EFFECT OF ANNEALING PROCESS ON PHYSICOCHEMICAL, MORPHOLOGICAL AND GELATINIZATION PROPERTIES OF CEREAL STARCHES

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ABSTRACT

Starch is one of the most important components in the food industry. However, the functional properties of native starch bring some disadvantages. Starch modification could overcome these weaknesses using several methods; one of them is the annealing process. This review provides information on the effects of the annealing process on the physicochemical, morphological and gelatinization properties of various types of cereal starch. The review also discusses the reasons for the variation in how the annealing process affects the properties of cereal starches. Overall, these different effects of the annealing process are caused by the different types of cereal starch, annealing conditions, and measurement methods. Annealed cereal starches have the potential for wider application in the food industry as ingredients in canned and frozen foods, noodles, and functional foods.

Keywords: annealing, cereal, gelatinization, morphological, physicochemical, starch.

1. Introduction

Starch, complex molecules that store mass energy in plants, have become an important material in the food industry (Sweedman *et al.*, 2013). Starch, in its native form, has many weaknesses such as low stability at high temperatures and under shear stress, and high levels of retrogradation (Jayakody and Hoover, 2008). The various modification methods used to overcome the weaknesses of native starch, can be divided into physical, chemical, and enzymatic modification (Zavarese and Dias, 2011). Chemical modification uses a chemical reagent to modify the properties of the starch using processes such as succinylation, acetylation, octenyl succinic acid modification, and hydroxypropylation. Enzymatic modification uses an enzyme to modify the properties of starch, using heat, moisture, shear or radiation (Zavarese and Dias, 2011). Physical modification leaves no chemical residue or chemical modification, so is safe for consumption (Wang *et al.*, 2014), some examples being pre-gelatinization, heat-moisture treatment, and annealing.

The annealing process modifies starch physically to an

intermediate moisture content (40-55% w/w) or excess water (> 60%) at above the glass transition temperature (T_g) but below the gelatinization temperature (Jacobs and Delcour, 1998). Many studies have investigated the effect of the annealing process on modifying different types of cereal starch (Krueger *et al.*, 1987a, 1987b; Knutson, 1990; Shi and Seib, 1992; Seow and Teo, 1993; Hoover and Vasanthan, 1994a, b; Jacobs *et al.*, 1995, 1996; Jacobs and Delcour, 1998; Tester *et al.*, 2000b; Qi *et al.*, 2004; Adebawale *et al.*, 2005a; Kiseleva *et al.*, 2005; Kohyama and Sasaki, 2006; Waduge *et al.*, 2006; Lan *et al.*, 2008 O'Brien and Wang, 2008; Liu *et al.*, 2009a, 2009b; Chung *et al.*, 2009; Dias *et al.*, 2010; Singh *et al.*, 2011; Rocha *et al.*, 2012; Vamadevan *et al.*, 2013; Wang *et al.*, 2014, 2017; Ali and Hasnain, 2016).

General reviews on the annealing process for starch have been provided by Tester and Debon (2000a), Zavarese and Dias (2011), and Jayakody and Hoover (2008) but none are available on its effects on the physicochemical, morphological and gelatinization properties of cereal starches. This review aims to provide an overview of current information on these effects.

2. Potential use of annealed cereal starches

The annealing process has been shown to increase the thermal stability and decrease the retrogradation of starch (Stute, 1992; Hoover & Vasanthan, 1994a; Jacobs *et al.*, 1995; Adebawale *et al.*, 2005b). Therefore, annealed cereal starches can be used in the production of canned and frozen foods (Jayakody and Hoover, 2008). Annealing decreased swelling power and amylose leaching but increased the heat and shear stability, suitable properties for the noodle industry (Zavarese and Dias, 2011). Using annealed rice starch for rice noodles was shown to improve their textural properties (adhesiveness, chewiness, and tensile strength) (Hormdok and Noomhorm, 2007).

The annealing process can also increase the proportion of resistant starch (Chung *et al.*, 2009). Therefore, annealed starch could be very useful in the functional food industry as a healthy food supplement. The annealing process also improved the clarity of starch paste, recommended for certain foods such as jellies and fruit fillings (Ali and Hasnain, 2016; Elliasson, 2004). The annealing process also increased gel formation (Adebawale *et al.*, 2005a) and produced harder gels (Singh *et al.*, 2011), properties suitable for certain sectors of the food industry with requirements for high gel-forming capability and harder gel properties.

3. Overview of annealing process on cereal starches

The information from several studies on the annealing process covering the various types of cereal starch, water to starch ratio, temperature, and annealing time has been summarized in Table 1. These studies included a range of cereal starches from maize, sorghum, wheat, rice, barley, oats and rye. The annealing process for maize starch has been studied most often.

Studies on the various water to starch ratios ranged from those using an excess of water to water to starch ratios of 2:1, 3:1, and 10:1 and adjusting the moisture content of the samples to 75%. In general, the annealing process uses a specific heating temperature: above the glass transition temperature (T_g) and below the gelatinization temperature (Jacobs and Delcour, 1998). Different sources of cereal starches have different glass transition and gelatinization temperatures. The studies in Table 1 investigated the annealing process with cereal starches using various temperatures: 55 °C, 50 °C, and 45 °C, below 45 °C, and above 55 °C.

The process times studied in research on the annealing process in cereal starches ranged from 24 h (1 day) to 168 h (7 days) and also included 48 and 72 h, below 24 h and above 72 h. Overall, research on the annealing process for various cereal starches has investigated different conditions of temperature, time, and water to starch ratio).

4. Variation in properties due to annealing process

4. 1. Effects of annealing process on the physicochemical properties of cereal starches

4.1.1. Effect of annealing on the amylose content

Starch consists of amylose and amylopectin, which have linear chains and highly-branched chains, respectively (Alcázar-Alay and Meireles, 2015). Studies on the effect of annealing on the amylose content or amylose leaching in different types of cereal starch have been summarized in Table 2. Some studies have shown that the annealing process did not change the amylose content of maize starch (Knutson, 1990; Liu *et al.*, 2009 and Rocha *et al.*, 2012; Wang *et al.*, 2014). Wang *et al.* (2014) reported that the annealing process did not significantly change the amylose content of maize starch. Wang *et al.* (2014) suggested that the annealing process modified starch using a purely physical process, which did not lead to any leaching of amylose. Rocha *et al.* (2012) have also shown that gelatinization process did not occur during the annealing process.

However, other studies have reported contrasting findings on the effect of the annealing process in decreasing the amylose leaching. It was determined with heating starch suspension in the above gelatinization temperature. Then, it was cooled to room temperature and centrifuged. The supernatant was used to measure the amylose content. Amylose leaching is the amount of amylose leached per 100 g of dry starch (Chung *et al.*, 2009). Several studies have found that annealing led to amylose leaching rice starch (Jacobs *et al.*, 1995), wheat starch (Hoover & Vasanthan, 1994a; sorghum starch (Singh *et al.*, 2011), oat starch (Hoover & Vasanthan, 1994b; Jacobs *et al.*, 1995), and barley starch (Waduge *et al.*, 2006). It has been suggested that amylose leaching after annealing are caused by the greater interaction between amylose-amylose and/or amylose-amylopectin chains (Hoover and Vasanthan, 1994a). The restructuring of the starch molecules leading to a stable structure also cause decrease in amylose leaching (Zavareze & Dias, 2011).

Another type of effect has been reported only by Chung *et al.* (2009) who found that the annealing process could slightly increase the amount of amylose leaching from maize starch. However, Chung *et al.* (2009) provided no explanation of this result. The effect of the annealing process on amylose content or amylose leaching in different types of cereal starches has been very controversial. Research studies show three different effects of the annealing process on amylose content or amylose leaching: no effect, and a decreased or increased amylose leaching. Thus, the annealing process can increase or decrease or not affect the amylose content or amylose leaching of different types of cereal starch depending on the conditions of the annealing process and the different sources of cereal starch.

Table 1. Overview of studies on the annealing process under different conditions and types of cereal starch

Starch	Temperature (°C)	Time (h)	Water:starch ratio	Reference
Maize (normal, high amylose, waxy maize)	50	48	Excess	Krueger <i>et al.</i> , (1987a)
	50	24	3:1	Knutson (1990)
	30	72	10:1	Liu <i>et al.</i> , (2009a)
	50	72	10:1	Kohyama and Sasaki (2006)
	45	24;72	2:1	Wang <i>et al.</i> , (2014)
	25-65	72	Excess	Tester <i>et al.</i> , (2000b)
	57;52	24	70% mc	Chung <i>et al.</i> , (2009)
	60	48	3:1	Shi <i>et al.</i> , (1992)
	50	72	10:1	Liu <i>et al.</i> , (2009b)
	63;62	24	Excess	Rocha <i>et al.</i> , (2012)
	40-60	24	3:1	O'Brien and Wang (2008)
	45	24	2:1	Jacobs <i>et al.</i> , (1995)
	42-50	72	3:1	Lan <i>et al.</i> , (2008)
	30;40;50	24	5:1	Wang <i>et al.</i> , (2017)
Wheat	45	24	2:1	Jacobs <i>et al.</i> , (1996)
	50	72	75% mc	Hoover and Vasanathan (1994a)
	48;53	24	2:1	Kiseleva <i>et al.</i> , (2005)
	60	0.5-10	2:1	
	55	24	2:1	Jacobs <i>et al.</i> , (1995)
	55	24	2:1	Jacobs <i>et al.</i> , (1996)
	70	48	3:1	Shi and Seib (1992)
Rice (normal, waxy rice)	45,50,55	16	9:1	Dias <i>et al.</i> , (2010)
	55	4-24	40 %mc-excess	Seow and Teo (1993)
	45,50,55	8, 16, 24	3:1	Horndok and Noomhorn, 2007
	50	72	75% mc	Waduge <i>et al.</i> , 2006
	49	24	Excess	Vamadevan <i>et al.</i> , 2013
	52	48	3:1	Shi and Seib (1992)
Barley (normal, waxy barley)	48	168	Excess	Qi <i>et al.</i> , (2004)
	55	72	75% mc	Ali and Hasnain (2016)
	50	24	4:1	Singh <i>et al.</i> , (2011)
	50	24	Excess	Adebawale <i>et al.</i> , (2005a)
Sorghum	44	24	Excess	Vamadevan <i>et al.</i> , (2013)
	50	72	75% mc	Hoover and Vasanathan (1994b)
Oat				
Rye	46	24	Excess	Vamadevan <i>et al.</i> , (2013)

mc = moisture content

4.1.2. Effect of annealing on swelling power

Table 3 shows the effect of annealing on the swelling power or swelling factor in native and annealed starches. Measuring the swelling power indicates the level of interplay between starch chains in the crystalline and amorphous regions of the native granule (Lan *et al.*, 2008). Generally, the annealing process can decrease the swelling power in maize starch (Wang *et al.*, 2014), barley starch (Waduge *et al.*, 2006), wheat starch (Hoover and

Vasanathan, 1994a), rice starch (Horndok and Noomhorn, 2007; Dias *et al.*, 2010), oat starch (Hoover and Vasanathan, 1994b), and sorghum starch (Adebawale *et al.*, 2005a; Singh *et al.*, 2011; Ali and Hasnain, 2016). The annealing treatment of maize starch resulted in a lower swelling power compared with that of native starch. Improving the long-range forces between amylopectin chains can lead to the rearrangement of amylose molecules. This prevents the free swelling of amylopectin molecules and results

Table 2. Overview of studies on the effect of the annealing process on amylose content and amylose leaching in various types of starch

Starch	Amylose content (%)	Amylose leaching (%)	Reference
Maize (native)	23.0±0.6		
Maize (annealed)	22.5±0.5		Wang <i>et al.</i> , (2014)
Maize (native)	27.9		
Maize (annealed)	28.1		Rocha <i>et al.</i> (2012)
Maize (native)	Ns		
Maize (annealed)	Ns		Knutson (1990)
Maize (native)		6	
Maize (annealed)		7	Chung <i>et al.</i> , (2009)
Maize (native)	23		
Maize (annealed)	23		Liu <i>et al.</i> , (2009)
Wheat (native)		10.9±0.8	
Wheat (annealed)		9.3±0.5	Hoover and Vasanthan (1994a)
Wheat (native)		9.2	
Wheat (annealed)		9.1	Jacobs <i>et al.</i> , (1995)
Rice (native)		4.5	
Rice (annealed)		4.3	Jacobs <i>et al.</i> , (1995)
Barley (native)		5	
Barley (annealed)		3	Waduge <i>et al.</i> , (2006)
Sorghum (native)		14.5	
Sorghum (annealed)		7.4	Singh <i>et al.</i> , (2011)
Oat (native)		12.3±0.4	
Oat (annealed)		11.8±0.2	Hoover and Vasanthan (1994b)

Ns = data not provided

in a lower swelling power (Wang *et al.*, 2014). Another study by Waduge *et al.* (2006) reported a decrease in the swelling power of barley starch after annealing, possibly because of the interactions of crystalline perfection and interplays between amylose-amylose during the annealing process.

Several factors influence swelling power: the structure of amylopectin (Shi and Seib, 1992; Sasaki and Matsuki, 1998), complexes of V-amylose lipid (Tester and Morrison, 1990), amylose content (Morrison *et al.*, 1993; Tester *et al.*, 2000a), an increase in crystalline perfection (Waduge *et al.*, 2006; Singh *et al.*, 2011), an increment in molecular organization (Gomes *et al.*, 2004), and the level of interaction between amylose-amylose and/or amylose-amylopectin chains (Hoover and Vasanthan, 1994b; Hoover and Manuel, 1996; Eerlingen *et al.*, 1997; Tester *et al.*, 2000a; Gunaratne and Hoover, 2002; Waduge *et al.*, 2006). Chung *et al.* (2009) found different results from others, reporting that the swelling factor increased slightly in maize starch after annealing, but no explanation was given.

4.1.3. Effect of annealing on pasting properties

Studies on the effect of the annealing process on pasting properties have included several types of cereal starch: maize starch (Wang *et al.*, 2014), wheat starch (Lan *et al.*, 2008), sorghum starch (Adebawale *et al.*, 2005a; Singh *et al.*, 2011; Ali and Hasnain, 2016) and rice starch (Dias *et al.*, 2010). According to Wang *et al.* (2014), the form of the amylograph curve did not change after annealing maize starch. There was a decrease in the viscosities (peak, through and final viscosity) of the maize starch after annealing. This could have been caused by the prevention of swelling of the annealed starch as a consequence of the improved reinforcement of the amylopectin groups by the realignment of amylose. Lan *et al.* (2008) also reported that the peak, breakdown, final, and setback viscosities of wheat starch decreased after the annealing process. The decrease in the swelling factor and amylose leaching were associated with the decreased peak and setback viscosities after the annealing process.

The annealing process decreased the peak viscosity in sorghum starch and was correlated with its swelling power (Singh

Table 3. Overview of studies on the effect of the annealing process on the swelling power and swelling factor of various types of starch

Starch	Swelling power (g/g)	Swelling factor (%)	Reference
Maize (native)	17.4±0.1		
Maize (annealed)	16.2±0.2		Wang <i>et al.</i> , (2014)
Maize (native)		8	
Maize (annealed)		9.75	Chung <i>et al.</i> , (2009)
Barley (native)		48	
Barley (annealed)		40	Waduge <i>et al.</i> , (2006)
Sorghum (native)	11.8±0.1		
Sorghum (annealed)	10.6±0.2		Ali and Hasnain (2016)
Sorghum (native)	9.93±0.03		
Sorghum (annealed)	9.24±0.04		Adebowale <i>et al.</i> , (2005a)
Sorghum (native)		12.2	
Sorghum (annealed)		8.1	Singh <i>et al.</i> , (2011)
Rice (native)	12		
Rice (annealed)	11		Dias <i>et al.</i> , (2010)
Rice (native)	14.11±0.31		
Rice (annealed)	10.15±0.04		Hormdok and Noomhorn (2007)
Wheat (native)	28.6±0.3		
Wheat (annealed)	18.9±0.2		Hoover and Vasanthan (1994a)
Oat (native)	25.7±0.2		
Oat (annealed)	19.8±0.4		Hoover and Vasanthan (1994b)

et al., 2011). A reduction in the peak viscosity was caused by inter- and intra-molecular hydrogen bonding in the starch chains (Hoover & Vasanthan, 1994c). They also found that the annealing process could decrease the through and final viscosities of the starch. This was consistent with findings by Dias *et al.* (2010), who showed that annealing could decrease the final viscosity of rice starch.

The value of the breakdown viscosity indicates the stability of the starch during heating and agitation (Singh *et al.*, 2011). Annealed starch exhibited a lower breakdown viscosity than native starch (Lan *et al.*, 2008; Dias *et al.*, 2010; Singh *et al.*, 2011; Ali and Hasnain, 2016). This decrease in breakdown viscosity is associated with a decrease in granular swelling and amylose content (Lan *et al.*, 2008; Singh *et al.*, 2011). The annealing process reduced the setback viscosity in sorghum and rice starches (Singh *et al.*, 2011; Dias *et al.*, 2010) because of several factors such as the extent of amylose leaching, granule size, and length of the amylose chain (Singh *et al.*, 2011).

However, some authors have postulated that the annealing process can increase the viscosity of starch (Jacobs *et al.*, 1995; Wang *et al.*, 2013, 2017). In rice and wheat starch, the shape of

the pasting profile exhibits a slightly increased viscosity after annealing (Jacobs *et al.*, 1995). Wang *et al.* (2013, 2017) found an increase in the viscosity of wheat starch after annealing which can occur because of the enhanced rigidity and a reduction in deformability (Wang *et al.*, 2017). This was also associated with an increment in the stability of the annealed starch during heat and shear condition (Jacobs *et al.*, 1995). The higher stability has meant that starch more resistant to heat and shear stress. It is indicated by low breakdown viscosity value (Corke *et al.*, 1997).

The different temperatures during annealing affected the pasting properties of wheat starch: annealing at 30 °C and 40 °C increased the overall paste viscosity. The annealing process at 50 °C also decreased the whole paste viscosity and increased the pasting temperature (Wang *et al.*, 2017). This finding was consistent with that of Dias *et al.* (2010), who showed that annealing at a higher temperature (55 °C) decreased the peak viscosity of high-amylose starch. However, annealing at a lower temperature (45 °C and 50 °C) increased the peak viscosity of low-amylose starch. The increase in peak viscosity after annealing was not caused by limited granular swelling in starch. Annealing also

Table 4. Overview of studies on the effect of the annealing process on the pasting properties of various types of starch

Starch	Pv	Tv	Bv	Fv	Sv	PT (°C)	Ref.
Maize (native)	1054±34	1002±15	52±3	1043±21	41±3	94.6±0.6	
Maize (annealed)	821±26	762±24	59±5	869±20	107±10	94.8±0.4	Wang <i>et al.</i> , (2014)
Sorghum (native)	2770±42	4905±7	935±7	Ns	2895±21	73.4±0	
Sorghum (annealed)	2420±42	4260±85	760±14	Ns	2675±21	75.8±0.1	Ali and Hasnain (2016)
Sorghum (native)	3213	2302	911	339	1088	79.3	
Sorghum (annealed)	2706	2185	521	2929	744	79.5	Singh <i>et al.</i> , 2011
Sorghum (native)	970	446.7	523.3	595	148.3	63.75	
Sorghum (annealed)	3650.4	2080.7	1500.4	1670.8	1261.9	64.55	Adebowale <i>et al.</i> , (2005a)
Rice (native)	2445±8.7	Ns	611±16.9	3289±13.4	1437±29	85.9±0.15	
Rice (annealed)	2689±5	Ns	598±11.7	3010±5.4	920±17.5	87.9±0.17	Dias <i>et al.</i> , (2010)
Rice (native)	2181.7±636	1904.6±44.2	277.1±19.4	2747.9±71.3	843±27.1	82.45±0.1	
Rice (annealed)	2093.3±271	1697.9±59.5	395.4±32.4	2888.8±102.4	1190.8±71.9	83.75±0.23	Hormdok and Noomhorn (2007)

Ns = data not provided, Pv = peak viscosity (mPas), Tv = through viscosity (mPas),

Bv = breakdown viscosity (mPas), Fv = final viscosity (mPas), Sv = setback viscosity (mPas),

PT = pasting temperature (°C)

Table 5. Overview of studies on the effect of the annealing process on the morphological properties of various types of starch

Starch	Granules shape	Reference
Maize (native)	small granules look spherical and large granules looks polyhedral	
Maize (annealed)	small granules look spherical and large granules looks polyhedral (no change)	Wang <i>et al.</i> , (2014)
Maize (native)	Round and polyhedral shaped	
Maize (annealed)	Round and polyhedral shaped (no change)	Rocha <i>et al.</i> , (2012)
Wheat (native)	Oval	
Wheat (annealed)	Oval at 30°C, 40°C but fusion and destruction shape at 50°C	Wang <i>et al.</i> , (2017)
Wheat (native)	Oval to elliptical to round	
Wheat (annealed)	Oval to elliptical to round (no change)	Lan <i>et al.</i> , (2008)
Sorghum starches (native)	Mixture of large (polygonal and spherical) and small (mostly spherical)	
Sorghum starches (annealed)	Mixture of large (polygonal and spherical) and small (mostly spherical) (no change)	Ali and Hasnain (2016)
Sorghum (native)	irregular, elongated as well as spherical in shape	
Sorghum (annealed)	irregular, elongated as well as spherical in shape (no change)	Singh <i>et al.</i> , (2011)
Barley (native)	a mixture of large (spherical, disc, and lenticular shaped) and small (irregularly shaped) granules (no change)	
Barley (annealed)	a mixture of large (spherical, disc, and lenticular shaped) and small (irregularly shaped) granules (no change)	Waduge <i>et al.</i> , (2006)
Rice (native)	No pores on the surface	
Rice (annealed)	Pores on surface and granules more agglomerated	Dias <i>et al.</i> , (2010)

increased the breakdown viscosity suggesting that a lower level of stability during heating (Adebowale *et al.*, 2005a). Hormdok and Noomhorn (2007) also found that the annealing process increased the breakdown viscosity of rice starch.

Annealed starch exhibits a higher pasting temperature

compared with native rice starch. It also strengthens the bonds, so requires a higher temperature to gelatinize (Gomes *et al.*, 2004). Hormdok and Noomhorn (2007) found that the annealing process increased the setback viscosity of rice starch. The different effects of annealing on the pasting temperature have been related to

Table 6. Overview of studies on the effect of the annealing process on the crystallinity of various types of starch

Starch	XRD Pattern Type	Relative Crystallinity (%)	Reference
Maize (native)	A-type	34.6	Wang <i>et al.</i> , (2014)
Maize (annealed)	A-type	33.5	
Maize (native)	A-type	32.6	Rocha <i>et al.</i> , (20,12)
Maize (annealed)	A-type	33.7	
Maize (native)	A-type	38.3 ± 0.4	Liu <i>et al.</i> , (2009b)
Maize (annealed)	A-type	40.1 ± 0.3	
Maize (native)	A-type	Ns	O'Brien and Wang (2008)
Maize (annealed)	A-type	Ns	
Wheat (native)	A-type	22.6	Wang <i>et al.</i> , (2017)
Wheat (annealed)	A-type	14.3	
Wheat (native)	A+B type	30.6	Lan <i>et al.</i> , (2008)
Wheat (annealed)	A type	30.9	
Barley (native)	A-type	44.3 ± 0.5	Waduge <i>et al.</i> , (2006)
Barley (annealed)	A-type	46.6 ± 0.6	
Rice (native)	A-type	Ns	Dias <i>et al.</i> , (2010)
Rice (annealed)	A-type	Ns	
Sorghum (native)	A-type	Ns	Singh <i>et al.</i> , (2011)
Sorghum (annealed)	A-type	Ns	

Ns = data not provided

Table 7. Overview of studies on the effect of the annealing process on the gelatinization properties of various types of starch

Starch	To (°C)	Tp (°C)	Tc (°C)	ΔH	Reference
Maize (native)	66.5 ± 0.3	70.7 ± 0.3	75.4 ± 0.2	14 ± 0.3	Wang <i>et al.</i> , (2014)
Maize (annealed)	68 ± 0.2	71.8 ± 0.2	75.0 ± 0.1	13.6 ± 0.4	
Maize (native)	67.3 ± 0.6	72.9 ± 0.7	82.7 ± 1.6	10.9 ± 0.5	Chung <i>et al.</i> , 2009
Maize (annealed)	72.5 ± 0.4	76.5 ± 0.8	85.0 ± 0.8	11.5 ± 0.6	
Maize (native)	66.1	Ns	Ns	3.7	Shi and Seib (1992)
Maize (annealed)	77.7	Ns	Ns	3.5	
Maize (native)	63.9	70.3	Ns	2.61	Krueger <i>et al.</i> , (1987a)
Maize (annealed)	68.9	72.6	Ns	3.10	
Maize (native)	61.2	67.3	Ns	2.28	Krueger <i>et al.</i> , (1987b)
Maize (annealed)	68.8	71.3	Ns	2.94	
Maize (native)	67.3 ± 0.4	69.9 ± 0.6	Ns	15.22 ± 0.42	Liu <i>et al.</i> , (2009)
Maize (annealed)	75.9 ± 0.2	77.1 ± 0.5	Ns	15.43 ± 0.31	
Maize (native)	62.9 ± 0.5	70.5 ± 0.4	81.1 ± 0.8	12.6 ± 0.2	Tester <i>et al.</i> , (2000b)
Maize (annealed)	Ns	80	Ns	12.1	
Maize (native)	Ns	72.3	Ns	12.3	O'Brien and Wang (2008)
Maize (annealed)	Ns	77.4	Ns	15.2	
Wheat (native)	56.2	61.1	66.6	9.7	Hoover and Vasanthan, (1994 a)
Wheat (annealed)	69.6	72.0	74.7	12.2	
Wheat (native)	52 ± 0.4	56.8 ± 0.3	63.5 ± 0.8	3.5 ± 0.4	Jacobs <i>et al.</i> , (1998 a)
Wheat (annealed)	60.2 ± 0.3	62.3 ± 0.4	65.6 ± 0.5	5.7 ± 1.1	

Wheat (native)	54.4±0	58.7±0.1	63.6±0.1	11.8±0.3	
Wheat (annealed)	61.6±0.1	63.7±0.2	66.9±0.2	12.2±0.4	Jacobs <i>et al.</i> , (1998 b)
Wheat (native)	51.5	56.2	61.6	10.6	
Wheat (annealed)	59.7	61.7	64.9	11.0	Jacobs <i>et al.</i> , (1995)
Wheat (native)	55.6±0.4	60.9±0.5	67.3±0.6	10.3±0.2	
Wheat (annealed)	67.7±0.1	69.9±0	73.7±0.1	5.6±0.2	Wang <i>et al.</i> , (2017)
Wheat (native)	58.3±0.2	63.5±0.1	72.2±0.2	12.3±0.2	
Wheat (annealed)	68.1±0.1	71.5±0.1	78.5±0.1	12.5±0.1	Lan <i>et al.</i> , (2008)
Barley (native)	58.1	Ns	Ns	3.3	
Barley (annealed)	70.6	Ns	Ns	2.8	Shi and Seib (1992)
Barley (Native)	54.6±0.1	58.0±0.0	63.4±0.1	10.9±0.1	
Barley (Annealed)	62.1±0.2	63.7±0.2	67.8±0.2	12.0±0.2	Vamadevan <i>et al.</i> , (2013)
Barley (native)	61.3±0.1	65.5±0	75.6±0.1	11.4±0	
Barley (annealed)	67.1±0.1	69.9±0	76.7±0.1	11.6±0	Waduge <i>et al.</i> , 2006
Waxy barley (native)	53.0±0.1	59±0.4	68.6±0.5	10.8±0.2	
Waxy barley (annealed)	65.4±0.1	67.4±0.1	73.3±0.2	11.0±0.5	Qi <i>et al.</i> , (2004)
Rice (Native)	59.7	67.8	82.6	13.0	
Rice (Annealed)	66.2	70	81.2	14.2	Jacobs <i>et al.</i> , (1995)
Rice (native)	76.2	Ns	Ns	4.6	
Rice (annealed)	86.9	Ns	Ns	4.7	Shi and Seib (1992)
Rice (native)	67.67	73.49	78.75	13.21	
Rice (annealed)	71.07	74.74	79.12	11.03	Hormdok and Noomhorn (2007)
Oat (Native)	50.0±0.1	55.9±0.1	61.6±0	8.9±0.5	
Oat (Annealed)	58.6±0.1	61.8±0.1	66.6±0.1	9.4±0.1	Vamadevan <i>et al.</i> , (2013)
Oat (native)	60.4	64.1	70.0	10.1	
Oat (annealed)	64.0	67.1	71.3	12.2	Hoover and Vassanthan, (1994 b)
Rye (Native)	51.9±0.1	57.6±0.1	65.3±0.2	9.0±0.1	
Rye (Annealed)	59.7±0	63.2±0.0	69.2±0.0	10.6±0.1	Vamadevan <i>et al.</i> , (2013)
Sorghum (native)	66.74	70.09	74.99	9.26	
Sorghum (annealed)	67.83	70.42	74.59	12.71	Singh <i>et al.</i> , (2011)

Ns = data not provided

the structural characteristics of the starch and the conditions of analysis (Jacobs *et al.*, 1996; Dias *et al.*, 2010).

4.1.4. Effect of annealing on retrogradation properties

Only a few studies have reported on the effect of the annealing process on retrogradation properties: Lan *et al.* (2008) on wheat starch; and Singh *et al.* (2011) and Ali and Hasnain (2006) on sorghum starch. Lan *et al.* (2008) postulated that the annealing process decreased the percentage transmittance of wheat starch, possibly attributed to a decrease in swelling power. Based on differential scanning calorimetry (DSC) data, they suggested that the annealing process could increase crystalline perfection and that the range of disconnection and unfolding of the double helices

during gelatinization would be slower. Therefore, the formation and lateral association of the unfolded double helices would be faster in the annealed starch than in native starch during storage of the starch gel (Lan *et al.*, 2008).

Retrogradation properties can also be determined using DSC measurements. Singh *et al.* (2011) showed that after the annealing process, the onset (T_o), peak (T_p), and conclusion temperatures (T_c), and enthalpy of retrogradation (ΔH_{ret}) were significantly higher compared with native starches. This implied that the crystalline structure of the annealed starches had been rearranged more than that of the native starch. During annealing, the rearrangement of the double helix between adjacent amylopectin is slower and less broad than in native starch (Singh *et al.*, 2011).

Different results have been found for annealed sorghum starch, where annealing increased the paste clarity compared with native starch (Ali and Hasnain, 2006). This increased clarity was correlated with decreased values of amylose leaching and solubility. Amylose with higher levels of leaching and amylopectin interaction resulted in higher turbidity values of starch pastes caused by the arrangement of junction zones (Perrera and Hoover, 1999).

4.2. Effect of annealing process on morphological properties

Many studies have investigated the effects of the annealing process on granule morphology including maize starch (O'Brien and Wang, 2008; Rocha *et al.*, 2012; Wang *et al.*, 2014), barley starch (Waduge *et al.*, 2006), sorghum starch (Singh *et al.*, 2011; Ali and Hasnain, 2016), wheat starch (Kiseleva *et al.*, 2005; Lan *et al.*, 2008; Wang *et al.*, 2017) and rice starch (Dias *et al.*, 2010). Generally, most of these studies found that the annealing process did not change the granule morphology of starch compared with that of native starch.

Wang *et al.* (2014) reported that the granule morphology of maize starch did not change significantly after annealing treatment. The granules showed a variety of shapes: small spherical granules and large polyhedral granules with an average particle size between 3 and 20 μm . Rocha *et al.* (2012) also observed no differences after annealing in the shape of maize starch granules which were round and polyhedral. Annealed starch has pores and the pore size was greater than that of native starch. The presence of a small amount of reducing sugar on the annealed starch indicated the activity of endogenous amylase which produced a greater number of pores (Rocha *et al.*, 2012). These findings agreed with those of Dias *et al.* (2010), who found that annealing caused pores on the surface of granules of rice starch.

Another study by Waduge *et al.* (2006) showed similar results where annealing did not change the shapes and pore size of barley starch granules which contained a mixture of large granules (rounded, spherical, and lenticular-shaped) and small irregularly-shaped granules. The annealing process also did not change the shape of wheat starch granules where both native and annealed wheat starch ranged in shape from oval to elliptical to spherical (Lan *et al.*, 2008).

However, there are some contrasting findings. Wang *et al.* (2017) showed that the annealing process at 50 °C changed the granules of wheat starch: the annealed starch was damaged and fused compared with granules of native wheat starch, agreeing with a previous study (Singh *et al.*, 2011). After annealing, the starch surface appeared coarse and grooved compared with native granules. Dias *et al.* (2010) also noted that annealed rice starch granules were larger than the native granules.

4.3. Effect of annealing on starch crystallinity

In general, starch exhibits three kinds of X-ray diffraction

pattern. Type-A is generally found in cereal starches and type-B in tuber and high-amylose starches. Type-C, a mixture of the A and B type is found in legume starches and some tuber starches such as yam (Jayakody and Hoover, 2008; Wang *et al.*, 2017). Other studies on the effect of the annealing process on starch crystallinity have included maize starch (O'Brien and Wang, 2008; Liu *et al.*, 2009; Rocha *et al.*, 2012; Wang *et al.*, 2014), wheat starch (Lan *et al.*, 2008; Wang *et al.*, 2017); barley starch (Waduge *et al.*, 2006); rice starch (Dias *et al.*, 2010) and sorghum starch (Singh *et al.*, 2011). These studies mostly found that the annealing process did not change the type of crystallinity of cereal starches compared with the native starch. Native cereal starches and annealed cereal starches have A-type crystallinity (Waduge *et al.*, 2006; O'Brien and Wang, 2008; Liu *et al.*, 2009b; Dias *et al.*, 2010; Singh *et al.*, 2011; Rocha *et al.*, 2012; Wang *et al.*, 2014, 2017).

Although annealing does not change the type of crystallinity pattern compared with native cereal starch, it had a different effect on relative crystallinity. In general, relative crystallinity is calculated as the percentage total crystallinity area divided by the total area of the XRD graph data. Wang *et al.* (2013, 2014) found that the relative crystallinity of maize starch did not change significantly after annealing because the annealing process occurred only in the amorphous regions so had no effect on the crystalline region. Wang *et al.* (2017) also reported that annealing wheat starch at 30 °C or 40 °C did not change the relative crystallinity.

Another different effect of the annealing treatment on starch crystallinity, increasing the relative crystallinity, was reported by Waduge *et al.* (2006) in barley starch, Lan *et al.* (2008) in wheat starch, and Rocha *et al.* (2012) in maize starch. Annealing could increase the relative crystallinity compared with native starch because of several factors: the amount of amylopectin, changes in the size and reorientation of starch crystallites, crystallite perfection, the improved ordering of the crystalline V amylose-lipid complex, and the formation of new crystallites (Waduge *et al.*, 2006; Lan *et al.*, 2008).

In contrast, Wang *et al.* (2017) showed that annealing wheat starch at 50 °C could reduce the crystallinity from 22.6% to 14.3%. Dias *et al.* (2010) also showed that the annealing process could decrease the relative crystallinity. This reduction was related to the disruption of the starch crystallites (Wang *et al.*, 2017 and Dias *et al.*, 2010).

4.4. Effect of the annealing process on the gelatinization properties of cereal starches

The gelatinization properties of starch can be determined using DSC measurements of T_o (onset temperature), T_p (peak temperature), T_c (conclusion temperature), and ΔH (gelatinization enthalpy). Many studies have investigated the effect of the annealing process on the gelatinization properties of various types

of cereal starch such as maize starch (Krueger *et al.*, 1987a, b; Shi and Seib, 1992; O'Brien and Wang, 2008; Chung *et al.*, 2009; Liu *et al.*, 2009; Wang *et al.*, 2014), wheat starch (Hoover and Vasanthan 1994a; Jacobs *et al.*, 1995, 1998a, b, Lan *et al.*, 2008, Wang *et al.*, 2017), barley starch (Shi and Seib, 1992; Qi *et al.*, 2004; Waduge *et al.*, 2006; Vamadevan *et al.*, 2013), rice starch (Shi and Seib, 1992; Jacobs *et al.*, 1995; Hormdok and Noomhorn, 2007), oat starch (Hoover and Vasanthan, 1994b; Vamadevan *et al.*, 2013), rye starch (Vamadevan *et al.*, 2013), and sorghum starch (Singh *et al.*, 2011). Generally, the annealing process increased the values of T_o , T_p and T_c in all sources of cereal starch because of the perfection of the pre-existing crystallites (Knutson, 1990; Hoover and Vasanthan, 1994b; Jacobs and Delcour, 1998; Tester *et al.*, 1998, 2000; Waduge *et al.*, 2006).

Regarding the enthalpy of gelatinization (ΔH) properties, the studies provided varying results. Some studies found that the annealing process had no effect on the enthalpy of gelatinization of maize starch (Tester *et al.*, 2000b; Chung *et al.*, 2009; Wang *et al.*, 2014), barley starch (Waduge *et al.*, 2006), rice starch (Hormdok and Noomhorn, 2007), and wheat starch (Lan *et al.*, 2008). No change in the enthalpy of gelatinization (ΔH) in the barley starch after annealing indicated that no new double helices had been formed (Waduge *et al.*, 2006).

Other studies found that annealing increased the enthalpy of gelatinization (ΔH) of maize starch (Krueger *et al.*, 1987a, b; O'Brien and Wang, 2008), wheat starch (Jacobs *et al.*, 1995, 1998a; Liu *et al.*, 2009), barley starch (Qi *et al.*, 2004; Vamadevan *et al.*, 2013), oat starch (Hoover and Vasanthan, 1994b; Vamadevan *et al.*, 2013;), sorghum starch (Singh *et al.*, 2011), rice starch (Shi and Seib, 1992) and rye starch (Vamadevan *et al.*, 2013).

After annealing the number of double helices remained unchanged but the crystalline order improved (Tester *et al.*, 1998 and Qi *et al.*, 2004). Annealing could improve crystalline order from less perfection order of double helices into an optimized crystalline registration without forming new double helices (Qi *et al.*, 2004). Enhancing the crystalline order needs more heat energy to gelatinize the starch, so that the enthalpy of gelatinization becomes high. In another study, Singh *et al.* (2011) found that the annealing process increased the enthalpy of gelatinization because the interaction between the double helices of adjacent amylopectin chains in the crystalline region produced a stable structure.

Contrasting results were found by Wang *et al.* (2017) on wheat starch and Shi and Seib (1992) on maize and barley starch. Wang *et al.* (2017) suggested that the reduction in the enthalpy of gelatinization for the annealing process at 50 °C could affect the ordered structure based on XRD and FTIR measurement but no explanation of the mechanism by which the annealing process decreased the enthalpy of gelatinization was provided.

5. Conclusions

The annealing process has been studied extensively using different sources of cereal starch. The varying results have covered the influence of the annealing process on amylose content, swelling power, retrogradation properties, granule morphology, starch crystallinity and gelatinization properties. The variations in the findings may have been caused by the different sources of cereal starch, the condition used in the annealing process (starch to water ratio, annealing temperature, and annealing time) and methods of measurement. Annealed starch has the potential for much greater application in the food industry as an ingredient in canned and frozen foods, noodles, and functional foods.

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