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Thermochimica Acta 246 (1994) 329–341

thermochimica acta

Retrogradation of starch and the role of its components

M. Gudmundsson

Department of Food Technology, Technological Institute of Iceland, 112 Reykjavik, Iceland

Received 1 November 1993; accepted 20 April 1994

Abstract

The retrogradation of starch is not a simple process: it manifests itself in apparently different processes, such as increased firmness and recrystallization of gelatinized starch gels with time. The components of starch, amylopectin and amylose, have different roles in retrogradation. Much evidence suggests that changes in the amylopectin are the main cause for what we call retrogradation because they are responsible for all long-term rheological and structural changes. The amylose, however, is responsible for the short-term changes. The water content and storage temperature greatly affect the rate and extent of retrogradation of starch gels. Other compounds added to the starch, such as lipids and surfactants, can retard or interfere with the retrogradation. In this paper, some suggestions concerning the effects of each component in the starch are discussed. Starches from different botanical sources, despite similar amylose/amylopectin ratios, can retrograde to different extents, indicating that the structure of the amylopectin seems to be a very important factor in retrogradation.

Keywords: Ageing; Amylopectin; Amylose; DSC; Gel; Gelatinization; Retrogradation; Starch; Water; XRD

1. Introduction

Retrogradation of starch is a term used for the changes that occur in gelatinized starch from an initially amorphous state to a more ordered or crystalline state. This occurs because pastes or gels of gelatinized starch are not in thermodynamic equilibrium. The changes that the starch gels undergo are manifested by apparently different processes. Their rheological properties change, as evidenced by increased firmness or rigidity. Loss of water-holding capacity and restoration of crystallinity

SSDI 0040-6031(94)01874-X

also become evident and increase on ageing. These processes are collectively called retrogradation and are thought to exert a major influence on texture leading to a decreased acceptability of many starch-containing foods.

Many studies support the idea that starch retrogradation is the main factor in the staling of bread and other baked products [1–4].

The kinetics of retrogradation have been thoroughly studied [1,2,4–7]. The mechanism involved on a molecular level is, however, still not completely known, because recrystallization and increased firmness are both referred to as retrogradation, and different experimental techniques are applied which are not necessarily measuring the same process. Factors other than the starch components themselves are also very important, such as the water content of the gel and the storage temperature which affect the rate and the extent of retrogradation. Moreover, many substances, such as lipids and surfactants can interfere with the retrogradation process. The botanical source may also play an important role in the starch retrogradation.

2. Methods used for estimating retrogradation and measured factors

X-ray diffraction analysis [2,8,9], thermal methods such as DSC [3,10–14], and several rheological techniques [5,15–17], more than any other methods, have been used to measure retrogradation, i.e. the rate and extent of recrystallization on ageing.

Because retrogradation is to a large extent a recrystallization process, it can be followed by changes in X-ray diffraction patterns. In the cereal starches, the A-pattern is lost during gelatinization and only the V-pattern is obtained owing to the formation of the amylose–lipid complex. On ageing, the B-pattern will develop, superimposed on the V-pattern [8]. The intensity of the B-pattern increases with time.

Rheological techniques (especially fundamental viscoelastic measurements) are well suited to monitor gel firmness (rigidity) on ageing. This is usually done by measuring the storage modulus (G'). Rheological techniques do not evaluate the role of only one component or process, but the combined effect of all the components of the gel.

Thermal methods like DSC are well fitted to follow the rate and extent of retrogradation as the starch molecules progressively reassociate on ageing. Aged gels and stale bread show a characteristic melting endotherm at around 55–60°C, which is absent in fresh gels and breads immediately after gelatinization. This transition enthalpy progressively increases in magnitude with storage time until a certain limit is reached, and then remains constant on further storage.

3. The role of amylose and amylopectin in retrogradation

It was first suggested by Schoch and French [1] that staling of bread essentially involves the retrogradation of the amylopectin but not the amylose fraction. Since

then, many investigations have been carried out to determine the respective role of amylopectin and amylose and their combined effects in the retrogradation of starch gels and the staling of baked products. The roles of amylose and amylopectin depend on the composite nature of the starch gels where swollen gelatinized starch granules are embedded within an amylose–gel matrix [18–21].

4. Evidence from X-ray diffraction analysis

When retrograded amylose gels (without granules) are compared to amylopectin gels (without granules) and starch gels, some important features emerge that explain the role of the two starch polymers in the retrogradation. Early X-ray diffraction studies on aged starch gels showed that the B-type diffraction pattern developed slowly [8]. Stored amylose gels and amylose precipitated from aqueous solution give a weak X-ray diffraction pattern of B-type [22]; the same has been reported for stored amylopectin gels [23,24]. It was suggested that one mechanism involved in gelling of amylose is phase separation into polymer-rich and polymer-deficient regions [15,16]. Crystal growth, as detected by X-ray diffraction, is slower than formation of the gel network and has been proposed as occurring in the polymer-rich regions of the gel [15,16]. For both amylose and starch gel, the initial development of crystallinity occurred at similar rates. However, the crystallization of amylose effectively reached a limit after 2 days, whereas the crystallinity of the starch gel continued to increase [16]. The amylopectin gels show only a slow increase in crystallinity with time and approach a limiting value after 30–40 days [24]. On heating fully retrograded starch gels to 90°C, about 70% of the crystallinity was lost, whereas that of the amylose gel was reduced by only 25% [15]. The crystallinity of amylopectin gels is fully reversible on heating [23]. The residual crystallinity of starch gels after heating is therefore due to crystallinity of the amylose fraction. Isolated gelatinized starch granules that have been washed free from all exudated amylose give no X-ray diffraction pattern immediately after cooling. After two weeks of storage, the B-type pattern is obtained, which completely disappears on heating to 70°C [15].

5. Evidence of retrogradation from DSC studies

DSC studies on retrogradation also attribute the long-term changes to the amylopectin fraction [10,12,15]. Aged bread, starch and amylopectin gels show a melting endotherm that slowly increases with time, whereas no melting endotherm is obtained from amylose gels in the temperature interval measured (10–130°C), see Fig. 1. The crystallinity of the amylose fraction can be seen as an endothermic peak at 153°C [24], which is a temperature rarely reached in connection with starch-based foods. When retrogradation of different ratios of amylopectin/amylose mixtures were studied [25], the melting endotherm decreased with increasing amount of amylose. The melting endotherm of starch gels and stale breads is

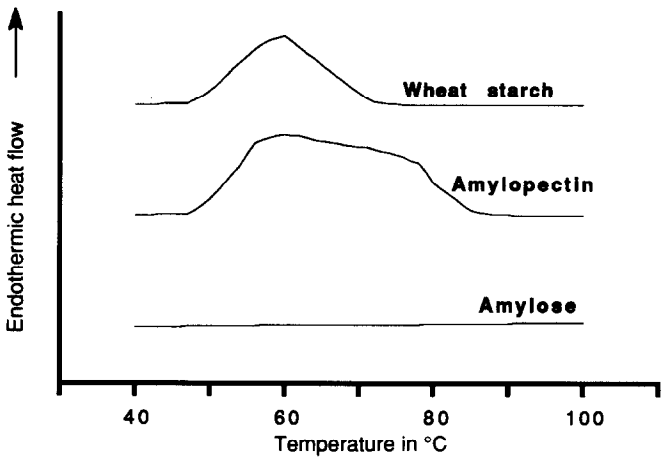

Fig. 1. Melting endotherms of retrograded wheat starch, amylopectin and amylose. Adapted from Ref. [12].

completely reversible; no endotherm is obtained immediately after the heating of an aged starch gel.

6. Evidence of retrogradation from rheological studies

Rheological studies give further support to the findings of the DSC and X-ray studies [15,16,23,24,26]. The amylose and starch gels quickly attain a nearly constant value of rigidity; starch gels, however, show a slow rigidity increase with time. The gelation of amylopectin gels is very slow, taking several weeks to approach the limiting value [24]. The starch and amylopectin gels are thermally reversible; they reattain nearly the initial values of the G' modulus on heating. Amylose gels do not change on heating to 100°C and can be regarded as thermally irreversible.

It seems clear that the slow increase in crystallinity, unique for starch and amylopectin gels, is related to the slow increase in rigidity (G') and to the development of the endothermic transition around 55–60°C. The long-term changes associated with retrogradation can therefore safely be attributed to the recrystallization of the amylopectin fraction within the starch granules. Likewise, the short-term changes can be attributed to the exudated amylose fraction that causes the initial gel network formation, i.e. the fast gelation of starch and amylose gels.

7. Cocrystallization of amylopectin and amylose in retrogradation

In the study of the retrogradation of gels from non-granular mixtures with different amylopectin/amylose ratios [25], some synergistic interactions were seen at

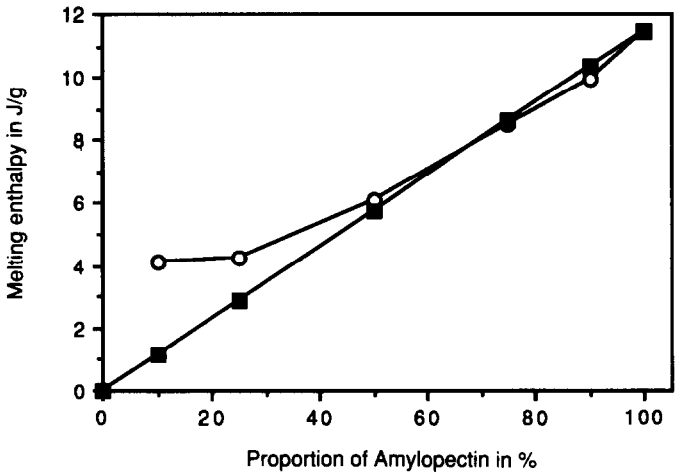

Fig. 2. Relation between the melting enthalpy and the proportion of amylopectin in the amylopectin/amylose mixtures: ■, theoretical line calculated from the enthalpy of 100% amylopectin; ○, measured values. From Ref. [25].

high amylose content (Fig. 2). Because the melting endotherm, as measured with the DSC, has been attributed to the recrystallization of the amylopectin fraction, one would expect the melting endotherm to be proportional to the amount of amylopectin. Gudmundsson and Eliasson [25] found unexpectedly high values for the melting enthalpy of gels with very high amylose content (75–90%). The possibility of limited co-crystallization has been proposed in relation to retrogradation [27]. Such co-crystallization could be promoted when the amylose content is high and the molecules are not granular. Schierbaum et al. [28] also found that linear segments of amylopectin and amylose, or linear dextrins of certain critical lengths, can interact in solution. However, the amylose and amylopectin in aqueous solution were shown to be immiscible at moderate concentrations where phase separation of the polymers is favoured [29]. Interactions of amylose and amylopectin are therefore limited in normal starch gels, because amylose is preferably leached out of the granules whereas the amylopectin is mainly within the granules.

8. Effects of storage temperature

Retrogradation is greatly affected by storage temperature. Compared to storage at room temperature, storage of starch gels containing 45–50% water at low temperatures but still above the glass temperature ($T_g \approx -5.0$°C), increases the retrogradation, especially during the first days of storage, compared to starch gels stored at room temperature. The glass temperature T_g is the temperature where the transition from glassy amorphous state to a more disordered rubbery state occurs. Storage at freeze temperatures below T_g virtually inhibits recrystallization [3,12]. Higher temperatures (above 32–40°C) effectively reduce retrogradation [3]. The

Avrami equation has frequently been used to account for the kinetics of the recrystallization process at different temperatures (and water content, see below) [3,4,7]. However, the analysis of retrogradation kinetics according to the Avrami equation implies a single-step process and has, therefore, limited applicability because retrogradation is a more complex process. This is indicated by the fact that at low storage temperatures (4–5°C) the crystallites formed are less perfect because they have lower melting temperatures than those formed at higher storage temperature [30,31]. Instead, a three-step mechanism of initial nucleation (junction point of two or more starch chains), followed by crystal growth/propagation and crystal perfection, has been proposed [32].

9. Effects of water content

Several studies have shown that the extent of retrogradation is very sensitive to the water content of starch gels. Longton and LeGrys [7] observed that crystallization during ageing occurred only in gels with starch contents between 10% and 80% and that maximum crystallization occurred in gels with 50–55% starch. Eliasson [11] and Zeleznak and Hoseney [14] have confirmed that maximum crystallinity occurs in gels with 50–60% starch. The retrogradation is only dependent on the water content during ageing, not during gelatinization [14].

In contrast to a native starch suspension, gelatinized starch gel is completely amorphous and its water is uniformly distributed. The recrystallization process depends on the T_g of the amorphous gel because the mobility of the chains determines their association rate. As a plasticizer, water controls the T_g of the amorphous gel. At very low water content, the T_g is above room temperature and the amorphous gel is in a highly viscous glassy state that effectively hinders molecular mobility. Recrystallization increases with increasing water content (depression of T_g below room temperature) up to 45–50%, because of progressively more effective plasticization (increased molecular mobility); with further increase of water content up to 90%, it decreases, apparently due to excess dilution [32].

Solutes such as sugars affect the retrogradation of starch gels by their anti-plasticizing effect, compared to water alone. That is, they reduce the mobility of the chains in the amoprhous matrix by increasing the T_g. As a consequence, the rate of propagation can decline and decrease the extent of retrogradation.

10. Effects of lipids and surfactants

Polar lipids, e.g. monoglycerides, and related compounds are known to have an anti-staling effect on bread and to extend its shelf-life [33,34]. The retarding mechanism of lipids/surfactants on retrogradation is thought to be dissimilar from that of other solutions, i.e. an anti-plasticizing effect, being instead related to their ability to form complexes with the amylose fraction [8,33,34]. These substances form a helical inclusion complex with amylose [35] with a V-type X-ray diffraction

pattern [8,36–38]. These complexes melt at 100–120°C at high or intermediate water content as measured with DSC [36,39–41].

Since Schoch and French [1] proposed that the amylopectin fraction, and not the amylose fraction, was responsible for the retrogradation, many investigations have attributed the long-term effects associated with retrogradation to the amylopectin fraction as discussed above. The question then arises of how lipids or surfactants affect the retrogradation as they are thought to form complexes only with the amylose molecule, and not with the amylopectin fraction [8,42].

A few possible answers to this question are listed below.

(1) The intact amylose–lipid complex, i.e. as one entity, interferes with the crystallization of the amylopectin in some unknown way and retards the retrogradation.

(2) The amylose–lipid complex interferes indirectly by changing or retarding the water distribution and hence the retrogradation [43].

(3) Co-crystallization of amylose and amylopectin is possible to some extent, and substances that form complexes with amylose eliminate the contribution of amylose in the recrystallization process [27].

(4) Lipids and surfactants interact directly with the amylopectin fraction, at least to a small extent, and retard retrogradation through the formation of an amylopectin–lipid complex [25,32,40,44–48].

These alternatives were investigated using the aforementioned methods, i.e. X-ray diffraction, DSC, and rheological methods. Lipids added to bread show increased V-type X-ray patterns when compared to control bread. The V-type pattern is virtually unchanged with time, but is superimposed by a B-type X-ray diffraction pattern that increases on ageing [8].

In the presence of lipids/surfactants, the DSC trace shows a depressed melting endotherm (the first peak) and an increased endotherm associated with the amylose–lipid complex transition [11,13]. Rheological measurements (mostly firmness measurements) usually show that added lipids decrease the firmness of breads on ageing, compared to control breads [49]. Other rheological measurements have shown that surfactants can have varied effects on rheological properties of starch gels, depending on the type of surfactant [33,40]. Because the alternatives are based on the hypothesis that lipids act through an amylose–lipid complex in various ways or that they interact directly with the amylopectin, one has to prove or refute the involvement of the amylose–lipid complex, or exclude interactions between lipids and amylopectin molecules.

We will now examine the evidence. Amylopectin in solution does not precipitate when monostearin is added [50], and no DSC endotherm is seen for a complex transition when amylopectin is heated and cooled in the presence of lysolecithin [42]. This has been regarded as evidence that interactions between amylopectin and lipids are negligible. However, lipids have been shown to depress the melting endotherm even for waxy starches and non-granular amylopectin: these effects cannot be explained by formation of an amylose–lipid complex. In Ref. [46], the possibility of retarding the retrogradation of some starches (maize, potato and waxy maize) and non-granular amylopectin by adding an intact CTAB–amylose

complex was explored. It was found that intact CTAB–amylose complexes added to cooled gelatinized starch gels, or to starch suspensions that were heated to temperatures below the transition temperature of the CTAB–amylose complex, had little effect on retrogradation. However, starch gels or starch suspensions with added CTAB–amylose complex that were heated to temperatures above its transition temperature, i.e. the complex melted, had a decreased retrogradation. Alternative (1) is therefore unlikely.

Because lipids and some surfactants retard or delay gelatinization, probably by complexing with leached amylose on the surface of the starch granules, it is possible that lipids/surfactants also retard the retrogradation by a similar mechanism, i.e. by acting as a barrier against water transport [43]. This mechanism could be involved in retarding the retrogradation of normal starches as it is known that water content is very important for recrystallization. However, it does not explain the effect of lipids/surfactants on decreasing the retrogradation of waxy starches, unless they interact with the surface molecules of the waxy starch granules. Furthermore, non-granular amylopectin gels have also been shown to decrease the extent of retrogradation when surfactants and monoglycerides are added [25,45], thus demonstrating that the granular form is not a limiting factor. If lipids and surfactants are added after the conclusion of gelatinization, such a barrier effect would not be obtained and the retrogradation would progress in a similar way as for starch gels without additives. In Refs. [46] and [48], there are some evidences against this. In Ref. [46], one treatment involved pre-gelatinization of the starches before addition of the CTAB–complex, followed by reheating of the starch gels above the transition temperature of the complex. Such treatment decreased the extent of retrogradation compared to control starch gels and those with intact complexes. This shows that lipids or surfactants affect the retrogradation even when the starch suspensions are fully gelatinized. In Ref. [48], the waxy starches used were either gelatinized with a surfactant or first gelatinized and then surfactant added, before being stored for 10 days. Both these treatments gave at least one X-ray diffraction line compatible with the V-type pattern for all the waxy starches, although the former treatment gave V-patterns with stronger intensity. Alternative (2), therefore, provides only a limited explanation for the effects of lipids/surfactants on retrogradation.

A possible co-crystallization of amylose and amylopectin as a part of the retrogradation has been proposed by Russell [27]. Lipids and surfactants would prevent the participation of amylose in the process. As before, this mechanism does not explain the effects of lipids on waxy starches and non-granular amylopectin gels. It could possibly assist in delaying the retrogradation of the normal starch gels, but according to Gudmundsson and Eliasson [25], the amylose content of amylopectin/amylose mixtures has to exceed 50% before having any effect on the retrogradation of the amylopectin fraction. Alternative (3) can therefore only account for a very small part of the retarding effects of lipids and surfactants.

Other explanations involving the amylose–lipid complex may be possible, but can never account for the effect of lipids/surfactants decreasing the extent of retrogradation of waxy starches and non-granular amylopectin gels.

Because the formation of the amylose–lipid complex cannot explain the effects of lipids/sufactants on retrogradation, another mechanism has been proposed. A direct interaction between the amylopectin molecule and lipids/surfactants via complex formation has been suggested [25,32,40,44–48]. However, in previous studies, direct evidence in the form of a transition endotherm of amylopectin–lipid complex for waxy starches with added lipids was not observed [40,42,45,51]. Because of this some difficulties arise in interpreting the observed decrease in retrogradation for waxy starch–lipid systems. It is thought that only the outer branches of the amylopectin can participate in the formation of such a complex [40,44,45]. The outer branches of the amylopectin molecule have the shortest average chain length [52], and many of them do not reach the minimum size to allow formation of a complex or a double helix [37,53–55]. The complex between amylopectin and lipids/surfactants is therefore not expected to produce an endothermic signal in the DSC trace [40]: its melting would be spread over a large temperature interval with a small transition enthalpy. This makes such a peak poorly distinguishable from the noise of the baseline. Recently, however, more direct evidence on amylopectin–lipid/surfactant interactions has been reported. Slade and Levine [32] obtained a transition endotherm with DSC for a complex between waxy maize starch and sodium stearoyl lactylate (SSL) at 70°C at very low water content (10%). They thought that such a complex is so unstable that it can only be observed at very low water contents, due to the plasticizing effects of water on the complex. In Ref. [25], however, a complex transition endotherm was obtained for non-granular amylopectin gel with added sufactants (CTAB and SDS) and monoglycerides at about 110°C and at an intermediate water content (50% w/w). It is possible that amylopectin in non-granular form can interact to a greater extent with surfactants than a waxy starch. This hypothesis is supported by Eliasson and Ljunger [45], as surfactants reduce the retrogradation in amylopectin gels more than in waxy starch gels. The amylopectin used in Ref. [25] was from potato, and has longer outer branches than that from waxy maize starch [56].

The minimum chain length at which the amylose molecule can form complexes has been reported to be 20–40 glucose residues when complexed with butanol [57]. Studies on synthetic amylopectin showed that a minimum of 15–20 glucose units of the outer branches were needed to complex with iodine at low temperatures [54]. In the case of lipids and surfactants, the complex formation is also dependent on the length of their carbon chains. Lipids and surfactants are required to have a minimum of 8 carbons in the chain [37] and optimal chain lengths are between 12 and 18 carbons [36,50,58]. The average chain length of the outer branches of amylopectin has been reported to be 16–20 glucose residues, depending on the botanical source [56]. Theoretically, outer branches with chain lengths longer than 20 glucose residues could reliably form complexes with a suitable compound with optimal chain length.

Further evidence for amylopectin–surfactant complex formation has been reported for both non-granular amylopectin [25] and waxy starches [48] with added surfactant (CTAB and/or SDS), which showed V-type X-ray diffraction lines. When the amount of surfactant (SDS) was increased in the case of non-granular amylopectin, the V-type X-ray pattern lines increased in intensity, indicating that stronger or more interactions took place.

11. Effects of botanical source

In addition to the above-mentioned factors, the botanical source is of great importance for the retrogradation of starch gels [26,47,48,52,59–62]. This does not concern differences in amylose content, because it has even been observed in starches with very similar amylose contents. This indicates that structural differences found in the amylopectin molecule may be the cause of differences in the recrystallization rate.

There are minimum requirements for the aggregation of chains. It has been observed for 10 glucose units for malto-oligosaccharides (short chain amylose) [55]. The short chains of the amylopectin have been shown to be responsible for the crystallization in the amylopectin molecule [53], although chains with less than 15 glucose units do not take part in the crystallization [24,53]. Amylopectin from potato, tapioca and kuzu starches, which are B-starches, retrograde to a different extent, which has been related to differences in average chain length [63]. Amylopectin from cereals has also been shown to retrograde to a lesser extent than pea, potato and canna amylopectin, which has been attributed to shorter average chain length in the cereal amylopectin [26,62].

In Refs. [46,52,60,61], retrogradation of different cereal starches was studied. Obviously some of the differences between the cereal starches can be attributed to differences in the amylopectin/amylose ratio and lipid contents. However, these factors account for only a part of the differences.

The transition temperature T_c at which the melting of the recrystallized starch occurs is nearly the same for all cereal starches (with the exception of amylomaize), despite differences in gelatinization temperatures of up to 24°C [48]. The gelatinized starches are fully hydrated (T_g depressed to ≈ -5.0°C) and the recrystallized (retrograded) starch melts at a temperature that depends on the water content. Because cereal starches have similar T_c values, their crystallites should have similar stability and therefore similar short-chain lengths. A higher melting temperature T_c is reported for B-starches with longer short chains [62]. The structural differences in cereal amylopectins related to retrogradation can be related either to differences in the amorphous regions or to differences in the ratio of short to long chains and the ratio of A- to B-chains. A greater amount of short chains over 15 glucose units and an increased ratio of A- to B-chains probably promote retrogradation. It has also been reported that very short chains (6–9 glucose units) can inhibit or retard retrogradation of starch gels [64,65]. A complete explanation of the retrogradation of starches from different botanical sources will therefore be possible only when all these structure-related factors are clearly understood.

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