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Pressure-Induced Gelatinization of Starch in Excess Water

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Pressure-Induced Gelatinization of Starch in Excess Water

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High pressure processing is a promising non-thermal technology for the development of fresh-like, shelf-stable foods. The effect of high pressure on starch has been explored by many researchers using a wide range of techniques. In general, heat and pressure have similar effects: if sufficiently high, they both induce gelatinization of starch in excess water, resulting in a transition of the native granular structure to a starch paste or gel. However, there are significant differences in the structural and rheological properties between heated and pressurized starches. These differences offer benefits with respect to new product development. However, in order to implement high-pressure technology to starch and starch-containing products, a good understanding of the mechanism of pressure-induced gelatinization is necessary. Studies that are published in this area are reviewed, and the similarities and differences between starches gelatinized by pressure and by temperature are summarized.

Keywords   High pressure, retrogradation, phase diagrams; glass transition

INTRODUCTION

Starch, the major reserve polysaccharide of green plants, consists of glucose polymers and naturally occurs as water-insoluble granules. As a major constituent of many cereal food products (such as bread, breakfast cereals, rice, and pasta) and of fruits and vegetables (such as potato), it provides 70–80% of the calories consumed by humans worldwide (Whistler and BeMiller, 1999). In addition, starch is widely used in industry (paper making and textile industry) and food applications due to its low cost and unique functional properties. It works as a thickener, a gelling agent, an absorber of water, a source of energy in fermentations, a bulking agent, or an antisticky/sticky agent (Eliasson and Gudmundsson, 2006). Commercial starches are obtained from cereal grains, particularly maize and wheat, and from tubers or roots, such as potato, cassava (tapioca starch), and sago. However, almost all the culinary and industrial uses of starch require the gelatinization of the native starch granules. Gelatinization has been defined as an irreversible phase transition of the starch granules from an ordered to a disordered state (Hermansson and Svegmark, 1996). Although heating starch in the presence of excess water is the most common method to induce gelatinization, it can also be induced by treating starch at high pressures (Stute et al., 1996). The use of high-pressure treatment for physical modifications of starch has attracted much attention, mainly because it results in starch pastes and gels with unique microstructural and rheological properties (Stute et al., 1996). Furthermore, high-pressure processing has the ability to affect and inactivate microorganisms and enzymes while preserving other favorable food components that are generally significantly reduced by traditional thermal processing. The investigations performed thus far on the effect of high pressure on starch can be divided into three categories (Stute et al., 1996). First are those in which the applied pressure was not high enough to provide a gelatinization effect (Thevelein and Van Assche, 1981; Liu et al., 2009a). Second are those in which the pressure application was performed on almost dry starch (Mercier et al., 1968; Kudla and Tomasik, 1992a, 1992b). And third are those that use where the investigations were carried out with excess water and pressures above 400 MPa (Hibi et al., 1993; Stute et al., 1996). This review will focus on the last category, and will compare gelatinization induced by high pressure to the better understood thermal gelatinization.

STARCH: AN ORDERED ENTITY

Starch consists of a mixture of two distinct polysaccharide fractions: amylose and amylopectin. They are both composed of α-(1,4)-linked D-glucose units. Amylose (M_w 10^4–10^5) is

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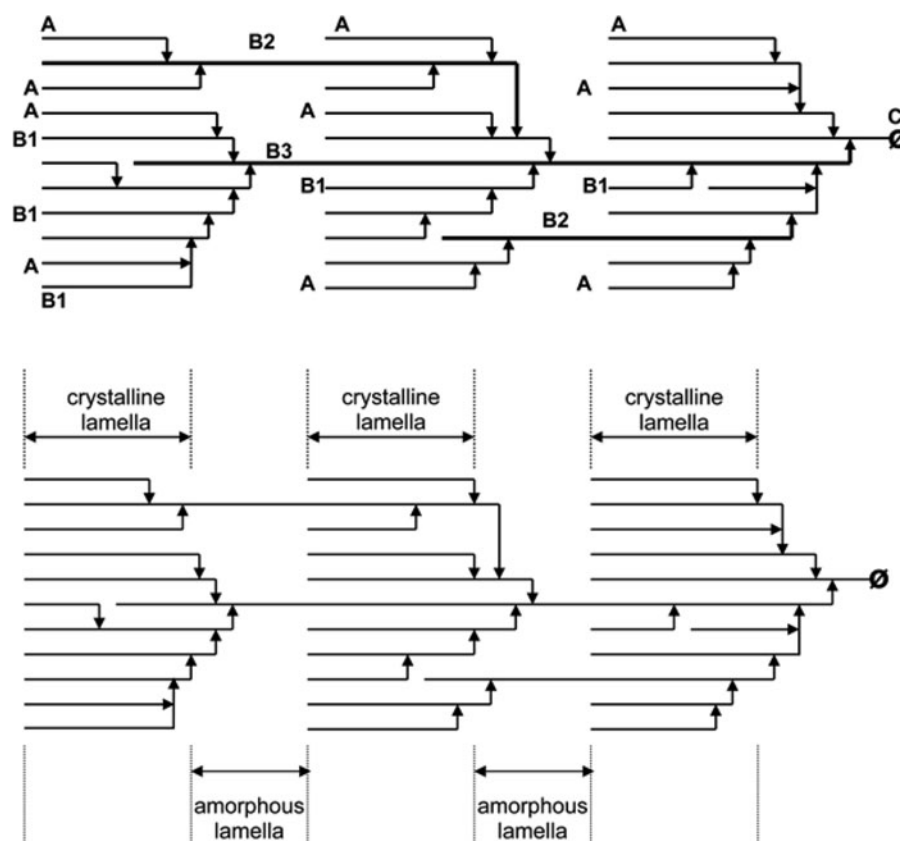
Figure 1 Cluster structure of amylopectin, with indication of A, B, and C chains and illustration of crystalline and amorphous lamellae. The solid lines represent α-1,4-linked glucose units; arrows indicate α-1,6 linkages. The only chain carrying a reducing end (ø) is the C chain. The external chains are A chains. B1 chains expand over one cluster only, while B2 and B3 chains expand over two and three clusters, respectively. (Adapted from Delcour and Hoseney, 2010 Copyright (2010), with permission from AACC International).

essentially linear, whereas amylopectin ($M_w \sim 10^8$) is a highly branched polymer due to 4–5% of α-(1,6)-links (Buléon et al., 1998). The amylopectin molecules contain three types of chains (Fig. 1): the C-chain is the central chain in the amylopectin molecule, containing side-chains and the reducing end; B-chains are side-chains carrying branches, while A-chains are side-chains who do not carry branches themselves (Peat et al., 1956). The cluster model for the structure of amylopectin, stating that the double helical side chains occur in clusters (Gallant et al., 1997), is widely accepted today. The B-chains expanding over one cluster are termed B1-chains, while B2 and B3 chains expand over two and three clusters, respectively (Fig. 1; Hizukuri, 1986).

Most commercial starches contain about 20–25% amylose (Parker and Ring, 2001). However, waxy starches consist nearly solely of amylopectin, while "high amylose" starches can contain up to 70% amylose (Oates, 1997). Starch contains several minor constituents that, although only present in small concentrations, affect the starch properties. Cereal starches contain lipids (0.5–1.2%) in amounts positively correlated with the amylose content (Swinkels, 1985). They occur either free or as amylose-lipid complexes. Other minor constituents found in starch include proteins, phosphorous and other minerals (Jacobs and Delcour, 1998)

Starch occurs naturally as water-insoluble, structurally complex granules whose shape and size (2–100 μm) are characteristic of their botanical origin. Figure 2 shows wheat starch, which contains of larger disk-shaped granules and smaller spherical granules. The internal architecture of native starch granules is characterized by alternating amorphous and semi-crystalline growth rings of 120–400 nm radial thickness formed around the
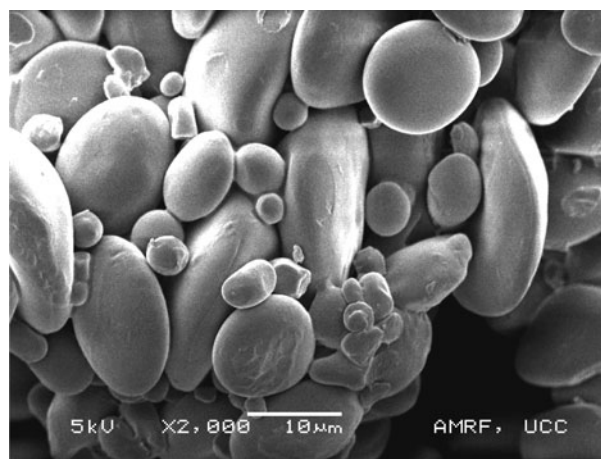

Figure 2 Scanning electron micrograph of isolated wheat starch granules.
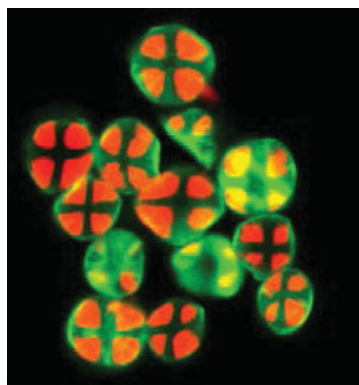
Figure 3 Confocal laser scanning micrograph of sorghum starch taken with a polarizing plate showing the Maltese cross. (Color figure available online.)

hilum (French, 1984). Inside these growth rings, polymers are oriented perpendicular to the surface. The hilum contains a large portion of the reducing ends of starch molecules and is usually less organized than the rest of the granule (Blanshard, 1987). The nonreducing ends of amylose and amylopectin radiate out toward the surface of the granules, allowing further extension of the chains (Oates, 1997). Amylopectin is the source of the semi-crystalline order of the granules, whereas amylose is present in the amorphous state (Oates, 1997).

Due to the high degree of molecular order of starch granules, they are birefringent. When viewed in polarized light, starch granules show birefringence in the form of a typical "Maltese cross." Figure 3 shows the "Maltese cross" of sorghum starch, imaged with a confocal laser-scanning microscope equipped with a polarizing plate. However, birefringence must not be confused with crystallinity, as materials can be very highly ordered, yet not crystalline (Delcour and Hoseney, 2010). Native starch granules contain between 15 and 45% crystalline material. It is accepted that double helices belonging to the same amylopectin cluster, are arranged in either an A- or B-type crystalline polymorph. The A-type is found in most cereal starches. Potato starch, certain other tuber starches, high amylose starches and retrograded starches exhibit B-type crystallinity. The C-type crystalline structure, a mixed organization of A and B-type, is found in some tuber starches (tapioca starch from cassava) as well as in most legume starches, such as smooth pea and bean starch (Gallant et al., 1997). Individual double helices in the different crystalline forms have very similar, if not identical conformations, but there are substantial differences in water content and the packing configuration of the double helices between the different polymorphs (Oates, 1997). The A-form consists of starch double helices packed into a monoclinic lattice. The unit cell consists of 12 glucose residues located in two left-handed double helices that contain four water molecules each (Parker and Ring, 2001). The B-form is a more highly hydrated and open structure, consisting of double helices packed in a hexagonal lattice. The unit cell has two left-handed double helices that are arranged in parallel. It contains 12 glucose molecules and 36 water molecules (Oates, 1997). X-ray diffraction of crystalline amylose helical inclusion compounds results in the V-type pattern. Such patterns can be found after gelatinization and complexing with lipid or related compounds (Czuchajowska et al., 1991; Cheetham and Tao, 1998).

REVERSIBLE CHANGES OF STARCH IN EXCESS WATER

The gelatinization process is always and necessarily preceded by a glass transition of the amorphous regions of the starch granules (Roos, 1998). These regions consist of the amorphous growth rings containing amylose and probably less ordered amylopectin, as well as the amorphous lamellae containing backbone and spacers (the length of a branch between the part of the side chain involved in double helix formation and the backbone) of amylopectin. Before the glass transition, the amorphous polymer chains have low mobility and are frozen in a random conformation, making the starch phase solid and glassy. Above the glass transition temperature (T_g), the polymers become less rigid and their molecular mobility increases, resulting in a rubbery material (Zeleznak and Hoseney, 1987). Water exerts a plasticizing effect on the amorphous zones and depresses T_g. When dry native starch granules are exposed to excess water at room temperature, the granules absorb about ∼30% of their weight as water. At that moisture level, water has exerted its maximum plasticizing effect and additional water forms a separate phase outside the granules. Therefore, at moisture contents higher than ∼30%, T_g is constant (Biliaderis et al., 1986). At lower water levels however, T_g increases with decreasing water level (Biliaderis et al., 1986). Several studies have shown that when starch is hydrated with excess water, the polymers will go through a glass transition below room temperature. Zeleznak and Hoseney (1987) postulated that the T_g is below room temperature at water levels above 22%. In agreement, Capron et al. (2007) concluded that at 20°C, the glassy to rubbery transition in native granular starch occurs at 15–21% water level. However, a glass transition at higher temperatures (50–60°C), immediately preceding the gelatinization process, has been reported by many other researches (Biliaderis et al., 1986; Slade and Levine, 1988; Liu and Shi, 2006; Liu et al., 2009b). Biliaderis et al. (1986) proposed that starch granules consist of three phases: a fully ordered crystalline phase, a bulk amorphous phase and a second nonordered inter-crystalline phase. This distinction of two amorphous phases could result in at least two glass transitions (Biliaderis et al., 1986; Slade and Levine, 1988; Liu and Shi, 2006). Liu and Shi (2006) suggested that the amorphous growth rings are readily available to hydration and show a T_g below room temperature in excess water, while the glass transition of the amorphous regions close to the crystallites immediately precedes the melting of the amylopectin crystals. On the contrary, Morgan et al. (1995) proposed that in moistened starch, the liquid-like properties are associated with amorphous amylopectin, whereas amylose possesses less intramolecular mobility and imparts a more solid-like structure. In agreement, it has
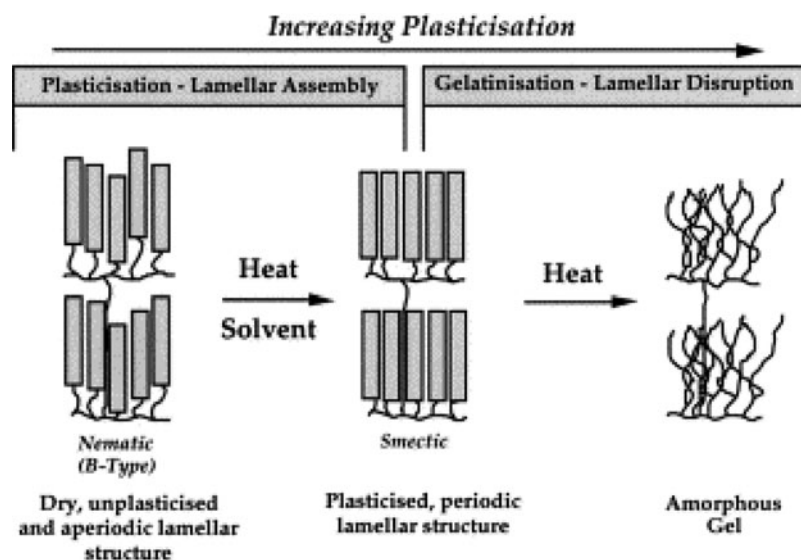
Increasing Plasticisation

Figure 4 A schematic representation of the progression of heat and solvent induced changes in B-type starch granule structure. The unplasticized state in A-type starch is more isotropic in character. (Adapted from Perry and Donald, 2002).

been widely accepted that upon starch hydration at room temperature, the self-assembly of alternating crystalline and amorphous lamellae will occur in the semi-crystalline growth ring due to plasticization of the amorphous parts of amylopectin (Waigh et al., 2000b). In the glassy, dry state, the rigid double helices are strongly coupled to the backbone of the polymer and they can only exhibit disordered nematic packing (Perry and Donald, 2000). Upon hydration at room temperature, plasticization of the backbone and spacers of amylopectin enables the double helices to form an aligned smectic phase (Waigh et al., 1998), resulting in the formation of a well-defined periodic lamellar arrangement with an average lamellar repeat distance of 9 nm. A schematic representation of plasticization and the self-assembly of the lamellae is shown in Figure 4.

Very little reports on the effect of pressure on the glass transition of the amorphous regions have been published, and responses to pressure treatment have been interpreted mainly on the basis of the crystalline aspects of starch. Kweon et al. (2008) conducted a study on the role of glassy and crystalline transitions in the response of corn starch to pressure treatment. They showed that pressure treatment at room temperature resulted in a significant impact on amorphous as well as crystalline transitions, and stated that annealing as well as gelatinization occurs during pressure treatment. At atmospheric pressure, annealing can only occur at temperatures between the glass transition of the amorphous regions and the melting temperature of the amylopectin crystals (Jacobs and Delcour, 1998). However, Kweon et al. (2008) observed that at sufficiently high pressures, annealing occurred at temperatures below the characteristic value of the glass transition temperature at atmospheric pressure. Liu et al. (2008) hypothesized that, under high-pressure treatment, the amorphous regions in starch were altered and have lower glass transition temperature. They suggested several possible alterations, including changed configuration of the amorphous

regions and plasticization by water in the amorphous regions through water redistribution forced by the high pressure. However, none of these alterations have been confirmed so far.

IRREVERSIBLE CHANGES OF STARCH IN EXCESS WATER

Phase Diagrams

Although the effect of temperature on starch has been studied much more widely, there is no doubt about the equivalently importance of pressure as thermodynamic variable. Only the experimental difficulties can explain the relative rareness of pressure studies. However, the number of high-pressure experiments performed on starch has considerably increased in the last decades and high pressure has proven to be an effective tool to gelatinize starch granules. The effects of temperature and pressure (or a combination of both) on the phase transition of starch can be visualized by a pressure–temperature phase diagram with the curves indicating constant degree of gelatinization. Similar to the phase diagram of the denaturation of proteins (Fig. 5), the starch gelatinization phase diagrams are elliptical (Smeller, 2002). An overview of isogelatinization curves of different starch–water suspensions was discussed by Buckow and Heinz (2008). Due to experimental difficulties, diagrams showing the phase transition of starches over a wide range of temperatures and pressures are rare. Furthermore, gelatinization phase diagram are characteristic for the type of starch, and are dependent on the treatment time and the moisture content.

Gelatinization phase diagrams give a good representation of the pressure dependence of the gelatinization temperature. Under atmospheric pressure and in excess water, the gelatinization occurs at a fixed temperature characteristic for the type
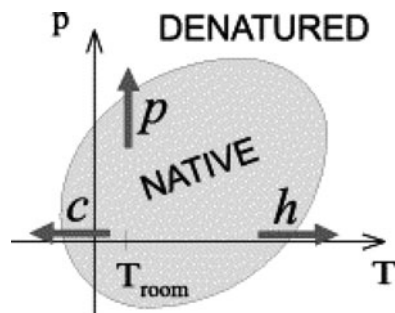
Figure 5 Schematic representation of the elliptic phase diagram of proteins. The arrows marked by the letters p, h, c show the specific denaturation ways known as pressure, heat and cold denaturation. (Adapted from Smeller, 2002).

of starch. Several studies on granule gelatinization at elevated pressures show the influence of pressure on the gelatinization temperatures (Thevelein and Van Assche, 1981; Muhr and Blanshard, 1982; Muhr et al., 1982; Douzals et al., 2001; Rubens and Heremans, 2001; Bauer and Knorr, 2005; Buckow et al., 2007; Sablani et al., 2007; Oh et al., 2008a; Buckow et al., 2009). Thevelein and Van Assche (1981) reported an antagonistic effect of low pressure (up to 150 MPa) and temperature on the degree of gelatinization for potato starch, indicating that low pressure stabilizes the granules against thermally induced gelatinization. These results were confirmed by Muhr and Blanshard (1982) and Muhr et al. (1982). Similar to pressure stabilization of proteins (Heremans and Smeller, 1998), this may be due to high-pressure promoting hydrogen bonds and Van der Waals interactions within the molecule, stabilizing the double-helical structure of amylopectin (Buckow et al., 2009). At pressures above 250 MPa, Muhr and Blanshard (1982) and Muhr et al. (1982) observed a decrease in gelatinization temperature with increasing pressure. The phase diagram of rice starch, as constructed by Rubens and Heremans (2001), did not show stabilization against thermal gelatinization at low pressures. Instead, a constant gelatinization temperature of 61°C up to 400 MPa was reported, followed by a decrease at higher pressures. The combined effects of pressure and temperature on wheat starch gelatinization was studied by Douzals et al. (2001) for pressures up to 400 MPa and temperatures from −25°C up to 100°C. Furthermore, pressure–temperature phase diagrams were constructed for wheat, tapioca and potato starch by Bauer and Knorr (2005) and for maize starch by Buckow et al. (2007). The effect of amylose on the phase diagram of maize starch was studied

by Buckow et al. (2009). In agreement with Chen et al., 2007, high amylose maize starch (50 and 80%) clearly showed higher pressure and temperature stability than normal or waxy maize starch. Several explanations such as differences in crystal type and the formation of amylase-lipid complexes have been given (Buckow et al., 2009).

The importance of treatment duration on starch gelatinization has been highlighted in a number of studies (Stolt et al., 1999; Bauer and Knorr, 2005; Sablani et al., 2007). Stolt et al. (1999) observed that the consistency of a starch–water suspension increased with increasing processing time until a plateau was reached where the consistency did not change further. The more severe the treatment conditions (higher temperature and/or pressure), the faster this plateau value was reached. The use of starch gelatinization as a pressure time temperature indicator, an indicator of the severity of the treatment, for monitoring high pressure processing conditions has been discussed by Bauer and Knorr (2005) and Sablani et al. (2007).

Temperature-Induced Gelatinization

When starch–water mixtures are heated above the gelatinization temperature, irreversible changes occur (Thomas and Atwell, 1999). Figure 6 envisages the temperature-induced gelatinization process of sorghum starch by scanning electron microscope images. Due to the ingress of hot water, the hydrogen bonds between starch molecules are broken and hydrogen bonds with water are formed instead. Water is able to further penetrate the granules, and irreversible swelling takes place (Vaclavic and Christian, 2003). The linear amylose solubilises and diffuses out of the granules (Hermansson and Svegmark, 1996). The granules loose their birefringence and crystalline order, becoming amorphous. More extensive granule swelling and amylose solubilization is responsible for a rapid increase in consistency of the starch–water mixture (termed pasting). A maximum paste viscosity is obtained during heating when there is a majority of swollen granules. At this point, the starch paste consists of a continuous phase of leached amylose containing dispersed granule remnants enriched in amylopectin. Upon further heating, the granules begin to break down and amylopectin solubilization increases, resulting in a decrease in consistency (Thomas and Atwell, 1999). As stated by Hoseney (1998), wheat starch is completely solubilized if heated to about 130°C, resulting in a minimum viscosity.
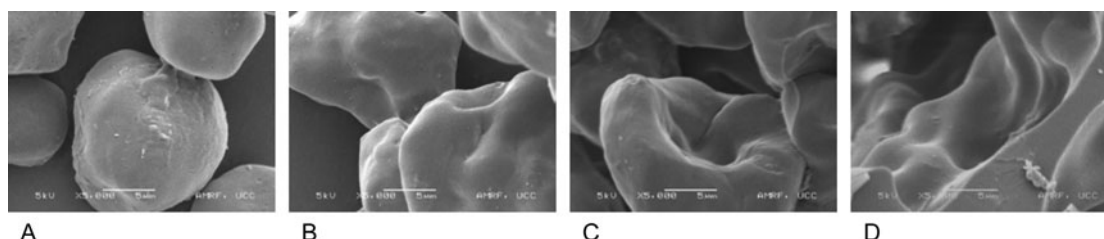

Figure 6 Scanning electron micrographs of sorghum starch at room temperature (A), after heating at 65°C (B), after heating at 75°C (C), and after heating at 95°C for 10 min.

As long as water is abundant, gelatinization will occur within a fixed temperature range, normally 60–70°C. However, this range is dependent on the botanical and genetic origin of the starch, the starch concentration and the measuring method. In general, the gelatinization temperatures of tuber and root starches such as potato and tapioca are slightly lower than those of cereal starches such as corn and wheat (Thomas and Atwell, 1999). As described in literature, DSC studies show a single symmetrical endotherm peak when starch is heated in excess water (Svensson and Eliasson, 1995). However, this single endotherm comprises several processes: the glass transition of the "rigid amorphous" phase (Liu and Shi, 2006), the disruption of the full three-dimensional crystal structure by helix–helix dissociation and the loss of helicity by helix-coil transitions (Waigh et al., 2000a). Gelatinization is a swelling-driven process, and expansion of the amorphous growth rings due to their glass transition, results in crystalline disruption. The process of loss of crystallinity and loss of helicity of starch was discussed in detail by Waigh et al. (2000a). In excess water, two possible scenarios were suggested. In the first scenario, which is most likely to occur in A-type starch, double helices are slowly stripped of the side of the crystals, and the fast helix-coil transition happens as an immediate consequence of this step. For B-type starches, it is more likely that a smectic–nematic transition is the first step, followed by the helix unwinding transition. However, as the rate of water penetration will be the same as the rate of crystallite disruption in excess water (Svensson and Eliasson, 1995), swelling of the granules, helix–helix dissociation and helix-coil transition occur nearly simultaneously.

Upon cooling of a gelatinized starch suspension, the viscosity increases and a starch paste is formed. Depending on the presence of a continuous amylose phase outside the swollen granules a starch gel might be formed (Delcour and Hoseney, 2010). In general, the higher the amount of leached amylose content, the more likely the paste will set to a firm and cuttable gel (Thomas and Atwell, 1999). During gelation, double helices are formed between the leached amylose molecules and a network develops. This network is reinforced by the embedded deformed gelatinized granules. Upon storage of starch gels, recrystallization occurs: due to the reassociation and crystallization of starch chains, a new semi-crystalline structure is formed. The newly formed crystals exhibit a B-pattern, independent of the crystalline pattern of the native starch (Miles et al., 1985). Recrystallization is a slow, two-phase process. The short-term (∼1–2 days) recrystallization is dominated by crystallization within the amylose matrix. The double helices form very stable crystals, as they have a melting temperature of about 150°C (Silverio et al., 1996). Amylopectin retrogradation is much slower (∼10 days) and the crystals have a lower thermal stability melting between 50 and 60°C (Miles et al., 1985). The greater thermal stability of the amylose crystallites can be ascribed to the linear character of amylose, resulting in inter-chain associations with other amylose molecules over many residues. Contrarily, inter-chain association in amylopectin can only extend over about 15 residues before it is interrupted by a branch point (Miles et al., 1985).

Pressure-Induced Gelatinization

It has been shown that the pressure-induced gelatinization, although similar to temperature-induced gelatinization in many ways, can result in unique microstructural and rheological properties (Stute et al., 1996). It has been shown that the pressure-induced gelatinization curves, representing the degree of gelatinization as function of pressure, have a similar sigmoid shape as the temperature-induced gelatinization curves (Stute et al., 1996; Vallons and Arendt, 2009b). This indicates that, in analogy with temperature-induced gelatinization, the pressure-induced gelatinization occurs within a pressure range. It has been shown that this range depends on the type of starch (Hibi et al., 1993; Stute et al., 1996). In agreement with Oh et al. (2008b), starches can largely be divided into three classes, based on their susceptibility to pressure. Waxy starches, with low baroresistence, form the first group. Their high susceptibility to pressure has been ascribed to low amylose content. Most of the normal starches exhibit medium susceptibility to pressure. Gelatinization of wheat starch begins below 300 MPa and is achieved completely at 600 MPa (Douzals et al., 1996). Similar gelatinization ranges were obtained for other starches, such as rice (Oh et al., 2008a; Tan et al., 2009), oat (Hüttner et al., 2009), sorghum (Vallons and Arendt, 2009a), buckwheat (Vallons and Arendt, 2009b), barley (Stolt et al., 2001), maize (Hibi et al., 1993; Fernández-Martín et al., 2008), tapioca starch (Bauer and Knorr, 2004; Vittadini et al., 2008), and pea (Fernández-Martín et al., 2008). The third group, containing potato and high-amylose starches, requires the highest pressures (≥700 MPa) to reach complete gelatinization (Muhr and Blanshard, 1982; Bauer and Knorr, 2005; Blaszczak et al., 2005a, 2005b; Kawai et al., 2007). The baroresistance of this third group has been ascribed to their B-type crystal structure (Katopo et al., 2002).

Rubens et al. (1999) studied the gelatinization of starches under pressure in situ with FTIR. Analysis of the spectra led to the proposition of a multistep gelatinization mechanism, similar to the temperature-induced gelatinization. First, the amorphous parts of the starch granules are hydrated. This hydration induces a swelling (1) of the granule leading to a distortion of the crystalline regions and (2) which can lead to a destruction of the granule structure. Next, the crystalline regions become more accessible for water. The two-step mechanism of pressure-induced gelatinization was further confirmed by Blaszczak et al. (2005a), who studied the gelatinization of potato starch treated at 600 MPa.

(1) Swelling of starch granules during pressure-induced gelatinization has been visualized by microscopy or by determining the swelling index (Hibi et al., 1993; Douzals et al., 1996; Oh et al., 2008a, 2008b). In situ microscopic observations of wheat starch granules during pressure treatment showed that about 25% of the granules were swollen above 300 MPa (Douzals et al. 1996). Swelling involved the entry of water into the starch granules and the creation of hydrogen bonds between water and starch. In agreement with *Le Chatelier's* principle, granule swelling was accompanied by reduction of the bulk suspension,

indicating that water molecules linked with starch occupy a smaller volume than molecules in pure water (Douzals et al., 1996). In comparison with heat gelatinization however, most starches show limited swelling upon pressurization (Stute et al., 1996; Oh et al., 2008b). Lower swelling indices were observed for pressure-treated wheat, corn and rice starch compared to heated starches (Douzals et al., 1998; Selmi et al., 2000; Tan et al., 2009). According to Douzals et al. (1998), limited granule expansion upon pressurization, is the result of lower starch hydration at higher pressure. In addition, these authors stated that lower water binding at higher pressures leads to a lower release of amylose from the granules (Douzals et al., 1998). In agreement, Stolt et al. (2001) reported no leaching of amylose during pressurization of a barley starch suspension at 550 MPa. As restricted swelling and lower release of amylose stabilizes the granular structure, pressure-treated starches exhibit better preservation of the granular structure (Douzals et al., 1998). A study by Vallons and Arendt (2009b) showed that, although preservation of granular structure was observed for buckwheat starch after treatment with 600 MPa, treatment with 75°C resulted in complete disintegration of the buckwheat granules (Fig. 7). Likewise, corn-starch granules appear swollen and deformed with rough surfaces at pressures above 400 MPa, while on heating at temperatures above 65°C, they fused with each other (Takahashi et al., 1994). It was postulated by Oh et al. (2008a) that during pressure treatment, amylose may form thermodynamically favorable complexes with displaced amylopectin molecules instead of leaching into the aqueous phase, resulting in limited swelling and more rigid granule remnants. In agreement, Debet and Gidley (2007) hypothesized that granule remnant or "ghost" formation is attributable to cross-linking of amylose and/or long amylopectin chains within swollen granules, most likely involving double helices. They stated that "ghost" formation involves a competition between swelling and cross-linking within the swollen granules. When swelling is rapid and extensive, cross-link formation is probably too slow to result in granule preservation. On the other hand, slower swelling results in the formation of robust granule remnants (Debet and Gidley, 2007). Consequently, difference in granule structure preservation between pressure- and temperature-induced gelatinization might be due to a shift in the balance between swelling and polymer cross-linking.

Although the restricted swelling is somehow typical for pressure-induced gelatinization, other starches show extensive swelling and subsequent granule disintegration upon pressurization. Stute et al. (1996) classified starches of different plant origin into those showing more limited swelling after pressure treatment and those with a swelling behavior similar to heat treatment. Starch suspensions of the latter class form pastes characterized by a viscosity, amounts of solubilized starch, and pasting properties similar to those obtained by heat gelatinization. It has been shown that waxy starches can be classified into the second group (Stute et al., 1996; Rubens et al., 1999; Blaszczak et al., 2005b; Oh et al., 2008a). As waxy starches contain very little amylose, no pressure-stable, swelling-restricting

network can be formed within the granules (Oh et al., 2008a). Besides waxy starches, Vallons and Arendt (2009a) classified sorghum starch in the group of starches characterized by microstructural and rheological properties of the pressurized starch suspension similar to those obtained by thermal gelatinization. In addition, Rubens et al. (1999) also showed a complete disintegration of the granules of rice and tapioca starch after pressure treatment.

(2) The effect of pressure on the crystalline structure of starch granules has been studied using X-ray diffraction (Hibi et al., 1993; Katopo et al., 2002; Blaszczak et al., 2005b), FTIR (Rubens et al., 1999; Rubens and Heremans, 2001; Blaszczak et al., 2005a), and NMR (Blaszczak et al., 2005a, 2005b; Doona et al., 2006; Blaszczak et al., 2007). Similar to temperature-induced gelatinization, pressure-induced gelatinization involves the melting of starch crystals. However, the extent of the pressure effect on the crystalline structure depends on the type of crystallinity. A higher resistance of B-type starches to pressure has been reported by Stute et al. (1996) and Rubens et al. (1999). The sensitivity of the C-type starches is located in between B- and A-type starches: Bauer and Knorr (2005) showed that the phase gelatinization of tapioca starch (C-type) occurred at higher pressures than the phase change of wheat starch (A-type) but below the melting of potato starch. In addition, Hibi et al. (1993) reported a destruction of the A-type crystalline structure of maize starch during pressure treatment. The A-type X-ray diffraction pattern tended to change into a faint B-type pattern. The X-ray diffraction pattern of rice starch, as observed by Katopo et al. (2002), displayed a conversion toward a combination of a weak B- and a V-type, indicating the presence of amylose-lipid complexes. Katopo et al. (2002) attributed the differences in pressure sensitivity between A- and B-type starches to their crystal structure. Water filling up the channel in the B-type crystallites as well as longer amylopectine side chains can explain the more stable structure. In contrast, the A-type crystals have a more scattered amylopectin branching structure, which is more flexible, and therefore allows rearrangement of double helices to generate a channel in which water molecules are included under pressure. On the other hand, Oh et al. (2008b) suggested that the external region of the starch granules of potato and high amylose starches might explain their higher baroresistance. Sevenou et al. (2002) concluded that potato and amylomaize exhibit a far greater level of ordered structure in the external region of their granules than other normal and waxy starches. In agreement, SEM analysis of pressure-treated potato starch performed by Blaszczak et al. (2005a) indicated that the potato starch granule surface was very resistant to high pressure, showing a very compact condensed layer. The inner part of the granule was less resistant, and hydration of the amorphous phase and/or melting of the crystalline structures resulted in the formation of gel-like structures inside the granules (Blaszczak et al., 2005a). Although for pressure-induced gelatinization B-type starches are the most stable, and A-type starches change into faint B-type patterns, the opposite has been reported for temperature-induced gelatinization. This difference in stability to pressure and temperature can
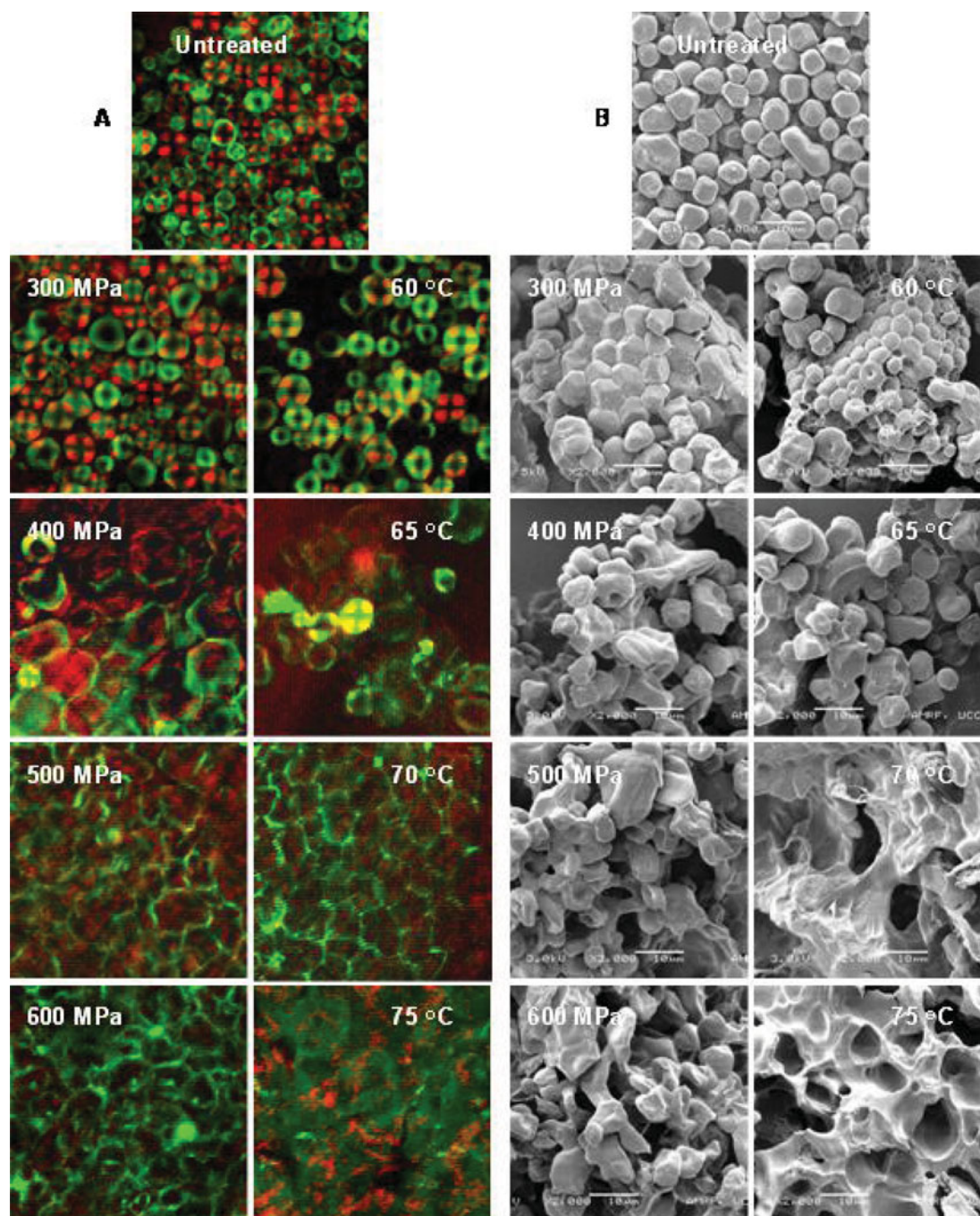
Figure 7   Confocal laser scanning micrographs (A) and scanning electron micrographs (B) of buckwheat starch suspensions after treatment for 10 min at different pressures and temperatures. (Adapted from Vallons and Arendt, 2009b). (Color figure available online.)

probably be explained by the differences in crystal structure of both types in combination with the differences in driving force: while temperature-induced gelatinization is an entropy-driven transition, pressure-induced gelatinization is a volume-driven transition (Smeller, 2002). However, to obtain a more detailed understanding of this difference in stability, further research is necessary.

Interestingly, many publications showed the presence of residual crystalline order after pressure treatment. Hibi et al.

(1993), Stute et al. (1996) and Katopo et al. (2002) reported the presence of a faint B-type pattern after pressure-treatment of A-type starches. In agreement with Stute et al. (1996), Katopo et al. (2002) stated that this residual B-type crystallinity results in a DSC melting peak with peak temperature around 50°C, resembling the thermal transition peak of retrograded starch. Kawai et al. (2007) observed a similar DSC peak for pressure-treated potato starch. As this peak is visible immediately after pressure treatment, the faint B-type pattern was the result of an

event during or immediately after pressurization (Stute et al., 1996). In literature, this event is referred to as "rapid retrogradation." In each case, the greater the degree of gelatinization induced by the pressure treatment, the greater the extent of "rapid retrogradation" (Kawai et al., 2008a). However, the melting enthalpies, as reported by Katopo et al. (2002) and Fernández-Martín et al. (2008), were small. Furthermore, Katopo et al. (2002) and Kawai et al. (2007) showed that the development of this crystalline structure upon pressurization is dependent on the starch concentration: no residual crystallinity was detected at lower starch concentrations (10–30%). In addition, Vallons and Arendt (2009b) found no residual order for the preserved buckwheat starch granules in a 25% suspension after treatment with 600 MPa.

Fernández-Martín et al. (2008) stated that the pressure-induced "rapid retrogradation" occurs inside the intact granules, indicating that it might be responsible for the limited swelling and higher rigidity of the pressure-treated starches. This indicates that the previously mentioned formation of amylose-amylopectin complexes might be the cause of the so-called "rapid retrogradation." However, the events occurring during "rapid retrogradation" are still unclear. Whether these B-type crystals are the result of retrogradation or crystal transformation cannot be decisively concluded. In addition, it remains unclear if this "rapid retrogradation" occurs during the pressure treatment, after pressure treatment or during the pressure drop at the end of the treatment, pointing out the importance of further investigation.

Upon storage, the starch pastes undergo further recrystallization. King and Kaletunç (2009) reported the crystallization of pressure-treated wheat and corn starch during storage. The melting enthalpy of starch crystals formed during storage increased as a function of time up to a constant value. However, Douzals et al. (1998) showed that the extent of retrogradation was higher for starch gelatinized by heat than for starch gelatinized by pressure. A lower sensitivity to aging of pressure-induced starch gels was also observed by Fernández-Martín et al. (2008) for pea and corn-starch and by Vittadini et al. (2008) for tapioca starch gels. On the contrary, Stolt et al. (2001) found similar retrogradation behavior of the pressure- and temperature-induced barley starch gels.

The events occurring during gelatinization and recrystallization of a starch suspension, especially the granule swelling and leaching of amylose/amylopectin, will strongly change the rheological properties of a starch suspension. Limited swelling, better granule preservation and lower amylose leaching upon pressurization compared to temperature treatment is expected to result in starch pastes and gels with unique rheological properties (Stute et al., 1996; Stolt et al., 2001). A few contrasting reports on the rheological properties of pressure-induced starch gels have been published. Stute et al. (1996) observed poor viscosity and gel forming properties for starches showing limited swelling. In agreement, Douzals et al. (1998) found that the elastic moduli of compression of pressure-induced wheat starch gels were significantly lower than those of temperature-induced

gels, related to the lower release of amylose from starch granules. On the contrary, pressure-induced barley, tapioca, japonica rice, and buckwheat starch gels were shown to be significantly harder (as indicated by higher elstic moduli) then temperature-induced gels (Stolt et al., 2001; Vittadini et al., 2008; Tan et al., 2009; Vallons and Arendt, 2009b). For these starches, the granular structure was better preserved upon pressurization. Vallons and Arendt (2009b) suggested that the viscosity of the buckwheat starch suspension was determined by the swollen granules and the granule–granule interactions, and that entanglement of leached amylose played a minor role. Consequently, the rigidity of the granules impacts the consistency with granule disintegration during heating resulting in a lower consistency. This is in agreement with Hoseney (1987), who stated that a mixture of solubilized starch and granule remnants will give a higher consistency than a totally solubilized starch-water mixture.

The possibility of enhancing the susceptibility of starch to amylase action by pressure treatment has been studied by a number of researchers. Hayashi and Hayashida (1989) and Takahashi et al. (1994) showed an increased digestibility by α-amylase and glucoamylase, respectively, of pressure-treated starches. Furthermore, Takahashi et al. (1994) observed no distinct differences between the pressure- and heat-treated starches as far as the digestibility and bindability with the enzymes was concerned. However, a lower degree of amyloglucosidase hydrolysis after pressure treatment was reported by Stute et al. (1996). "Rapid retrogradation" during pressure treatment was suggested as a possible explanation. On the contrary, Selmi et al. (2000) showed higher glucose yield (after 30 min) for wheat starch treated at high pressure compared to heated starch. Besides changing the structure of starch, pressure also alters the conformation of proteins, thereby changing the activity of the starch-hydrolysing enzymes (Raabe and Knorr, 1996). Gomes et al. (1998) treated slurried of wheat and barley flour at pressures up to 800 MPa. Pressure-treatment of the slurries at 300–600 MPa caused an increased α- and β-amylase activity due to starch gelatinization, while higher pressures resulted in inactivation of the enzymes due to conformation changes. Furthermore, Raabe and Knorr (1996) showed a protective effect of the substrate against pressure inactivation of α-amylase.

CONCLUSIONS

The effects of high pressure on starch have been presented, and a comparison with temperature has been made. Pressure- as well as temperature-treatment of starches in excess water result in the gelatinization of starch. However, differences in the final products were observed. Pressure-induced gelatinization was characterized by limited granule swelling, lower amylose leaching, and better granule preservations resulting in starch pastes and gels with unique functional properties. However, the pressure-induced gelatinization mechanism is still not fully understood. Many gaps in the knowledge exist, and a lot of the

observation made cannot be explained so far. Consequently, more research needs to be done. The authors believe that some of the experimental differences and limitations in the high pressure research today will be overcome by further progress and commercialization of the technology and the equipment. Process development efforts are currently based mainly on observations of end effects from trial and error experiments. The authors would like to emphasize the importance of performing studies in a more consistent and rational manner, as up till today, comparing different studies is difficult due to inconsistency in term such as gelatinization, pasting, retrogradation, and "rapid retrogradation." Better understanding of high-pressure-induced gelatinization can result in new interesting industrial applications of high pressure, such as "cold pasteurization" of starch-containing products and the production of new "clean label" starches with desired functionality.

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