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Effect of annealing on the molecular structure and physicochemical properties of starches from different botanical origins – A review

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ABSTRACT

Annealing is a hydrothermal treatment that changes the physicochemical properties of starches by improving crystalline perfection and by facilitating interactions between starch chains. The extent of these changes being influenced by starch composition and by the arrangement of the starch chains within the amorphous and crystalline domains of the native starch granules. During annealing, starch granules in excess or at intermediate water content are heated for a certain length of time, at a temperature above the glass transition but below the gelatinization temperature. This review summarizes the current knowledge on the effect of annealing on the granule morphology, composition, crystallinity, X-ray pattern, granular swelling, amylose leaching, pasting properties, gelatinization parameters, and acid and α-amylase hydrolysis of starches from cereals, legumes and tubers. The physical probes used in studying the mechanism of annealing, *in-vivo* annealing and the application of annealing in the food industry is also reviewed. Recommendations for future research is outlined.

1. Introduction

Starch is a semicrystalline biopolymer and is stored in various plant locations, for example in cereal grains, roots, tubers, stem-piths, leaves, seed, fruit and pollen. Starch granules in storage tissues can vary in shape, size and composition. The shape and size of the granules depend on the source. The chemical composition, structure and properties are also essentially typical of the biological origin of the starch (Smith, 2001). The importance of starch as a food stuff may be judged by the fact that it accounts for over 30% of the average diet on a dry weight basis and more than 25% on an available energy basis (Galliard, 1987). Starch granules in higher plants, regardless of the plant source, contain two principal types of polysaccharides, namely amylose and amylopectin. Amylose is a relatively long, linear polymer containing 99% α $(1 \rightarrow 4)$ and 1.0% α $(1 \rightarrow 6)$ linkages. The structure and size of amylose have been shown to vary among botanical sources (Biliaderis, 1998; Buléon, Colonna, Planchot, & Ball, 1998). The degree of polymerization (DPn) of amylose has been shown to vary from 324 to 4920 with 9 to 20 branch points (Hizukuri, 1993; Yoshimoto, Tashiro, Takenouchi, & Takeda, 2000). The molecular weight of amylose has been shown to range from 1×10^5 to 1×10^6 (Buléon et al., 1998). Amylopectin contains 95% α $(1 \rightarrow 4)$ and 5% α $(1 \rightarrow 6)$ linkages. The molecular weight and DPn of amylopectin has been shown to range from 1×10^7 to 1×10^9 and 9600 to 15,900, respectively (Buléon et al., 1998; Morrison & Karkalas, 1990; Takeda, Shibahara, & Hanashiro, 2003). Hizukuri (1996) has classified the amylopectin unit chains as A, B and C. The A chains are the shortest (DP 6–12) and are linked by a single α $(1 \rightarrow 6)$ linkage to the amylopectin molecule. B chains are classified into B1, B2, B3 and B4 depending on their respective length and the number of clusters they span (Hizukuri, 1996; Jane et al., 1999). The chain lengths ($\overline{\mathrm{C}}$L) of A, B_1–B_4 chains of amylopectins from different starch sources have been shown to be in the range 12–16, 20–24, 42–48, 69–75 and 101–119, respectively (Hizukuri, 1988; Wang & White, 1994). The most exterior chains (A and B1) have been shown to form double helices within the native granules, whereas the B2 to B4 chains act as connecting chains in the amylopectin molecule. The amylopectin component inside starch granules crystallizes into either A- or B-type structures (Katz and Van Itallie, 1930). The A-type structure is characteristic of cereal starches and the B-type of many tuber and high amylose starches. The C-type structure, which is a mixture of A- and B-type X-ray patterns, is characteristic of legume and some tuber starches. The A-type starch has a mono clinic unit cell, which is closely packed. In contrast, the B-type polymorphic starch has a hexagonal unit cell, which is relatively loosely packed with an open channel of water in the unit cell (Imberty, Buléon, Tran, & Péréz, 1991). The exact location of amylose and amylopectin within the granule interior is still in dispute. Blanshard (1986) proposed that amylose is present in the amorphous regions partially co-crystallized with amylopectin in potato starch. Jane and Shen (1993) have shown that in corn and potato starches, amylose is more concentrated at the

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granule periphery than at the core. Atkin, Cheng, Abeysekera, and Robards (1999) have shown the presence of alternating layers of densely packed amylopectin and amylose molecules. Whereas, in amylomaize starch, granules were shown to possess an amylopectin center surrounded by an amylose periphery encapsulated by an amylopectin surface. Jenkins and Donald (1995) have shown by small angle X-ray scattering studies on maize starches of varying amylose contents, that amylose disrupts the packing of amylopectin double helices within the crystalline lamella. Waduge, Hoover, Vasanthan, Gao, and Li (2006) have suggested, based on their study of barley starches of varying amylose content, that when the amylose content reaches a certain threshold, amylose chains may interact with amylopectin chains.

Native starches, are not widely utilized in the food industry due to their poor functional properties (poor thermal, shear and acid stability, and high rates and extent of retrogradation). Therefore, most starches currently incorporated into foods are chemically modified by cross-linking and/or substitution. At the present time, there is a great interest in the use of physical modification techniques such as annealing and heat–moisture treatment which modify the physicochemical property of starch without destroying its granular structure. Both heat–moisture treatment and annealing involve storage of starch at a specific temperature and at a certain moisture level during a certain time period. The term heat–moisture treatment is used when low moisture levels (<35% w/w) are applied. Whereas, annealing refers to treatment of starch in excess water (<65% w/w) or at intermediate water (40–55% w/w). Both heat–moisture treatment and annealing occur below the onset temperature of gelatinization and have been shown to modify starch structure and properties to different extents. Research geared to physical modification is important, since it is unlikely that any new chemical or genetic modification will be allowed to alter the functional properties of existing commercially based starches. Thus, this review will attempt to summarize, the present knowledge, on the impact of annealing on starch structure and properties.

2. Annealing (overview)

Annealing of starch, is a physical treatment of starch granules in the presence of heat and water. The effect of moisture content on '*in vitro*' annealing of wheat starch (Tester, Debon, & Sommerville, 2000) has shown (by the use of differential scanning calorimetry [DSC]) that annealing can be initiated at room temperature when the moisture content exceeds 22% on a total weight basis, but is restricted (in terms of its effect on increasing the gelatinization temperature) unless it exceeds 60% by weight. During annealing starch granules in excess (>60% [w/w]) or at intermediate water content (40% [w/w]) are held at a temperature above the glass transition temperature (T_g) but below the onset (T_o) temperature of gelatinization (Table 1) for a set period of time (Hoover & Vasanthan, 1994a; Jacobs & Delcour, 1998; Tester & Debon, 2000). T_g refers to the temperature at which the amorphous domains of the starch granule are transformed from a rigid glassy to a mobile rubbery state when heated in the presence of solvents such as water or glycerol. These solvents are referred to as plasticizers (Tester & Debon, 2000). The plasticizing effect of water increases glucan chain mobility within the amorphous lamella regions of the semicrystalline growth ring (Perry & Donald, 2000). Recently, Kweon, Slade, and Levine (2008) have shown that treatment of corn starch for 15 min at elevated pressures (600 MPa) resulted in annealing even at 25 °C. The above authors suggested that elevated pressure can induce annealing at a temperature significantly lower than the characteristic T_g at atmospheric pressure. The above pressure and temperature was shown to cause structural changes in the crystalline regions of amylopectin. Several authors (Jacobs & Delcour, 1998; Larsson & Eliasson, 1991; Lorenz, Collins, & Kulp, 1984; Muhrbeck & Svensson, 1996; Seow & Teo, 1993, Slade & Levine, 1987; Tester & Debon, 2000; Tester & Morrison, 1990) have described starch annealing as a crystal growth/perfection, diffusion controlled non-equilibrium process.

In semicrystalline polymers, annealing has been interpreted as: (1) a 'sliding diffusion', which entails the movement of complete molecular sequences within a crystalline lattice (this mechanism being favoured by high mobility of the chains in the crystals), and/or (2) a 'complete or partial fusion' of crystals and subsequent re-crystallization of the melted materials at the annealing temperature. There is experimental evidence that supports both proposed mechanisms (Martuscelli & Pracella, 1974). According to the side-chain liquid crystalline analogy of Waigh et al. (2000), the rigid amylopectin double helices are attached to an amorphous backbone (Fig. 1). Perry and Donald (2000) and Waigh, Jenkins, and Donald (1996) have proposed that double helices of the unhydrated form of starch are intact, but are not arranged regularly side by side (Fig. 1), due to the differing lengths of radial and tangential branches (Fig. 1). This state is called a nematic, collapsed or a 'withered state' (Fig. 1). The amorphous region of the granule is the area most vulnerable to the initial water absorption and plasticization. Before hydration the amorphous area is more glassy and immobile (Fig. 1); hydration of the starch granule increases the mobility of the amorphous regions. This induces vibrational movement of tangential and radial chains in both amorphous and crystalline domains (Fig. 1). Simultaneously hydration causes limited but reversible granule swelling, allowing mobility of crystalline domains (Fig. 1). An increase in annealing temperature (>T_g but <T_o) and excess water accelerates the rate of hydration and increases glucan chain mobility (Fig. 1). This dynamic nature allows limited side by side movement of the double helices (Perry & Donald, 2000; Waigh et al., 2000) resulting in the formation of a smectic-type structure (Fig. 1). An increase in the incubation temperature enhances initially, the order of the amorphous lamellae and, subsequently, the order of double helices of amylopectin (Tester, Debon, Davies, & Gidley, 1999). At this stage, molecules are closely aligned in a distinct series of layers, with their axes lying perpendicular to the plane of the layers (Fig. 1). With the progress of annealing the initially weaker or imperfect crystallites gradually disappear, while the rest of the crystallites become more perfect due to fusion and re-crystallization. The crystallite perfection on annealing was first suggested by Lorenz, Collins, and Kulp (1980). Stute (1992) postulated that crystalline perfection may also occur due to: (1) larger crystal formation from smaller crystals, (2) a change of crystal shape, (3) a change in direction of crystal growth, (4) orientation of crystallites, (5) interactions between crystallites, and (6) changes within the amorphous regions. This clearly indicates that crystalline perfection does not necessarily correlate with an increase in crystallinity. Native starch contains crystallites of varying stabilities. However, annealing decreases the above variations resulting in more homogenous crystallites (Hoover & Vasanthan, 1994a; Jacobs et al., 1998b; Larsson & Eliasson, 1991; Paredes-Lopez & Hernández-Lopez, 1991; Tester & Debon, 2000; Tester, Debon, & Karkalas, 1998; Tester & Morrison, 1990; Yost & Hoseney, 1986). Hoover and Vasanthan (1994a) and Jacobs, Eerlingen, Rouseu, Colonna, and Delcour (1998a) postulated that amylose chain mobility could increase on annealing, resulting in the formation of double helices arising from interactions between amylose–amylose and/or amylose–amylopectin chains.

2.1. Single, double and multi-step annealing

Studies on annealing have been mainly conducted as a single cycle event [single step annealing] (Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a; Hormdok & Noomhorm, 2007; Genkina, Wasserman, & Yuryev, 2004b; Genkina et al., 2004a; Genkina,

Table 1
Annealing parameters and gelatinization parameters for tuber, legume and cereal starches

Starch source	Annealing parameters				Gelatinization parameters						Reference
	Temp (°C)	Steps (≠)	Time (h)	W:S[a]	S:W[b]	T_o[c] (°C)	T_p[c] (°C)	T_c[c] (°C)	T_c–T_o[d]	Δ[e] (J/g)	
Potato (native)					1:03	54	58.8	64.5	10.5	16.8	Hoover and Vasanthan (1994a)
Potato (annealed)	50	Single	72	3:01	1:03	71.2	74.2	78.4	7.2	20.2	Hoover and Vasanthan (1994a)
Potato (native)						59.1	61.9	66.8	7.7	18.3	Vermeylen et al. (2006)
Potato (annealed)	51	Single	24	2:01		64.9	66.8	71.1	6.2	18.3	Vermeylen et al. (2006)
Potato (native)						*	*	*	*	*	Kohyama and Sasaki (2006)
Potato (annealed)	50	Single	72	10:01		61.1	63.1	70.7	9.6	18	Kohyama and Sasaki (2006)
Potato (native)						58.6	63	72.2	13.6	19.2	Jacobs et al. (1995, 1996)
Potato (annealed)	50	Single	24	2:11		64.8	67.7	73	8.2	19.9	Jacobs et al. (1995, 1996)
Potato (native)						58	62.5	70.5	12.5	18.7	Jacobs et al. (1998c)
Potato (annealed)	50 (1st step)	Two step	24	2:11		64.7	67.5	72.7	8	20	Jacobs et al. (1998c)
	55 (2nd step)		24	2:11		67.3	69.8	74.2	6.9	20.5	Jacobs et al. (1998c)
Potato (native)						60.4	64.4	69.7	9.3	16.9	Nakazawa and Wang (2004)
Potato (annealed)	40 (1st step)	Multi	24	3:01		–	–	–	–	–	Nakazawa and Wang (2004)
	45 (2nd step)		24	3:01		–	–	–	–	–	Nakazawa and Wang (2004)
	50 (3rd step)		24	3:01		71.4	74.5	78.5	7.1	18.5	Nakazawa and Wang (2004)
Cassava (native)						65.4	71.5	81.5	16.1	8.8	Atichokudomchai et al. (2002)
Cassava (annealed)	51	Single	72	3:01		70.7	74	81.3	10.6	9.4	Atichokudomchai et al. (2002)
Black bean (native)					1:03	58.5	67	74.2	15.7	8.4	Hoover and Manuel (1996)
Black bean (annealed)	50	Single	24	3:01	1:03	69.6	74	80.3	10.7	12.2	Hoover and Manuel (1996)
Pinto bean (native)					1:03	59	68	73	14	9.2	Hoover and Manuel (1996)
Pinto bean (annealed)	50	Single	24	3:01	1:03	64	73.5	79	9.6	9.6	Hoover and Manuel (1996)
Field pea (native)					1:03	58.7	69.3	72	13.3	9.6	Hoover and Manuel (1996)
Field pea (annealed)	50	Single	24	3:01	1:03	66.6	73.3	76.2	11.6	11.6	Hoover and Manuel (1996)
Lentil (native)					1:03	58.6	65.4	70.9	12.3	8	Hoover and Manuel (1996)
Lentil (annealed)	50	Single	24	3:01	1:03	66.9	70	74.9	8	10.2	Hoover and Manuel (1996)
Wheat (native)						–	–	–	*	–	Kohyama and Sasaki (2006)
Wheat (annealed)	20	Single		10:01	1:03	48.2	56.2	68.5	20.3	10.6	Kohyama and Sasaki (2006)
	50	Single		10:01	1:03	60.1	62.5	68.1	8.1	9.9	Kohyama and Sasaki (2006)
Wheat (native)						56.2	61.1	66.6	10.4	9.7	Hoover and Vasanthan (1994a)
Wheat (annealed)	50	Single	72	3:01	1:03	69.6	72	74.7	5.1	12.2	Hoover and Vasanthan (1994b)
Waxy barley (native)					01:04.5	53	59	68.6	15.6	10.8	Qi et al. (2004)
Waxy barley (annealed)	48	Single	168	Excess	01:04.5	65.4	67.4	73.3	7.9	11	Qi et al. (2004)
Normal maize (native)					1:05	56.9	67.7	76.5	19.6	17.6	Qi et al. (2005)
Normal maize (annealed)	55	Single	168	Excess	1:05	72.1	76.4	82.3	10.2	16.9	Qi et al. (2005)
Waxy maize (native)					1:05	62.2	70.7	78.7	16.5	17.3	Qi et al. (2005)
Waxy maize (annealed)	55	Single	168	Excess	1:05	73.3	77.3	83.1	9.8	17.3	Qi et al. (2005)
Normal maize (native)					1:03	64.7	71.1	–	–	2.6	Krueger et al. (1987a, 1987b)
Normal maize (annealed)	50	Single	48	Excess	1:03	68.4	73.4	–	–	3	Krueger et al. (1987a), Krueger et al. (1987b)
Waxy maize (native)					1:03	66.7	71.5	–	–	3.5	Krueger et al. (1987a, 1987b)
Waxy maize (annealed)	50	Single	48	Excess	1:03	69	73.3	–	–	3.4	Krueger et al. (1987a), Krueger et al. (1987b)
High Amylose maize (native)					1:03	70.6	79.8	–	–	4.5	Krueger et al. (1987a, 1987b)
High Amylose maize (annealed)	50	Single	48	Excess	1:03	72.3	79.2	–	–	5.7	Krueger et al. (1987a, 1987b)
Normal maize (native)					1:03	69.2	73.2	–	–	3.3	Knutson (1990)
Normal maize (annealed)	50	Single	24	3:01	1:03	70.4	74	–	–	3.2	Knutson (1990)
Waxy maize (native)					1:03	67.2	72.8	–	–	3.7	Knutson (1990)
Waxy maize (annealed)	50	Single	24	3:01	1:03	68.4	73.5	–	–	3.7	Knutson (1990)
High amylose maize (native)					1:03	70.1	75.6	–	–	2.1	Knutson (1990)
High amylose maize (annealed)	50	Single	24	3:01	1:03	70.9	77.6	–	–	3.2	Knutson (1990)
Sago (native)						–	70.1	–	–	15.1	Wang et al. (1997)
Sago (annealed)	60	Single	5	5:01	3:02	–	72.8	–	–	15.1	Wang et al. (1997)
Oat (native)						60.4	64.1	70	9.6	10.1	Hoover and Vasanthan (1994a)
Oat (annealed)	50	Single	72	3:01	1:03	64	67.1	71.3	7.3	12.2	Hoover and Vasanthan (1994b)
Wheat (native)					1:01	52	56.8	63.5	11.5	3.5	Jacobs et al. (1998b)
Wheat (annealed)	48 (1st step)	Two	24	2:01	1:01	60.2	62.3	65.6	5.4	5.7	Jacobs et al. (1998b)
	53 (2nd step)		24	2:01	1:01	63.1	65.1	68.4	5.3	6.2	Jacobs et al. (1998b)

(*continued on next page*)

Table 1 (*continued*)

Starch source	Annealing parameters				Gelatinization parameters						Reference
	Temp (°C)	Steps (≠)	Time (h)	W:S[a]	S:W[b]	T_o[c] (°C)	T_p[c] (°C)	T_c[c] (°C)	T_c–T_o[d]	Δ[e] (J/g)	
Wheat (native)						54.4	58.7	63.6	9.2	11.8	Jacobs et al. (1998c)
Wheat (annealed)	48 (1st step)	Two	24	2:01	1:02	61.6	63.7	66.9	5.3	12.2	Jacobs et al. (1998c)
	53 (2nd step)		24	2:01	1:02	64.2	66.3	69.7	5.5	12.3	Jacobs et al. (1998c)
Wheat (native)					1:05	52.5	58.7	71.5	19	10.4	Tester et al. (1998)
Wheat (annealed)	25		144	Excess	1:05	54.6	59.2	71.3	16.7	10.3	Tester et al. (1998)
	35	Single	144	Excess	1:05	59.2	59.7	72.9	13.7	11	Tester et al. (1998)
	45		144	Excess	1:05	63.7	59.4	76.3	12.6	10.4	Tester et al. (1998)
Wheat (native)					1:03	58.4	63.2	69	10.6	100	Shi (2008)
Wheat (annealed)	52	Single	4	3:01	1:03	67	69.4	73.2	6.2	8.8	Shi (2008)
Wheat (native)					1:03	58.4	63.2	69	10.6	10	Shi (2008)
Wheat (annealed)	51 (1st step)	Two	0.5	3:01	1:03	63.5	66	69.2	5.7	9.2	Shi (2008)
	56 (2nd step)		0.5	3:01	1:03	65.9	65.9	72.5	6.6	6.7	Shi (2008)
Waxy rice (native)					1:03	65	76.7	90.5	25.5	17.2	Tester and Morrison (1990)
Waxy rice (annealed)	55	Single	72	–	1:03	67.3	78.6	93	25.7	21.4	Tester and Morrison (1990)
	65		72	–	1:03	74	82.7	95.7	21.7	20	Tester and Morrison (1990)
Waxy rice (native)					1:03	76.2	81.2	87.1	10.9	19.2	Shi (2008)
Waxy rice (annealed)	70	Single	48	3:01	1:03	86.9	90	93.7	6.8	19.6	Shi (2008)
Normal rice (native)					1:03	67.7	73.5	78.7	11	13.2	Hormdok and Noomhorm (2007)
Normal rice (annealed)	55	Single	24	3:01	1:03	71.1	74.7	79.1	8	11	Hormdok and Noomhorm (2007)
Normal barley (native)					1:03	61.3	65.3	72.8	11.4	10	Waduge et al. (2006)
Normal barley (annealed)	50	Single	72	3:01	1:03	66.7	69.8	77	10.3	10	Waduge et al. (2006)
Waxy barley (native)					1:03	59.3	64.9	81.8	22.5	13	Waduge et al. (2006)
Waxy barley (annealed)	50	Single	72	3:01	1:03	66.2	70.2	82.9	16.7	13.4	Waduge et al. (2006)
High amylose barley (native)					1:03	61	67.9	76.6	15.6	6	Waduge et al. (2006)
High amylose barley (annealed)	50	Single	72	3:01	1:03	67.9	72.1	79	11.1	7	Waduge et al. (2006)

–, signifies that the data were not reported.

[a] Water: starch.

[b] Starch: water.

[c] Onset (T_o), mid-point (T_p) and conclusion (T_c) temperatures of gelatinization.

[d] Gelatinization temperature range.

[e] Enthalpy of gelatinization.

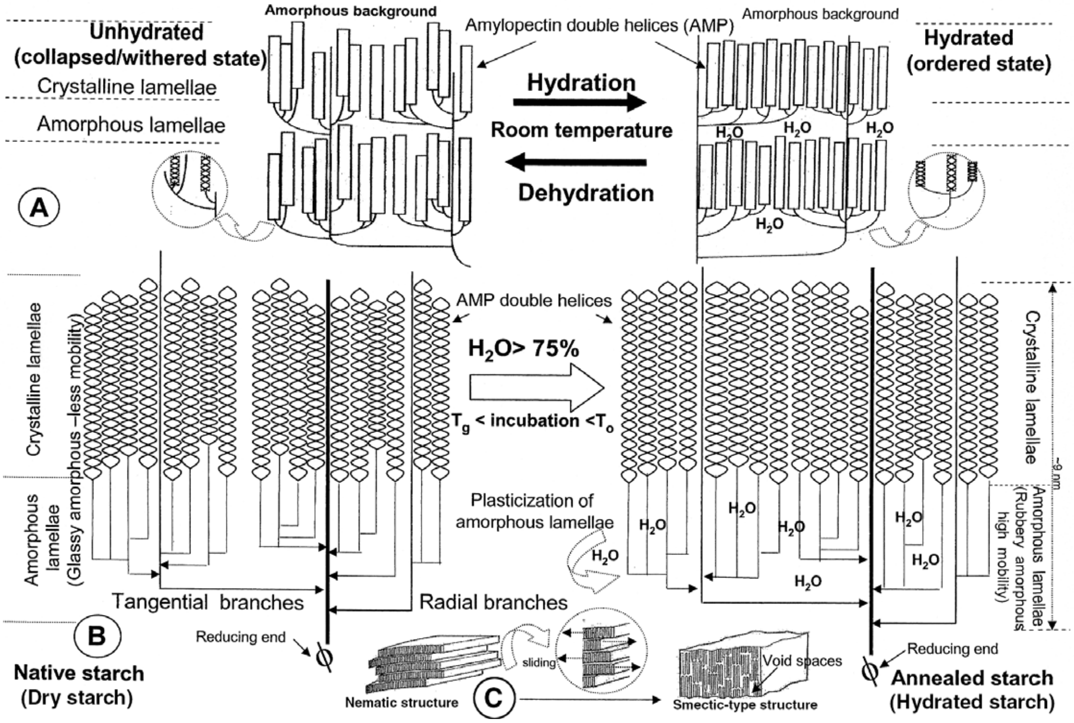

Fig. 1. Mechanism of annealing. (Adapted from Tester and Debon (2000), Waigh et al. (2000) and Martuscelli and Pracella (1974) with permission of The Royal Society of Chemistry Elsevier BV, and Elsevier.)

Wilkman, Bertoft, & Yuryev, 2007; Jacobs, Eerlingen, Clauwaert, & Delcour, 1995; Jacobs, Eerlingen, & Delcour, 1996; Karlsson & Eliasson, 2003a; Karlsson & Eliasson, 2003b; Kiseleva et al., 2004; Kiseleva et al., 2005; Kohyama & Sasaki, 2006; Koroteeva et al., 2007; Kozlov, Blennow, Krivandin, & Yuryev, 2007; Krueger, Knutson, Inglett, & Walker, 1987a; Krueger, Walker, Knutson, & Inglett, 1987b; Larsson & Eliasson, 1991; Lin, Wang, & Chang, 2008; Muhrbeck & Svensson, 1996; Muhrbeck & Wischmann, 1998; Ozcan & Jackson, 2003; Qi, Tester, Snape, & Ansell, 2005; Seow & Teo, 1993; Seow & Vasanti-nair, 1994; Stute, 1992; Tester et al., 1998; Tukomane, Leerapongnum, Shobsngob, & Varavinit, 2007; Vermeylen, Goderis, & Delcour, 2006; Waduge et al., 2006). Whereas, double (Genkina et al., 2007; Jacobs, Eerlingen, Spaepen, Grobert, & Delcour, 1998c; Jacobs et al., 1998a, 1998b; Shi, 2008) and multi-step (Knutson, 1990; Nakazawa & Wang, 2003, 2004; Shi, 2008) annealing have been carried out to a limited extent. The multi-step annealing involves initial annealing below T_o of the native starch, then re-annealing below T_o of the annealed starch. Since the first annealing increases T_o, the sample could be held at a higher annealing temperature, that is just below the new T_o, without triggering gelatinization. This process could be repeated until no further increase in T_o of the annealed starch.

2.2. Starch to water ratio on annealing treatment

Annealing of starches has been studied at various starch: water ratios (1:1, 1:3, 1:4, 1:5) and at temperatures ranging from 40 to 75 °C (Andreev, Kalistratova, Wasserman, & Yuryev, 1999; Atichokudomchai, Varavinit, & Chinachoti, 2002; Cameron & Donald, 1992; Genkina et al., 2004a, 2004b; Gomez, Mendes da Silva, Ricardo, Sasaki, & Germani, 2004; Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a, 1994b; Hormdok & Noomhorm, 2007; Jacobs, Eerlingen, Clauwaert, & Delcour, 1995; Jacobs et al., 1998b, 1998c; Kiseleva et al., 2004, 2005; Knutson, 1990; Kohyama & Sasaki, 2006; Kozlov et al., 2007; Krueger et al., 1987a, 1987b; Kuge & Kitamura, 1985; Larsson & Eliasson, 1991; Lawal, 2005; Lopez & Lopez, 1991; Muhrbeck & Svensson, 1996; Nakazawa & Wang, 2003, 2004; Ozcan & Jackson, 2003; O'Brien & Wang, 2008; Qi et al., 2004; Seow & Teo, 1993; Seow & Vasanti-Nair, 1994; Shi, 2008; Shih, King, Daigle, An, & Ali, 2007; Stute, 1992; Tester et al., 1998, 2000; Tukomane et al., 2007; Vermeylen et al., 2006; Wang, Powell, & Oates, 1997; Yost & Hoseney, 1986).

2.3. Probes used in the study of annealing

The effect of annealing on the morphology, structure and properties of starches has been probed using scanning electron microscopy (Hoover & Vasanthan, 1994a; Jacobs et al., 1998c; Kiseleva et al., 2005; Stute, 1992; Tukomane et al., 2007; Waduge et al., 2006; Wiegel, 1993), X-ray diffraction (Cameron & Donald, 1992; Gough & Pybus, 1971; Hoover & Manuel, 1996; Jacobs et al., 1998b; Lorenz et al., 1980; Muhrbeck & Wischmann 1998; Qi et al., 2005; Stute, 1992; Waduge et al., 2006), DSC (Freitas, Paula, Feitosa, Rocha, & Sierakowski, 2004; Genkina et al., 2007; Hoover & Vasanthan, 1994a; Hormdok & Noomhorm, 2007; Jacobs & Delcour, 1998; Jacobs et al., 1995, 1998b, 1998c; Kiseleva et al., 2004; Knutson, 1990; Krueger et al., 1987a, 1987b; Kuge & Kitamura, 1985; Larsson & Eliasson, 1991; Lin et al., 2008; Liu & Lelievre, 1991; Lorenz & Kulp, 1978; Lorenz et al., 1980, 1984; Muhrbeck & Eliasson, 1991; Muhrbeck & Svensson, 1996; Nakazawa & Wang, 2003; Ozcan & Jackson, 2003; Paredes-Lopez & Hernández-Lopez, 1991; Qi et al., 2005; Shi, 2008; Slade & Levine, 1987; Stute, 1992; Tester, Ansell, Snape, & Yusuph, 2005; Tester & Morrison, 1990; Tester et al., 1998, 2000; Tsutsui, Katsuta, Matoba, Takemasa, & Nishinari, 2005; Waduge et al., 2006; Wang et al., 1997; Yost & Hoseney, 1986; Zeleznak & Hoseney, 1987; Ziegler, Thompson, & Casasnovas, 1993), ^{13}C cross polarization magic angle spinning/NMR (Jacobs et al., 1998c; Lin et al., 2008; Tester & Karkalas, 1996; Tester & Debon, 2000), microscopy (Gough & Pybus, 1971; Hoover & Vasanthan, 1994a; Jacobs et al., 1998c; Kiseleva et al., 2005; Stute, 1992; Waduge et al., 2006; Wiegel, 1993), susceptibility to acids (Hoover & Vasanthan, 1994a; Jacobs et al., 1998a; Nakazawa & Wang, 2003; Tester et al., 1998; Waduge et al., 2006), enzymes (Gough & Pybus, 1971; Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a; Jacobs et al., 1998c; Kuge & Kitamura, 1985; Lauro et al., 1999; Lorenz et al., 1980; Wang et al., 1997), granule swelling (Adebowale, Olu-Owolabi, Olawumi, & Lawal, 2005a; Hoover & Vasanthan, 1994a; Hormdok & Noomhorm, 2007; Nakazawa & Wang, 2004; Tester et al., 1998; Tsutsui et al., 2005; Waduge et al., 2006), amylose leaching (Eliasson & Gudmundsson, 1996; Hoover & Vasanthan 1994a; Jacobs et al., 1998b; Knutson, 1990; Krueger et al., 1987a; Lorenz et al., 1984; Tsutsui et al., 2005, 1994a; Waduge et al., 2006), pasting (Hoover & Vasanthan, 1994a; Hormdok & Noomhorm, 2007; Jacobs et al., 1995; Stute, 1992; Tsutsui et al., 2005), in the presence of α-amylase (Tukomane et al., 2007), and after treatment of starch with acid and methanol (Lin et al., 2008).

2.4. Effect of annealing on granule morphology

Granule morphology, granule size distribution and surface characteristics play an important role in many food and non-food applications of starch, it was surprising to find that there is a dearth of information (especially for tuber and root starches) on the effect of annealing on the above parameters. Several authors (Hoover & Vasanthan, 1994a; Jacobs et al., 1998c; Stute 1992; Waduge et al., 2006; Wiegel, 1993) have found no changes to granule morphology on annealing of wheat, oat, lentil, barley (certain cultivars) and potato starches. However, Kiseleva et al. (2005) observed that the lens shaped granules of high amylose and waxy wheat starches were slightly deformed on annealing. The extent of this deformation being greater in the latter. Gough and Pybus (1971) observed a granule size increase (5 μm) on annealing of normal wheat starch. Wang et al. (1997) have postulated that annealing could create pores or fissures. The pore size of some barley cultivars have been shown to increase slightly on annealing (Waduge et al., 2006). Kiseleva et al. (2005) reported that the Maltese-cross and concentric growth rings in wheat starches remain unchanged on annealing. However, concentric growth rings were much denser after annealing.

2.5. Effect of annealing on starch structure

The following changes have been shown to occur on annealing: decrease in B-type crystallinity in high amylose barley (Waduge et al., 2006) and sweet potato (Genkina, Wasserman, Noda, Yuryev, & Tester, 2004c) starches, increase in granule stability (Hoover & Vasanthan, 1994a; Jacobs et al., 1995), crystallite growth and perfection/optimization (Hoover & Vasanthan, 1994a; Jacobs et al., 1998b; Larsson & Eliasson, 1991; Paredes-Lopez & Hernández-Lopez, 1991; Tester & Debon, 2000; Tester & Morrison, 1990; Tester et al., 1998; Yost & Hoseney, 1986), twisting of unordered ends of double helices (Tester et al., 1998, 1999), starch chain interactions within the amorphous and crystalline domains of the granule (Hoover & Vasanthan, 1994a; Jacobs & Delcour, 1998; Stute, 1992), increase in order within the amorphous domain without increase in crystallinity (Jacobs & Delcour, 1998; Tester & Debon, 2000) formation of double helices and compartmentalization of amylose–amylose (AM–AM) amylopectin–amylopectin (AMP–AMP) and AM–AMP helices (Atichokudomchai et al., 2002; Hoover & Vasanthan, 1994a; Jacobs et al., 1998a, 1998b; Knutson, 1990; Morrison, Tester, Gidley, & Karkalas, 1993a; Seow & Vasanti-Nair, 1994; Shi, Capitani, Trzasko, & Jeffcoat, 1998; Tester et al., 2000), amylose–lipid interactions (Jacobs et al., 1998b), extra reinforcing of the -D-(16) linkages (Jacobs et al., 1998a), polymer chain realignment within granules and partial crystallite melting (Marchant & Blanshard, 1980), mobility differences in amorphous or crystalline regions (Nakazawa, Noguchi, Takahashi, & Takada, 1984; Stute, 1992) and an increase in the glassy nature (more rigid and less mobile) of the amorphous material (Tester & Debon, 2000). However, annealing has been shown to have no influence on the wide angle X-ray diffraction pattern of maize (Muhrbeck & Wischmann, 1998; Qi et al., 2005; Waduge et al., 2006) legume (Hoover & Manuel, 1996) Cassava (Tukomane et al., 2007) and potato (Stute, 1992) starches. Vermeylen et al. (2006) have shown by small angle X-ray scattering studies on potato starch, that on annealing the 9 nm scattering intensity was more pronounced at 51 °C (closer to T_o) than at 44 or 47 °C. The enhanced intensity was attributed to more efficient packing of the double helices. The enhanced density contrast between the crystalline and amorphous lamellae was also observed in wheat starches by Jacobs et al. (1998b) and Kiseleva et al. (2005).

2.6. Effect of annealing on gelatinization characteristics

Annealing has been shown to increase the gelatinization temperatures (T_o, T_p, T_c) and decrease the gelatinization temperature range (Table 1) in all starches (Genkina et al., 2007; Hoover & Vasanthan, 1994a; Jacobs & Delcour, 1998; Jacobs et al., 1995, 1998c; Kiseleva et al., 2004; Knutson, 1990; Kohyama & Sasaki, 2006; Krueger et al., 1987a, 1987b; Kuge & Kitamura, 1985; Larsson & Eliasson, 1991; Lawal, 2005; Liu & Lelievre, 1991; Liu & Shi, 2006; Lorenz & Kulp, 1978; Lorenz et al., 1980, 1984; Muhrbeck & Eliasson, 1991; Muhrbeck & Svensson, 1996; Paredes-Lopez & Hernández-Lopez, 1991; Slade & Levine, 1987; Stute, 1992; Tester & Morrison, 1990; Tester et al., 1998, 2000, 2005; Tsutsui et al., 2005; Vermeylen et al., 2006; Waduge et al., 2006; Wang et al., 1997; Yost & Hoseney, 1986). However, the effect of annealing on the gelatinization enthalpy (ΔH) has been shown to vary among starch sources. For instance, on annealing, ΔH has been reported to increase (Atichokudomchai et al., 2002; Genkina et al., 2004b; Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a; Jacobs et al., 1995, 1998b, 1998c; Kiseleva et al., 2004; Kiseleva et al., 2005; Knutson, 1990; Krueger et al., 1987a, 1987b; Larsson & Eliasson, 1991; Muhrbeck & Svensson, 1996; Nakazawa & Wang, 2003; Slade & Levine, 1987; Waduge et al., 2006), remain unchanged (Eerlingen, Jacobs, Win, & Delcour, 1996; Muhrbeck & Wischmann, 1998; Jacobs et al., 1998c; Larsson & Eliasson, 1991; Qi et al., 2005; Seow & Teo, 1993; Shi & Seib, 1995; Stute, 1992; Waduge et al., 2006, Wang et al., 1997; Yost & Hoseney, 1986) or decrease (Kohyama & Sasaki, 2006; Larsson & Eliasson, 1991). The increase in gelatinization temperature has been shown to be most pronounced for T_o and least for T_c (Table 1). Annealing has a greater influence on T_o, since T_o represents melting of the weakest crystallites (Larsson & Eliasson, 1991; Nakazawa & Wang, 2003; Wang et al., 1997). These crystallites are more susceptible to crystallite perfection on annealing than crystallites that have higher stability (represent by T_c) (Jacobs et al., 1998b). The decrease in T_c–T_o on annealing indicates greater homogeneity and cooperative melting of crystallites (Jacobs & Delcour, 1998). Increase in starch mobility within the amorphous regions leads to a molecular re-organization which involves interaction between AM–AM and/or AM–AMP chains (Atichokudomchai et al., 2002; Hoover & Vasanthan, 1994a; Jacobs et al., 1998a, 1998b; Knutson, 1990; Morrison, Law, & Snape, 1993c; Morrison, Tester, Snape, Law, & Gidley, 1993b; Morrison et al., 1993a; Seow & Vasanti-Nair, 1994; Shi et al., 1998; Tester et al., 2000). This interaction together with crystallite perfection increases T_g. Consequently, this increases T_o, T_p and T_c in the annealed starches. Genkina et al. (2004b), Kiseleva et al. (2004), Qi et al. (2005), Tester et al. (2000, 1998) have postulated that changes to the gelatinization transition temperatures on annealing could also be due to lengthening of the double helices that were not optimized during biosynthesis. Kiseleva et al. (2004) have postulated that the lengthening of amylopectin pre-existing double helices on annealing could occur due to twisting of uncoiled ends resulting from an increase in glucan chain mobility. This twisting leads to the formation of additional intrahelical hydrogen bonds resulting in an increase in crystalline lamella thickness, which in turn elevates the melting temperature of amylopectin double helices. However, for such a mechanism to have a significant impact on gelatinization temperatures, the free ends of the double helices in the native starch, should be long enough to intertwine and form strong intrahelical hydrogen bonds.

Cooke and Gidley (1992) have shown by ^{13}C cross polarization magic angle spinning/NMR and DSC, that ΔH reflects the number of double helices that unravel and melt during gelatinization. Thus, starches in which ΔH remains the same pre- and post-annealing, suggests that the only molecular reorganization that occurs in these starches is crystalline perfection, and that the double helical order (number of double helices and stabilizing hydrogen bonds) is not influenced by annealing. Evidence for the constancy of ΔH pre- and post-annealing in normal wheat (Tester et al., 1998) and normal corn (Tester et al., 2000) starches was shown by ^{13}C-CP MAS/NMR. However, significant increases in ΔH have been shown to occur in high amylose barley (Waduge et al., 2006) and corn starches (Tester et al., 2000). Knutson (1990), Tester et al. (2000) and Waduge et al. (2006) hypothesized, that when amylose content reaches a certain threshold, amylose chains may be in close proximity to each other and/or with amylopectin chains. Consequently, on annealing interactions could occur between AM–AM and/or AM–AMP chains resulting in the formation of new double helices. Tester et al. (2000) showed using ^{13}C-CP MAS/NMR that the amount of double helices in amylomaize starch (63.1% amylose) increased by 11% on annealing (single step). The corresponding increase in ΔH being ~5%. Waduge et al. (2006) showed by studies on barley starches of varying amylose content (0–55.3%) that a particular cultivar (SB 94893) having the highest amylose content (55.3%) exhibited the largest increase in ΔH (~28%) on annealing. However, its unit amylopectin chain length distribution was higher (DP 5–17: 56.9%) than the barley cultivar SB 948907 (DP 5–17: 52.6%) [amylose content 43.7%] in which ΔH remained unchanged on annealing. This clearly demonstrates that the increase in ΔH is influenced by the interplay of: (1) amylose content, (2) location of amylose and amylopectin within the starch granule interior, and (3) amylopectin unit chain length distribution.

2.6.1. Impact of annealing temperature, moisture content and annealing time on gelatinization parameters

Several studies (Hoover & Vasanthan, 1994a; Knutson, 1990; Krueger et al., 1987a; Larsson & Eliasson, 1991; Lorenz et al., 1984; Slade & Levine, 1987; Tester & Debon, 2000) have shown that the effect of annealing on starch structure is more pronounced if the annealing temperature is set (close) to but below T_o. However, if the annealing temperature is set very close to T_o, then it would trigger starch gelatinization. Therefore, annealing temperatures are generally kept at about 5–15 °C (Table 1) below T_o (Eliasson & Gudmundsson, 1996; Tester & Debon, 2000). However, annealing temperatures (15–28 °C) below T_o have also been shown to have a significant impact on the gelatinization parameters of starches (Nakazawa & Wang, 2003; Tester et al., 1998). Krueger et al. (1987a) showed that on annealing T_o and T_p of maize starch increased gradually up to a moisture content of 67% (w/w), after which excess water had no further effect. Hoover and Vasanthan (1994a) reported steep increases in T_o, T_p and T_c at an annealing moisture of 50% in wheat and lentil starches and at 10% and 70%, respectively, in potato and oat starches. For ΔH, a steep increase was shown to occur at moisture contents of 40% and 50% in potato and wheat starches, respectively. Whereas, changes in ΔH for oat and lentil starches were gradual (Hoover & Vasanthan, 1994a). Interaction between AM–AM and/or AM–AMP chains would allow enthalpically driven assembly of the lamellar structure to be initiated with amylopectin double helices moving into alignment (Fig. 1). This would then explain the increase in gelatinization parameters with increase in moisture content.

The impact of annealing time on T_o, T_p, T_c and ΔH was studied by Hoover & Vasanthan, 1994a; Genkina et al., 2004a; Genkina et al., 2004b; Jacobs et al., 1998a; Kiseleva et al., 2005; Knutson, 1990; Larsson & Eliasson, 1991; Krueger et al., 1987a; Muhrbeck & Wischmann, 1998; Seow & Vasanti-Nair, 1994; Seow & Teo, 1993. In general, T_o, T_p and T_c increases with annealing time. The increase being more pronounced in T_o and least in T_c. Hoover and Vasanthan (1994a) showed that in oat, wheat, potato and lentil starches, increases in T_o, T_p, T_c and ΔH do not begin simultaneously during the time course of annealing (at 50 °C). The rates of increase in T_o, T_p and T_c were gradual in wheat and oat starches, but rapid in potato (during the first 30 min). Annealing beyond 24 h, did not significantly increase T_o, T_p, and T_c of oat, potato and lentil starches. However, those of wheat starch became more pronounced as the annealing time exceeded 24 h. Increases in ΔH were slower and were evident in wheat, oat, potato and lentil starches only after annealing had been in progress for 48, 6, 2 and 1 h, respectively. Genkina et al. (2004a) showed that T_o of sweet potato starches increased rapidly during the first 60 min of annealing (at 45 °C). After that, increments were much lower tending towards constant value after 8 h. Larsson and Eliasson (1991) reported that for wheat starch the largest changes in T_o, T_p, T_c and T_c–T_o occurred during the first 4 h of annealing (at 50 °C). No changes were observed after 6 h.

2.6.2. Impact of phosphorylation on gelatinization parameters

The extent of increase in gelatinization parameters on annealing has been shown to be influenced by the level of negatively charged phosphate groups located on the A-chains and on the inner and outer sections of the B-chains of amylopectin (Muhrbeck & Svensson, 1996). Studies on potato starches of varying degrees of phosphorylation (13–24 μmol G-6-P/g starch) showed that largest increase in T_p on annealing occurred for those samples with the lowest degree of phosphorylation. Whereas, the largest increase in ΔH was observed for the highly phosphorylated starches (Muhrbeck & Svensson, 1996). Muhrbeck, Svensson, and Eliasson (1991) showed that the degree of crystallinity (due mainly to amylopectin) is reduced by a high phosphate level. This was attributed to dislocations in the amylopectin clusters induced by bulky phosphate groups interfering with the building up of the structures during starch biosynthesis. Muhrbeck and Svensson (1996) postulated that reorientation of phosphate groups occur during annealing. Consequently, after annealing, the ΔH would be increased, since the double helices would be better aligned than in the native starch (phosphate groups in the native starch could hinder double helical chain realignment), resulting in stronger interhelical and intrahelical hydrogen bonding. The extent of this increase was found to be more pronounced in the high phosphate level starches, since in their native state ΔH is lower (due to greater extent of crystallite disruption) than in the low phosphate level starches. The increase in T_p on annealing was found to higher in the low phosphate level starches, presumably due to less crystallite disruption in the native state. Muhrbeck and Svensson (1996) and Muhrbeck and Wischmann (1998) have reported that covalently bound starch–phosphate esters are not hydrolyzed during annealing.

2.7. Impact of annealing on amylose–lipid complex formation

Morrison, Tester, Snape, Law, and Gidley (1993b) and Morrison, Law, and Snape (1993c) have shown (^{13}CCP-MAS NMR, DSC, X-ray) the presence of amylose–lipid complexes in native starch granules of barley, maize, rice and oat starches. DSC studies have shown that the amylose–lipid complex transition occurs in the range 85–115 °C (Biliaderis, Page, & Maurice, 1986; Biliaderis, Page, Slade, & Sirett, 1985; Kugimiya & Donovan, 1981; Russell, 1987; Slade & Levine, 1988), 96–125 °C (Karkalas, Ma, Morrison, & Pethrick, 1995), ~110 °C (Nakazawa & Wang, 2004) and 93.2–96.8 °C (Andreev et al., 1999). Tester et al. (2005) postulated that since amylose–lipid complexes are distinct entities and they are unlikely to be formed during annealing (Tester et al., 2005). Several reports have indicated that new amylose–lipid complexes are not formed during single or double step annealing (Jacobs et al., 1998c; Kiseleva et al., 2005; Larsson & Eliasson, 1991; Nakazawa & Wang, 2004). This was based on the DSC amylose–lipid complex melting endotherm (Jacobs et al., 1995, 1998a; Kiseleva et al., 2005; Kohyama & Sasaki, 2006; Larsson & Eliasson, 1991; Nakazawa & Wang, 2004; Wasserman, Misharine, & Yuryev, 2002), the ^{13}C.CP/MAS NMR Signal at 31 ppm (Jacobs et al., 1998a) and the apparent amylose content (Kohyama & Sasaki, 2006) remaining unchanged on annealing. This was attributed to the annealing temperature range (35–50 °C) being much lower than the melting temperature range (85–125 °C) of the amylose–lipid complex (Larsson & Eliasson, 1991). Andreev et al. (1999) have shown by DSC studies on normal (maize, wheat, barley, rye) and high amylose (barley) starches, that only maize starch has the ability to form additional amylose–lipid complexes on annealing. Wasserman et al. (2002) have postulated that the ability of maize starch to form additional amylose–lipid complexes on annealing may be due to the entry of surface lipids (via the channels on granule surface) into the granule interior. It is likely, that once inside the granule interior, the thermal energy imparted to the fatty acid chain during annealing may increase its mobility, thereby facilitating its interaction with the amylose helix. Lorenz et al. (1984) and Waduge et al. (2006) have shown increases in the intensity of V-amylose–lipid complex ($2\theta \sim 20°$) in barley starches on annealing. However, the enthalpy of the melting of amylose–lipid complex remained unchanged on annealing (Waduge et al., 2006). Waduge et al. (2006) have proposed that the increased intensity of the amylose–lipid peak on annealing was not due to formation of additional amylose–lipid complexes, but to enhanced ordering of lipid molecules that were present as amylose–lipid complexes within granules of native barley starches.

2.8. Impact of annealing on X-ray diffraction pattern and crystallinity

Gough and Pybus (1971) were the first to study X-ray diffraction patterns of annealed starches. Muhrbeck and Wischmann (1998) reported that the effect of annealing is more pronounced in B-type starches than on A-type starches. Annealing of barley (Waduge et al., 2006), potato (Hoover & Vasanthan, 1994a; Jacobs et al., 1998a; Vermeylen et al., 2006), new coco yam (Lawal, 2005), cassava (Tukomane et al., 2007), wheat (Gough & Pybus, 1971; Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a; Jacobs et al., 1998a; Qi et al., 2005; Stute, 1992), oat (Hoover & Vasanthan, 1994a), pea (Hoover & Manuel, 1996), lentil (Hoover & Vasanthan, 1994a) and maize (Ozcan & Jackson, 2003; Qi et al., 2005) starches have shown no effect on their polymorphic pattern. However, in some varieties of barley (Waduge et al., 2006), sweet potato (Genkina et al., 2004c), and cassava (Gomez et al., 2004), starches, the A+B X-ray diffraction pattern changes to a A-type pattern on annealing. The X-ray intensities has been shown to increase slightly in potato, lentil, oat, wheat (Hoover & Vasanthan, 1994a), and barley (Jacobs et al., 1998b; Waduge et al., 2006) starches on annealing.

X-ray crystallinity has been shown to increase on annealing in high amylose barley (Waduge et al., 2006), normal wheat (Hoover & Vasanthan, 1994a), and to decrease in potato (Vermeylen et al., 2006) or remain unchanged in potato (Jacobs & Delcour, 1998), normal wheat (Jacobs & Delcour, 1998; Slade & Levine, 1987), normal maize (Ozcan & Jackson, 2003), pea (Jacobs & Delcour, 1998), and in normal and waxy barley (Waduge et al., 2006) starches. Tukomane et al. (2007) showed that annealing of tapioca starch close to the onset temperature of gelatinization combined with the addition of α-amylase were found to increase the relative crystallinity of starch by removal of the amorphous region without changing the X-ray pattern. The increase in crystallinity on annealing reflects the interplay of the following factors: (1) amylopectin content (Waduge et al., 2006), (2) changes in orientation of the starch crystallites (Tester & Debon, 2000), (3) crystallite perfection (Jacobs & Delcour, 1998; Larsson & Eliasson, 1991; Lorenz et al., 1984; Muhrbeck & Svensson, 1996; Seow & Teo, 1993; Slade & Levine, 1987; Tester & Debon, 2000; Tester & Morrison, 1990), (4) enhanced ordering of the V-amylose–lipid complex (Lorenz et al., 1984) and (5) formation of amylose crystallites (Krueger et al., 1987a, 1987b). The unchanged crystallinity observed in some starches on annealing is indicative that changes in factors 2 to 5 may have been of a low order of magnitude. The slight decrease in crystallinity reported by Vermeylen et al. (2006) may be a reflection of crystallite disruption or crystallite reorientation. However, the above authors have not provided any explanation for this phenomenon.

2.9. Impact of annealing on granular swelling

Annealing has been shown to reduce granular swelling in potato (Debon & Tester, 2000; Hoover & Vasanthan, 1994a; Nakazawa & Wang, 2004), cassava (Nakazawa & Wang, 2004), breadfruit (Adebowale et al., 2005a), wheat (Hoover & Vasanthan, 1994a; Lorenz & Kulp, 1978; Tester et al., 1998), corn (Nakazawa & Wang, 2004; Qi et al., 2005), lentil (Hoover & Vasanthan, 1994a), oat (Hoover & Vasanthan, 1994a), pea (Hoover & Manuel, 1996), and barley (Waduge et al., 2006) starches. The decrease in granular swelling has been attributed to the interplay of the following factors: (1) increased crystalline perfection and decreased hydration (Tester et al., 1998; Waduge et al., 2006), (2) AM–AM and/or AMP–AMP interaction (Jacobs et al., 1998b), (3) increased intragranular binding forces and reinforcement of the granule (Hizukuri, 1996; Jacobs et al., 1995), and (4) V-amylose–lipid complex formation (Hoover & Vasanthan, 1994a; Jacobs et al., 1998b; Waduge et al., 2006).

2.10. Impact of annealing on amylose leaching (AML)

Annealing has been shown to reduce amylose leaching at all temperatures (below 100 °C) in potato (Hoover & Vasanthan, 1994a; Jacobs et al., 1995; Kuge & Kitamura, 1985; Nakazawa & Wang, 2004), wheat (Hoover & Vasanthan, 1994a; Lorenz & Kulp, 1978), lentil and oat (Hoover & Vasanthan, 1994a), pea and rice (Jacobs et al., 1995), cassava (Gomez et al., 2004), and certain cultivars of barley (Waduge et al., 2006) starches. However, an increase in AML has been reported for wheat (Jacobs et al., 1995) and in certain cultivars of barley starches (Waduge et al., 2006) on annealing. The reduction in AML has been attributed to the interplay of the following: (1) interactions between AM–AM and/or AM–AMP (Hoover & Vasanthan, 1994a; Waduge et al., 2006), (2) decrease in granular swelling (Tester et al., 2000), and (3) increase in V-amylose–lipid content (Tester et al., 2000; Waduge et al., 2006).

2.11. Impact of annealing on pasting properties

The effects of annealing on pasting properties are complex and vary among starches. The information currently available on the pasting properties of annealed starches is for wheat (Jacobs, Eerlingen, & Delcour, 1996; Jacobs et al., 1995), lentil (Hoover & Vasanthan, 1994a), rice (Shih et al., 2007), oat (Hoover & Vasanthan, 1994a), potato (Hoover & Vasanthan, 1994a; Jacobs et al., 1995; Stute, 1992), pea (Jacobs et al., 1995, 1996), rice (Hormdok & Noomhorm, 2007; Jacobs et al., 1995), breadfruit [*Artocarpus artilis*] (Adebowale et al., 2005a), sorghum (Adebowale, Olu-Owolabi, Olayinka, & Lawal, 2005b), and bambarra ground nut [*Voandzeia subterranean*] (Adebowale & Lawal, 2002) starches. Generally, annealing has been shown to increase the pasting temperature, thermal stability and decrease peak viscosity and the viscosity at the end of the cooling cycle (Adebowale & Lawal, 2002; Adebowale et al., 2005a; Hoover & Vasanthan, 1994a; Jacobs et al., 1995, 1996; Stute, 1992). The exceptions being, rice (Jacobs et al., 1995), wheat (Hoover & Vasanthan, 1994a; Jacobs et al., 1995), and pea (Jacobs et al., 1995) starches which exhibit a higher peak viscosity (wheat > pea > rice) on annealing. The reduced viscosity and improved shear stability on annealing has been attributed to reduced granular swelling and amylose leaching, and increased interaction between starch chains during annealing (Hoover & Vasanthan, 1994a; Jacobs et al., 1995; Stute, 1992). The increase in viscosity exhibited by wheat starch on annealing was attributed by Jacobs et al. (1995) to an increase in granule rigidity and resistance to shear. Hoover and Vasanthan (1994a) have shown by DSC studies, that on annealing, wheat starch exhibits a higher decrease in T_c–T_o than potato starch. They attributed this to interaction between double helices (in the crystalline domain) being more extensive in wheat than in potato starch. Thus, although, the extent of granular swelling is reduced (wheat > potato) as a result of annealing, the increase in granular stability of wheat starch on annealing is so high that it negates the effect of decreased granular swelling on peak viscosity. This would then explain why the viscosity of wheat starch increases on annealing, whereas that of potato starch decreases.

2.12. Impact of annealing on acid hydrolysis

The impact of annealing on acid hydrolysis has been shown to be influenced by the method used for annealing (single step, double step, and multi-step), annealing temperature and starch source (Waduge et al., 2006, Qi et al., 2005; Nakazawa & Wang, 2003; Jacobs et al., 1998a; Tester et al., 1998; Hoover & Vasanthan, 1994a). Waduge et al. (2006) reported that in starches extracted from different cultivars of barley, the difference in acid hydrolysis [single step, 0.25 g starch/10 mL 2.2 M HCl, at 35 °C/18 days] between native and annealed starches was only marginal. No difference in hydrolysis was observed between native and annealed wheat and pea starches subjected to double step annealing [0.167 g starch/10 mL 2.2 M HCl, at 35 °C/20 days] (Jacobs et al., 1998a). However, Nakazawa and Wang (2003) showed by studies on potato, wheat, cassava, maize and high amylose maize starches that annealing increased acid susceptibility [multi-step, 15.3% H_2SO_4, 0.5 g starch/10 mL, at 30 °C/30 days] in all starches, with potato starch showing the greatest and high amylose maize starch showing the smallest change. Tester et al. (1998) reported that during the rapid phase of acid hydrolysis [single step, 0.1 g starch/10 mL, 2 M HCl, at 35 °C/10 days], annealed wheat starch was more extensively degraded than its native counterpart, while during the slow phase of hydrolysis, there was no difference in the extent of hydrolysis. Hoover and Vasanthan (1994a) reported that in potato, lentil, oat, and wheat the difference in acid hydrolysis [single step, 0.25 g starch/10 mL 2.2 M HCl, at 35 °C/20 days] between native and annealed starches were ~5%.

The decrease in acid hydrolysis on annealing has been attributed to: (1) perfection of starch crystallites (Waduge et al., 2006), (2) formation of double helical structures between amylose chains (Jacobs et al., 1998a), (3) increased embedding of -(16) branch points within the crystalline structure (Jacobs et al., 1998a), and (4) formation of V-amylose–lipid complexes (Hoover & Vasanthan, 1994a; Jacobs et al., 1998a; Waduge et al., 2006). The increase in acid hydrolysis on annealing has been attributed to: (1) an increase in the concentration of -glucan in the amorphous region as a consequence of crystalline perfection (Tester et al., 2000) and (2) formation of void spaces in the crystalline lamellae due to crystalline perfection (Nakazawa & Wang, 2003). Similarity in acid hydrolysis between native and annealed starches during the slow phase of hydrolysis has been attributed to: (1) limited crystallite perfection and (2) unchanged double helical content pre- and post-annealing (Nakazawa & Wang, 2003; Tester et al., 2000).

In summary, there is conflicting information with respect to the susceptibility of annealed starches towards acid hydrolysis. For instance, the same type of starch (e.g. potato or corn or wheat) has been shown to behave differently towards H_3O^+ after annealing (Hoover & Vasanthan, 1994a; Jacobs et al., 1998a; Nakazawa & Wang, 2003; Tester et al., 2000). This could be attributed to differences in: (1) variety of the starch source, (2) number of steps used in annealing [single vs double vs multi-step], (3) type of acid [HCl vs H_2SO_4], (4) acid concentration [1.7 M H_2SO_4 vs 2.2 M HCl] and (5) temperature of the reaction mixture [35 °C vs 38 °C].

2.13. Impact of annealing on α-amylase hydrolysis

There is a dearth of information on the impact of annealing on α-amylase hydrolysis, and what is available is often conflicting. It is difficult to find a consensus of the action pattern of α-amylase on native and annealed starches reported in the literature (Gough & Pybus, 1971; Hoover & Manuel, 1996; Hoover & Vasanthan, 1994a; Jacobs et al., 1998c; O'Brien & Wang, 2008; Wang et al., 1997). This could be attributed to differences in α-amylase sources, enzyme purity, enzyme concentration, time of hydrolysis, varietal differences, annealing temperature, time and the number of annealing steps. Annealing has been shown to increase the susceptibility of wheat starch towards fungal α-amylase (Lorenz et al., 1980) and bacterial α-amylase (Gough and Pybus (1971)). However, Jacobs et al. (1998c) showed by using pancreatin (a mixture of α-amylase from porcine pancreatic stomach mucosa, lipase and protease) that during early stages of hydrolysis (<20 h), susceptibility of one step and double step annealed wheat starches is lower than that of its native counterpart. However, during the latter stages (>20 h) this trend is reversed. Hoover and Vasanthan (1994a) reported that the susceptibility of annealed (single step) wheat starch towards porcine pancreatic α-amylase was lower than its native counterpart throughout the time course of hydrolysis. Both single step (Hoover & Vasanthan, 1994a; Jacobs et al., 1998c) and double step (Jacobs et al., 1998c) annealing have been shown to decrease the susceptibility of potato starch towards porcine pancreatic α-amylase (Hoover & Vasanthan, 1994a) and pancreatin (Jacobs et al., 1998c). Legume starches such as pinto bean, black bean, lentil and field pea starches have been shown (Hoover & Manuel, 1996) to exhibit increased susceptibility towards porcine pancreatic α-amylase on annealing (single step). A similar finding was also reported by Jacobs et al. (1998c) for pancreatin hydrolyzed single and double step annealed pea starch. An increase in hydrolysis on annealing (single step) has also been observed in sago (*Metroxylon* sp.) starch (Wang et al., 1997), waxy corn, normal corn, high amylose (hylon V and hylon VII) and potato (O'Brien & Wang, 2008) starches. Tukomane et al. (2007) showed that annealing of cassava starch at 60 °C for 90 min followed by hydrolysis with α-amylase from *Bacillus subtulis* at 60 °C, results in an increase in starch crystallinity. The percentage crystallinity was found to increase with increasing hydrolysis time and with decreasing amylose content.

The decrease in α-amylase susceptibility on annealing has been attributed to the interplay of the following factors: (1) crystallite perfection and double helical content, (2) crystal type (3) annealing steps, (4) interaction between AM–AM and/or AM–AMP chains and (5) amylose–lipid complex formation on annealing (Hoover & Vasanthan, 1994a; Jacobs et al., 1998c). Wang et al. (1997) have speculated that annealing may create pores or fissures which alter the pattern of α-amylase hydrolysis from surface to internal erosion. X-ray and DSC studies (O'Brien & Wang, 2008) has shown that annealing facilitates the entry of α-amylase into the amorphous and crystalline domains of corn (normal, waxy, high amylose) and potato starches due to an increase in granule porosity. This suggests, that changes to the granule surface on annealing could negate the effect of glucan chain interaction and crystallite perfection on α-amylase hydrolysis and thereby facilitate the entry of α-amylase into the granule interior. This could then explain the increase in hydrolysis observed in some starches on annealing. However, a clear relationship between pore/fissures development on annealing, and its influence on hydrolysis cannot be made, until a systematic study is carried out on the nature of the granule surface of different starches before and after annealing.

2.14. Growth temperature induced 'in vivo' annealing

Debon, Tester, Millam, and Davies (1998) and Tester et al. (1998, 1999) have shown by studies on starches in potato microtubers and potato starches, that when there is a constant background of amylopectin structure and amylose to amylopectin ratio, the gelatinization and swelling characteristics of starches can be modified during biosynthesis by increasing growth temperature. This is analogous to annealing of starches isolated in the laboratory. Both elevated growth temperature (*in-vivo* annealing) or heating of starches in excess water below T_o but above T_g (*in-vitro* annealing) causes double helical realignment (resulting in crystalline perfection) without the formation of more double helices in crystalline regions. Tester et al. (1999) showed that the gelatinization temperatures of potato starch increased as growth temperature was increased from 10 to 25 °C, although ΔH remained constant. Tester and Debon (2000) have postulated that the major molecular reorganization underlying both '*in-vivo*' and '*in-vitro*' annealing are: (1) improved perfection of starch crystallites and (2) improved ordering of starch chains within the amorphous domains. The effect of '*in-vivo*' annealing on starch structure was also reported by Genkina et al. (2004c) and Protserov et al. (2002) for potato and sweet potatoes grown at different soil temperatures (15 and 33 °C). It was shown that crystallites of starches formed at higher soil temperatures were more perfect than those formed at a lower soil temperature. A similar observation was reported by Kiseleva et al. (2004) for normal, waxy and high amylose barley starches.

Tester and Debon (2000) have stated that the effects of growth temperature during starch biosynthesis potentially have important industrial consequences such as the energy needed for starch gelatinization in food products or for malting and brewing. Modifying starch structure by '*in vivo*' and/or '*in-vitro*' annealing would be a way of reducing the processing cost associated with chemical modification of starches.

2.15. Storage temperature induced 'in-vivo' annealing

Tester et al. (2005) have shown that in '*in vivo*' annealing could be achieved by storage of potato tubers at 55 °C for 7 days. The extent of annealing (monitored by DSC) was comparable with that achieved by subjecting extracted potato starches in excess water to the same time/temperature protocol. The author's concluded that there may be potential commercial values of using annealing '*in situ*' to create new products in the food and non-food sectors.

2.16. Annealing during starch isolation

Krueger et al. (1987a) showed that annealing occurs during isolation of corn starch by the wet milling process. Prior to wet milling, shelled corn is steeped in a bath of dilute sulfurous acid at 52 °C for 48 h. The steeping temperature being close to T_o is able to trigger annealing. Lorenz and Kulp (1978) also reported annealing in wheat and barley grains steeped in water (50 °C for 72 h) prior to starch isolation.

3. Potential uses of annealed starches

Annealing has been shown to improve thermal stability and decrease the extent of set-back (Adebowale et al., 2005a; Hoover & Vasanthan, 1994a; Jacobs et al., 1995; Stute, 1992). Therefore, annealed starches could be utilized in the canned and frozen food industries, for their respective advantages. Rice noodles prepared from rice flour are widely consumed in South East Asia. Traditionally, rice noodles are prepared from long-grain rice which has been stored for a period of time. This process limits starch granule swelling and improves the paste or gel quality (Zhou, Robards, Helliwelt, & Blanchard, 2003), making the rice flour suitable for preparing good quality noodles. The decrease in granular swelling and amylose leaching, and the increase in heat and shear stability that occur on annealing are all desirable properties for noodle manufacture. Hormdok and Noomhorm (2007) evaluated rice starch (native and annealed), fresh rice flour, aged flour and compound rice flours with 50/100 g native rice starch or annealed rice starch as replacement ingredients for the manufacture of noodles of acceptable quality. The study showed that the textural (adhesiveness, chewiness, tensile strength) quality of the rice noodle prepared using annealed rice starch was comparable to that of commercial noodles. 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; Haralampu & Gross, 1998). In these studies, high amylose maize starch (HAMS) has been used for enhancing resistant starch, since HAMS is digested very slowly (Wolf, Khoo, & Inglett, 1977). Brumovsky and Thompson (2001) showed that partial acid (HCl) hydrolysis of HAMS (hylon VII) for 6 h at 25 °C, followed by annealing (24 h, 70 °C, moisture content, 67%) gave a resistant starch content of ∼32% by total dietary fiber (TDF) analysis. The author's have postulated that limited acid hydrolysis enhances the mobility of the starch chains, to allow more efficient rearrangement of starch chains during annealing. Haralampu and Gross (1998) showed that the resistance starch content of HAMS can be increased by heating to 95 °C for 1 h, followed by debranching with pullalanase and storage at 57 °C overnight. The retrograded starch was then annealed at 90 °C for 2 h, leading to about 32% resistant starch by TDF analysis. Resistant starch can be incorporated in foods without altering the appearance and texture, partly due to its bland taste, white color and microparticulate structure. It can thus be used as a fat mimetic or to increase the dietary fiber content of food (Würsch, 1999).

Tukomane et al. (2007) showed that spherical agglomerates obtained by spray drying (at 160 °C) of annealed (60 °C, 90 min) – enzymatically (α-amylase) hydrolyzed (120 min) tapioca starch were suitable for preparation of tablet fillers by direct compression. These agglomerates exhibited high compressibility, increased disintegration time, high crystallinity and low friability. The author's have stated that these tablet fillers could be introduced as a new directly compressible excipient with other commercial fillers available in the market.

4. Directions for future research

This review has shown that the contribution of amylose to the observed changes to starch structure and physicochemical properties is still not fully understood. Recently, Kozlov et al. (2007) have postulated that defects in crystalline structure are more pronounced in high amylose (due to the presence of amylose tie-chains in the crystalline lamella) than in regular amylose starches. Therefore, it would be interesting to investigate whether changes to physicochemical properties on annealing in starches (regular, waxy, high amylose and their blends) belonging to a particular starch source (rice, maize, wheat, barley) can also be explained on the basis of variation in crystalline defects.

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