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Retrogradation of Amylopectin and the Effects of Amylose and Added Surfactants/Emulsifiers

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ABSTRACT

The retrogradation of mixtures with different amylopectin/amylose ratios and 50% (w/w) water content was followed by differential scanning calorimetry. The effect of the addition of surfactants/emulsifiers (sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB) and monoglycerides) was investigated. The results showed that the relationship beween the melting enthalpy of recrystallized amylopectin and the proportion of amylopectin was not linear. Mixtures with less than 50% amylopectin showed a higher melting enthalpy than expected. The effect of surfactants/emulsifiers on that relationship was to decrease the retrogradation of all the mixtures, but they had their greatest effect on 100%-amylopectin samples and least effect on mixtures with 50% amylopectin. Thermograms obtained for 100% amylopectin with added surfactants/emulsifiers showed transitions above 100°C, thus indicating the formation of a complex between amylopectin and the surfactants/emulsifiers. This was supported by X-ray diffraction analysis, as amylopectin samples with added SDS and CTAB showed a mixture of B- and V-patterns. This complex formation between amylopectin and surfactants/emulsifiers can explain the large reducing effect of the addition of surfactants/emulsifiers on retrogradation of 100% amylopectin samples, and partly the retrogradation of other mixtures.

INTRODUCTION

The retrogradation of starches or starch based products is of great importance to the food industry, as it affects texture and taste of starchy food products. It would be of great value if it was possible to control this process, but that would necessitate understanding on the molecular level

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of the interactions involved. The phenomenon that the concept 'retrogradation' describes has mainly been used for the process of starch, after gelatinization, recrystallizing during storage. The amylose component in the starch recrystallizes very fast, but the amylopectin component much more slowly (Miles *et al.*, 1985; Russell, 1987), so the concept of retrogradation often refers to recrystallization of the amylopectin component, as it is the long-term effects of recrystallization of starches that have been associated with changes in texture.

It was first suggested by Schoch and French (1947) that the amylopectin was responsible for the retrogradation of starch in bread. This is further supported by differential scanning calorimetry (DSC) studies (Eberstein *et al.*, 1980; Russell, 1983; Eliasson, 1985) and X-ray diffraction studies (Miles *et al.*, 1985; Ring, 1985). With the DSC technique, one can obtain both the gelatinization and the melting enthalpies and temperatures of starches, and also transition enthalpies and temperatures of starch/lipid complexes. The X-ray diffraction technique gives information about the crystallinity and diffraction patterns of starches (A-, B-, C- or V-pattern). It is well-known that several substances, e.g. lipids, pentosans and sugars, retard retrogradation of starches. The effects of lipids have been reported by several investigators (Krog & Jensen, 1970; Lagendijk & Penning, 1970; Knightly, 1977; Kulp & Ponte, 1978). Lipids form inclusion complexes with amylose (Mikus *et al.* 1946; Acker, 1977), and these can be seen as a transition in the DSC thermogram. So far, complex formation between amylopectin and lipids has not been demonstrated. DSC studies have shown that lipids decrease crystallization of amylopectin and increase the amount of the amylose/lipid complex (Eliasson, 1983; Russell, 1983). But how lipids or the amylose/lipid complexes retard recrystallization of amylopectin is still not clear.

It would be of importance to find out if lipids interact directly with amylopectin, but the presence of an amylopectin/lipid complex has been difficult to prove. Kugimiya *et al.* (1980), Batres and White (1986), Evans (1986) and Eliasson and Ljunger (1988) could not demonstrate the presence of an amylopectin/lipid complex, even though certain facts pointed in that direction. Recently, Slade and Levine (1987) stated that they had formed a complex between waxy maize starch and sodium stearoyl lactylate (SSL).

The possibility of adsorption of lipids on starch and amylopectin has also been discussed (Lagendijk & Pennings, 1970; van Lonkhuysen & Blankestijn, 1974). Lipids are not the only substances that affect retrogradation: sugars and pentosans do so too (Kim & D'Appolonia, 1977*a*; Kim & D'Appolonia, 1977*b*; Krusi & Neukom, 1984; Germani

et al., 1983). From our own study (Gudmundsson & Eliasson, 1989) on oat starches, native and defatted, it was obvious that the oat lipids were not the only factor influencing the retrogradation tendency of oat starches, as one oat starch showed a great difference between native and defatted state, whereas another one did not.

The relationship between amylose and amylopectin in the retrogradation process has only recently been reported (Orford *et al.*, 1987; Russell, 1987). Orford *et al.* found that the initial rate of development of stiffness of the gels they investigated was dependent on botanical source and the amount of amylose solubilized during gelatinization. This initial gelation was not reversed on heating to 100°C. There was also a long-term increase in gel stiffness, which was thermally reversible and involved amylopectin crystallization. Russell (1987) analysed his DSC data by fitting them to the Avrami equation. His results indicated that the rate constants were unrelated to amylopectin content, and the limiting melting enthalpy (staling endotherm enthalpy) was proportional to starch amylopectin. By extrapolation of his plot, the enthalpy becomes zero at an amylopectin content of 24%. Therefore, we considered it of importance to study retrogradation in its own right, and decided to investigate the effects of amylose on the retrogradation of amylopectin and how certain surfactants/emulsifiers affect that relationship. Mixtures of amylopectin and amylose from potato starch with the amylopectin proportion from 10 to 100% were studied with DSC both with and without surfactants/emulsifiers. X-ray diffraction analysis was performed on some surfactant/amylopectin mixtures.

MATERIALS AND METHODS

Materials

The amylopectin and amylose used were from potato starch (Sigma, St Louis, USA). The lipid material used was cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) from BDH Biochemicals (Poole, UK), and Dimodan LS (a mixture of 70% monolinoleic glyceride, 18% monooleic glyceride and 11% saturated monoglycerides) from Grindsted Products (Brabrand, Denmark). Sodium cholate was from Sigma.

Methods

Preparation of lipids

The surfactants were used at concentrations 1·9 and 2·9% based on dry weight of the amylose/amylopectin mixture. CTAB and SDS were added

directly to water to give a micellar solution, which was added to the amylopectin/amylose mixture to give 50% (w/w) water and 1·9 or 2·9% (w/w) surfactant.

Monoglycerides (100 mg) were mixed with 1 ml of 1% sodium cholate solution. The dispersion was sonicated for 5 min at 40°C (Riisom *et al.*, 1984) to give a liposomal dispersion of the monoglycerides. The solution was added to the amylopectin/amylose mixtures to 1·9 or 2·9% (w/w) monoglycerides, and then water was added to the suspension to give 50% (w/w) water.

DSC measurements

The DSC measurements were performed on a Perkin-Elmer DSC-2 instrument. The retrogradation of amylopectin/amylose mixtures of different ratios (100/0, 90/10, 75/25, 50/50, 25/75, and 10/90) was followed at 50% water content. Retrogradation of identical mixtures with added surfactants/emulsifiers at two different concentrations (1·9 and 2·9 mg/100 mg mixture on a dry weight basis) were also followed.

Samples (10–20 mg) were transferred to weighed sample pans, which were then sealed and reweighed. The sample pans were heated in an oven at 105°C for 15 min, and then stored for 1, 2, 3, 7 or 14 days at room temperature before DSC analysis. The samples were heated from 17 to 147°C at a heating rate of 10°C/min using an empty sample pan as a reference. The water content was determined by puncturing the pans, drying them in an oven at 105°C for 24 h and then reweighing.

Each measurement was at least duplicated. The melting enthalpy of recrystallized amylopectin (ΔH_c) was calculated from the thermograms. The standard deviation of the ΔH_c measurements was generally less than 10% of the mean (>85%) and many were less than 5% of the mean (50%). ΔH_c (J/g) is calculated on dry-substance basis. For Figs 2, 8–12, 14 and 15, the ΔH_c is the mean enthalpy value obtained from measurements at five different storage times (1, 2, 3, 4 and 14 days).

X-ray diffraction analysis

Amylopectin/water samples (1/1 w/w) with added surfactants CTAB (6 mg/100 mg amylopectin) and SDS (3 and 10 mg/100 mg amylopectin) were examined by X-ray diffraction. The samples were transferred to a cassette, which was then heated in an oven at 105°C for 15 min. The cassettes were then stored for 6–10 days before measurements were taken to allow recrystallization to occur. The X-ray source was a Philip fine-focus tube with Cu anode (X-ray wavelength 1·5418 Å). All measurements were made at 21°C and the exposure time was from 4 to 11 h. Tristearine was used for reference ($d = 4{\cdot}6$ Å), where d is the interplanar spacing.

RESULTS

Retrogradation of amylopectin/amylose mixtures and the amylopectin/amylose interaction

Retrogradation of mixtures of amylose and amylopectin, with the amylopectin ratio ranging from 10 to 100% (w/w), was followed by DSC, by measuring the enthalpy of the endotherm assigned to the melting of crystallized amylopectin (ΔH_c) (Fig. 1).

It is clear from Fig. 1 that the mixtures with no additives retrograde in the expected order: 100% > 90% > 50% > 10% amylopectin (75% and 25% are in the right order but not shown), i.e. the higher the amount of amylopectin, the higher the ΔH_c value.

If there were no interactions between amylopectin and amylose in the mixtures, then the DSC measurements should give a linear relationship between the proportion of amylopectin and the enthalpy of melting of the amylopectin crystallites.

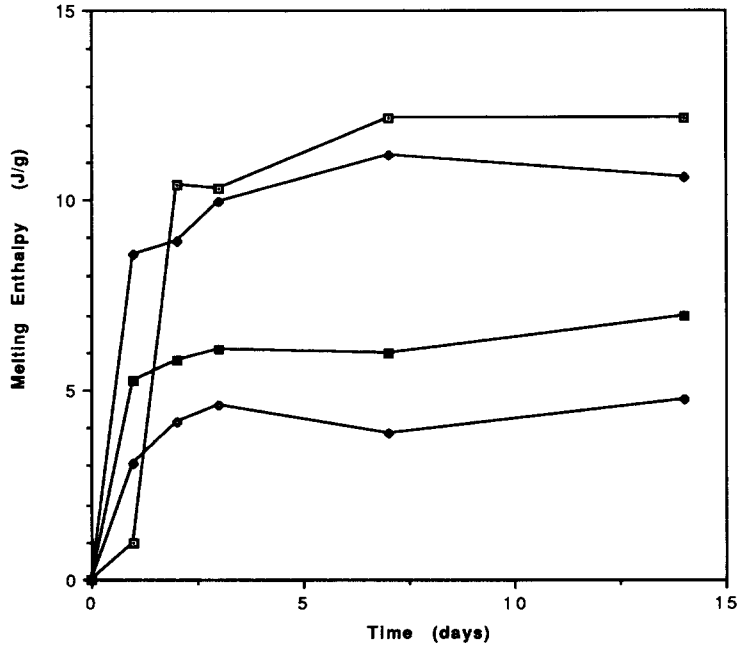

Fig. 1. Retrogradation, measured as melting enthalpy versus time, of mixtures with different amylopectin/amylose ratios. (⊡, 100% amylopectin; ◆, 90% amylopectin; ■, 50% amylopectin; ◇, 10% amylopectin; 75% and 25% amylopectin mixtures are not shown.)

In Fig. 2, ΔH_c is plotted against the proportion of amylopectin in the mixture. The measured values deviate from the theoretical line (obtained if amylopectin is independent of amylose) when the amylopectin content is lower than 50% in the mixtures. This indicates that there are some interactions between amylopectin and amylose.

In Figs 3 and 4, the effects of monoglycerides (2·9 mg/100 mg mixture) on retrogradation are shown. The reducing effect on the retrogradation is greatest for 100% amylopectin, but least for mixtures with 50% amylopectin. In Figs 5–7, the effects of different concentrations of surfactants on retrogradation are shown (the monoglycerides behaved very similar in a way). Increasing the concentration does further decrease retrogradation for all mixtures (including 90, 75 and 25% amylopectin, the data for which are not shown).

The influence of the surfactants/emulsifiers on the relationship between amylopectin/amylose ratio and ΔH_c (Figs 8 and 9) is clearly that the surfactants/emulsifiers lower ΔH_c, and the greatest effects are obtained for 100% amylopectin. The relationship is, though, still non-linear. The three additives (Figs 8 and 9) show that the surfactants SDS and CTAB are somewhat more effective than the monoglycerides.

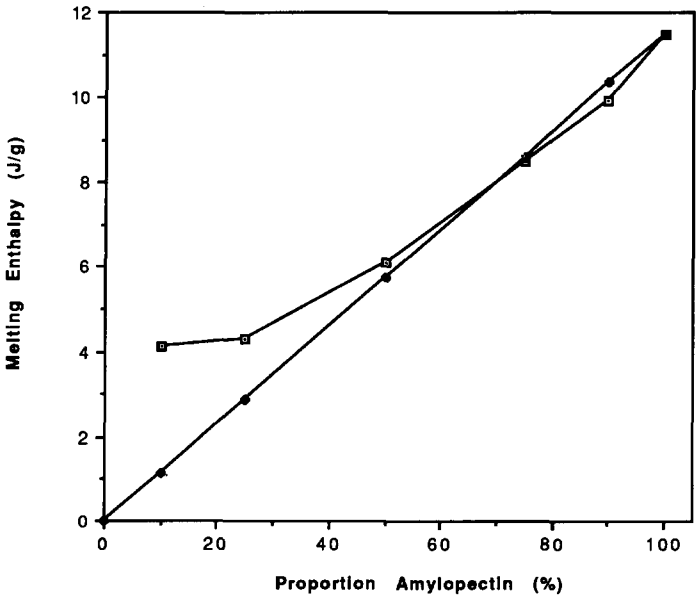

Fig. 2. Relation between the melting enthalpy and the proportion of amylopectin in the mixtures. (■, theoretical line, calculated from the enthalpy of 100% amylopectin; ◘, measured values.) (In this and Figs 8–12, 14 and 15, the ΔH_c values are obtained from the mean of measurements at 1, 2, 3, 4 and 14 days of storage.)

Increasing the concentration of surfactants/emulsifiers from 1·9 to 2·9 mg/100 mg mixture does further decrease ΔH_c for CTAB and SDS, but only for the 50–100% mixtures when monoglycerides are used, as shown in Figs 10–12. Still, the effects are greatest on 100% amylopectin compared to other mixtures. It thus seems that the food-grade monoglycerides and the surfactants CTAB and SDS have their greatest effect on lowering the retrogradation for a 100% amylopectin suspension. The effect of surfactants/emulsifiers seems to decrease as the amylopectin content in the mixture is reduced from 90 to 50%, where the effect is least. At still lower amylopectin contents the effects of the surfactants/emulsifiers seem to increase again.

Complex formation and the amylopectin/amylose ratio

Thermograms of 100% amylopectin with added surfactants/emulsifiers clearly showed transitions at temperatures usually associated with

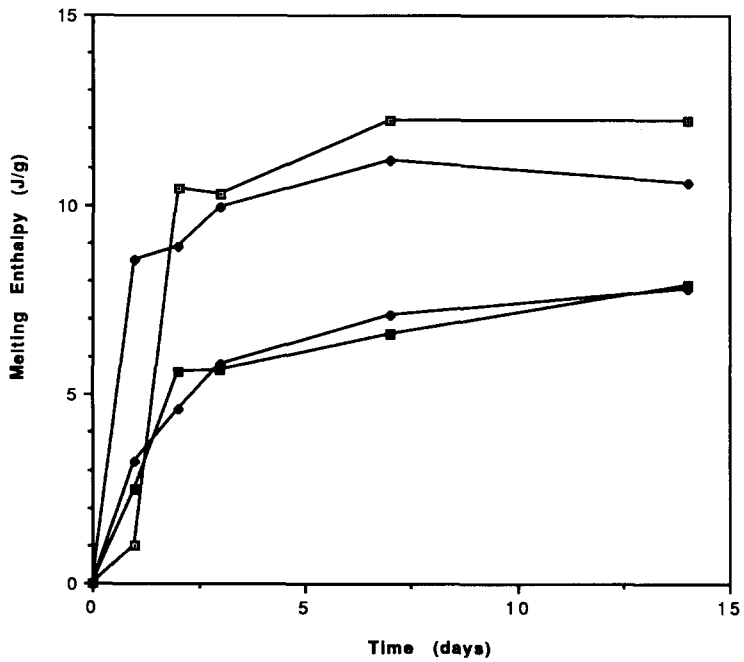

Fig. 3. Retrogradation, measured as melting enthalpy versus time for mixtures with 90 and 100% amylopectin with and without monoglycerides (2·9 mg/100 mg mixture). (□, 100% amylopectin without monoglycerides; ◆, 90% amylopectin without monoglycerides; ■, 100% amylopectin with added monoglycerides; ◆, 90% amylopectin with added monoglycerides.)

amylose/lipid complexes. An example is given in Fig. 13, compared with two other mixtures. The DSC results indicated complex formation between amylopectin and the surfactants/emulsifiers. These peaks were not seen for mixtures with no additives.

To further investigate the presence of an amylopectin/lipid complex, an X-ray diffraction analysis was done on amylopectin with added CTAB (6 mg/100 mg amylopectin) and SDS (3 and 10 mg/100 mg amylopectin) at 50% (w/w) water content. The X-ray diffraction analysis revealed, as seen in Table 1, that some diffraction lines could be identified with the B-pattern and other lines could be assigned to the V-pattern according to Zobel (1964). Furthermore, increasing the concentration of SDS from 3 to 10 mg/100 mg amylopectin made the B-pattern nearly disappear, whereas the V-pattern became stronger.

CTAB and SDS were added to the amylopectin samples above their Krafft point, which is 24 and 10°C, respectively (Fontell, 1981) and they formed micellar solution at least up to 30% (w/w) (see the phase diagram in Fontell, 1981). Micellar solutions exhibit a few, fairly broad bands at

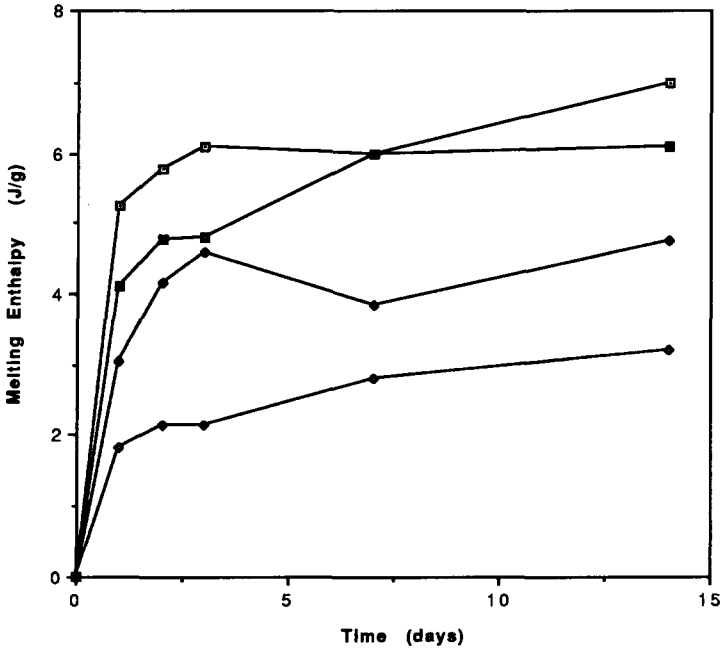

Fig. 4. Retrogradation, measured as melting enthalpy versus time for mixtures with 10 and 50% amylopectin with and without monoglycerides (2·9 mg/100 mg mixture). (⧈, 50% amylopectin without monoglycerides; ■, 50% amylopectin with added monoglycerides; ◆, 10% amylopectin without monoglycerides; ❖, 10% amylopectin with added monoglycerides.)

large spacings, between 20 and 100 Å and a diffuse halo at about 4·5 Å (Chapman, 1965).

As seen in Figs 14 and 15, the enthalpy of transition for the complexes changes with proportion of amylopectin. There are two transition endotherms for monoglycerides, and one for CTAB and SDS. For mixtures with SDS, the enthalpy values decrease with increasing amylopectin content, whereas mixtures with CTAB show varying values throughout the entire amylopectin range. The baseline for the transitions of the complexes can be somewhat difficult to draw, as they are usually small and broad, so the estimation of the transition enthalpy is not accurate, especially for mixtures with CTAB.

The mixtures with monoglycerides have two complex transitions; this is somewhat peculiar, but can be explained by the fact that the monoglycerides used are a mixture which contains both unsaturated and saturated monoglycerides, which might give rise to two complexes with different transition temperatures. Different explanations could be given, one similar to Kowblansky (1985), who has shown that two transitions of

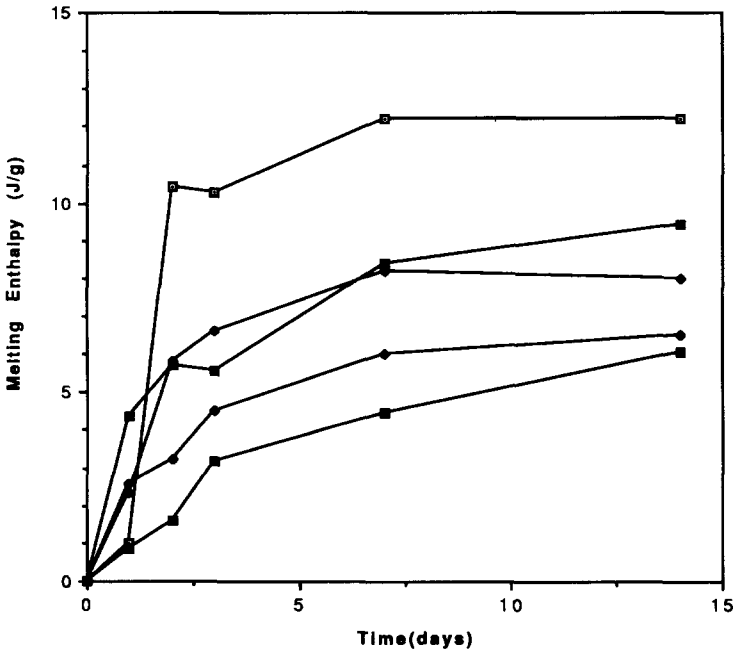

Fig. 5. Retrogradation, measured as melting enthalpy versus time for 100% amylopectin; a comparison between amylopectin without additives and with added CTAB and SDS (1·9 and 2·9 mg/100 mg). (▫, without additives; ▪, with added SDS (1·9%); ◆, with added CTAB (1·9%); ◆, with added CTAB (2·9%); ■, with added SDS (2·9%).)

inclusion complexes are possible with straight-chain aliphatic compounds, depending on the previous thermal history of the sample. The explanation could also be a multiple transition of the inclusion complex as Biliaderis *et al.* (1986) explain it. The first transition (at 105–107°C) increases with increasing amount of amylopectin, but the second (128–131°C) decreases with increasing amylopectin content.

Despite the fact that the higher concentration of surfactants/emulsifiers decreased the retrogradation further compared to the lower concentration of surfactants/emulsifiers, the enthalpy of transition of the complexes were very similar for these two concentrations, as seen in Figs 14 and 15. This might indicate that only a certain amount of amylose and/or amylopectin complexes with the surfactants/emulsifiers. However, it must be pointed out that optimal conditions for complex formation are probably not achieved in this experiment, as it is known that reheating the samples gives higher enthalpy values (Eliasson *et al.*,

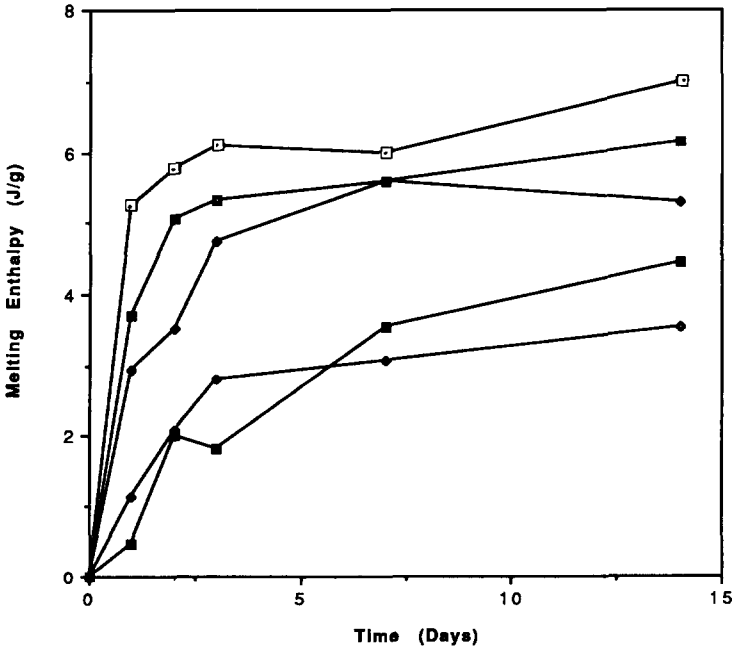

Fig. 6. Retrogradation, measured as melting enthalpy versus time for 50% amylopectin mixtures; a comparison between mixtures without additives and with added CTAB and SDS (1·9 and 2·9 mg/100 mg mixture). (⊡, without additives; ◘, with added SDS (1·9%); ◆, with added CTAB (1·9%); ■, with added SDS (2·9%); ◆, with added CTAB (2·9%).)

1988), so some of the surfactants/emulsifiers are prior to reheating either uncomplexed or complexed and subsequently dispersed.

DISCUSSION

If amylopectin retrogrades independently of amylose, it should be expected that the relationship between melting enthalpy (ΔH_c) and the proportion of amylopectin in the mixture would be linear. There have been no reports of amylose affecting the retrogradation of amylopectin, as far as the authors are aware of. The melting enthalpy measured by the DSC method has only been associated with the amylopectin component in starches (Eberstein *et al.*, 1980; Russell, 1983; Eliasson, 1985).

However, the relationship shown in Fig. 2 was not linear. Mixtures with more than 50% amylopectin retrograded as expected, whereas mixtures with less than 50% amylopectin retrograded to a greater extent

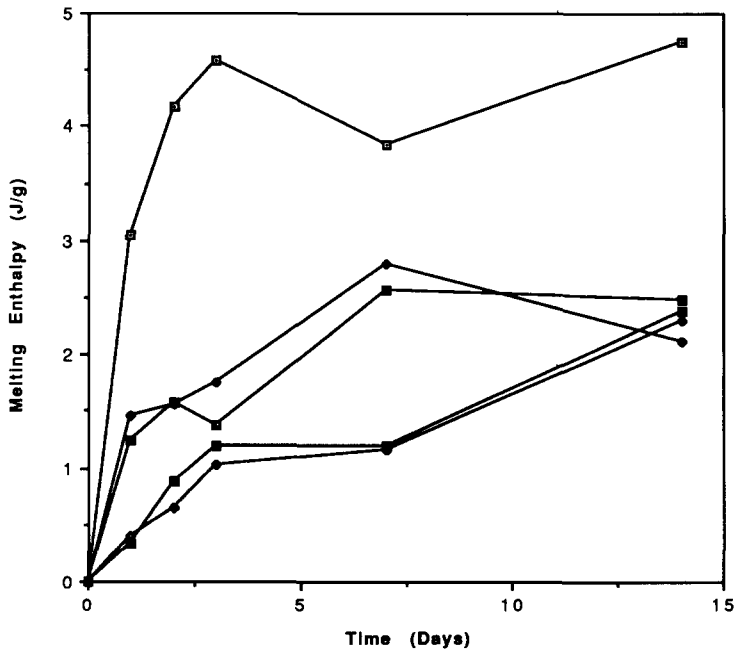

Fig. 7. Retrogradation, measured as melting enthalpy versus time for 10% amylopectin mixtures; a comparison between mixtures without additives and with added CTAB and SDS (1·9 and 2·9 mg/100 mg mixture). (▫, without additives; ◆, CTAB (1·9%); ▪, SDS (1·9%); ◈, CTAB (2·9%); ■, SDS (2·9%).

than expected. One explanation of this behavior might be that at low amylopectin content the amylose component functions as a nuclei and/or co-crystallizes with the amylopectin to some degree, i.e. at least to a greater extent than for mixtures which are high in amylopectin content.

Russell (1987), when discussing the effects of addition of glyceryl monostearate (GMS) to bread to reduce the staling endotherm, gave the explanation of limiting co-crystallization of amylose and amylopectin so that the staling endotherm induced some fraction of amylose. Added GMS complexes with some of the amylose, thus making it unavailable to participate in co-crystallization during gel ageing, but that explanation seems to rule out the possibility of the monoglycerides affecting amylopectin directly in the retrogradation process, even though it can be partly true. It seems clear, though, that amylose affects crystallization of amylopectin at least when amylose is present in greater amounts than amylopectin.

The purpose of adding surfactants/emulsifiers to these amylopectin/amylose mixtures was to see if the relationship between melting enthalpy (ΔH_c) and the proportion of amylopectin changed to any degree.

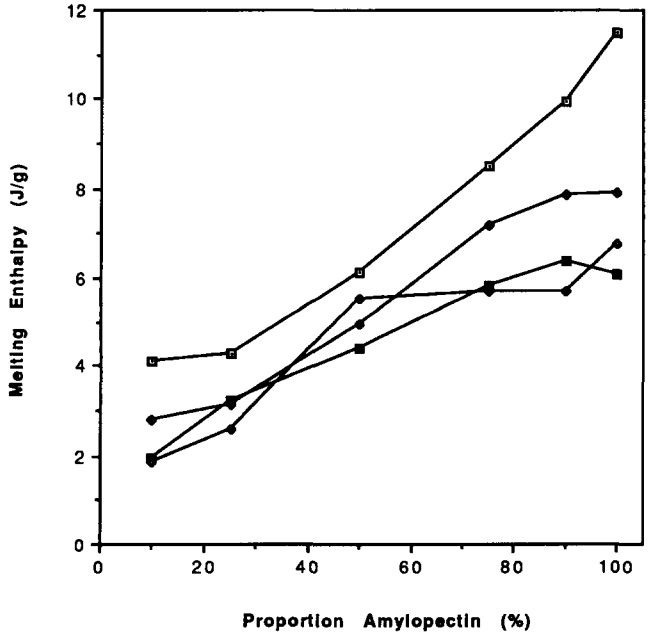

Fig. 8. Comparison of melting enthalpies of different mixtures with and without additives versus the proportion of amylopectin in the mixture. (⊡, without additives; ◆, with added monoglycerides; ◇, with added CTAB; ◘, with added SDS; all additives are 1·9 mg/100 mg mixture.)

It was expected that the surfactants/emulsifiers would form a complex with the amylose component and thus make the amylopectin component independent of the amylose, at least in the low amylopectin region. The mixtures would then retrograde more normally and a linear or near-linear relationship would be obtained. The results seen in Figs 8 and 9 do not bear this out; on the contrary, the surfactants/emulsifiers have their greatest effect in terms of decreasing ΔH_c for 100% amylopectin suspensions, the effect decreasing down to an amylopectin content of 50%, and then increasing slightly as the amylopectin content is reduced further. These results indicate that surfactants/emulsifiers have a strong, direct effect on amylopectin. The smaller effects of the surfactants/emulsifiers on mixtures with 50–90% amylopectin can be explained by the formation of amylose/lipid complexes, and hence the retardation of the interaction between amylopectin and the surfactants/emulsifiers.

The effects of the surfactants/emulsifiers on mixtures with less than 50% amylopectin can be explained along similar lines to those given by Russell (1987) — namely, that the amylose cannot co-crystallize with

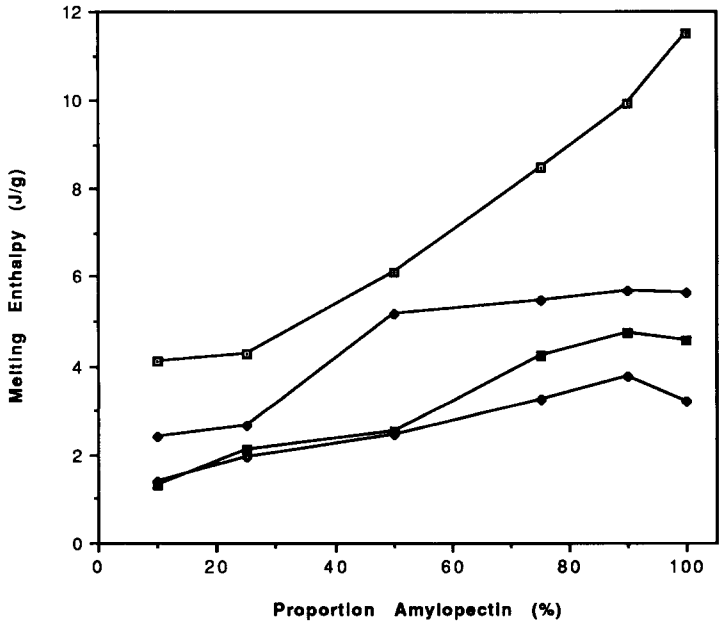

Fig. 9. Comparison of melting enthalpies of different mixtures with and without additives versus the proportion of amylopectin in the mixture. (□, without additives; ◆, with added monoclyerides; ■, with added CTAB; ◆, with added SDS; all additives are 2·9 mg/100 mg mixture.)

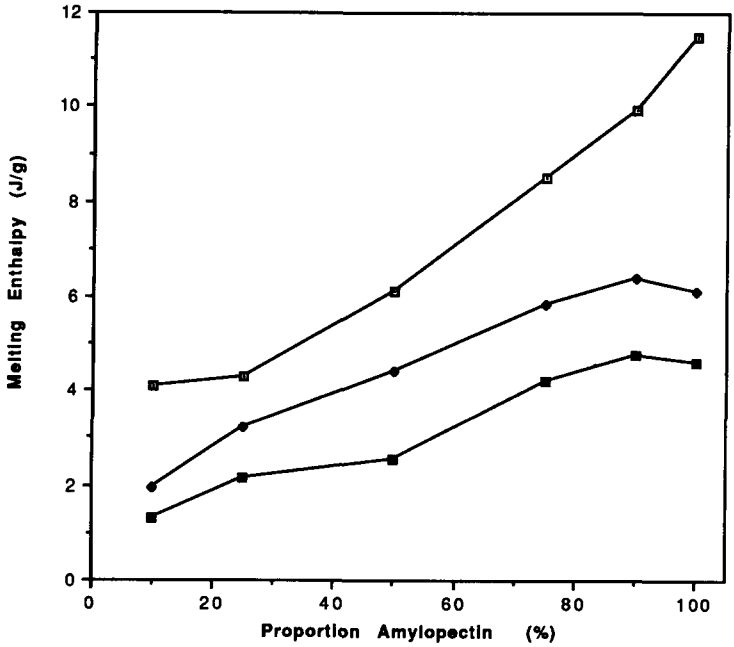

Fig. 10. Comparison of melting enthalpies of mixtures without additives and with added CTAB (1·9 and 2·9 mg/100 mg mixture) versus the proportion of amylopectin. (□, without additives; ◆, with added CTAB (1·9%); ◘, with added CTAB (2·9%).)

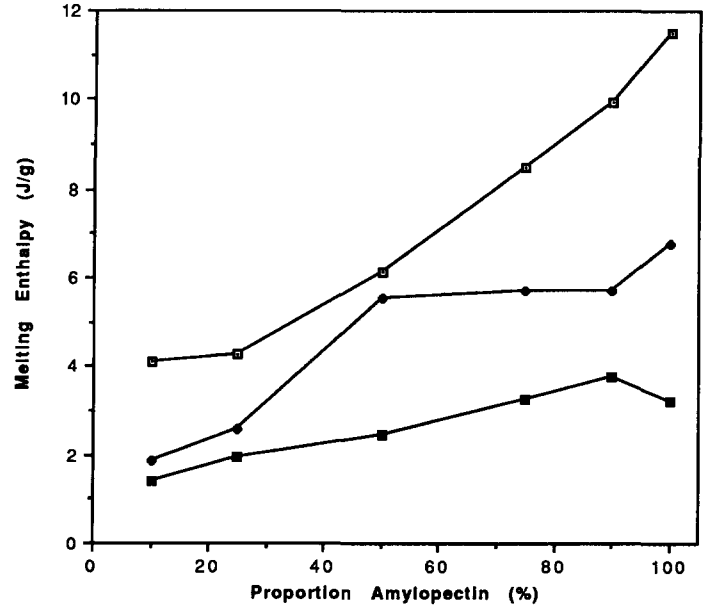

Fig. 11. Comparison of melting enthalpies of mixtures without additives and with added SDS (1·9 and 2·9 mg/100 mg mixture) versus the proportion of amylopectin. (◘, without additives; ◆, SDS (1·9%); ◘, SDS (2·9%).)

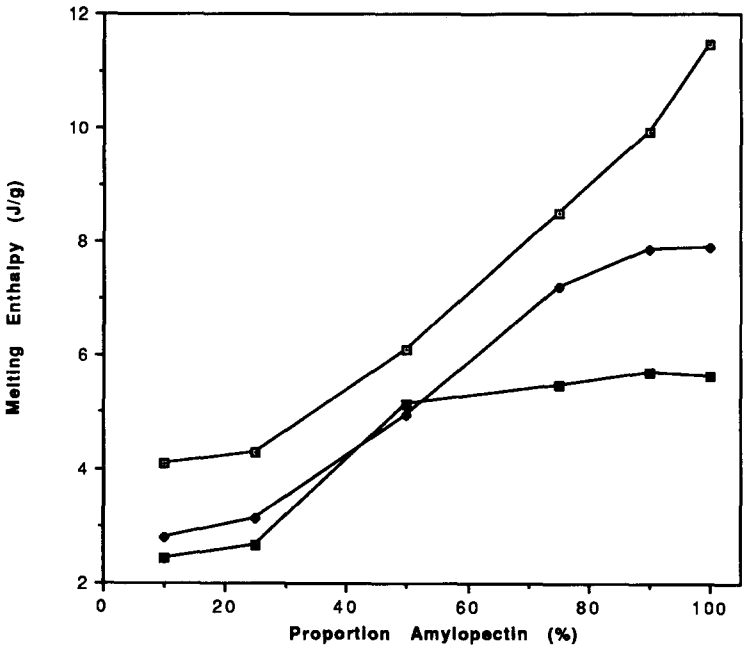

Fig. 12. Comparison of melting enthalpies of mixtures without additives and with added monoglycerides (1·9 and 2·9 mg/100 mg mixture) versus the proportion of amylopectin. (□, without additives; ◆, monoglycerides (1·9%); ■, monoglycerides (2·9%).)

amylopectin to the same extent when it is complexed with the surfactants/emulsifiers and thus cannot contribute to the melting enthalpy of amylopectin. There has been increasing non-direct evidence that lipids interact with amylopectin to some extent, as they do with amylose (Batres & White, 1986; Evans, 1986; Hahn & Hood, 1987; Slade & Levine, 1987; Eliasson & Ljunger, 1988). In this study, the results show that adding 1·9 mg/100 mg mixture of surfactants/emulsifiers to a 100% amylopectin suspension has the same effect as decreasing the amount of amylopectin to 60–70% (see Fig. 8). Eliasson and Ljunger (1988) showed that the effect of lipids on amylopectin is in the order surfactants > unsaturated monoglycerides > lecithin > triglycerides, the triglycerides having hardly any effect at all. This is the same ranking as for the effectiveness of complex formation of these substances with amylose. A similar effect was found in this study, as monoglycerides had a smaller effect than either CTAB or SDS. It has been shown that thermal stability of amylose/lipid complexes increases with increasing chain length and decreases with increasing unsaturation (Morrison, 1985), and the charged nature of the surfactants is likely to contribute to more rigid complexes with amylopectin because of charge-

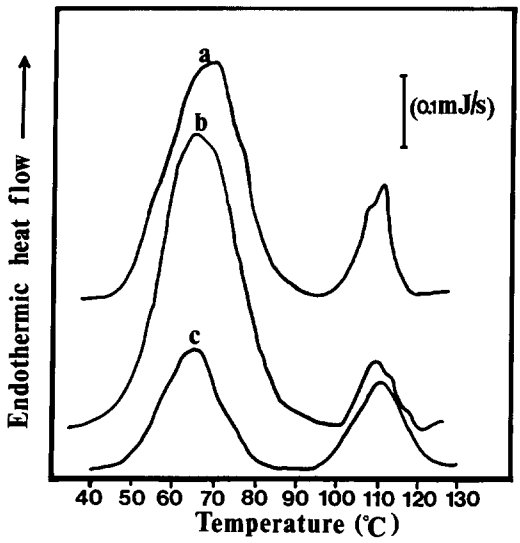

Fig. 13. Examples of the influence of CTAB on the DSC thermograms of (a) 100% amylopectin stored for 2 days (9·3 mg); (b) mixture with the amylopectin/amylose ratio of 25/75, stored for 3 days (13·37 mg); and (c) mixture with the amylopectin/amylose ratio of 10/90, stored for 3 days (8·33 mg). All samples had a water content of 50% (w/w) and contained CTAB (1·9 mg/100 mg mixture); they were heated in an oven (105°C, 15 min) before storage.

TABLE 1
X-ray Diffraction Lines for Amylopectin with CTAB (6%) and SDS (3 and 10%)

Amylopectin + CTAB (6%)		*Amylopectin + SDS (3%)*		*Amylopectin + SDS (10%)*		*Zobel (1964)*	
d-spacing (Å)	*Intensity*[a]	*d-spacing (Å)*	*Intensity*[a]	*d-spacing (Å)*	*Intensity*[a]	*d-spacing (Å)*	*Pattern*
15·6	S	15·6	S	15·6	W	15·8(S)	B
12·0	W	12·0	W	12·0	M	12·0(M)	V
—	—	—	—	6·80	W	6·75(S)	V
5·17	S	5·17	S	—	—	5·16(S)	B
4·46	S	4·47	S	4·47	S	4·42(S)	V
4·01	W	4·03	W_+	3·98	W	4·00(M)	B
3·73	W_+	—	—	—	—	3·70(M)	B

[a]S = strong, W = weak, M = medium.

repulsion effect (Evans, 1986). It has been speculated (Batres & White, 1986; Evans, 1986; Eliasson & Ljunger, 1988) that the outer branches of the amylopectin molecule assist in the formation of a helical inclusion complex with suitable lipids.

The appearance of a transition for 100% amylopectin suspension at temperatures usually associated with amylose/lipid complex has not been reported earlier, except by Slade and Levine (1987) for waxy maize starch and sodium stearoyl lactylate.

X-ray diffraction lines (Table 1) for 100% amylopectin suspension in the presence of SDS and CTAB seem to support the possibility of an amylopectin/lipid complex similar to the amylose/lipid complex, as at the lower concentration of CTAB and SDS a mixture of B- and V-patterns is found, but at high concentration of SDS (10%) the V-pattern is stronger whereas the B-pattern has almost completely disappeared. These findings seem to provide direct evidence of an interaction between amylopectin and the surfactants/emulsifiers used, similar to the interaction of amylose and lipids in helical inclusion complexes. The fact that others (Kugimiya *et al.*, 1980; Evans, 1986) could not find direct evidence for the presence of an amylopectin/lipid complex might be because they used waxy starches, whereas in this study amylopectin was

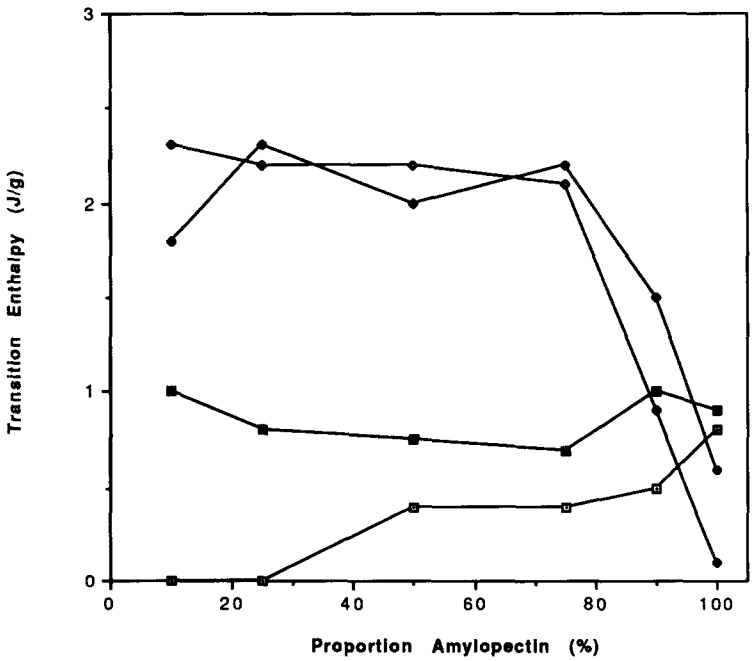

Fig. 14. Transition enthalpies for the surfactants/emulsifiers complexes versus the proportion of amylopectin, for 3 additives: CTAB, SDS and monoglycerides. (◈, SDS complex; ◆, high temperature transition of the monoglycerides; ■, CTAB complex; ⊡, low temperature transition of the monoglycerides. All additives were 1·9 mg/100 mg mixture.)

used as it is, not bound into starch granules and therefore more free to interact with the surfactants/emulsifiers. This is supported by findings of Eliasson and Ljunger (1988), who showed that CTAB had a greater effect on decreasing the ΔH_c of amylopectin than on waxy maize starch.

It might be concluded that amylopectin forms a complex with a suitable lipid. However, this complex formation is restrained when amylopectin is present in the native starch granule. If amylose is present the amylose/lipid complex will probably be formed first. The possibility of complex formation of both amylose and amylopectin at the same time, though, cannot be ruled out.

The enthalpy of transition of complexes for 100% amylopectin is generally much lower than for the other mixtures, indicating, as said before, that the amylopectin does not form a complex as easily as amylose. However, the transition temperatures are very similar over the whole range of mixtures, which indicates that the complexes have about the same stability.

One peculiar finding is the two complex peaks for mixtures with monoglycerides. The complex peak at the lower transition temperature

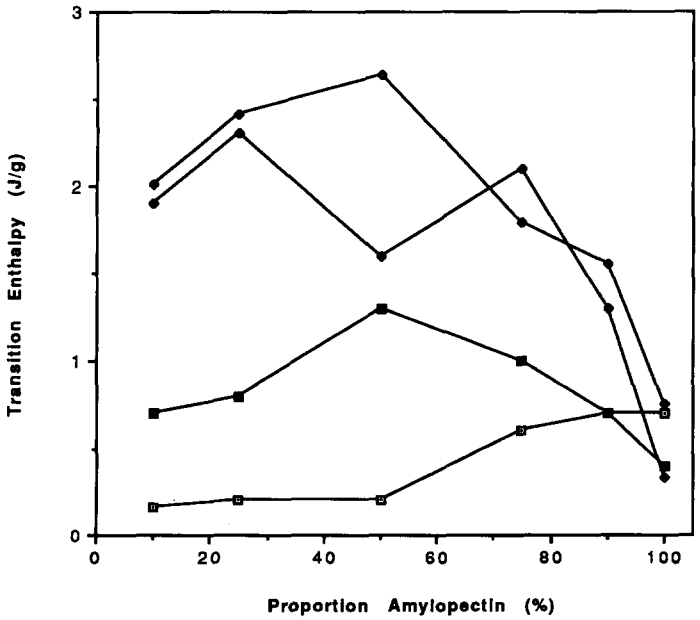

Fig. 15. Transition enthalpies for the surfactants/emulsifiers complexes versus the proportion of amylopectin, for 3 additives: CTAB, SDS and monoglycerides. (◆, SDS complex; ◆, high temperature transition of the monoglycerides; ■, CTAB complex; ▫, low temperature transition of the monoglycerides. All additives were 2·9 mg/100 mg mixture.)

(105–107°C) increases with increasing amylopectin content, and the other peak at higher temperature (128–131°C) increases with increasing amylose content. It is difficult to say which component of the monoglyceride mixture forms better complexes with amylose or amylopectin, but as said before, saturated or longer chains give more thermally stable complexes than unsaturated or shorter chains (Morrison, 1985). It is, therefore, likely that the unsaturated monoglycerides complex better with amylopectin, and the saturated monoglycerides complex better with amylose. For SDS, which is a straight-chain molecule, the enthalpy value increased with increasing amylose content, but for CTAB, which is also a straight-chain molecule, the values varied considerably.

CONCLUSIONS

How starches retrograde depends among other things on the amylopectin/amylose ratio. When the amylopectin content is less than 50%, it co-crystallizes with amylose to some extent, and the amylose then contributes to a higher melting enthalpy than is expected. When the amylopectin content is over 50%, the amylose content does not significantly affect the melting enthalpy.

The effects of surfactants/emulsifiers on retrogradation are as follows:

1. They can form a complex with amylopectin and therefore have their greatest reducing effect on the melting enthalpy for 100% amylopectin samples, i.e. if nothing else disturbs that effect.
2. In mixtures containing 50–90% amylopectin, they primarily form complexes with the amylose component, and can therefore have a smaller reducing effect on the melting enthalpy.
3. In mixtures containing less than 50% amylopectin, they also primarily form complexes with amylose. The consequence is that the amylose cannot co-crystallize with amylopectin to the same extent as before, and also the surfactants/emulsifiers cannot affect the amylopectin. The result is also a smaller reduction in retrogradation.

The small effect on mixtures with 50% amylopectin can be explained by the fact that they contain too little amylose to co-crystallize with amylopectin, so the surfactants/emulsifiers do not affect that part; and on the other hand, too much amylose as it neutralizes all the surfactants/emulsifiers, so they cannot influence the amylopectin component.

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