robin, F. (2007). Slowly digestible starch-its structure and health implications: A review. *Trends in Food Science and Technology*, *18*, 346–355.

Leliévre, J., & Liu, H. (1994). A review of thermal analysis studies of starch gelatinization. *Thermochimica Acta*, *246*, 309–315.

Lin, J. H., Wang, S. W., & Chang, Y. H. (2008). Effect of molecular size on gelatinization thermal properties before and after annealing of rice starch with different amylose contents. *Food Hydrocolloids*, *22*, 156–163.

Liu, H., Corke, H., & Ramsden, L. (2000). The effect of autoclaving on the acetylation of ae, wx and normal maize starches. *Starch/Stärke*, *52*, 353–360.

Liu, H., Yu, L., Simon, G., Dean, K., & Chen, L. (2009). Effects of annealing on gelatinization and microstructures of corn starches with different amylose/amylopectin ratios. *Carbohydrate Polymers*, *77*, 662–669.

Liu, Q. (2005). Starch modifications and applications. In S. W. Cui (Ed.), *Food carbohydrates: Chemistry, physical properties, and applications* (pp. 357–406). CRC Press, cap. 8.

Liu, Q., & Thompson, D. B. (1998). Effects of moisture content and different gelatinization heating temperatures on retrogradation of waxy-type maize starches. *Carbohydrate Research*, *314*, 221–235.

Lopez-Rubio, A., Flanagan, B. M., Gilbert, E. P., & Gidley, M. J. (2008). A novel approach for calculating starch crystallinity and its correlation with double helix content: A combined XRD and NMR study. *Biopolymers*, *89*, 761–768.

Maache-Rezzoug, Z., Zarguili, I., Loisel, C., Queveau, D., & Buléon, A. (2008). Structural modifications and thermal transitions of standard maize starch after DIC hydrothermal treatment. *Carbohydrate Polymers*, *74*, 802–812.

Miao, M., Zhang, T., & Jiang, B. (2009). Characterizations of kabuli and desi chickpea starches cultivated in China. *Food Chemistry*, *113*, 1025–1032.

Miyazaki, M., & Morita, N. (2005). Effect of heat-moisture treated maize starch on the properties of dough and bread. *Food Research International*, *38*, 369–376.

Morrison, W. R. (1995). Starch lipids and how they relate to starch granule structure and functionality. *Cereal Food World*, *40*, 437–446.

Nakazawa, Y., & Wang, Y. J. (2003). Acid hydrolysis of native and annealed starches and branch-structure of their Naegeli dextrins. *Carbohydrate Research*, *338*, 2871–2882.

Niba, L. L. (2003). Processing effects on susceptibility of starch to digestion in some dietary starch sources. *International Journal of Food Sciences and Nutrition*, *54*, 97–109.

O'Brien, S., & Wang, Y. J. (2008). Susceptibility of annealed starches to hydrolysis by a-amylase and glucoamylase. *Carbohydrate Polymers*, *72*, 597–607.

Olayinka, O. O., Adebowale, K. O., & Olu-Owolabi, B. I. (2008). Effect of heat-moisture treatment on physicochemical properties of white sorghum starch. *Food Hydrocolloids*, *22*, 225–230.

Parker, R., & Ring, S. G. (2001). Aspects of the physical chemistry of starch. *Journal of Cereal Science*, *34*, 1–17.

Pomeranz, Y. (1992). Research and development regarding enzyme resistant starch (RS) in the USA: A review. *European Journal of Clinical Nutrition*, *46*, S63–S68.

Pukkahuta, C., Suwannawat, B., Shobsngob, S., & Varavinit, S. (2008). Comparative study of pasting and thermal transition characteristics of osmotic pressure and heat-moisture treated corn starch. *Carbohydrate Polymers*, *72*, 527–536.

Pukkahuta, C., & Varavinit, S. (2007). Structural transformation of sago starch by heat-moisture and osmotic-pressure treatment. *Starch/Stärke*, *59*, 624–631.

Qi, X., Tester, R. F., Snape, C. E., & Ansell, R. (2005). The effect of annealing on structure and gelatinization of maize starches with amylose dosage series. *Progress in Food Biopolymers Research*, *1*, 1–27.

Ratnayake, W. S., & Jackson, D. S. (2008). Thermal behavior of resistant starches RS 2, RS 3, and RS 4. *Journal of Food Science*, *73*, 356–366.

Saibene, D., & Seetharaman, K. (2010). Amylose involvement in the amylopectin clusters of potato starch granules. *Carbohydrate Polymers*, *82*, 376–383.

Sanz, T., Salvador, A., Baixauli, R., & Fiszman, S. M. (2009). Evaluation of four types of resistant starch in muffins. II. Effects in texture, colour and consumer response. *European Food Research & Technology*, *229*, 197–204.

Sasaki, T., & Matsuki, J. (1998). Effect of wheat starch structure on swelling power. *Cereal Chemistry*, *75*, 525–529.

Serrano, P. O., & Franco, C. M. L. (2005). Modificação hidrotérmica (annealing) e hidrólise enzimática do amido de mandioca. *Brazilian Journal of Food and Technology*, *8*, 220–232.

Shin, S. I., Kim, H. J., Ha, H. J., Lee, S. H., & Moon, T. W. (2005). Effect of hydrothermal treatment on formation and structural characteristics of slowly digestible non-pasted granular sweet potato starch. *Starch/Stärke*, *57*, 421–430.

Singh, G. D., Bawa, A. S., Riar, C. S., & Saxena, D. C. (2009). Influence of heat-moisture treatment and acid modifications on physicochemical, rheological, thermal and morphological characteristics of Indian water chestnut (*Trapa natans*) starch and its application in biodegradable films. *Starch/Stärke*, *61*, 503–513.

Smith, A. M. (2001). The biosynthesis of the starch granule. *Biomacromolecules*, *2*, 335–341.

Stute, R. (1992). Hydrothermal modification of starches. The differences between annealing and heat-moisture treatment. *Starch/Stärke*, *44*, 205–214.

Suzuki, A., & Sekiya, S. (1994a). Application of heat-moisture treated starch, "derica star" to food materials. I: The application to pouchpacked and canned foods. *Food Chemicals*, *10*, 67–73.

Suzuki, A., & Sekiya, S. (1994b). Application of heat-moisture treated starch, "derica star" to food materials. II: The application to fillings. *Food Chemicals*, *10*, 93–98.

Tatge, H., Marshall, J., Martin, C., Edwards, E. A., & Smith, A. M. (1999). Evidence that amylose synthesis occurs within the matrix of the starch granule in potato tubers. *Plant, Cell and Environment*, *22*, 543–550.

Tester, R. F., & Debon, S. J. J. (2000). Annealing of starch—A review. *International Journal of Biological Macromolecules*, *27*, 1–12.

Tester, R. F., Debon, S. J. J., & Sommerville, M. D. (2000). Annealing of maize starch. *Carbohydrate Polymers*, *42*, 287–299.

Tester, R. F., & Karkalas, J. (1996). Swelling and gelatinization of oat starches. *Cereal Chemistry*, *73*, 271–273.

Tester, R. F., & Morrison, W. R. (1990). Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids. *Cereal Chemistry*, *67*, 551–557.

Thomas, D. J., & Atwell, W. (1999). *Starches: Practical guides for the food industry*. MN: Eagan Press., 94p.

Tsai, M. L., Li, C. F., & Lii, C. Y. (1997). Effects of granular structures on the pasting behaviors of starches. *Cereal Chemistry*, *74*, 750–757.

Van der Maarel, M. J. E. C., Van der Veen, B., Uitdehaag, J. C. M., Leemhuis, H., & Dijkhuizen, L. (2002). Properties and applications of starch-converting enzymes of the α-amylase family. *Journal of Biotechnology*, *94*, 137–155.

Varatharajan, V., Hoover, R., Liu, Q., & Seetharaman, K. (2010). The impact of heat-moisture treatment on the molecular structure and physicochemical properties of normal and waxy potato starches. *Carbohydrate Polymers*, *81*, 466–475.

Vermeylen, R., Goderis, B., & Delcour, J. A. (2006). An X-ray study of hydrothermally treated potato starch. *Carbohydrate Polymers*, *64*, 364–375.

Vieira, F. C., & Sarmento, S. B. S. (2008). Heat-moisture treatment and enzymatic digestibility of Peruvian carrot, sweet potato and ginger starches. *Starch/Stärke*, *60*, 223–232.

Waduge, R. N., Hoover, R., Vasanthan, T., Gao, J., & Li, J. (2006). Effect of annealing on the structure and physicochemical properties of barley starches of varying amylose content. *Food Research International*, *39*, 59–77.

Walter, M., Silva, L. P., & Denardin, C. C. (2005). Rice and resistant starch: Different content depending on chosen methodology. *Journal of Food Composition and Analysis*, *18*, 279–285.

Wang, W. I., Powel, A. D., & Oates, C. G. (1997). Effects of annealing on the hydrolysis of sago starch. *Carbohydrate Polymers*, *33*, 195–202.

Watcharatewinkul, Y., Puttanlek, C., Rungsardthong, V., & Uttapap, D. (2009). Pasting properties of a heat-moisture treated canna starch in relation to its structural characteristics. *Carbohydrate Polymers*, *75*, 505–511.

You, S., Stevenson, S. G., Izydorczyk, M. S., & Preston, K. R. (2002). Separation and characterization of barley starch polymers by a flow field-flow fractionation technique in combination with multiangle light scattering and differential refractive index detection. *Cereal Chemistry*, *79*, 624–630.

Zavareze, E. R., Storck, C. R., Castro, L. A. S., Schirmer, M. A., & Dias, A. R. G. (2010). Effect of heat-moisture treatment on rice starch of varying amylose content. *Food Chemistry*, *121*, 358–365.

Zhang, J., Wang, Z. W., & Shi, X. M. (2009). Effect of microwave heat/moisture treatment on physicochemical properties of canna edulis ker starch. *Journal of the Science of Food & Agriculture*, *89*, 653–664.

Zhang, T., & Oates, C. G. (1999). Relationship between α-amylase degradation and physico-chemical properties of sweet potato starches. *Food Chemistry*, *65*, 157–163.

Zhong, F., Li, Y., Ibanz, A. M., Oh, M. H., Mckenzie, K. S., & Shoemaker, C. (2009). The effect of rice variety and starch isolation method on the pasting and rheological properties of rice starch pastes. *Food Hydrocolloids*, *23*, 406–414.

Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch/Stärke*, *40*, 1–7.