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Starch Gelatinization under Shearless and Shear Conditions

Fengwei Xie, Hongshen Liu, Pei Chen, Tao Xue, Ling Chen, Long Yu, and Penny Corrigan

Abstract

This article reviews the development of studying starch gelatinization under shear and shearless conditions, in particular the technologies used to detect the degree of gelatinization. Advantages and disadvantages of each technology were discussed and then some examples were presented to demonstrate their application. A new technology RheoScope, an instrument that can measure viscosity under shear stress and simultaneously observes variation of starch particles using a microscope, was also introduced. It was found the definition of "gelatinization" could be different for different detection technologies. Under shearless condition full gelatinization of starch needs about ratio of water 3/starch 1, while the gelatinization under shear condition requires less water content since shear stress enhances the processing. The number of endotherm and enthalpy of gelatinization depends on amylose/amylopectin, moisture and lipid content.

KEYWORDS: starch, gelatinization, shear, shearless, DSC, microscope, extrusion

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1. Introduction

Gelatinization of starch is very important in food processing and has been extensively studied in food science (Stevens, Elton et al. 1971; von Eberstein, Hopcke et al. 1980; Zobel 1984; Tester and Morrison 1990; Hermansson and Svegmark 1996) for decades, in particularly with higher water content. Recently starches have been used as important raw materials for biodegradable plastics and its gelatinization process has attracted much attention since it acts as an important and unique characterization in the processing of starch-based materials (Lelievre 1974; Lelievre 1976; Biladeris, Page et al. 1985; Russell 1987; Svensson and Eliasson 1995).

Starch based foods are traditionally processed under shearless condition, such as bread, steam bread and biscuits, etc. Extrusion foods have been developed later with early developments in the preparation of ready-to-eat cereals (Harper 1989). The use of twin-screw extruders for food processing began in the 1970's and expanded dramatically in the 1980's. Starches are gelatinized under shear stress during extrusion cooking. More recently extrusion has been used to processed starch-based materials, especially for lower moisture formulations. The processing of thermoplastic starches is much more complex than that of conventional thermoplastics because the processing involves gelatinization, melting, volume expansion, molecular degradation, and various physicochemical changes in starches. The gelatinization of starches is of particular importance because the melting points of starches exceed their decomposition temperature before the gelatinization. Study of the gelatinization behavior of starch is not only important to control the processing conditions but also useful to understand the mechanical properties of starch-based materials, which will be discussed in a separate paper.

To study the gelatinization, various technologies have been developed, such as microscope with hot-stage, viscometry, DSC, XRD, NMR etc. In this paper, the gelatinization of starch under shear and shearless conditions was reviewed; various technologies used to detect the gelatinization are introduced and discussed.

2. Principle of Starch Gelatinization

The well-accepted conception of "gelatinization" means destroying the crystalline structure in starch granular (Lelievre 1974; Atwell, Hood et al. 1988). Starch gelatinization is an irreversible process and includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization (Sullivan and Johnson 1964). The gelatinization of starches has been extensively studied previously. Many methods have been developed to study the gelatinization in food and thermoplastics field, for examples, the estimation of maltose (Roberts, Potter et al. 1954); determination of iodine blue complex (Roberts, Potter et al. 1954); observe polarizing patterns under microscope (Olkku and Rha 1978; Ghiasi, Hoseney et al. 1982; Tester and Morrison 1992; Ziegler, Thompson et al. 1993; Yeh and Li 1996). In the last 20 years, DSC has been widely used to study the thermal behaviour of starches, including gelatinization (Yu and Christie 2001). However, all these previous methods can either study gelatinisation under shear less conditions (DSC or optical microscope with hot-stage) or just measuring viscosity without directly observation (Zobel 1984).

Atwell et al (1988) surveyed starch chemists and struggle to propose more precise definition gelatinization and pasting. In their definition, gelatinization is an irreversible process and includes granule swelling, native crystallite melting, loss of birefringence and starch solubilization. In a short words, gelatinization is used to describe physical transition include “the collapse of molecular orders within the starch granule”, whereas pasting was proposed to include “the phenomenon following gelatinization in the dissolution of starch” (Cooke and Gidley 1992; Fisher and Thompson 1997).

The gelatinization of starch is a multi-stage process. Previous researchers distinguished various phases in the breakdown of the starch molecular structure. In the first phase, which occurs before the onset of gelatinization, water is slowly and reversibly taken up. At this stage the mobility of water decreases as the temperature is increased from 20 to 60°C and it is thought that water is being reversibly complexed with the starch molecules in the granule (Olkku and Rha 1978). But starch granular is still in stable state. The constituent molecules exist in spherulites held together by van der Waals’ force or hydrogen bonds. And these granules exhibit a typical birefringence under polar light (Lim, Wu et al. 2000). Gough & Pybus (1971) treated undamaged wheat starch granules within this temperature range, and found that: the change is reversible at temperatures below the onset of gelatinization, but continued exposure of the starch to water can cause changes in the granule itself. When aqueous suspensions of starch granules are heated gradually, a temperature is reached at which hydrogen bonding forces are weakened to the point where water can be absorbed by the granules. This temperature is usually called “initial gelatinization temperature”. At the temperature, the granules swell irreversible and some granules begin to lose their birefringence. The transition involves dissociation of double helices (most of which are in crystalline regions) and expansion of granules as the polymer (and granule interstices) hydrate (Tester and Debon 2000). These phenomena start at the hilum or botanical center of the granules and spread rapidly to the periphery. Gelatinization begins in the intercellular areas where the hydrogen bondings are weakest. It occurs in different temperature ranges for different starches (Olkku and Rha 1978).

Further heating of the aqueous suspension above gelatinization temperature, hydrogen bondings continue to be disrupted and water molecules become attached to hydroxyl groups, results in greater swelling of the granules and melting of crystallites (Lim, Wu et al. 2000). And as a direct result of granule swelling, there is an increase in starch solubility, paste consistency and paste clarity. In a concentrated starch paste, the individual granules gelatinize and swell freely until all the available water has been imbibed. As they swell, the swollen starch granules become increasingly susceptible to shear disintegration. When temperature is above T_c, all amylopectin double helices have dissociated, although swollen granule structure will be retained until more extensive temperature and shear have been applied (Tester and Debon 2000). After melting of the crystallites, the granules hydrate and swell irreversibly. The granules collapse or become disrupted as their integrity is lost. As soluble components (primarily amylose) leach out of the granules during the process they form a solution. Thus the hot starch pastes may be viewed as a mixture of swollen starch granules and granule fragments, together with colloidal and molecularly dispersed starch molecular (Olkku and Rha 1978).

Caesar (1950) also explained gelatinization by hydrogen bonding of the starch hydroxyl groups through water molecules as follows: "Hydrogen bonds are continuously broken and reformed throughout the heating period, the dissociating water molecules force their way into the micellar jungle of bristling hydroxyl groups which entrap and bind them (Fig. 1); free water is consumed or 'bound', and viscosity increases until the peak viscosity is reached. The energy supplied by increased temperature and the shear from agitation then begin to destroy the O–H…O links holding the bound water molecules to the starch hydroxyl groups, and the viscosity rapidly decreases" (McGrane, Mainwaring et al. 2004).

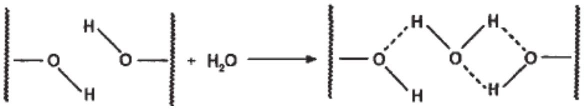

Fig. 1. Schematic representation of the reaction between amylose and water to form a hydrogen-bonded network, where the dashed lines represent hydrogen bonds.

In limited water condition such as thermoplastic starch, destruction of the starch granules is performed at relatively high temperature, high-shear conditions, and with limited amounts of water, the latter hindering both granule swelling and disintegration, yielding a microscopically homogeneous material (Hulleman, Janssen et al. 1998).

3. Starch Gelatinization under Shearless Conditions

3.1 Phase Transition of Starch Granules Observed under Microscope

3.1.1 Principle and advantages

The most sensitive methods of measuring starch gelatinization are based on the loss of birefringence by gelatinized starch (Shetty, Lineback et al. 1974). One widely accepted definition of gelatinization is based on loss of granular birefringence as microscopically viewed under polarized light, which is that: gelatinization is the loss of birefringence upon the slow heating of a dilute aqueous suspension of starch granules (Atwell, Hood et al. 1988). Because of the regular orientation of D-glucosyl units in amorphous and crystalline regions, most granules show some degree of birefringence (optical anisotropy or double refraction) (Zobel 1984).

Microscope with a hot stage examine granules undergoing gelatinization permits one to observe swelling duration, degree of swelling, and swollen granule integrity and size, and the loss of birefringence (Zobel 1984). Besides, it also permits one to record the onset temperature and end temperature of the gelatinization simultaneously. Hai et al. (1989) used the DSC, hot stage microscopy and viscography studied the gelatinization temperatures of starch and hydroxyethyl starch, and compared the gelatinization temperature obtained by the three methods. They found that hot stage microscopy based on visual observation gave the correct gelatinization temperature.

However, microscopy with hot stage has some disadvantages such as temperature lag.

3.1.2 Technology Description

Determination of starch gelatinization requires ways of heating the starch slurry and of sensing the structural changes that occur. Thus Loss of birefringence measurements requires an optical microscope with cross polarizers and a heating stage, such as the Kofler (Zobel 1984).

A light microscope with heating stage attachment connected to a camera and a computer was used to visually observe swelling of starch granules upon heating at an preseted rate (Chatakanonda, Varavinit et al. 2000). Starch suspensions were usually at high water content due to the fact that too many granules that crowed together interfere with the observation of the size of the granules (Hai, Garg et al. 1989; Liu, Lelievre et al. 1991; Yeh and Li 1996; Chatakanonda, Varavinit et al.

2000), and were usually heated between glass and cover slips from ambient temperature to preseted temperature (Yeh and Li 1996; Chatakanonda, Varavinit et al. 2000). Sometimes for the sake of preventing water from volatilization, silicon glue may used. The images of the heated samples were continuously taken and saved in the computer, and then analyzed by a software program. The rupture temperature (a granule was considered ruptured when losing its border) and the birefringence end point temperature of starch granules were recorded. The experiments could be carried out under both normal light and polarized light modes in order to observe the swelling and the loss of birefringence, respectively (Chatakanonda, Varavinit et al. 2000).

3.1.3 Applications

Microscope has been used to observe the structure of starch granules for a long time. Probably the first person to view starch granules undergoing dissolution in hot water was the inventor of the microscope, Antoni van Leeuwenhoek (1719). Then Kofler hot-state microscopy has been used in a method described by Watson (1964). Other microscopic measurements have been reported by Seidemann (1963) and by Kainuma et al. (1968), who used photopastegraphs. Miller et al. (1973) also used photomicrographs which are photographs, taken through a microscope, of the samples taken during gelatinization in an Amylograph. Often polarized light microscopy was used in combination with other methods such as DSC, scanning electron microscopy, viscography and the blue dextran method to measure gelatinization of starch.

Varriano-Marston et al. (1980) studied starch gelatinization in bakery food using viscosity, enzymatic, and crystallographic methods, complemented with results from x-ray diffraction, polarized microscopy, enzymatic methods. They found that for baked products the degree of starch gelatinization and swelling paralleled moisture content. Ghiasi et al. (1982) compared the results of gelatinization of wheat starch obtained by DSC and light microscopy and found that low water contents restrict swelling and deformation of granules.

Burt et al. (1983) found that the temperature at which gelatinization was complete, i.e. at which complete loss of birefringence occurred, increased as the water content was reduced. Liu et al. (1991) measured the gelatinization of potato and corn starches using polarized light and scanning electron microscopy, and they observed that in the presence of sufficient diluent, individual granules gelatinized over a narrow temperature range of 1 or 2°C, and higher temperatures resulted in greater deformation of granules. Yeh et al. (1996) suggested that the loss of birefringence starts to occur at a lower temperature than that of granule rupture.

Yeh et al. (1996) have measured the changes in size distribution of rice starch granules during heating continuously using a polarized light microscope in combination with a hot stage and an image analysis system. They found that the size of starch granules increased slightly as the temperature was raised from 35°C to 55°C, and increased dramatically at 65°C. The swelling of the starch granules reached a maximum increase in average area at 75°C. They were probably the first ones who quantitatively analyze changes of starch granules. Srikaeoa et al. (2006) have studied the changes of starch microstructure in soft and hard wheat grains after cooking in a pressure cooker using a scanning electron microscope and a light microscope in conjunction with image analysis. They found that with increased cooking time or temperature, the number of starch granules decreased and the area increased as a result from the swelling and melting of starch granules.

Tester et al. (1990) found that swelling is evidently a property of amylopectin and amylose is a dilutent. They also suggested that amylose and lipids in the normal starch inhibit swelling under conditions when amylose-lipid complexes are likely to be formed.

3.2 Starch Gelatinization Studied by DSC

3.2.1 Principle and advantages

Differential scanning calorimetry (DSC) monitors changes in the physical and chemical properties of starches, offering a thermodynamic approach to the study of starch gelatinization.

DSC has proven to be an extremely valuable tool to quantify the gelatinization of starch and has been widely used to study the thermal behaviors of starches (Donovan 1979; Eliasson 1980; Wootton and Bumunuarachchi 1980; Takahashi, Shiraai et al. 1982; Lund 1984; Shogren 1992; Yu and Christie 2001; Tufvesson, Wahlgren et al. 2003; Tananuwong and Reid 2004). The DSC thermograms give the possibility of analysing transition temperatures as well as transition enthalpies. The enthalpy (ΔH) of a transition was interpreted as corresponding to the amount of crystal order (or double-helical structure) in the starch suspensions that disrupted at heating scans. However, the reported results are not consistent and are sometimes controversial because of the complexity of thermal behaviors of starches, differing measurement conditions and sometimes even using unsuitable facilities. Yu & Christie (2001) have discussed various factors affecting on the measurement results considering pan selection, sample preparation and measurement conditions etc.

3.2.2 Technology description

Basically, DSC is a technique to measure the difference in energy input into a substance and a reference material as a function of temperature while both materials are subjected to programmed heating or cooling. In DSC, when a thermal transition occurs, the energy absorbed by the samples is replenished by increased energy input to maintain the temperature balance. Since the energy input is precisely equivalent in magnitude to the energy absorbed during transition, a recording of this balancing energy yields a direct calorimetric measurement of the energy transition which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change (ΔH) and its direction indicates the occurred thermal event is endothermic or exothermic (Abd Karim, Norziah et al. 2000). In the case of starch gelatinization, the DSC thermograms give the possibility of transition enthalpies occurred during melting of the semi-crystallization (or double-helical structure) in the starch as well as precise measurement of the transition temperatures (i.e. onset, T_o; peak, T_p; and conclusion, T_c) (Wootton and Bamunuarachchi 1979; Russell 1987; Sahai and Jackson 1999).

3.2.3 Applications

Since Stevens and Elton first used differential scanning calorimetry (DSC) to measure gelatinization and retrogradation of starch in 1971, DSC has been widely accepted as the most suitable method for the evaluation of starch gelatinization (Eliansson 1986; Russell 1987; Yu and Christie 2001; Tananuwong and Reid 2004). A water-dependent relationship has been established from DSC measurement for the starch endotherms during gelatinization. One single symmetric endotherm, usually denoted by G, is observed in the lower temperature region (54-73°C) for different starches with excess water (Wootton and Bamunuarachchi 1979; Russell 1987). A reduction in the amount of water available causes a biphasic endotherm with a trailing shoulder, M1. Further reducing the water content causes the first endotherm, G, to fade, and it will only be possible to observe the second endotherm, M1, with a temperature shift towards a higher region (Sahai and Jackson 1999; Gonera and Cornillon 2002). In addition to the G and M1 endotherms, a further endotherm was observed at a higher temperature than the M1 endotherm in the condition with about ~50% water content and was assigned as Z endotherm. It was suggested to be resulted from annealing of the amylopectin crystallites during heating (Russell 1987; Liu, Yu et al. 2006). Moreover, an endotherm at higher temperature, M2, is attributed to the melting of the amylose-lipid complex and is absent for potato or defatted starches (Shogren 1992; Matveev, Elankin et al. 1998; Andreev, Kalistratova et al. 1999). In our previous paper (Liu, Yu et al. 2006), an unique endotherm, labeled M3, was observed only existing in the high amylose maize starch at higher temperature.

Yu et al (2001) has systematically studied some key factors that affect the results of thermal behavior determination of starch measured by DSC, such as sample preparation, type of pan and measurement conditions. A practical guide to studying the thermal behavior of starch using DSC was introduced.

More recently, Liu et al (2006) systematically studied the gelatinization behaviours of cornstarch with different amylose/amylopectin content (waxy: 0/100, maize: 23/77, Gelose 50: 50/50, Gelose 80: 80/20) by DSC using stainless steel high pressure pan as functions of water content (9-75%) and temperature (0-200 °C). The number of endotherm and enthalpy of gelatinization depends on amylose/amylopectin, moisture and lipid content. A unique endotherm for the high amylose starch Gelose 80 was detected and labelled as M3. Gelatinization endotherms G, M1 and M2 in different cornstarches showed similar thermal behaviors and variation patterns. The enthalpy of gelatinization was calculated individually and through summarization of all the gelatinization endotherms. The gelatinization enthalpy of amylopectin rich starch is higher than that of amylose rich starch. Total enthalpy of gelatinization increased with increasing amylopectin and water contents.

3.3 Other Methods Used to Detect Gelatinization

3.3.1 XRD

Because the starch granules posses both short-range (crystalline double helices) and long-range (alternation of crystalline and amorphous lamellae) order, both of wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) have been employed to obtain information regarding the internal structures (Jenkins, Cameron et al. 1994). Power WAXS diffraction patterns show relatively broad peaks superimposed on an amorphous “halo”. The relative intensity of these two features is used to estimate the level of crystalline order. Broad diffraction peaks indicate either imperfect or relatively small crystallites (Cooke and Gidley 1992). Previous researches have assigned the typical peaks for varied polymorphs: A typical A-type pattern has strong reflections at 2θ of about 15° and 23°, and an unresolved doublet at 17°, 18° 2θ. A typical B-type pattern gives the strongest diffraction peak at around 17° 2θ and a few small peaks at around 2θ values of 23°, 22° and 20°. An additional peak appeared at about 5° 2θ with a d spacing of 5.4 Å. As for a C-type pattern, only one peak appears at 23° 2θ and the peak at ~ 18° is converted into a shoulder. These are indicative of the A pattern, while the peaks at 5° 2θ are characteristic of the B pattern. Compared to native starch samples, the observation that none of the wide-angle diffraction peaks shift position during gelatinization provides evidence for a lack of swelling within the crystallite regions. Since any swelling would involve either an increase in the average interhelix spacing, or an increasing in the helical pitch, this would result in a shift in the WAXS peaks associated with such spacing to lower angles (Jenkins, Cameron et al. 1994).

Kate was probably the first reported using X-ray diffraction diagrams to illustrate the different crystalline forms of starch in 1920's (Sarko and Wu 1978; Wu and Sarko 1978; Imberty, Chanzy et al. 1988). Kainuma & French (1972) were the first to suggest a double-stranded helix for the B-polymorph. Wu & Sarko (1978; 1978) analyzed X-ray diffraction diagrams of amylose fibers and Imberty (1988) investigated crystals to show that all (A, B and C) polymorphs are composed of ordered arrays of double helices, most likely left-handed with parallel strands. Individual double helices in these two structures have very similar conformation. Polymorphic variation is centered on packing differences with the A-type adopting a nearly close-packed arrangement and B-type structure being more open and containing more correspondingly more water (Gidley and Bociek 1985; Imberty, Chanzy et al. 1988; Cooke and Gidley 1992; Aggarwal and Dollimore 1998). Hizukuri (1985) studied the relationship between distribution of amylopectin chain-length and the crystalline forms of starch granules, and found that A-type starches have shorter chains in both the long and short chain fractions and larger amounts of the short-chain fractions than those of the B-type starches (Hizukuri 1985; Shi, Capitani et al. 1998). On the other hand, another polygraph V has been found due to left handed single amylose helix structure (Winter and Sarko 1974; Gidley and Bociek 1988; Kawada and Marchessault 2004). Lorenz and Kulp (1982) claimed that amylose chains in cereal starches form complexes with the residual lipids, and this could hinder the amylose rearrangements. Kawabata et al. (1994) also reported the evidence for amylose-lipid complex formation in cereal starch from the appearance of a new peak on the X-ray diffractogram (Lim, Chang et al. 2001).

However, unlike WAXS which quantifies crystalline order throughout starch granules, SAXS quantifies differences (periodicity) at the level of amorphous-crystalline lamellae radiating from the hilum to the periphery of starch granules. Using this technique, Jacobs et al. (Jacobs, Mischenko et al. 1998) showed that (for wheat and potato starches) the repeat distances of the crystalline and amorphous lamellae remain unchanged (10.5 nm in wheat and 9.9 nm in potato), although there was an increase in peak intensity (Cameron and Donald 1993; Tester and Debon 2000).

By modeling the SAXS data from starch slurries of various concentrations, gelatinization in limiting and excess water was studied. The degree and mode of the absorption of water and the loss of crystalline order give insight into the gelatinization process, and the results can be compared with those obtained in the literature by DSC (Cameron and Donald 1993).

Previous papers (Jenkins, Cameron et al. 1994; Oates 1997) have reported that the SAXS from starch can be accurately fitted by a scattering function generated for a proposed model structure. The model comprises a linear paracrystalline stack of alternating crystalline and amorphous lamellae embedded in a background medium. The crystalline lamellae are believed to correspond to regions containing ordered amylopectin double helices, the amorphous lamellae to regions of amylopectin branch points, and the background medium to the amorphous growth ring. With regard to the SAXS data, only the parameters of electron densities within the mode were observed to vary during gelatinization. It is significant that the average repeat distance between crystalline lamellae remains invariant. This invariance indicates that the semicrystalline lamellar stack, representing the semicrystalline growth ring, dose not expand radially during gelatinization (Jenkins, Cameron et al. 1994).

3.3.2 NMR

Although X-ray powder diffraction can monitor crystal structure and relative amounts of crystalline and amorphous phases in starch, it is only sensitive to long range order, while NMR is sensitive to short range order, being especially suitable for less crystalline samples. Combination of both techniques has provided much important information about secondary structures and molecular order of a number of molecular systems (Cheetham and Tao 1998). The study of the equilibria between configurational and conformational isomers of carbohydrates in solution is a classical application of NMR spectroscopy (Jeffrey, Wood et al. 1983).

^{13}C cross polarization/ magic angle spinning NMR (^{13}C CP/MAS NMR) has been widely used as an analytical tool for studying the presence of isomers in starch. The simple rule for detecting would seem to be that the number of signals should relate direct to the number of carbon atoms in the asymmetric unit (Marchessault, Taylor et al. 1985). Previous papers (Gidley and Bociek 1985; Veregin, Fyfe et al. 1986) have assigned the distribution of the resonance. Signal at 99-104, 81-84 ppm are attributed to C-1 and C-4 respectively. A- and B-type **α-**(1,4) glucan polymorphs have asymmetric units which contain and two glucose residues, respectively, and hence triples and double C-1 signal peaks appear in the spectrum, respectively (Marchessault, Taylor et al. 1985; Gidley and Bociek 1988). The signal at 59-62ppm is assigned to hydroxymethyl carbon-6 in hexopyranoses. The large signal around 70-73ppm, is associated with C-2, 3, 5 in hexopyranoses. The signal at ~81.6 ppm for C-4 is about 4 ppm downfield from the solution value. This downfield shift and the shoulder at ~95 ppm are believed to arise from noncrystalline material. As for the chemical shift differences between solid and liquid spectra is due to ^{13}C chemical shifts in the solid state are determined by a range of fixed values of the dihedral angles, while those in aqueous solution are time averaged as a result of rapid conformational isomerisation (Saitô, Izumi et al. 1982; Cheetham and Tao 1998).

Previous papers (Gidley and Bociek 1985; Gidley and Bociek 1988; Cheetham and Tao 1998) have reported the amylose content has a different effect on ^{13}C NMR spectra of starches in the solution and solid state. In the solid state, ^{13}C CP/MAS spectras of maize starches with different amylose contents are similar, indicating that their overall conformation is almost independent of the amylose/amylopectin ratio, although amylose and amylopectin differ in average chain length, linkage mode, physical and chemical properties (Cheetham and Tao 1998). In addition, non-crystalline amylose and amylopectin yield spectra in which the resonances have similar chemical shift ranges to those of the semi-crystalline starches. Saitô et al. (1986) also reported similar results with curdlan, pachyman and lentina. It was suggested that a-(1-4) linked glucans probably exist in a partially-ordered extended conformation. Orientation manner and proportion of α-(1-6) linked side-chains do not significantly affect the resulting main chain conformation (Cheetham and Tao 1998). However in aqueous solution, the non-reducing end-unit of branches shows distinctive minor resonances in ^{13}C NMR, and the differences in average branched chain lengths are reflected in the differences in the relative signal intensities (Dais and Perlin 1982). Quantitative analysis can provide an estimate of the proportion of branched molecules present, i.e. the ration of (1-4) and (1-6) linkages, as well as a measure of the degree of branching in the amylopectin components (Gidley 1985; Peng and Perlin 1987). Cheetham el al. (1998) compared the NMR spectra of hydrated maize starches with different amylose contents and demonstrated the presence of lipid-amylose complexes (V-type amylose). Furthermore, he also found that A-type starches with high amylopectin levels seem more sensitive to the degree of hydration. Gidley et al. (1988) observed that ^{13}C CP/MAS spectra of model amorphous materials showed marked similarities to that of single helical amyloses. It indicates that a substantial portion of the amorphous phase of starch granules consists of local conformations similar to those characteristic of V-type structure.

4. Starch Gelatinization under Shear Condition

4.1 Starch Gelatinization during Extrusion Processing

Over the last 4 decades, the use of extrusion cooking was an attractive process in food and feed industries; this is due to the advantages of versatility, high productivity, low cost, energy efficiency and no effluents causing waste problems, and to the greater demand for convenience and snack-type foods. The introduction of twin-screw extruders widened the scope of food extrusion in the manufacture of cereals and starches, ready-to-eat cereals, infant formulas, snack foods, soft moist pet foods, breadings, and coatings. Its basic principle is to convert a solid material to a fluid state by applying moisture and heat, then to extrude the material through a die to form a product of predetermined geometric and physical characteristics (Chiang and Johnson 1977).

Starch gelatinization is reported as an essential factor providing instant properties of starch-based products (Schubert 1993). In the extrusion cooking of starch-containing materials, starch is heated under pressure, between 30 to 60 atm at up to 40% moisture, to 200-250 °C (Harper 1981). At this temperature and moisture content, starch granules undergo both gelatinization and melting processes. Donovan (1979) examined the order-disorder transitions of starch over water contents ranging from a large excess to a volume fraction of less than 0.3. He suggested that the gelatinization process takes place at a moisture content higher than 61% (w/w), while at a lower moisture content, the crystallites undergo the melting process, upon continuous heating, at a significantly higher temperature than that for gelatinization.

The process such as extrusion cooking or cereal based product is dependent on proper conversion of starch within the raw materials. Under extrusion cooking environment, typically with low amount of water available, starch is gelatinized and melted in a short period of time (Wang, Chiang et al. 1989). As it is important in extrusion cooking of starch-based products, fully understanding of starch gelatinization during extrusion is required. Development of extrusion cooking technology requires an understanding of how process variables and their interactions affect the thermomechanical transformation of a feed material (Vainionpää 1991). The knowledge of the kinetics of starch gelatinization and melting is required for food process design engineers to design and optimize the extrusion process (Wang, Chiang et al. 1989).

Lawton et al. (1972) investigated the effects of 15 variables including screw geometry and operating parameters on gelatinization of corn starch. The important variables were found to be moisture, barrel and die temperatures, screw speed and screw geometry, among which, product moisture content and extruder barrel temperature had the greatest effects on gelatinization of starch. A strong interaction between moisture and barrel temperature was found to occur. The maximum gelatinization occurred at higher moisture content and lower barrel temperature or vice versa. Chiang and Johnson (1977) studied the influence of extrusion variables on the gelatinization of wheat flour and reported that temperature, moisture content, screw speed, and interaction between temperature and moisture significantly affected starch gelatinization during extrusion. Owusu-Ansah et al. (1983) found the three major extrusion variables—temperature, feed moisture, and screw speed—were significant factors affecting the physicochemical changes evaluated in their study. In the study of Ibanoglu et al. (1996), it was indicated that barrel temperature had the most pronounced effect on starch gelatinization at constant moisture content, followed by feed rate and screw speed. Besides them, similar findings were also reported by other researchers

(Anderson, Conway et al. 1969; Anderson, Conway et al. 1969; Gomez and Aguilera 1983; Gomez and Aguilera 1984; Bhattacharya and Hanna 1987).

4.1.1 Temperature

Bhattacharya and Hanna (1987) found that as the extruder barrel temperature increased from 115 to 164°C, the percent gelatinization increased from 73.6 to 98.4 in the waxy corn (1% amylose) while it increased from 40 to 55.2 in the ordinary corn samples (30% amylose). The gelatinization rate constants for both samples increased with increasing temperature. Similar result was observed by Govindasamy et al. (1996) who found that increasing barrel temperature (81-149°C) enhanced the degree of gelatinization of sago starch in a twin-screw extruder under a high moisture system (34-47%). Ibanoglu et al. (1996) also suggested that starch gelatinization increases with increase in the barrel temperature, but this increase is less dramatic at high feed rates, which possibly shows a minimum residence time needed for gelatinization. They explained that with an increase in barrel temperature hydrogen bondings would be disrupted to a greater extent so that more amylose would be solubilized increasing the degree of gelatinization.

It was also suggested that the increasing rate of the degree of starch gelatinization by increasing the temperature was affected by the moisture content. In Chiang and Johnson (1977)'s study of extrusion of wheat flour with a single-screw extruder, they showed that starch gelatinization increased sharply with increasing temperature when moisture contents were 24 or 27%, but increased more gradually when moisture contents were 18 or 21%. Cai and Diosady (1993) reported similar results for extrusion of wheat starch in a twin-screw extruder.

Owusu-Ansah et al. (1983) observed that gelatinization was affected in an anomalous manner, decreasing with increasing temperature. They attributed its cause to the choice of screw profile, which leaded to complete gelatinization at low temperature, probably because of mechanical shear associated with the profile used. Under these conditions, further heating led to the formation of water-soluble carbohydrate not accounted for in the Birch and Priestley (1973) method of determining the degree of gelatinization. When a low-pressure profile was used, the expected increase in gelatinization with increasing temperature was observed.

4.1.2 Moisture content

Many researchers (Gomez and Aguilera 1983; Bhattacharya and Hanna 1987; Lin, Hsieh et al. 1997) reported that decreasing moisture content results in increase in degree of starch gelatinization. It was suggested that the increase of initial water would decrease dough temperature during extrusion (Fletcher, McMaster et al. 1985; Hsieh, Huff et al. 1991; Huang 1993; Lin, Hsieh et al. 1997), which presumably impedes starch gelatinization. Water in the extruder also could work as a lubricant and decrease friction (Miller 1985; Hayashi, Hayakawa et al. 1993).

Chiang and Johnson (1977) suggested some interaction between moisture content and temperature. In their research, starch gelatinization decreased slightly with increasing moisture contents (18-27%) at low extrusion temperature (65°C and 80°C), but at higher temperature (95°C and 110°C), increased moisture content significantly increased starch gelatinization.

Govindasamy et al. (1996) studied the gelatinization of sago starch in a co-rotating twin-screw extruder and suggested that feed moisture content exerted the greatest effect on gelatinization. It was also suggested that increasing or decreasing the moisture content around 40% led to an elevation in the degree of gelatinization. Processing under conditions of low moisture content of starch (below 40%) may restrict the material flow inside the extruder barrel, and increase the viscosity and residence time which would increase the degree of gelatinization. With excess water (above 40%) acting as a lubricant, it should also be observed that at high moisture, the viscosity of the starch would be low, allowing for extensive internal mixing and uniform heating which would account for enhanced gelatinization (Lawton, Henderson et al. 1972).

Lawton et al. (1972) suggested that at 27% moisture sufficient water is associated with the gelatinized corn starch granules to satisfy all the theoretical requirements of bound water. Hence additional water will not be so tightly bound and may be regarded as free water and could under certain circumstances act as lubricant. This empirical finding was substantiated by Gomez and Aguilera (1984) who observed that maximum gelatinization occurred at about 28-29% moisture in case of corn starch.

4.1.3 Screw speed

Lawton et al. (1972) and Chiang and Johnson (1977) reported that increasing screw speed (shear rate) decreased starch gelatinization. They explained it as a result of a decreasing retention time in the extruder. Cai and Diosady (1993) however observed a reverse phenomenon that an increase in screw speed from 200 to 300 rpm increased degree of gelatinization for all given combinations of moisture content (25% and 30%) and barrel temperature (100-160 °C) used, which confirmed that shear is a significant contributor to starch gelatinization. This was agreed by the study of Ibanoglu et al. (1996) who found that increasing the screw speed usually resulted in an increase in tarhana temperature indicating viscous dissipation which could cause greater gelatinization. As in the case of temperature, hydrogen bonding could be weakened by mechanical action of the screws, which could enhance the leaching of amylose out of the starch granules thereby increasing gelatinization.

Govindasamy et al. (1996) reported that increasing or decreasing the screw speed around 410 rpm results in a rise in the degree of gelatinization. Raising screw speed (325 to 410 rpm) increases shear rate but also lowers the residence time, which reduced swelling making the granule less susceptible to shearing action. At higher screw speeds (410 to 485 rpm) the shearing action presumably predominates over residence time accounting for the enhanced gelatinization at these conditions.

Lin et al. (1997) investigated the starch gelatinization of extruded dry pet food and found that the way the screw speed affected the degree of starch gelatinization was related to its fat content. At 25 g/kg fat addition, the degree of starch gelatinization of the sample obtained at a lower screw speed (200 rpm) was lower than those at 300 and 400 rpm. On the contrary, at higher fat contents (50 and 75 g/kg), a higher screw speed (400 rpm) resulted in a lower degree of starch gelatinization as compared to the samples obtained at 200 and 300 rpm. Lin et al. (1997) explained that the degree of starch gelatinization was associated with the final dough temperatures, which would be dependent on the result of the combination effect of friction and conduction. It appeared that the friction effect dominated with low fat addition, causing an increase in the dough temperature with an increase in screw speed. With high fat addition (50 and 75 g/kg), the lubricating effect of fat reduced the friction (Mälkki, Kervinen et al. 1984) and the lower residence time associated with higher screw speed resulted in a lower dough temperature. The degree of starch gelatinization seemed to follow the trends of the product temperatures of the extrudates with changing screw speeds. The changes of screw speed resulted in changes of product temperature, thus affecting starch gelatinization.

4.1.4 Fat and lipid

Addition of lipid in extrusion is generally found to retard the degree of gelatinization and affect dough rheology in the barrel (Madeleine 1979; Schweizer, Reimann et al. 1986), which would reduce dough viscosity and change dough flow properties (Mälkki, Kervinen et al. 1984), respectively.

Besides the effect of interaction between fat content and screw speed that mentioned above, Lin et al. (1997) also pointed out that fat content had the most prominent influence on starch gelatinization of the samples among the factors involved. Increasing the fat content significantly decreased the degree of starch gelatinization of the extrudates. This is mainly due to its lubrication effect, which resulted in the decrease of product temperature and thus the degree of gelatinization. Moreover, it was confirmed that this effect of fat addition is more significant that feed moisture on the starch gelatinization. Lin et al. (1997) also found that addition of beef tallow resulted in a lower degree of starch gelatinization as compared to poultry fat.

4.1.5 Other factors

Lawton et al. (1972) reported that increasing the compression ratio of the screw results in an increase in the degree of gelatinization and shear of the starch. Chiang and Johnson (1977) reported that increasing the die nozzle size decreased starch gelatinization. It was assumed that pressure and surface shear decreases caused decreased starch gelatinization because of reduced residual time of flour in the extruder.

Ibanoglu et al. (1996) reported that increasing feed rate does not change the degree of gelatinization at relatively low barrel temperatures because at this condition the temperature of the barrel may not be high enough to cause much starch gelatinization. It was observed during tarhana extrusion that an increase in feed rate reduces the mean residence time at a given screw speed (59-135 s^{-1}), which could reduce the gelatinization due to a shorter processing time (Anderson, Conway et al. 1969). Ibanoglu et al. (1996) concluded that a high degree of starch gelatinization can be achieved when tarhana is extruded at high barrel temperature and screw speeds but low feed rates (i.e. high residence times).

Chuang and Yeh (2004) suggested that the degree of starch gelatinization increased with the $\bar{t}$ as the degree of starch gelatinization is a function of cooking temperature and time. In their study, the extrudate temperature was lower than the T_p (peak temperature in differential scanning calorimeter, about 87 °C) (Chuang and Yeh 2002) of rice starch, thus the degree of starch gelatinization in extrudates was a function of the mean residence time.

4.1.6 Extruder channel

By the “dead-stop” shutdown and quick opening of the barrel, Cai and Diosady (1993) and Lin et al. (1997) observed basically two different sections in the extruder from the product transformation viewpoint: (1) a solid granule conveying zone which begins from the feed inlet to the position where cooking of the material starts; and (2) a “reaction” or cooking zone which was defined as the region after the solid granule conveying zone and before the die nozzle.

In the experiment of Cai and Diosady (1993), starch gelatinization did not occur in the first zone. At about the last flight of the conveying screw before the kneading disc section, starch was transformed from powder to melt within a very short section, defined as the transition section. The length of the transition section was about 2-2.5 cm without significant difference in length for the range of operating conditions used in their study. Starch gelatinization in the extruder channel started at the beginning of the cooking zone and continued through the entire cooking zone.

Cai and Diosady (1993) explained for this phenomenon that the temperature of the material in the solid granule conveying zone did not increase rapidly enough until the material reached the cooking zone. In the fully filled segment, the heat transfer area between material and barrel was increased to the maximum due to the filling of the channel, and the increased mixing action which also improved heat transfer. Meanwhile, the increased shear action developed heat through the dissipation of mechanical energy.

Cai and Diosady (1993) revealed that the length of the cooking zone was determined by the position of the transition section. The transition section was always at the beginning of the first fully filled segment. Locations of the fully filled segments were affected only by screw configuration and die size in the range of extrusion conditions used.

In Lin et al. (1997)'s study, It was observed that the cooking zone always occurred at the second fully filled segment. Moreover, Lin et al. (1997) found that the length of the cooking zone for pet food extrusion was affected by the level of fat addition and screw speed. In the low fat content (25g/kg) treatment, increasing screw speed increased the length of the cooking zone. This was due to the friction effect dominant in low fat extrusion. A higher screw speed generated a higher friction and, therefore, a higher energy input into the material, which resulted in a longer cooking zone and a higher degree of starch gelatinization at the end of the barrel even though the residence time of the material was shorter. For the extrusion runs at a high fat addition (75g/kg), the degree of starch gelatinization of the material increased gradually along the cooking zone. The cooking zone seemed to start at the same position (about 14 cm from the die nozzle) for both operations at low and high screw speeds. However, the degree of starch gelatinization of the materials along the extruder barrel for 200 rpm operation was higher than at 400 rpm operation. Lin et al. (1997) attribute this phenomenon to the lubricating effect of the lipid with a higher fat content reduced the friction generated at a higher screw speed, and, therefore, resulted in a lower degree of starch gelatinization.

4.1.7 Kinetics

Based on measurements using differential scanning calorimetry, the kinetics of starch gelatinization at high temperature and low moisture content were reported to be pseudo-first-order for corn meal (Burros, Young et al. 1987), and pseudo-zero-order for waxy corn starch (Wang, Chiang et al. 1989). However, the cooking environment for starch in an extruder channel is not the same as in a differential scanning calorimeter, since shear forces in the extruder channel can not be reproduced in the calorimeter cell. Bhattacharya and Hanna (1987) published the results of an investigation of the kinetics of starch gelatinization during extrusion at 17.8, 20, 30, 40, and 42.2% moisture contents with a single-screw extruder. They found that the process followed pseudo-zero-order reaction kinetics and the rate constants decreased with decreasing temperature. Lai and Kokini (1991) indicated that starch gelatinization during extrusion followed a first order reaction. These findings indicate that starch gelatinization is not an elementary reaction; a series of reaction may be involved in this process so that only global reaction kinetics can be obtained as long as the reaction mechanism of gelatinization is not fully understood.

As mentioned in the previous part, Cai and Diosady (1993) observed that the extruder channel could be divided into two major functional zones: a solid conveying zone and a cooking zone. The physical transition from solid to melt occurred in a relatively short section at the beginning of the cooking zone. Based on this observation, starch gelatinization in an extruder does not follow a simple reaction mechanism. The reaction initially followed a pseudo-second-order rate law in the transition section, but it soon reverted to pseudo-first-order. Starch gelatinization during extrusion cooking could be predicted with reasonable accuracy by the first-order model where the rate constant was a function of both temperature and shear stress. Unfortunately, while this first-order model empirically predicted the extent of gelatinization of extrudates, it did not adequately represent the true reaction mechanism in the extruder channel.

4.2 Viscosity Variation under Shear Stress (Viscometry as a Method for Determining Starch Gelatinization)

It is well know the viscosity of starch various significantly during and after gelatinization. A Brabender Visco/amylo/Graph provides information, not only on gelatinization, but also on the properties of the cooled paste (Zobel 1984). This instrument records the torque required to balance the viscosity that develops when starch slurry is subjected to a programmed heating and cooling cycle. The Amylograph Handbook covers the theory, construction, applications, sources of error, troubleshooting, and adjustment of units (Gonera and Cornillon 2002). Addition of carboxymethyl cellulose (CMC), which binds part of the water, to the starch slurry permits detection of the initial gelatinization or swelling temperature (Crossland and Favor 1948). Data obtained by this technique are compared with light transmission, water adsorption, and solubility data by Sandstedt (Sandstedt and Abbott 1964). Reported Amylograph data should include instrument model, torsion spring used, bowl speed, volume of slurry, slurry concentration (including basis), and start, hold, and final temperature.

Freeman and Verr (1972) measured gelatinization and paste development by heating starch in a closed bottle submerged in a water bath with a shaking mechanism. At specified times or temperature, samples were removed and viscosities determined with a Brookfield Synchro-Lectric viscometer. Samples were also cooled and viscosity again measured to determine setback. The authors

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claim the procedure is rapid and that it gives precise viscosity values when measuring the effects of starch concentration, cooking times, temperature range, and pH.

5. Study of Starch Gelatinization using RheoScope

A new technology RheoScope, an equipment can measure viscosity under shear stress at same time observes variation of starch particulars using a microscope, was developed to study starch gelatinization under shear stress.

5.1 Principle and Advantages

RheoScope is a controlled rate/controlled stress (CR/CS) rheometer, but has the advantage of containing a built-in, high resolution, black and white video camera with microscope lens and light source. The camera and 150W visible, white, light source are positioned in such a manner that the objective lens is trained through a window in the lower fixture of the measuring geometry. The radial location of the objective can be altered with a servo driven motor, to view the material between the outer edge of the measuring geometry and the centre. The field in which the microscope is focused can also be altered, by servo motor, allowing the interested scientist to focus between the upper and lower fixtures to a field depth of 5μm. The resolution of the microscope used for these analyses is 1μm. The RheoScope also has an additional feature, which allows the use of polarized light, in cases where the boundary between phases is not distinct under non-polarized, visible light.

The camera captures one image for each rheological data point, up to a maximum of 15 images every second. These images may be played back consecutively as a video file, or selectively saved as individual images. The heat exchanger consists of fluid filled tubing, connected to a water bath with refrigeration, heating and a pump. In this way the temperature of the sample in the measuring gap was altered or maintained. The major restriction of this instrument is that the camera arrangement can not function above 95 °C. So, samples that had not dissolved at this temperature could not be tested further.

5.2 Application in Studying Gelatinization of Cornstarch

Recently Yu et al. (2006) studied the gelatinization of cornstarches with different amylose content using RheoScope. Cornstarches with different ratio of amylose/amylopectin were used in this experimental work. Experiments were carried out to assess the rheological behavior of four different starch samples as the starch particles dissolved in a water carrier at up to a maximum temperature of 90 °C.

The rheological data show distinct types of generalized behavior for the starch suspensions and solutions, according to the dominance of different mechanisms affecting the rheological data for each sample. The images collected help with the interpretation of this complicated system.

One important effect observed during experiments, by comparing successive images, is that all of the starch systems tested appear to have a distinct process of dissolution. At first the particle size increases, this swelling is caused by ingress of moisture through the amorphous region, expanding the particle. The swelling is accompanied by a reduction in the disparity or definition of the location of the epidermis, which one would intuitively suspect is due to the stretching it undergoes due to the expansion and the softening it experiences as a result of the elevated temperature. These phenomena are followed by partial or complete dissolution by the tiring force through particle swelling. In some cases there was evidence that some epidermal remnants did not change phase but remained, in a much expanded and transparent state.

It is first time that viscosity and microstructure variations were recorded at same time. The camera captures one image for each rheological data point, up to a maximum of 15 images every second. A direct relationship between viscosity and variation of starch granular for starch gelatinization under shear stress was established. Cornstarches with different amylose content (0, 26, 50, 80%) was used in this work. It was found that amylopectin (wax starch) gelatinized at lower temperature and starch particulars are completely destroyed after gelatinization. Since out layer of starch granular is gradually dissolved under shear stress the size increase of starch granular by swelling during gelatinization is not clearly observed.

From the point of starch granular dissolving, there are two steps during gelatinization under shear stress: starch granular swelling and outside layer dissolving gradually, than whole particles dissolved in a relative short time.

6. Summary

This article reviews the development of studying starch gelatinization under shear and shearless conditions, in particular the technologies used to detect the degree of gelatinization. The gelatinization of starch is a multi-stage process. To study the gelatinization, various technologies have been developed, such as microscope with hot-stage, viscometry, DSC, XRD, NMR etc. It was found the definition of “gelatinization” could be different for different detection technologies. Recently starches have been used as important raw materials for biodegradable plastics and its gelatinization process has attracted much attention since it acts as an important and unique characterization in the processing of starch-based materials. Gelatinization processing for starch-based materials is normally carried under shear stress with less water content.

The well-accepted conception of “gelatinization” means destroying the crystalline structure in starch granular. Starch gelatinization is an irreversible process and includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization. Microscope with a hot stage examine granules undergoing gelatinization permits one to observe swelling duration, degree of swelling, and swollen granule integrity and size, and the loss of birefringence. Besides, it also permits one to record the onset temperature and end temperature of the gelatinization simultaneously. DSC is a technique to measure the difference in energy input into a substance and a reference material as a function of temperature while both materials are subjected to programmed heating or cooling. In the case of starch gelatinization, the DSC thermograms give the possibility of transition enthalpies occurred during melting of the semi-crystallization (or double-helical structure) in the starch as well as precise measurement of the transition temperatures. The number of endotherm and enthalpy of gelatinization depends on amylose/amylopectin, moisture and lipid content.

Under shearless condition full gelatinization of starch needs about ratio of water 3/starch 1, while the gelatinization under shear condition requires less water content since shear stress enhances the processing. The process such as extrusion cooking or cereal based product is dependent on proper conversion of starch within the raw materials. Under extrusion cooking environment, gelatinization is typically with low amount of water available and higher pressure conditions. Recently, a new technology RheoScope, an equipment can measure viscosity under shear stress at same time observes variation of starch particulars using a microscope, was developed to study starch gelatinization under shear stress. RheoScope is a controlled rate/controlled stress (CR/CS) rheometer, but has the advantage of containing a built-in, high resolution, black and white video camera with microscope lens and light source.

References

Abd Karim, A., M. H. Norziah, et al. (2000). "Methods for the study of starch retrogradation." Food Chemistry **71**(1): 9-36.

Aggarwal, P. and D. Dollimore (1998). "A thermal analysis investigation of partially hydrolyzed starch." Thermochimica Acta **319**(1-2): 17-25.

Anderson, R. A., H. F. Conway, et al. (1969). "Gleatinization of Corn grits by roll and extrusion cooking." Cereal Science Today **14**(1): 4-7, 11-12.

Anderson, R. A., H. F. Conway, et al. (1969). "Roll and extrusion cooking of grain sorghum grits." Cereal Science Today **14**: 372-376, 381.

Andreev, N. R., E. N. Kalistratova, et al. (1999). "The influence of heating rate and annealing on the melting thermodynamic parameters of some cereal starches in excess water." Starch/Stärke **51**(11-12): 422-429.

Atwell, W. A., L. F. Hood, et al. (1988). "The terminology and methodology associated with basic starch phenomena." Cereal Foods World **33**: 306-311.

Bhattacharya, M. and M. A. Hanna (1987). "Kinetics of Starch Gelatinization During Extrusion Cooking." Journal of Food Science **52**(3): 764-766.

Biladeris, C. G., C. M. Page, et al. (1985). "Thermal behavior of amylose-lipid complexes." Carbohydrate Polymers **5**: 367-389.

Birch, G. G. and R. J. Priestley (1973). "Degree of gelatinization of cooked rice." Starch/Stärke **25**: 98.

Burros, B., C., L. A. Young, et al. (1987). "Kinetics of Corn Meal Gelatinization at High Temperature and Low Moisture." Journal of Food Science **52**(5): 1372-1380.

Burt, D. J. and P. L. Russell (1983). "Gelatinization of low water content wheat starch-water mixtures." Starch/Stärke **10**: 354-360.

Caesar, G. V. (1950). Chapter IX. The hydrogen bond in starch as a basis for interpreting its behavior and reactivity. Chemistry and Industry of Starch. R. W. Kerr. New York, Academic Press Inc.**:** 249-258.

Cai, W. and L. L. Diosady (1993). "Model for Gelatinization of Wheat Starch in a Twin Screw Extruder." Journal of Food Science **58**(4): 872-887.

Cameron, R. E. and A. M. Donald (1993). "A samll-angle X-ray scattering study of the absorption of water into the starch granule." Carbohydrate Research **244**: 225-236.

Chatakanonda, P., S. Varavinit, et al. (2000). "Effect of Crosslinking on Thermal and Microscopic Transitions of Rice Starch." Lebensmittel-Wissenschaft und-Technologie **33**(4): 276-284.

Cheetham, N. W. H. and L. P. Tao (1998). "Solid state NMR studies on the structural and conformational properties of natural maize starches." Carbohydrate Polymers **36**(4): 285-292.

Chiang, B. Y. and J. A. Johnson (1977). "Gelatinization of Starch in Extruded Products." Cereal Chemistry **54**(3): 436-443.

Chuang, G. C.-C. and A.-I. Yeh (2002). "Effects of product temperature and moisture on viscoelastic properties of glutinuous rice extrudates." Cereal Chemistry **79**: 36-40.

Chuang, G. C.-C. and A.-I. Yeh (2004). "Effect of screw profile on residence time distribution and starch gelatinization of rice flour during single screw extrusion cooking." Journal of Food Engineering **63**(1): 21-31.

Cooke, D. and M. J. Gidley (1992). "Loss of crystalline and molecular order during starch gelatinization: origin of the enthalpic transition." Carbohydrate Research **227**: 103-112.

Crossland, L. B. and H. H. Favor (1948). "Starch gelatinization studies. II. A method for showing the stages in swelling of starch during heating in the amylograph." Cereal Chemistry **25**: 213.

Dais, P. and A. S. Perlin (1982). "High-field C-NMR sepctroscopy of β-D-glucans, amylopectin and glycogen." Carbohydrate Research **100**: 103-116.

Donovan, J. W. (1979). "Phase transition of the starch-water system." Biopolymers **18**: 263.

Eliansson, A.-C. (1986). "On the effects of surface active agents on the gelatinization of starch---a calorimetirc investigation." Carbohydrate Polymers: 463-474.

Eliasson, A.-C. (1980). "Effect of water content on the gelatinization of wheat starch." Starch/Stärke **32**: 270-272.

Fisher, D. K. and D. B. Thompson (1997). "Retrogradation of maize starch after thermal treatment within and above the gelatinization temperature range." Cereal Chemistry **74**(3): 344-351.

Fletcher, S. I., T. J. McMaster, et al. (1985). "Rheology and extrusion of maize grits." Chemical Engineering Communications **32**: 239-262.

Freeman, J. E. and W. J. Verr (1972). Cereal Science Today **17**(2): 46.

Ghiasi, K., R. C. Hoseney, et al. (1982). "Gelatinization of wheat starch.3.Comparison by differential scanning calorimetry and light microscopy." Cereal Chemistry **59**: 258-262.

Gidley, M. J. (1985). "Quantification of the structural features of starch polysaccharides by N.M.R. spectroscopy." Carbohydrate Research **139**: 85-94.

Gidley, M. J. and S. M. Bociek (1985). "Molecular organization in starches: A 13C CP/MAS NMR study." Journal of American Chemistry Society **107**: 7040-7044.

Gidley, M. J. and S. M. Bociek (1988). "^{13}C CP/MAS NMR studies of amylose inclusion complexes, cyclodextrins, and the amorphous phase of starch granuels: relationships between gylcosidic linkage conformation and solid-state ^{13}C chemical shifts." Jouranl of American Chemistry Society **110**: 3820-3829.

Gomez, M. H. and J. M. Aguilera (1983). "Changes in the starch fraction during extrusion-cooking of corn." Journal of Food Science **48**: 378-381.

Gomez, M. H. and J. M. Aguilera (1984). "A Physicochemical Model for Extrusion of Corn Starch." Journal of Food Science **49**: 40-43 + 63.

Gonera, A. and P. Cornillon (2002). "Gelatinization of starch/gum/sugar systems studied by using DSC, NMR, and CSLM." Starch/Stärke **54**(11): 508-516.

Gough, B. M. and J. N. Pybus (1971). "Effect on the Gelatinization Temperature of Wheat Starch Granules of Prolonged Treatment with Water at 55 °C." Starch/Stärke **23**: 210-212.

Govindasamy, S., O. H. Campanella, et al. (1996). "High moisture twin-screw extrusion of sago starch: 1. Influence on granule morphology and structure." Carbohydrate Polymers **30**(4): 275-286.

Hai, P. K., S. Garg, et al. (1989). "Gelatinization of starch and modified starch." Starch/Stärke **41**: 88-91.

Harper, J. M. (1981). Extrusion of Foods. Boca Raton, Fl, CRC Press.

Harper, J. M. (1989). Food Extruders and Their Applications. Extrusion Cooking. C. Mercier, P. Linko and J. M. Harper. St. Paul, MN, Am. Assoc. Cereal Chem.**:** 1-15.

Hayashi, N., I. Hayakawa, et al. (1993). "Flow behavior of soy protein isolate melt with low and intermediate moisture levels at an elevated temperature." Journal of Food Engineering **18**: 1-11.

Hermansson, A. M. and K. Svegmark (1996). "Development in the understanding of starch functionality." Trends in Food Science & Technology **7**(11): 345-353.

Hizukuri, S. (1985). "Relationship between the distribution of the chainlength of amylopectin and the crystalline structure of starch granules." Carbohydrate Research **141**: 295-306.

Hsieh, F., H. E. Huff, et al. (1991). "Twin-screw extrusion of sugar beet fiber and corn meal." Lebensmittel-Wissenschaft und-Technologie **24**: 495-500.

Huang, S. (1993). Extrusion cooking of rapeseed meal. Department of Agricultural Engineering. Columbia, University of Missouri. **Master**.

Hulleman, S. H. D., F. H. P. Janssen, et al. (1998). "The role of water during plasticization of native starches." Polymer **39**(10): 2043-2048.

Ibanoglu, S., P. Ainsworth, et al. (1996). "Extrusion of tarhana: effect of operating variables on starch gelatinization." Food Chemistry **57**(4): 541-544.

Imberty, A., H. Chanzy, et al. (1988). "The double-helical nature of the crystalline part of A-starch." Journal of Molecular Biology **201**: 365-378.

Jacobs, H., N. Mischenko, et al. (1998). "Evaluation of the impact of annealing on gelatinisation at intermediate water content of wheat and potato starches: A differential scanning calorimetry and small angle X-ray scattering study." Carbohydrate Research **306**(1-2): 1-10.

Jeffrey, G. A., R. A. Wood, et al. (1983). "Crystal structure and solid-state NMR analysis of lactulose." Jouranl of American Chemistry Society **105**: 2128-2133.

Jenkins, P. J., R. E. Cameron, et al. (1994). "In situ simultaneous small and wide angle X-ray scattering: A new technique to study starch gelatinization." Jouranl of polymers science: Part B: Polymer physics **32**: 1579-1583.

Kainuma, K. and D. French (1972). "Naegeli Amylodextrin And Its Relation To Starch Granule Structure. II. Role Of Water In Crystallization Of B-Starch." Biopolymers **11**: 2241-2250.

Kainuma, K. T., T. Oda, et al. (1968). "Observation of changes of starch granules during gelatinization by a novel photopastegraphy method. I. Design of the photopastegraph." S.J. Technol. Soc. Starch (Tokyo) **16**: 51-4.

Kawabata, A., N. Takase, et al. (1994). "Microscopic observation and X-ray diffractometry of heat/moisture-treated starch granules." Starch/Stärke **46**: 463-469.

Kawada, J. and R. H. Marchessault (2004). "Solid state NMR and X-ray studies on amylose complexes with small organic molecules." Starch/Stärke **56**(1): 13-19.

Lai, L. S. and J. L. Kokini (1991). "Physicochemical changes and rheological properties of starch during extrusion." Biotechnology Progress **7**: 251-266.

Lawton, B. T., B. A. Henderson, et al. (1972). "The effects of extruder variables on the gelatinisation of corn starch." The Canadian Journal of Chemical Engineering **50**: 168-172.

Lelievre, J. (1974). "Starch Gelatinization." Journal of Applied Polymer Science **18**(1): 293-296.

Lelievre, J. (1976). "Theory of gelatinization in a starch water solute system." Polymer **17**: 854-858.

Lim, M. H., H. B. Wu, et al. (2000). "The effect of starch gelatinization and solute concentrations on T-g ' of starch model system." Journal of the Science of Food and Agriculture **80**(12): 1757-1762.

Lim, S. T., E. H. Chang, et al. (2001). "Thermal transition characteristics of heat-moisture treated corn and potato starches." Carbohydrate Polymers **46**(2): 107-115.

Lin, S., F. Hsieh, et al. (1997). "Effects of Lipids and Processing Conditions on Degree of Starch Gelatinization of Extruded Dry Pet Food." Lebensmittel-Wissenschaft und-Technologie **30**(7): 754-761.

Liu, H., J. Lelievre, et al. (1991). "A study of starch gelatinization using differential scanning calorimetry, X-ray, and birefringence measurements." Carbohydrate Research **210**: 79-87.

Liu, H., L. Yu, et al. (2006). "Gelatinization of cornstarch with different amylose/amylopectin content." Carbohydrate Polymers **65:** 357-363.

Lorenz, K. and K. Kulp (1982). "Cereal and root starch modification by heat-moisture treatment." Starch/Stärke **34**: 76-81.

Lund, D. B. (1984). "Influence of time, temperature, moisture, ingredients, and processing conditions on starch gelatinization." CRC Critical Reviews in Food Science and Nutrition **20**(4): 249-273.

Madeleine, A. M. (1979). "The effect of extractable lipid on the viscosity characteristics of corn and wheat starches." Journal of the Science of Food and Agriculture **30**: 731-738.

Mälkki, Y., R. Kervinen, et al. (1984). Effects of monglycerides during extrusion cooking of wheat flour. . Fats (lipids) in Baking and Extrusion. R. Marcuse. Göteborg, Sweden, LIPIDFORUM Symposium**:** 130-137.

Marchessault, R. H., M. G. Taylor, et al. (1985). "Solid state ^{13}C-c.p.-m.a.s. n.m. r. of starches." Carbohydrate Research **144**: C1-C5.

Matveev, Y. I., N. Y. Elankin, et al. (1998). "Estimation of contributions of hydration and glass transition to heat capacity changes curing melting of native starches in excess water." Starch/Stärke **50**(4): 141-147.

McGrane, S. J., D. E. Mainwaring, et al. (2004). "The role of hydrogen bonding in amylose gelation." Starch/Stärke **56**(3-4): 122-131.

Miller, B. S., R. I. Derby, et al. (1973). "A pictorial explanation for the increase in viscosity of a heated wheat starchwater suspension." Cereal Chemistry **50**: 271-80.

Miller, R. C. (1985). "Low moisture extrusion: Effects of cooking moisture on product characteristics." Journal of Food Science **55**: 249-253.

Oates, C. G. (1997). "Towards an understanding of starch granule structure and hydrolysis." Trends in Food Science & Technology **8**(11): 375-382.

Olkku, J. and C. Rha (1978). "Gelatinization of starch and wheat flour starch- a review." Food Chemistry **3**: 293.

Owusu-Ansah, J., F. R. V. D. Voort, et al. (1983). "Physiochemical changes in cornstarch as a function of extrusion variables." Cereal Chemistry **60**(4): 319-324.

Peng, Q.-J. and A. S. Perlin (1987). "Obervations on N.M.R. spectra of starches in dimethyl sulfoxide, iodine-complexing and solvation in water-dimethyl sulfoxide." Carbohydrate Research **160**: 57-72.

Roberts, R. L., E. L. Potter, et al. (1954). "Effect of processing conditions on the explanded volume, color, and soluble starch of parboiled rice." Cereal Chemistry **31**: 121-125.

Russell, P. L. (1987). "Gelatinisation of starches of different amylose/amylopectin content. A study by DSC." Journal of Cereal science **6**: 133-145.

Sahai, D. and D. S. Jackson (1999). "Enthalpic transitions in native starch granules." Cereal Chemistry **76**(3): 444-448.

Saitô, H., G. Izumi, et al. (1982). "A ^{13}C cross polariztion-magic angle spinning (cp-mas) N. M. R. study of crystalline cyclohexa-amylose inclusion complexes. Conformation dependent ^{13}C chemical shifts are related to the dihedral angels of glycosidic linkages." Journal of Chemistry Society, Chemisty Communication: 1386-1388.

Saitô, H., R. Tabeta, et al. (1986). "A high-resolution solid-state ^{13}C NMR study of (1-3)-β-D-glucans from various sources conformation characterisation as viewed from the conformation dependent ^{13}C chemical shifts and its consequence to gelation property." Bulletin of the Chemical Society of Japan **50**: 2093-2101.

Sandstedt, R. M. and R. C. Abbott (1964). "A comparison of methods for studying the course of starch gelatinisation." Cereal Science Today **9**(1): 13-26.

Sarko, A. and H.-C. H. Wu (1978). "The crystal structures of A-, B-, and C-polymorphs of amylose and starch." Starch/Stärke **30**: 73-78.

Schubert, H. (1993). "Instantization of powdered food products." International Chemical Engineering **33**: 28-45.

Schweizer, T. F., S. Reimann, et al. (1986). "Influence of drum-drying and twin-screw extrusion cooking on wheat carbohydrates, II, Effect of lipids on physical properties, degradation and complex formation of starch in wheat starch." Journal of Cereal Science **4**: 249-260.

Seidemann, J. (1963). "Identification of different kinds of starches by microscopic determination of the swelling range." Starch/Stärke **15**: 291.

Shetty, R. M., D. R. Lineback, et al. (1974). "Determining the degree of gelatinization in parboiled rice: Comparison of a subjective and an objective method." Cereal Chemistry **51**: 364-375.

Shi, Y. C., T. Capitani, et al. (1998). "Molecular structure of a low-amylopectin starch and other high-amylose maize starches." Journal of Cereal Science **27**(3): 289-299.

Shogren, R. L. (1992). "Effect of moisture content on the melting and subsequent physical aging of cornstarch." Carbohydrate Polymers **19**: 83-90.

Srikaeo, K., J. E. Furst, et al. (2006). "Microstructural changes of starch in cooked wheat grains as affected by cooking temperatures and times." LWT - Food Science and Technology **39**(5): 528-533.

Stevens, D. J., G. A. H. Elton, et al. (1971). "Thermal properties of the starch/water system. 1.meausrement of heat of gelatinization by DSC."

Sullivan, J. W. and J. A. Johnson (1964). "Measurement of starch gelatinization by enzyme susceptibility." Cereal Chemistry **41**: 73-77.

Svensson, E. and A.-C. Eliasson (1995). "Crystalline changes in native wheat and potato starches at intermediate water levels during gelatinization." Carbohydrate Polymers **66**: 181-187.

Takahashi, K., K. Shiraai, et al. (1982). "Structural Changes in Starch Granules of Low Moisture Content during Heating." Agric. Biol. Chem **46**(10): 2505-2511.

Tananuwong, K. and D. S. Reid (2004). "DSC and NMR relaxation studies of starch-water interactions during gelatinization." Carbohydrate Polymers **58**(3): 345-358.

Tester, R. F. and S. J. J. Debon (2000). "Annealing of starch - A Review." International Journal of Biological Macromolecules **27**(1): 1-12.

Tester, R. F. and W. R. Morrison (1990). "swelling and gelatinization of cereal starch. I. effects of amylopectin, amylose, and lipids." Cereal Chemistry **67**(6).

Tester, R. F. and W. R. Morrison (1992). "Swelling and gelatinization of cereal starches. III. Some properties of waxy and normal. nonwaxy barley starches." Cereal Chemistry **69**: 654-658.

Tufvesson, F., M. Wahlgren, et al. (2003). "Formation of amylose-lipid complexes and effects of temperature treatment. Part 1. Monoglycerides." Starch/Stärke **55**(2): 61-71.

Vainionpää, J. (1991). "Modelling of extrusion cooking of cereals using response surface methodology." Journal of Food Engineering **13**(1): 1-26.

van Leeuwenhoek, A. (1719). Epistolae physiologicae, super compluribus naturae arcanis. Delphis, Apud Adrianum Beman.

Varriano-Marston, E., V. Ke, et al. (1980). "comparison of methods to determine starch gelatinization in bakery foods." Cereal Chemistry **57**(4): 242-248.

Veregin, R. P., C. A. Fyfe, et al. (1986). "Characterisation of the crystalline A and B starch polymorphs and investigation of starch crystallization by high-resolution ^{13}C CP/MAS NMR." Macromolecules **19**: 1030-1034.

von Eberstein, K., R. Hopcke, et al. (1980). "DSC investigation of starch: Part I. Feasibility of thermalytical methods to characterize starches." Starch/Stärke **32**: 397-403.

Wang, S. S., W. C. Chiang, et al. (1989). "Kinetics of Phase transition of waxy corn starch at extrusion temperatures and moisture contents." Journal of Food Science **54**(5): 1298-132- (some pages mising in between).

Watson, S. A. (1964). Dertermination of starch gelatinization temperature. Methods in carbohydrate chemistry, Vol. IV, Starch. R. L. Whistler. New York, Academic Press**:** 240-2.

Winter, W. T. and A. Sarko (1974). "Crystal and molecular structure of V-anhydrous amylose." Biopolymers **13**: 1447-1460.

Wootton, M. and A. Bamunuarachchi (1979). "Application of DSC to starch gelatinization: 1. Commerical native and modified starches." Starch/Stärke **31**: 201-204.

Wootton, M. and A. Bumunuarachchi (1980). "Application of differential Scanning Calormetry to Starch Gelatinization: III Effect of Sucrose and sodium chloride." Starch/Stärke **33**(4): 126-129.

Wu, H.-C. H. and A. Sarko (1978). "The double -helical molecular structure of crystalline A-amylose." Carbohydrate Research **61**: 27-40.

Wu, H.-C. H. and A. Sarko (1978). "The double -helical molecular structure of crystalline B-amylose." Carbohydrate Research **61**: 7-25.

Yeh, A.-I. and J.-Y. Li (1996). "A continuous measurement of swelling of rice starch during heating." Journal of Cereal Science **23**: 277-283.

DOI: 10.2202/1556-3758.1162

Yu, L. and G. Christie (2001). "Measurement of starch thermal transitions using differential scanning calorimetry." Carbohydrate Polymers **46**(2): 179-184.

Yu, L., T. Kealy and Chen P. (2006). "Study of Starch Gelatinization in a Flow Field using Simultaneous Rheometric Data Collection and Microscopic Observation." International Polymer Processing **3:** 283-289.

Ziegler, G. R., D. B. Thompson, et al. (1993). "Dynamic measurement of. starch granule swelling." Ceral Chemistry **70**: 247-251.

Zobel, H. F. (1984). Chapter IX. Gelatinization of starch and mechanical properties of starch pastes. Starch: Chemstry and Technology. R. L.

Whistler, J. N. BeMiller and B. F. Paschall. New York, Academic Press.