JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

AUGUST 1998
VOLUME 46, NUMBER 8

REVIEWS

Hydrothermal Modifications of Granular Starch, with Retention of the Granular Structure: A Review

Heidi Jacobs and Jan A. Delcour*

Laboratory of Food Chemistry, Katholieke Universiteit Leuven, K. Mercierlaan 92, B-3001 Heverlee, Belgium

Annealing and heat−moisture treatment are two hydrothermal treatments that modify the physicochemical properties of starch, without destroying granular structure. They involve incubation of starch granules in excess water/intermediate water content (annealing) or at low moisture levels (heat−moisture treatment) during a certain period of time, at a temperature above the glass transition temperaturr but below the gelatinization temperature. The impact of hydrothermal treatments on starch physicochemical properties is extensively discussed. Such physicochemical properties include granule morphology and crystallinity, double-helix content, amount and appearance of amylose−lipid complexes, gelatinization and pasting, swelling power and solubility, gel properties, and susceptibilities to acid and enzymic hydrolysis. Finally, the major differences between the effects of annealing and heat−moisture treatment are pointed out and an overview is given of possible explanations for the observed effects of hydrothermal treatments.

Keywords: *Starch; hydrothermal modification; annealing; heat−moisture treatment*

INTRODUCTION

Starch is synthesized in the form of granules within cellular organelles (amyloplasts). The shape and size of a starch granule is typical of its botanical origin. Cereal starch granules (such as from maize or wheat) are generally small and polyhedral, potato starch granules are elliptical, and legume starches (such as from pea) are kidney-like ovoidal. Granule sizes range from <5 μm in diameter (e.g., rice) to >80 μm in diameter (e.g., potato). The two major components of starch are amylose and amylopectin. Amylose is an essentially linear polymer, built up by α-(1−4) linked D-glucose units. The degree of polymerization (DP) is usually in the range of 500−6000 glucose units. Only very few α-(1−6) linkages are present. Amylopectin is a very large branched molecule with a DP ranging from 3×10^5 to 3×10^6 glucose units (Zobel, 1988). It is composed of linear α-(1−4) glucan chains linked together at the α-(1−6) branch points. One molecule contains 4−5% α-(1−6) linkages (Manners, 1989). Minor constituents commonly found in starch include lipids (up to 1% in cereal starches), proteins, phosphorus, and other minerals.

For a wide range of starch applications (foods, plastics, paper, textile, . . .) properties of native starches do not meet industrial needs. However, native starch

* Author to whom correspondence should be addressed [telephone (+32) 16 321634; fax (+32) 16 321997; e-mail jan.delcour@agr.kuleuven.ac.be].

S0021-8561(98)00169-1 CCC: $15.00
Published on Web 07/30/1998

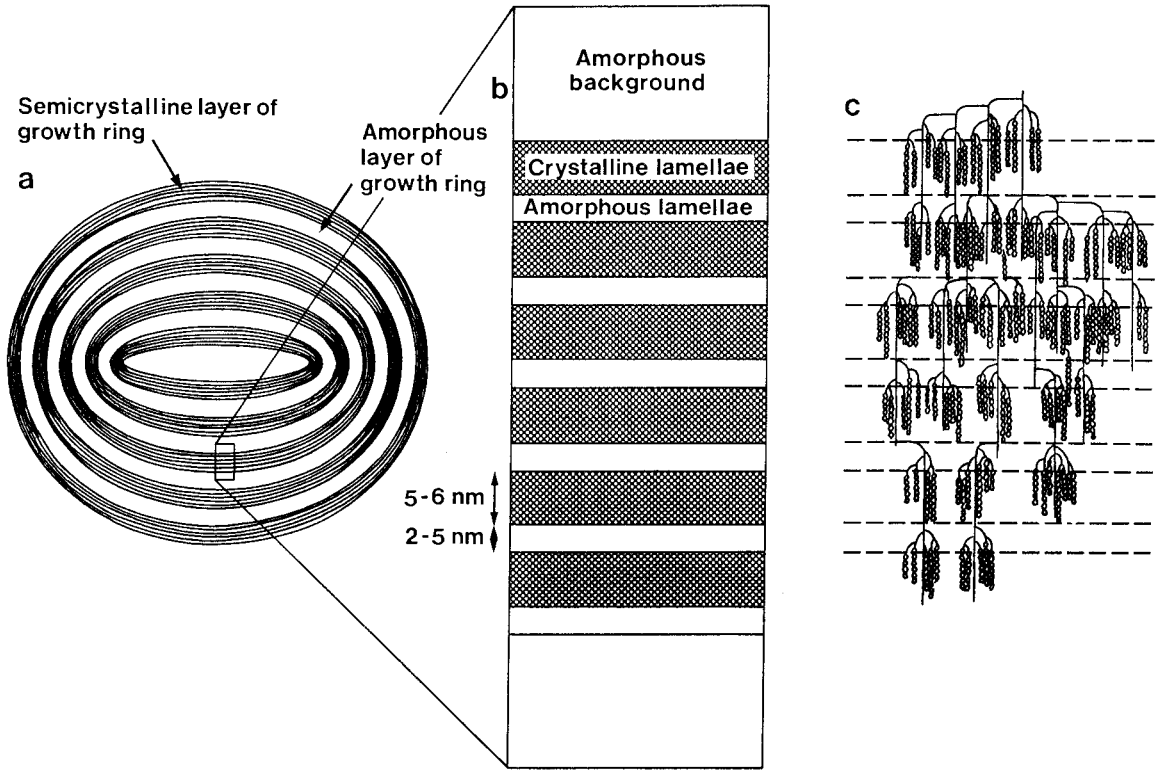

Figure 1. Schematic representation of starch granule structure (Jenkins et al., 1994): (a) a single granule with alternating amorphous and semicrystalline layers, representing growth rings; (b) expanded view of the semicrystalline layer of a growth ring, consisting of alternating crystalline and amorphous lamellae; (c) the cluster structure of amylopectin within the semicrystalline layer of the growth ring.

granules can be modified to obtain desired properties. Mostly, chemical modification (such as cross-linking and/or acetylation) is used, but there is a growing interest in physical modification (heat, moisture, shear, or radiation) of starch, especially for food applications. In fact, such physically modified starches are considered to be natural materials with high safety.

In this work, only hydrothermal modifications (action of heat and moisture) of starch granules, which do not destroy the granule structure, will be reviewed. The impact of such hydrothermal treatments on starch physicochemical properties will be discussed and is of significance not only for the development of novel starches for food and nonfood applications but also for understanding the impact of process steps during the industrial isolation of starch on its functionality.

STARCH GRANULE STRUCTURE

A model of the starch granule structure is schematically shown in Figure 1. The more or less concentric layers (Figure 1a) show alternating high and low refractive indices, densities, crystallinities, and resistance to acid and enzymic hydrolysis and presumably represent growth rings (French, 1984). These growth rings arise from a periodicity in the biosynthesis. The dense layer in a growth ring consists of ~16 (Cameron and Donald, 1992) repeats of alternating crystalline (5−6 nm) and amorphous (2−5 nm) lamellae (semicrystalline layer, Figure 1b). It has a thickness between 120 and 400 nm (French, 1984). The less dense layer is largely amorphous, contains more water, and, according to Cameron and Donald (1992), is at least as thick as the dense layer. Starch granules are thus partially crystalline with a degree of crystallinity of 20−40% (Hizukuri, 1996).

With small-angle X-ray and neutron scattering, a periodicity of 9−11 nm has been found for starches of various botanical sources (Sterling, 1962; Blanshard et al., 1984; Muhr et al., 1984; Oostergetel and Van Bruggen, 1989; Cameron and Donald, 1992; Jenkins et al., 1993). Kassenbeck (1978) and Yamaguchi et al. (1979) ascribed the periodicity to the repeat distances of crystalline and amorphous lamellae.

The crystalline lamellae are made up by amylopectin double helices, which are packed in a parallel fashion, whereas the amylopectin branch points are in amorphous zones (Figure 1c). The crystallinity of the granule is thus mainly ascribed to double helices formed by amylopectin branches rather than to amylose (Jenkins et al., 1993). Wide-angle X-ray scattering (WAXS) has revealed three forms of packing of amylopectin double helices, A-, B-, and C-crystal types, and the features of starch ^{13}C CP/MAS spectra are consistent with starch being a combination of amorphous (single-chain) and ordered (double-helix components) material (Gidley and Bociek, 1985).

The exact location of amylose in the granule remains unknown. However, these linear molecules are believed to be interspersed between amylopectin, rather than being located in bundles (Jane et al., 1992). According to Jenkins et al. (1994), most of the amylose is located in the largely amorphous layers of the growth rings. Recent research (Morrison et al., 1993a,b) has indicated that in cereal starches two amorphous forms of amylose are present: lipid-free amylose and lipid-complexed amylose. Limited cocrystallization between amylose and amylopectin has been suggested by Blanshard (1987) and Jenkins and Donald (1995).

TRANSFORMATIONS OF STARCH DURING HEATING AND COOLING IN THE PRESENCE OF WATER

An important property of partially crystalline materials, such as starch granules, is the **glass transition** of the amorphous regions, at the glass transition temperature (T_g). When passing T_g during heating, the amorphous regions are transformed from a rigid glassy to a mobile rubbery state. The softening of the amorphous regions is required before melting of crystallites can take place (Slade and Levine, 1987). Thus, the glass transition always precedes gelatinization (see below).

At temperatures at or above a characteristic temperature, referred to as the gelatinization temperature, the molecular order of the starch granules is irreversibly destroyed by a process termed **gelatinization**. The structural changes that take place during gelatinization include changes of shape and size of granules, absorption of water and swelling, crystallite melting, and leaching of amylose (amylopectin) from the granules (Atwell et al., 1988). Differential scanning calorimetry (DSC) measures the gelatinization temperatures (onset temperatures of gelatinization typically 50−60 °C in excess water), and the heat energy (10−20 J/g) required for gelatinization is believed to mainly reflect the loss of molecular (double-helical) order (Cooke and Gidley, 1992).

The changes that occur following starch gelatinization, during further heating, are termed **pasting**. These changes involve further swelling of granules, leaching of molecular components from the granules, and eventually disruption of the granules (at ∼85 °C) (Tester and Morrison, 1990a,b). The changes that occur during gelatinization and pasting greatly affect the rheological properties of the starch suspension. Therefore, starch pasting characteristics are commonly evaluated by viscometry.

When starch pastes cool, molecules reassociate in an ordered structure. This process is referred to as **retrogradation** (Atwell et al., 1988). At starch concentrations >∼6%, it leads to the formation of a gel. Such a starch gel can be viewed as a composite, in which deformable gelatinized granules (enriched in amylopectin) are embedded in and reinforce, on crystallization, a continuous amylose matrix (Miles et al., 1985). Retrogradation consists of two separable processes: (1) gelation and crystallization of amylose and (2) recrystallization of amylopectin (Miles et al., 1985).

HYDROTHERMAL TREATMENTS

Two hydrothermal treatments that modify the physicochemical properties of starch, without destroying granule structure, are annealing (ANN) and heat−moisture treatment (HMT). Both treatments involve storage at a certain moisture level and a specific temperature, during a certain period of time. In most publications, treatments in "excess" water (>60% w/w) or at "intermediate water content" (40−55% w/w) are referred to as "annealing", whereas the term "heat−moisture treatment" is used when "low moisture levels" (<35% w/w) are applied. Both physical modifications occur at temperatures above the T_g but below the gelatinization temperature (determined at the specific moisture conditions used during the treatment) of the starch granules. Thus, hydrothermal modifications can only take place when starch polymers in the amorphous phase are in the mobile rubbery state. A treatment time of only a few minutes often suffices to result in detectable changes in physicochemical properties of the starch.

Annealing. *Definition.* In the context of this work, annealing of starch is defined as a **physical treatment** that involves incubation of starch granules in **excess water** or at **intermediate water content**, that is, at or above 40% water (w/w), during a certain period of **time**, at a **temperature** above the glass transition temperature but below the gelatinization temperature. Annealing conditions for starches of different botanical origin are summarized in Table 1. Krueger et al. (1987a) reported that commercial maize starch is already annealed during the isolation process because wet milling includes a lengthy steeping step at temperatures >45 °C and that annealing either is less extensive or occurs much more slowly when starch content is equal to or higher than water content. Also, when wheat or barley is steeped during 72 h at 50 °C prior to isolation of starch, annealing can occur (Lorenz and Kulp, 1978, 1984). While Seow and Teo (1993) noted that annealing of rice starch can also occur at temperatures below its T_g, their definition of T_g is rather unconventional.

Impact of Annealing on Starch Granule Morphology and Crystallinity. After annealing of starch, no changes in granule size and shape were observed (Wiegel, 1933; Stute, 1992; Hoover and Vasanthan, 1994b). Also, no leaching of carbohydrates (Lorenz and Kulp, 1984; Krueger et al., 1987a; Knutson, 1990; Hoover and Vasanthan, 1994b) was detected during the annealing treatment.

For wheat starch, Gough and Pybus (1971) observed no changes in the wide-angle X-ray scattering (WAXS) patterns as a result of annealing. A slight sharpening of the X-ray diffraction lines and a decrease in the background for annealed wheat and barley starches were observed by Lorenz and Kulp (1980, 1984). For annealed potato starch, Stute (1992) found unchanged WAXS patterns. Hoover and Vasanthan (1994b) found unchanged *d* spacings with only marginally changed intensities for annealed wheat, potato, lentil, and oat starches. We also found no significant changes in crystal type and degree of crystallinity after one- and two-step annealing of wheat, potato, and pea starches (Jacobs, 1998).

Small-angle X-ray scattering (SAXS) peak positions after one- and two-step annealing of wheat and potato starches were unchanged, indicating that the repeat distance of crystalline and amorphous lamellae was not altered as a result of annealing (Jacobs et al., 1998b). However, annealing may affect the individual lamellar sizes (without affecting the overall repeat distance). The more pronounced peaks for the annealed starches indicated a higher electron density contrast between the amorphous and crystalline regions (Jacobs et al., 1998b).

Impact of Annealing on Starch Double-Helix Content. ^{13}C CP/MAS NMR spectra of native and annealed wheat, potato, and pea starches were not significantly different (Jacobs, 1998), indicating no changes in double-helix content as a result of annealing or changes below the detection limit.

Impact of Annealing on Amylose−Lipid Complexes in the Starch Granule. Lorenz and Kulp (1984) observed development of a V-type pattern (attributed to crystalline amylose−lipid complexes) after annealing of normal- and high-amylose barley starches. Evidence of *crystalline* amylose−lipid complexes has not been found after annealing of other lipid-containing starches. For

Table 1. Annealing Conditions for Starches, Cited in the Literature

starch	temp (°C)	time	water content (%)	reference
amaranth	45−55	2/12 h	excess[a]	Parades-Lopez et al. (1989); Parades-Lopez and Hernandez-Lopez (1991)
barley (normal, waxy, high amylose)	25−50	24/72 h	excess	Lorenz and Kulp (1984)
	45/55	72 h	excess	Tester et al. (1991)
	52	2/48 h	excess	Shi and Seib (1992)
maize (normal, waxy, high amylose)	50/55	2−48 h	excess	Krueger et al. (1987a,b)
	50	48 h	excess	Deffenbaugh and Walker (1989a)
	50−70[b]	2−72 h	excess	Knutson (1990)
	30−50	24 h	50	Larsson and Eliasson (1991)
	60	2/48 h	excess	Shi and Seib (1992)
lentil and oat	50	0.5−72 h	excess	Hoover and Vasanthan (1994b,c)
pea	50−56[b]	24 h	excess	Jacobs et al. (1995, 1996, 1997c)
potato	52	0.5−10 h	excess	Wiegel (1933)
	50−60[b]	?	excess	Hjermstad (1971)
	50	72 h	excess	Kuge and Kitamura (1985)
	30−50	24 h	50	Larsson and Eliasson (1991)
	52−64[b]	14/92 h	excess	Stute (1992)
	50 °C	0.5−72 h	excess	Hoover and Vasanthan (1994b,c)
	50−55[b]	24 h	excess	Jacobs et al. (1995, 1996, 1997a,b)
	52−54	16 h	40−excess	Eerlingen et al. (1996)
	50	2 min−21 h	excess	Muhrbeck and Svensson (1996)
rice (normal, waxy)	40	114 h	50	Nakazawa et al. (1984)
	55/65	72 h	excess	Tester and Morrison (1990b)
	50	1 week	50	Liu and Lelièvre (1991)
	60/70	2/48 h	excess	Shi and Seib (1992)
	55	4−24 h	40−excess	Seow and Teo (1993)
	50	15 min−24 h	excess	Seow and Vasanti-Nair (1994)
	55	24 h	excess	Jacobs et al. (1995, 1996)
rye	45	16 h	excess	Münzing (1989)
	50	1 h	excess	Schierbaum and Kettlitz (1994)
wheat	50	72 h	excess	Gough and Pybus (1971)
	40/50	24/72 h	excess	Lorenz and Kulp (1978, 1980)
	50	72/96 h	excess	Marchant and Blanshard (1978, 1980)
	42/47	30 min	50	Yost and Hoseney (1986)
	25	55 days	55	Slade and Levine (1987)
	50	48 h	excess	Deffenbaugh and Walker (1989a)
	40	3 h	excess	Münzing (1989)
	30−50	10 min−48 h	50	Larsson and Eliasson (1991)
	50	0.5−72 h	excess	Hoover and Vasanthan (1994b,c)
	45−53[b]	24 h	excess	Jacobs et al. (1995, 1996, 1997a,b)

[a] Excess water content means >60%. [b] Including multistep annealing temperatures.

wheat starch, based on the unchanged DSC amylose−lipid dissociation endotherm (Larsson and Eliasson, 1991; Jacobs et al., 1995, 1998a) and the unchanged ^{13}C CP/MAS NMR signal at 31 ppm [attributed to carbons of fatty acids that are immobilized in amylose-lipid complexes (Morrison et al., 1993a,b; Jacobs et al., 1997)], the amount of amylose−lipid complexes was found to be unchanged by annealing.

Impact of Annealing on Starch Gelatinization Characteristics. Using hot-stage polarization microscopy, an increase of the gelatinization temperature and a decrease of the gelatinization temperature range as a result of annealing were observed (Gough and Pybus, 1971; Lorenz and Kulp,1978, 1980, 1984). Their findings were confirmed later by DSC experiments (Nakazawa et al., 1984; Kuge and Kitamura, 1985; Yost and Hoseney, 1986; Slade and Levine, 1987; Krueger et al., 1987a,b; Münzing, 1989; Parades-Lopez et al., 1989; Knutson, 1990; Tester and Morrison, 1990b; Larsson and Eliasson, 1991; Liu and Lelièvre, 1991; Parades-Lopez and Hernandez-Lopez, 1991; Tester et al., 1991; Stute, 1992; Shi and Seib, 1992; Seow and Teo, 1993; Hoover and Vasanthan, 1994b; Seow and Vasanti-Nair, 1994; Jacobs et al., 1995, 1997, 1998b; Eerlingen et al., 1996; Muhrbeck and Svensson, 1996) and by small-angle light scattering (Marchant and Blanshard, 1978, 1980). Gelatinization enthalpies were increased (Kuge and Kitamura, 1985; Krueger et al., 1987a,b; Slade and Levine, 1987; Münzing, 1989; Knutson, 1990; Tester and Morrison, 1990b; Parades-Lopez and Hernandez-Lopez, 1991; Seow and Teo, 1993; Hoover and Vasanthan, 1994b; Seow and Vasanti-Nair, 1994; Jacobs et al., 1995; Eerlingen et al., 1996; Muhrbeck and Svensson, 1996; Jacobs et al., 1997, 1998b) or unchanged (Nakazawa et al., 1984; Yost and Hoseney, 1986; Larsson and Eliasson, 1991; Stute, 1992; Shi and Seib, 1992; Seow and Teo, 1993; Jacobs et al., 1995, 1997; Eerlingen et al., 1996).

Annealing studies of maize starches with different amylose contents (Krueger et al., 1987b; Knutson, 1990) showed that the largest changes in DSC characteristics were observed for starches with the highest amylose content. When annealing potato starches with varying degrees of phosphorylation, Muhrbeck and Svensson (1996) found the largest increase in gelatinization temperature for those samples with the lowest degree of phosphorylation, whereas the largest increase in gelatinization enthalpy was observed for the highly phosphorylated starches.

Using synchrotron radiation, SAXS patterns were recorded during gelatinization of native and one- and two-step annealed wheat and potato starches (Jacobs et al., 1998b). The major difference between SAXS gelatinization patterns of native and annealed starches was the lack of increase in integrated intensity at the onset of gelatinization for the annealed starches. Thus,

Table 2. Changes in Starch Pasting Characteristics, Measured by Viscometry, after Annealing (+, Increase; −, Decrease; =, Unchanged; 0, Not Determined)

technique	starch	onset temp[a]	visc max[b]	visc cooling[c]	reference
Ostwald viscometer[d]	potato	+	−	0	Wiegel (1933)
Corn Industries viscometer[e]	potato	+	−	+	Hjermstad (1971)
viscoamylograph[e]	potato	+	−	=	Kuge and Kitamura (1985)
		+	−	+	Stute (1992)
		+	−	+	Hoover and Vasanthan (1994b)
		+	−	+	Jacobs et al. (1995, 1996)
	wheat	=	+	+	Hoover and Vasanthan (1994b)
		−	+	+	Jacobs et al. (1995, 1996)
	lentil	+	−	−	Hoover and Vasanthan (1994b)
	oat	+	+	−	Hoover and Vasanthan (1994b)
	rye	+	=/−	=/−	Schierbaum and Kettlitz (1994)
	pea	=	+	+	Jacobs et al. (1995, 1996)
	rice	-	+	+	Jacobs et al. (1995, 1996)
rapid viscoanalyzer[f]	maize	=	−	−	Deffenbaugh and Walker (1989a)
	wheat	+	−	=	Deffenbaugh and Walker (1989a)
		+/−	+	+	Jacobs et al. (1995, 1996)
	potato	+	−	+	Jacobs et al. (1995, 1996); Eerlingen (1997)
	pea	+/=	+/-	+/−	Jacobs et al. (1995, 1996)
	rice	=	+	+	Jacobs et al. (1995, 1996)

[a] Onset temperature of viscosity development. [b] Maximum viscosity during heating. [c] Viscosity on cooling. [d] 1% starch suspension. [e] 5−6.6% stach suspension. [f] 6.6−10% starch suspension.

in the case of the annealed starches, SAXS measurements indicated that the water uptake is not only retarded but that there is less water absorption in the first phase of gelatinization than for the native starches (Jacobs et al., 1998b).

Impact of Annealing Temperature, Time, and Moisture Content on the Magnitude of Changes in DSC Gelatinization Characteristics. Annealing occurs most rapidly, and to the largest extent, just below the *temperature* at which gelatinization starts (Lorenz and Kulp, 1984; Krueger et al., 1987a; Slade and Levine, 1987; Knutson, 1990; Larsson and Eliasson, 1991). Nevertheless, the phenomenon has been reported to occur at temperatures down to 25 °C [after 3 days for barley starch (Lorenz and Kulp, 1984); after 55 days for wheat starch (Slade and Levine, 1987)]. The latter seems to be in conflict with the proposed location of the glass transition temperature just before DSC gelatinization (Maurice et al., 1985; Biliaderis et al., 1986; Slade and Levine, 1988). However, it must be kept in mind that T_g depends on operative conditions of moisture, temperature, *and* time. In other words, the operative T_g relative to annealing can decrease with increasing holding time, in the presence of water, due to the effect of dynamic plasticisation (Slade and Levine, 1988).

Multistep annealing allows higher annealing temperatures than can be obtained by one-step annealing (Hjermstad, 1971; Knutson, 1990; Stute, 1992; Eerlingen et al., 1996; Jacobs et al., 1997, 1998b). Thus, annealing temperatures were 48 °C (first step) and 53 °C (second step) for wheat starch and 50 °C (first step) and 55 °C (second step) for potato starch (Jacobs et al., 1998b).

The impact of annealing *time* on the magnitude of changes in DSC gelatinization characteristics was studied by Krueger et al. (1987a), Knutson (1990), Larsson and Eliasson (1991), Seow and Teo (1993), Hoover and Vasanthan (1994b), Seow and Vasanti-Nair (1994), and Muhrbeck and Svensson (1996). Generally, increases in gelatinization temperatures and enthalpies were more pronounced with longer incubation times. Krueger et al. (1987a) and Larsson and Eliasson (1991) reported the largest changes in gelatinization temperature for maize and wheat starches to occur during the first 2−6 h (at 50 °C). Increases in enthalpy as a result of annealing at 50 °C were evident after only 48, 6, 2, and 1 h, for wheat, oat, potato, and lentil starches, respectively (Hoover and Vasanthan, 1994b). These observations may have implications for process steps in the isolation of starch as well as for their end use.

With regard to *moisture content* during annealing, Krueger et al. (1987a) observed slightly larger and at the same time significant changes in gelatinization temperature of maize starch with increasing moisture content up to 67% (w/w), with no further effect at higher water content. The change in gelatinization enthalpy was practically not affected by increasing moisture content. Hoover and Vasanthan (1994b) found that the magnitude of changes in gelatinization temperatures and enthalpies of wheat, oat, potato, and lentil starches increased with increasing moisture content up to 80% (w/w).

Impact of Annealing on Starch Pasting Characteristics. A schematic overview of changes in pasting properties, measured by viscometry, that are observed after annealing is shown in Table 2. Wiegel (1933) reported a decreased viscosity, at temperatures between 70 and 95 °C, of a potato starch suspension, after preliminary treatment of the starch suspension at 52 °C during 1−2 h. Hjermstad (1971) also found a decreased viscosity during heating of annealed potato starch, together with an increased onset temperature of swelling, an increased stability on cooking, and an increased tendency to form a gel on cooling. Using the viscoamylograph, Kuge and Kitamura (1985), Stute (1992), Hoover and Vasanthan (1994b), and Jacobs et al. (1995, 1996) confirmed results of Hjermstad (1971): a higher onset temperature, a lower peak viscosity, and a higher (or unchanged) viscosity on cooling, as a result of annealing of potato starch, were observed. Hoover and Vasanthan (1994b) studied the pasting of native and annealed wheat, lentil, and oat starches, and Schierbaum and Kettlitz (1994) did so for native and annealed rye starches. Annealing of wheat, pea, and rice starches resulted in increased amylograph peak viscosities and viscosities upon cooling (Jacobs et al., 1995). However, it was equally reported that different results are obtained when the effects of annealing of pea and wheat starch were analyzed with the rapid viscoanalyzer (Jacobs et al., 1996).

Deffenbaugh and Walker (1989) detected differences in rapid viscoanalyzer (rva) pasting properties between native and annealed wheat and maize starches (Table 2). Rva pasting characteristics of native and annealed wheat, potato, pea, and rice starches were studied (Jacobs et al., 1995, 1996). The published data show that the effects of annealing on the pasting curves depend on the botanical source of the starch investigated and the measuring instrument (Table 2). Furthermore, the heating/cooling rate applied in the instrument was found to be important in determining the way in which the starch pasting curve is altered by annealing (Jacobs et al., 1996). Apparently, annealed starches are less sensitive toward heating rate and shearing time than the corresponding native starches (Jacobs et al., 1996). Hoover and Vasanthan (1994c) studied the flow properties of gelatinized suspensions of native and annealed starches with a cone and plate viscometer. Depending on the starch botanical source, they found an increase or a decrease in the apparent viscosity as a result of annealing.

Impact of Annealing on Starch Swelling Power and Solubility. Swelling power and amylose leaching were found to decrease after annealing of wheat (Lorenz and Kulp, 1978; Hoover and Vasanthan, 1994b,c; Jacobs, 1998), potato (Kuge and Kitamura, 1985; Hoover and Vasanthan, 1994b,c), and oat and lentil (Hoover and Vasanthan, 1994b,c) starches.

Impact of Annealing on Dynamic Rheological Characteristics of Starch Gels. The elastic moduli (G') of 20.0 and 9.9% gels of annealed wheat starches were higher than those of the starting materials, indicating an increased rigidity of the annealed starch granules (Jacobs, 1998).

Impact of Annealing on the Susceptibility of Granular Starch to Acid Hydrolysis. The annealing treatment affects the susceptibility of granular starches to acid hydrolysis. Hoover and Vasanthan (1994b) found a ~5% decrease in the degree of hydrolysis of annealed wheat, potato, and lentil starches after 20 days of acid hydrolysis (2.2 M HCl, 35 °C) but an increased susceptibility (+14%) of annealed oat starch. We also found a slight (~5%) decrease in the susceptibility of potato starch to acid hydrolysis (20 days, 2.2 M HCl, 35 °C). However, for wheat and pea starches, no differences in susceptibility were observed between native and annealed starches (Jacobs et al., 1997). After lintnerization of wheat, potato, and pea starches, differences in DSC characteristics between native and one- and two-step annealed samples almost disappeared (Jacobs et al., 1998a). For 7 and 20 days lintnerized wheat starches, 7 days lintnerized potato starches, and 20 days lintnerized pea starches, the chain length distribution patterns [determined by high-performance anion exchange chromatography (HPAEC)] showed a higher average DP and/or a slightly higher proportion of singly branched (DP 22−30) to short linear (DP 10−18) chains for the annealed than for the corresponding native samples. It is suggested that, as a result of annealing, the branch points of amylopectin become more resistant to acid attack, leading to a higher proportion of singly branched to short linear chains and/or a higher relative amount of multiply branched (DP > 35) chains (Jacobs et al., 1998a).

Impact of Annealing on the Susceptibility of Granular Starch to Enzymic Hydrolysis. Gough and Pybus (1971) and Lorenz and Kulp (1980) found annealing to increase the susceptibility of wheat starch to degradation with *Bacillus subtilis* α-amylase or a fungal α-amylase, respectively. Likewise, annealing was found to increase enzymic susceptibility of annealed barley (Lorenz and Kulp, 1984; Lauro et al., 1993) and oat (Hoover and Vasanthan, 1994b) starches. For annealed potato starch, however, Kuge and Kitamura (1985) observed a decreased susceptibility to *B. subtilis* α-amylolysis. A slightly decreased degree of solubilization of wheat, potato, and lentil starches, after 72 h of porcine pancreatic α-amylolysis, was reported by Hoover and Vasanthan (1994b). In a recent study (Jacobs et al., 1997), we found the impact of one- and two-step annealing on susceptibility to pancreatin hydrolysis to depend on starch botanical origin and/or the crystal type. In the first rapid phase of hydrolysis, the enzyme resistance was increased for one-step-annealed pea starch and annealed potato starches and was approximately unchanged for annealed wheat starches and two-step annealed pea starch. However, in the second slower phase, annealed wheat and pea starches were hydrolyzed to a larger extent than the corresponding native starches (although not significantly for wheat), whereas annealed potato starches were even more resistant to pancreatic α-amylolysis than native potato starch (Jacobs et al., 1997). DSC and ^{13}C CP/MAS NMR evidence indicated that annealing increased the susceptibility of double-helical structures in the wheat starch granule toward pancreatin hydrolysis (Jacobs et al., 1997).

Heat−Moisture Treatment. *Definition.* Heat−moisture treatment of starch is defined as a **physical treatment** that involves incubation of starch granules at **low moisture levels**, that is, below 35% water (w/w), during a certain period of **time**, at a **temperature** above the glass transition temperature but below the gelatinization temperature. Temperature−moisture conditions for heat−moisture treatments, however, have often been chosen without consideration of the exact gelatinization temperature of the starch at the moisture level investigated. Therefore, some of the reported results on heat−moisture treatments may have been influenced by partial gelatinization (Eerlingen et al., 1996). Heat−moisture treatment conditions for starches of different botanical origin are summarized in Table 3. Heat−moisture treatment is suggested to occur during drying of wheat grains (temperature reaching 80 °C and moisture content reaching 9.7%) (Zamponi et al., 1990).

Effects of Heat−Moisture Treatment on Starch Granule Morphology and Crystallinity. After heat−moisture treatment of maize, wheat, yam, lentil, and potato starches, no changes in external morphology were observed (Kulp and Lorenz, 1981; Stute, 1992; Hoover and Vasanthan, 1994a; Franco et al., 1995; Hoover and Manuel, 1996). However, Kawabata et al. (1994) observed formation of cracks on the surface of treated maize and potato starches, together with a hollow inside the granule.

A characteristic effect of heat−moisture treatment is the evolution of the WAXS pattern from the B- to the A- (or C-) type for potato starch (Sair, 1967; Donovan et al., 1983; Kuge and Kitamura, 1985; Stute, 1992; Hoover and Vasanthan, 1994c; Kawabata et al., 1994) and also for yam starch (Hoover and Vasanthan, 1994c). Such a shift from B- to A-crystal type as a result of heat−moisture treatment was confirmed by ^{13}C CP/MAS NMR based on variations in C-1 multiplicity

Table 3. Heat−Moisture Treatment Conditions for Starches, Cited in the Literature

starch	temp (°C)	time	water content (%)	reference
arrowroot and barley	100	16 h	18−27	Lorenz and Kulp (1982)
cassava	100	16 h	18−27	Lorenz and Kulp (1982)
	110	3−16 h	18−24	Abraham (1993)
maize (normal, waxy,	95−110	16 h	18−27	Sair (1967)
high amylose	120	30/180 min	25	Fukui and Nikuni (1969)
	?	?	?	Kobayashi (1993)
	125	5/20 min	14	Kawabata et al. (1994)
	100	4 h	25	Schierbaum and Kettlitz (1994)
	100	16 h	18−27	Franco et al. (1995)
	100	16 h	30	Hoover and Manuel (1996)
lentil and oat	100	16 h	10−30	Hoover and Vasanthan (1994a,c); Hoover et al. (1994)
pea	100	16 h	30	Hoover et al. (1993)
potato	95−110	16 h	18−27	Sair (1967)
	100	16 h	18−27	Lorenz and Kulp (1981); Kulp and Lorenz (1981); Donovan et al. (1983)
	80−120	15−60 min	5−27	Kuge and Kitamura (1985)
	110/120	140/240 min	20	Stute (1992)
	?	?	?	Kobayashi (1993)
	100	16 h	10−30	Hoover and Vasanthan (1994a,c); Hoover et al. (1994)
	110	30 min	16.5	Kawabata et al. (1994)
	84−105	16 h	20−35	Eerlingen et al. (1996, 1997)
rice	120	30/180 min	25	Fukui and Nikuni (1969)
rye	100	4 h	22/25	Radosta et al. (1992); Schierbaum and Kettlitz (1994)
triticale	100	16 h	18−27	Lorenz and Kulp (1982)
wheat	120	30/180 min	25	Fukui and Nikuni (1969)
	100	16 h	18−27	Lorenz and Kulp (1981); Kulp and Lorenz (1981); Donovan et al. (1983)
	100	16 h	10−30	Hoover and Vasanthan (1994a,c); Hoover et al. (1994)
	100	4 h	25	Schierbaum and Kettlitz (1994)
yam	100	16 h	10−30	Hoover and Vasanthan (1994c)

(Gidley and Bociek, 1985). However, for potato starch, not all temperature−moisture conditions induce such a shift from B- to A-type crystallinity (R. C. Eerlingen, Katholieke Universiteit Leuven, Heverlee, Belgium, unpublished results). For arrowroot and cassava starches, a shift from C- to A-type was observed (Lorenz and Kulp, 1982). Such transitions were not observed after annealing. The A-type pattern of cereal starches is unchanged after heat−moisture treatment and shows unchanged or increased intensities (Sair, 1967; Fukui and Nikuni, 1969; Donovan et al., 1983; Radosta et al., 1992; Hoover and Vasanthan, 1994a; Franco et al., 1995; Hoover and Manuel, 1996). However, some authors found decreased X-ray intensities for some heat−moisture-treated barley and triticale (Lorenz and Kulp, 1982), cassava (Abraham, 1993), and maize (Franco et al., 1995) starches.

Impact of Heat−Moisture Treatment on Starch Double-Helix Content. ^{13}C CP/MAS NMR spectra of native and heat−moisture-treated potato starches were not significantly different (Eerlingen, unpublished results). On the basis of the work by Gidley and Bociek (1985), this means that there are either no changes in double-helix content as a result of heat−moisture treatment or that they are below the detection limit.

Impact of Heat−Moisture Treatment on Amylose−Lipid Complexes in the Starch Granule. In some cases, for cereal starches, development of two new peaks, characteristic for the V-type pattern (attributed to crystalline amylose−lipid complexes), was observed (Fukui and Nikuni, 1969; Kawabata et al., 1994). Such indication of formation of crystalline amylose−lipid complexes as a result of annealing was found only for barley starches (Lorenz and Kulp, 1984).

Donovan et al. (1983) found an unchanged DSC amylose−lipid dissociation endotherm after heat−moisture treatment of wheat starch. For wheat and maize starches, Hoover and Vasanthan (1994a) and Hoover and Manuel (1996) observed a decreased apparent amylose content, indicating extra formation of amylose−lipid complexes as a result of heat−moisture treatment.

Impact of Heat−Moisture Treatment on Starch Gelatinization Characteristics. As for annealing, heat−moisture treatment increases the gelatinization temperature, but, in contrast with the narrower gelatinization temperature range observed after annealing, this range was broadened (Sair, 1967; Kulp and Lorenz, 1981; Donovan et al., 1983; Radosta et al., 1992; Stute, 1992; Kobayashi, 1993; Hoover et al., 1993, 1994; Hoover and Vasanthan, 1994a; Eerlingen et al., 1996; Hoover and Manuel, 1996) or unchanged (Eerlingen et al., 1996; Hoover and Manuel, 1996) after heat−moisture treatment. In some cases, a biphasic endotherm (in excess water) was observed after treatment of wheat, potato, or rye starches (Donovan et al., 1983; Radosta et al., 1992; Kobayashi et al., 1993). The gelatinization enthalpies were decreased (Donovan et al., 1983; Kuge and Kitamura, 1985; Radosta et al., 1992; Stute, 1992; Kobayashi, 1993; Hoover et al., 1994; Hoover and Vasanthan, 1994c; Eerlingen et al., 1996) or unchanged (Kuge and Kitamura, 1985; Hoover et al., 1993, 1994; Hoover and Vasanthan, 1994c; Eerlingen et al., 1996; Hoover and Manuel, 1996).

Impact of Heat−Moisture Treatment on Starch Pasting Characteristics. Kulp and Lorenz (1981), Kuge and Kitamura (1985), Stute (1992), and Hoover and Vasanthan (1994c) investigated the impact of heat−moisture treatment on the viscograph or rapid viscoanalyzer pasting properties of potato starch. A higher onset temperature of viscosity development, a lower peak viscosity, and a higher or lower end viscosity (depending on the treatment conditions) were observed. The same observations were made for cassava (Lorenz and Kulp, 1982; Abraham, 1993), maize (Schierbaum and Kettlitz, 1994; Franco et al., 1995; Hoover and Manuel, 1996),

wheat (Kulp and Lorenz, 1981), rye (Schierbaum and Kettlitz, 1994), and lentil, oat, and yam (Hoover and Vasanthan, 1994a) starches. An overall increase in heat−moisture-treated wheat starch viscosity was noted by Hoover and Vasanthan (1994a). Hoover and Vasanthan (1994c) also found significant effects of heat−moisture treatment on the flow properties of gelatinized starch suspensions, using a cone and plate viscometer.

Impact of Heat−Moisture Treatment on Starch Swelling Power and Solubility. Swelling power and carbohydrate leaching were generally found to decrease as a result of heat−moisture treatment (Sair, 1967; Kulp and Lorenz, 1981; Kuge and Kitamura, 1985; Hoover et al., 1993, 1994; Hoover and Vasanthan, 1994a,c; Hoover and Manuel, 1996), as was also found after annealing. Eerlingen et al. (1996) found no direct relationship between temperature and/or moisture content during treatment and the extent of the effect on swelling power or solubility. An increased solubility was observed for heat−moisture-treated wheat (Kulp and Lorenz, 1981), rye (Radosta et al., 1992), and barley and triticale (Lorenz and Kulp, 1982) starches.

Impact of Heat−Moisture Treatment on Dynamic Rheological Characteristics of Starch Gels. The extent to which the elastic moduli (G') of the potato starch gels were affected after different temperature−moisture treatment conditions could, on the basis of the theory of Steeneken (1989), be explained for all starch concentrations investigated (3.0, 6.6, and 20% w/w), in terms of swelling power, close packing concentration, and the starch concentration used. Thus, for those starches in the concentrated regime, G' values were determined by the rigidity of the granules and G' increased with decreasing swelling power. For the starches in the diluted regime, G' increased with increasing swelling power (Eerlingen et al., 1997).

Impact of Heat−Moisture Treatment on the Susceptibility of Granular Starch to Acid Hydrolysis. The susceptibility to acid hydrolysis decreased after treatment of maize (Hoover and Manuel, 1996), pea (Hoover et al., 1993), potato (Hoover and Vasanthan, 1994a), and wheat, lentil, oat, and yam (Hoover and Vasanthan, 1994a) starches. However, for oat, potato, and yam starches, Hoover and Vasanthan (1994a) noted an increased solubilization during the first 7 days of hydrolysis. The increase in DSC transition temperature of lintnerized potato starches was less for the heat−moisture-treated samples than for the native one (Eerlingen, unpublished results). Despite differences in the degree of hydrolysis, no significant changes in chain length distibutions (measured by HPAEC) of lintnerized native or heat−moisture-treated potato starches, before and after debranching, were found (Eerlingen, unpublished results). This contrasts with observations made after annealing (Jacobs et al., 1998a). The difference in behavior cannot be rationalized at present.

Impact of Heat−Moisture Treatment on the Susceptibility of Granular Starch to Enzymic Hydrolysis. Depending on botanical origin and treatment conditions, increased or decreased susceptibilities to enzymic hydrolysis were observed as a result of heat−moisture treatment (Kulp and Lorenz, 1981; Lorenz and Kulp, 1982; Kuge and Kitamura, 1985; Hoover et al., 1993; Kobayashi, 1993; Hoover and Vasanthan, 1994a; Kawabata et al., 1994; Franco et al., 1995; Hoover and Manuel, 1996). The reasons for the different behaviors are likely to be ascribed to variations in starch source as well as to differences in treatment conditions.

Major Differences between the Effects of Annealing and Heat−Moisture Treatment. The effects of annealing and heat−moisture treatment on starch are most readily differentiated using WAXS and DSC.

(1) Whereas annealing hardly affects WAXS patterns, heat−moisture treatment changes B-type patterns into A- (or C-) type patterns.

(2) Whereas annealing drastically narrows DSC gelatinization endotherms, these endotherms are broadened after heat−moisture treatment.

DISCUSSION AND SUGGESTIONS FOR FUTURE WORK

Despite a broad description in the literature of the changes in physicochemical properties of starches of different botanical origin that occur as a result of hydrothermal treatments, the exact molecular mechanism(s) of these treatments remain(s) unknown.

Possible explanations for the observed effects of annealing (ANN) and heat−moisture treatment (HMT) on starch properties include the following:

(1) Changes with Respect to the Crystallinity. These are either (a) crystallite growth or perfection of already existing crystallites (ANN: Lorenz and Kulp, 1980, 1984; Yost and Hoseney, 1986; Slade and Levine, 1987; Tester and Morrison, 1990b; Larsson and Eliasson, 1991; Parades-Lopez and Hernandez-Lopez, 1991; Tester et al., 1991; Seow and Teo, 1993; Muhrbeck and Svensson, 1996; Jacobs et al., 1997, 1998,a,b; HMT: Donovan et al., 1983; Hoover and Vasanthan, 1994a) as also also observed when synthetic polymers are annealed (Wunderlich, 1976); (b) changes in packing arrangement of double helices in starch crystallites from B- to A-type crystallinity (HMT: Sair, 1967; Donovan et al., 1983; Kuge and Kitamura, 1985; Stute, 1992; Hoover and Vasanthan, 1994a; Kawabata et al., 1994); (c) partial melting and realignment of polymer chains (ANN: Marchant and Blanshard, 1978), or (d) development of new crystallites in the amorphous regions. This may be formation of amylose crystallites (ANN: Krueger et al., 1987a,b; HMT: Hoover and Manuel, 1996) or formation of crystalline amylose−lipid complexes (ANN: Lorenz and Kulp, 1984; HMT: Fukui and Nikuni, 1969; Kawabata et al., 1994; Hoover and Manuel, 1996).

(2) Changes with respect to the amorphous fraction which have to do with increase in order, without increase in crystallinity. Mentioned were (a) increased interactions between amylose chains or between amylose and amylopectin (ANN: Nakazawa et al., 1984; Knutson, 1990; Seow and Teo, 1993; Hoover and Vasanthan, 1994b; Seow and Vasanti-Nair, 1994; Jacobs et al., 1997, 1998a, 1998b; HMT: Hoover et al., 1993, Hoover and Vasanthan, 1994a; Kawabata et al., 1994); (b) extra formation of amylose−lipid complexes (ANN: Lorenz and Kulp, 1984; HMT: Hoover and Vasanthan, 1994a), or (c) transformation of amorphous amylose into a helix (HMT: Lorenz and Kulp, 1982).

(3) Alterations of the interactions (coupling forces) between crystallites and the amorphous parts, for example, a reorientation of the crystallites within the amorphous matrix (ANN: Stute, 1992).

Because, in a semicrystalline structure such as the starch granule, crystalline and amorphous parts are interdependent, in our opinion, changes with respect to the crystallinity (1) and/or the amorphous fraction (2)

evidently also affect these interactions between crystalline and amorphous parts.

For several starch physicochemical properties, the observed effects of the treatments depend on starch botanical origin and/or the treatment conditions (temperature and moisture level). Most likely, the changes that occur in the starch granule on a molecular level during annealing or heat−moisture treatment, are a combination of the above-mentioned possible explanations.

SAXS, using synchrotron radiation, is a promising technique for elucidating some unknown features of starch granule structure (Cameron and Donald, 1992, 1993a,b; Jenkins et al., 1993, 1994; Jenkins and Donald, 1995; Jacobs et al., 1998b). In this respect, time-resolved SAXS *during* the annealing (or heat−moisture) treatment may provide more information on molecular mechanisms of hydrothermal treatments. Also, small-angle neutron scattering (SANS), which has been applied to native starches by Blanshard et al. (1984) and more recently by Jenkins and Donald (1996) and Waigh et al. (1996), seems promising for the investigation of hydrothermal treatment effects on water distribution in granular starches, because with SANS experiments water concentrations in different regions of the granule can be determined. Recently (Buléon et al., 1997; Waigh et al., 1997) X-ray microfocus diffraction experiments, using a synchrotron source, made it possible to study ~2 μm regions within one starch granule. The latter technique could also be applied in the study of the effects of hydrothermal treatments on starch molecular structure.

ABBREVIATIONS USED

ANN, annealing; HMT, heat−moisture treatment; DP, degree of polymerization; WAXS, wide-angle X-ray scattering; SAXS, small-angle X-ray scattering; SANS, small-angle neutron scattering; ^{13}C CP/MAS NMR, solid state ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance; T_g, glass transition temperature; DSC, differential scanning calorimetry; HPAEC, high-performance anion exchange chromatography.

ACKNOWLEDGMENT

We thank the Belgian Fonds voor Wetenschappelijk Onderzoek−Vlaanderen for a research position as aspirant (H.J.). Helpful discussions with Dr. R. C. Eerlingen are highly appreciated.

LITERATURE CITED

Abraham, T. E. Stabilization of paste viscosity of cassava starch by heat-moisture treatment. *Starch* **1993**, *45*, 131−135.

Atwell, W. A.; Hood, L. F.; Lineback, D. R.; Varriano-Marston, E.; Zobel, H. F. The terminology and methodology associated with basic starch phenomena. *Cereal Foods World* **1988**, *33*, 306−311.

Biliaderis, C. G.; Page, C. M.; Maurice, T. J.; Juliano, B. O. Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* **1986**, *34*, 6−14.

Blanshard, J. M. V. Starch granule structure and function: a physicochemical approach. In *Starch: Properties and Potential*; Galliard, T., Ed.; Wiley: New York, 1987; pp 16−54.

Blanshard, J. M. V.; Bates, D. R.; Muhr, A. H.; Worcester, D. L.; Higgins, J. S. Small-angle neutron scattering studies of starch granule structure. *Carbohydr. Polym.* **1984**, *4*, 427−442.

Buléon, A.; Pontoire, B.; Riekel, C.; Chanzy, H.; Helbert, W.; Vuong, R. Crystalline ultrastructure of starch granules revealed by synchrotron radiation microdiffraction mapping. *Macromolecules* **1997**, *30*, 3952−3954.

Cameron, R. E.; Donald, A. M. A small-angle X-ray scattering study of the annealing and gelatinization of starch. *Polymer* **1992**, *33*, 2628−2635.

Cameron, R. E.; Donald, A. M. A small-angle X-ray scattering study of starch gelatinization in excess and limiting water. *J. Polym. Sci., Polym. Phys. Ed.* **1993a**, *31*, 1197−1203.

Cameron, R. E.; Donald, A. M. A small-angle X-ray scattering study of the absorption of water into the starch granule. *Carbohydr. Res.* **1993b**, *244*, 225−236.

Cooke, D.; Gidley, M. J. Loss of crystalline and molecular order during starch gelatinisation: origin of the enthalpic transition. *Carbohydr. Res.* **1992**, *227*, 103−112.

Deffenbaugh, L. B.; Walker, C. E. Student laboratory experiments with the rapid visco-analyzer. In *Rapid Visco-Analyzer Operation Manual*; 1989; pp 13−14.

Donovan, J. W.; Lorenz, K.; Kulp, K. Differential scanning calorimetry of heat-moisture treated wheat and potato starches. *Cereal Chem.* **1983**, *60*, 381−387.

Eerlingen, R. C.; Jacobs, H.; Van Win, H.; Delcour, J. A. Effect of hydrothermal treatment on the gelatinisation properties of potato starch as measured by differential scanning calorimetry. *J. Therm. Anal.* **1996**, *47*, 1229−1246.

Eerlingen, R. C.; Jacobs, H.; Block, K.; Delcour, J. A. Effects of hydrothermal treatment on the rheological properties of potato starch. *Carbohydr. Res.* **1997**, *297*, 347−356.

Franco, C. M. L.; Ciacco, C. F.; Tavares, D. Q. Effect of heat-moisture treatment on the enzymatic susceptibility of corn starch granules. *Starch* **1995**, *47*, 223−228.

French, D. Organization of starch granules. In *Starch Chemistry and Technology*, 2nd ed.; Whistler, R. L., BeMiller, J. N., Paschal, E. F., Eds.; Academic Press: New York, 1984; pp 183−212.

Fukui, T.; Nikuni, Z. Heat-moisture treatment of cereal starch observed by X-ray diffraction. *Agric. Biol. Chem.* **1969**, *33*, 460−462.

Gidley, M. J.; Bociek, S. M. Molecular organization in starches: a ^{13}C CP/MAS NMR study. *J. Am. Chem. Soc.* **1985**, *107* (7), 7040−7044.

Gough, B. M.; Pybus, J. N. Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50 °C. *Starch* **1971**, *23*, 210−212.

Hizukuri, S. Starch: analytical aspects. In *Carbohydrates in Food*; Eliasson, A.-C., Ed.; Dekker: New York, 1996; pp 347−429.

Hjermstad, E. T. Potato starch properies by controlled heating in aqueous suspension. U.S. Patent 3,578,497, 1971.

Hoover, R.; Manuel, H. The effect of heat-moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylomaize V starches. *J. Cereal Sci.* **1996**, *23*, 153−162.

Hoover, R.; Vasanthan, T. Effect of heat-moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydr. Res.* **1994a**, *252*, 33−53.

Hoover, R.; Vasanthan, T. The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. *J. Food Biochem.* **1994b**, *17*, 305−325.

Hoover, R.; Vasanthan, T. The flow properties of native, heat-moisture treated, and annealed starches from wheat, oat, potato and lentil. *J. Food Biochem.* **1994c**, *18*, 67−82.

Hoover, R.; Swamidas, G.; Vasanthan, T. Studies on the physicochemical properties of native, defatted, and heat-moisture treated pigeon pea (*Cajanus cajan* L.) starch. *Carbohydr. Res.* **1993**, *246*, 185−203.

Hoover, R.; Vasanthan, T.; Senayake, N. Y.; Martin, A. M. The effects of defatting and heat-moisture treatment on the

retrogradation of starch gels from wheat, oat, potato and lentil. *Carbohydr. Res.* **1994**, *261*, 13−24.

Jacobs, H. Impact of annealing on physico-chemical properties of starch. Ph.D. Dissertation, Leuven, Belgium, 1998.

Jacobs, H.; Eerlingen, R. C.; Clauwaert, W.; Delcour, J. A. Influence of annealing on the pasting properties of starches from varying botanical sources. *Cereal Chem.* **1995**, *72*, 480−487.

Jacobs, H.; Eerlingen, R. C.; Delcour, J. A. Factors affecting the visco-amylograph and rapid visco-analyzer evaluation of the impact of annealing on starch pasting properties. *Starch* **1996**, *48*, 266−270.

Jacobs, H.; Eerlingen, R. C.; Spaepen, H.; Grobet, P. J.; Delcour, J. A. Impact of annealing on the susceptibility of wheat, potato and pea starches to hydrolysis with pancreatin. *Carbohydr. Res.* **1997**, *305*, 193−207.

Jacobs, H.; Eerlingen, R. C.; Rouseu, N.; Colonna, P.; Delcour, J. A. Acid hydrolysis of native and annealed wheat, potato and pea starches, *Carbohydr. Res.* **1998a**, in press.

Jacobs, H.; Mischenko, N.; Koch, M. H. J.; Eerlingen, R. C.; Delcour, J. A.; Reynaers, H. Evaluation of the impact of annealing on gelatinisation at intermediate water content of wheat and potato starches: a differential scanning calorimetry and small-angle X-ray scattering study. *Carbohydr. Res.* **1998b**, 306, 1−10.

Jane, J.-L.; Xu, A.; Radosavljevic, M.; Seib, P. A. Location of amylose in normal starch granules. I. Susceptibility of amylose and amylopectin to cross-linking reagents. *Cereal Chem.* **1992**, *69*, 405−409.

Jenkins, P. J.; Donald, A. M. The influence of amylose on starch granule structure. *Int. J. Biol. Macromol.* **1995**, *17*, 315−321.

Jenkins, P. J.; Donald, A. M. Application of small-angle neutron scattering to the study of the structure of starch granules. *Polymer* **1996**, *37*, 5559−5568.

Jenkins, P. J.; Cameron, R. E.; Donald, A. M. A universal feature in the structure of starch granules from different botanical sources. *Starch* **1993**, *45*, 417−420.

Jenkins, P. J.; Cameron, R. E.; Donald, A. M.; Bras, W.; Derbyshire, G. E.; Mant, G. R.; Ryan, A. J. In situ simultaneous small and wide-angle X-ray scattering: a new technique to study starch gelatinization. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 1579−1583.

Kassenbeck, P. Beitrag zur Kenntnis der Verteilung von Amylose und Amylopectin in Stärkekörnern. *Starch* **1978**, *30*, 40−46.

Kawabata, A.; Takase, N.; Miyoshi, E.; Sawayama, S.; Kimura, T.; Kudo, K. Microscopic observation and X-ray diffractometry of heat/moisture-treated starch granules. *Starch* **1994**, *46*, 463−469.

Knutson, C. A. Annealing of maize starches at elevated temperatures. *Cereal Chem.* **1990**, *67*, 376−384.

Kobayashi, T. Susceptibility of heat-moisture-treated starches to pancreatic α-amylase, and the formation of resistant starch by heat-moisture treatment. *Denpun Kagaku* **1993**, *40*, 285−290.

Krueger, B. R.; Knutson, C. A.; Inglett, G. E.; Walker, C. E. A differential scanning calorimetry study on the effect of annealing on gelatinization behavior of corn starch. *J. Food Sci.* **1987a**, *52*, 715−718.

Krueger, B. R.; Walker, C. E.; Knutson, C. A.; Inglett, G. E. Differential scanning calorimetry of raw and annealed starch isolated from normal and mutant maize genotypes. *Cereal Chem.* **1987b**, *64*, 187−190.

Kuge, T.; KitamurA, S. Annealing of starch granules − warm water treatment and heat-moisture treatment. *J. Jpn. Soc. Starch Sci.* **1985**, *32*, 65−83.

Kulp, K.; Lorenz, K. Heat-moisture treatment of starches. I. Physicochemical properties. *Cereal Chem.* **1981**, *58*, 46−48.

Larsson, I.; Eliasson, A.-C. Annealing of starch at an intermediate water content. *Starch* **1991**, *43*, 227−231.

Lauro, M.; Suortti, T.; Autio, K.; Linko, P.; Poutanen, K. Accessibility of barley starch granules to alpha-amylase during different phases of gelatinisation. *J. Cereal Sci.* **1993**, *17*, 125−136.

Liu, H.; Lelievre, J. A differential scanning calorimetry study of glass and melting transitions in starch suspensions and gels. *Carbohydr. Res.* **1991**, *219*, 23−32.

Lorenz, K.; Kulp, K. Steeping of wheat starches at various temperatures—Effects on physicochemical characteristics of the starch. *Starch* **1978**, *30*, 333−336.

Lorenz, K.; Kulp, K. Steeping of starch at various temperatures—Effects on functional properties. *Starch* **1980**, *32*, 181−186.

Lorenz, K.; Kulp, K. Heat-moisture treatment of starches. II. Functional properties and baking potential. *Cereal Chem.* **1981**, *58*, 49−52.

Lorenz, K.; Kulp, K. Cereal and root starch modification by heat-moisture treatment. I. Physico-chemical properties. *Starch* **1982**, *34*, 50−54.

Lorenz, K.; Kulp, K. Steeping of barley starch. Effects on physicochemical properties and functional characteristics. *Starch* **1984**, *36*, 116−121.

Manners, D. J. Recent developments in our understanding of amylopectin structure. *Carbohydr. Polym.* **1989**, *11*, 87−112.

Marchant, J. L.; Blanshard, J. M. V. Studies of the dynamics of the gelatinization of starch granules employing a small angle light scattering system. *Starch* **1978**, *30*, 257−264.

Marchant, J. L.; Blanshard, J. M. V. Changes in the birefringent characteristics of cereal starch granules at different temperatures and water activities. *Starch* **1980**, *32*, 223−226.

Maurice, T. J.; Slade, L.; Sirett, R. R.; Page, C. M. Polysaccharide-water interactions—Thermal behaviour of rice starch. In *Properties of Water in Foods*; Simatos, D., Multon, J. L., Eds.; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1985; pp 211−227.

Miles, M. J.; Morris, V. J.; Orford, P. D.; Ring, S. G. Recent observations on starch retrogradation. In *New Approaches to Research on Cereal Carbohydrates*; Hill, R. D., Munch, L., Eds.; Elsevier Science Publishers: Amsterdam, 1985; pp 109−115.

Morrison, W. R.; Law, R. V.; Snape, C. E. Evidence for inclusion complexes of lipids with V-amylose in maize, rice and oat starches. *J. Cereal Sci.* **1993a**, *18*, 107−109.

Morrison, W. R.; Tester, R. F.; Snape, C. E.; Law, R.; Gidley, M. J. Swelling and gelatinisation of cereal starches. IV. Some effects of lipid-complexed amylose and free amylose in waxy and normal barley starches. *Cereal Chem.* **1993b**, *70*, 385−391.

Muhr, A. H.; Blanshard, J. M. V.; Bates, D. R. The effect of lintnerization on wheat and potato starch granules. *Carbohydr. Polym.* **1984**, *4*, 399−425.

Muhrbeck, P.; Svensson, E. Annealing properties of potato starches with different degrees of phosphorylation. *Carbohydr. Polym.* **1996**, *31*, 263−267.

Munzing, K. Demonstration of changes in structure in cereal starches by heat flux DSC. *Thermochim. Acta* **1989**, *151*, 57−62.

Nakazawa, F.; Noguchi, S.; Takahashi, J.; Takada, M. Thermal equilibrium state of starch-water mixture studied by differential scanning calorimetry. *Agric. Biol. Chem.* **1984**, *48*, 2647−2653.

Oostergetel, G. T.; Van Bruggen, E. F. J. On the origin of a low angle spacing in starch. *Starch* **1989**, *41*, 331−335.

Parades-Lopez, O. P.; Hernandez-Lopez, D. H. Application of differential scanning calorimetry to amaranth starch gelatinization—influence of water, solutes and annealing. *Starch* **1991**, *43*, 57−61.

Parades-Lopez, O. P.; Schevenin, M. L.; Hernandez-Lopez, D. H.; Carabez-Trejo, A. Amaranth starch—isolation and partial characterization. *Starch* **1989**, *41*, 205−207.

Radosta, S.; Kettlitz, B.; Schierbaum, F.; Gernat, C. Studies on rye starch properties and modification. Part II. Swelling and solubility behaviour of rye starch granules. *Starch* **1992**, *44*, 8−14.

Sair, L. Heat-moisture treatment of starch. *Cereal Chem.* **1967**, *44*, 8−26.

Schierbaum, F.; Kettlitz, B. Studies on rye starch properties an modification. Part III. Viscograph pasting characteristics of rye starches. *Starch* **1994**, *46*, 2−8.

Seow, C. C.; Teo, C. H. Annealing of granular rice starches. Interpretation of the effect on phase transitions associated with gelatinization. *Starch* **1993**, *45*, 345−351.

Seow, C. C.; Vasanti-Nair, C. K. Sub-T_g annealing of granular rice starch: effects on enthalpy relaxation and starch-sucrose interactions. *Carbohydr. Res.* **1994**, *261*, 307−316.

Shi, Y.-C.; Seib, P. A. The structure of four waxy starches related to gelatinisation and retrogradation. *Carbohydr. Res.* **1992**, *227*, 131−145.

Slade, L.; Levine, H. Recent advances in starch retrogradation. In *Industrial Polysaccharides. The Impact of Biotechnology and Advanced Methodologies*; Stivala, S. S., Crescenzi, V., Dea, I. C. M., Eds.; Gordon and Breach Science: New York, 1987; pp 387−430.

Slade, L.; Levine, H. Nonequilibrium melting of native granular starch: Part I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. *Carbohydr. Polym.* **1988**, *8*, 183−208.

Steeneken, P. A. M. Rheological properties of aqueous suspensions of swollen starch granules. *Carbohydr. Polym.* **1989**, *11*, 23−42.

Sterling, C. A low angle spacing in starch. *J. Polym. Sci.* **1962**, *56*, S10−12.

Stute, R. Hydrothermal modification of starches: the difference between annealing and heat-moisture treatment. *Starch* **1992**, *44*, 205−214.

Tester, R. F.; Morrison, W. R. Swelling and gelatinisation of cereal starches. I. Effects of amylopectin, amylose and lipids. *Cereal Chem.* **1990a**, *67*, 551−557.

Tester, R. F.; Morrison, W. R. Swelling and gelatinization of cereal starches. II. Waxy rice starches. *Cereal Chem.* **1990b**, *67*, 558−563.

Tester, R. F.; South, J. B.; Morrison, W. R.; Ellis, R. P. The effects of ambient temperature during the grain-filling period on the composition and properties of starch from barley genotypes. *J. Cereal Sci.* **1991**, *13*, 113−127.

Waigh, T. A.; Jenkins, P. J.; Donald, A. M. Quantification of water in carbohydrate lamellae using SANS. *Faraday Discuss.* **1996**, *103*, 325−337.

Waigh, T. A.; Hopkinson, I.; Donald, A. M.; Butler, M. F.; Heidelbach, F.; Riekel, C. Analysis of the native structure of starch granules with X-ray microfocus diffraction. *Macromolecules* **1997**, *30*, 3813−3820.

Wiegel, E. Verlauf der Warmverkleisterung von Kartoffelstärke inbesondere bei verschiedener thermischer Vorgeschichte. *Kolloid-Z.* **1933**, *LXII62*, 310−324.

Wunderlich, B. *Macromolecular Physics, Vol. 2, Crystal Nucleation, Growth, Annealing*; Academic Press: New York, 1976.

Yamaguchi, M.; Kainuma, K.; French, D. Electron microscopic observations of waxy maize starch. *J. Ultrastruct. Res.* **1979**, *69*, 249−261.

Yost, D. A.; Hoseney, R. C. Annealing and glass transition of starch. *Starch* **1986**, *38*, 289−292.

Zamponi, R. A.; Giner, S. A.; Lupano, C. E.; Anon, M. C. Effect of heat on thermal and functional properties of wheat. *J. Cereal Sci.* **1990**, *12*, 279−287.

Zobel, H. F. Molecules to granules: a comprehensive starch review. *Starch* **1988**, *40*, 44−50.

Received for review February 20, 1998. Revised manuscript received June 11, 1998. Accepted June 17, 1998.

JF980169K