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Thermochimica Acta 246 (1994) 343–356

thermochimica acta

Interactions between starch and lipids studied by DSC

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Received 29 December 1993; accepted 20 April, 1994

Abstract

Differential scanning calorimetry is a valuable method for obtaining information about starch–lipid interactions. The transition of the amylose–lipid complex and the influence of lipids on starch gelatinization and retrogradation have been studied.

The thermal transition of the amylose–lipid complex depends on monoacyl chain length and the polar head of the lipid, on the water content and on the type of starch, i.e. when amylose is present in the form of starch granules. Different polymorphic forms of the amylose–lipid complex exist.

Food processing, e.g. extrusion cooking and drum drying, might lead to very different types of complexes. Chemical modification of the starch also affects the thermal properties of the amylose–lipid complex.

Indirect evidence is given for the formation of an amylopectin–lipid complex. This evidence includes the decrease in gelatinization enthalpy for a waxy maize starch in the presence of lipids, and the reduced retrogradation of waxy maize starch in the presence of lipids.

The influence of the lipid on the complex formation is shown. It is stated that not only the monoacyl chain length and the polar head but also the phase behaviour of the lipid influence the properties of the complex. The lamellar liquid-crystalline phase is much more effective for complex formation than, for example, the cubic phase.

Keywords: Amylose; DSC; Gelatinization; Heat of gelatinization; Heat of transition; Lipid; Starch; XRD

1. Introduction

The interaction between starch and lipids is a well-known phenomenon in the food industry. It is made use of to increase the shelf-life of bread, to decrease the

SSDI 0040-6031(94)01875-8

stickiness of pasta and potato flakes, and to affect the rheological behaviour of starch. There are also nutritional implications of these interactions. The effects of polar lipids on starch properties are often explained by the formation of an amylose–lipid complex. As will be discussed in this paper, the existence of an amylopectin–lipid complex has also been suggested.

The interaction between starch and lipid manifests itself in many different ways. It is thus possible to use a range of methods to study the interaction, including iodine absorption [1], enzymatic analysis [2–5], rheological methods [6–9], equilibrium dialysis [10,11], X-ray diffraction analysis [12–16], electron spin resonance [17–19] and Raman spectroscopy [20]. When DSC (differential scanning calorimetry) began to be used in the early eighties to study starch gelatinization, a thermal transition that could be attributed to the amylose–lipid complex was detected in the thermogram [21–23]. Since then, DSC is the method that has contributed the most to our understanding of starch–lipid interactions.

When starch is heated in the presence of lipids in the DSC the resulting thermogram might look like the one in Fig. 1. The thermogram shows the heating of potato starch (a starch essentially free of lipids) in a mixture of β-hydrate crystals of monolaurin and monomyristin (ratio 30:70). The water content is so high that it does not influence the gelatinization enthalpy. The first endotherm is due to melting of the monoglyceride crystals, and it is even possible to differentiate between monolaurin (I_a) and monomyristin (I_b). The next peak is the starch gelatinization, and the third peak is due to the transition of the amylose–lipid complex. The small fourth peak could be due to a transition between liquid-crystalline phases of the lipids. Of these transitions the starch gelatinization is irreversible, whereas the other transitions, including the transition of the amylose–lipid complex, are all reversible. The transitions observed in this thermogram and the

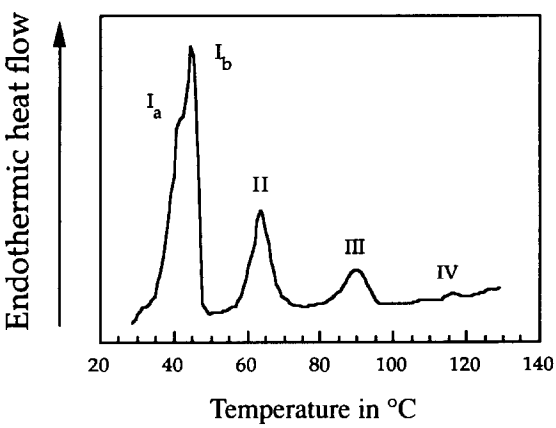

Fig. 1. A DSC thermogram (scanning rate 10°C min^{-1}) of potato starch heated in the presence of monoglycerides (monolaurin and monomyristin added as β-hydrate crystals).

information that can be obtained from this kind of experiment is the topic of the present review; the discussion will start with the amylose–lipid complex (peak III in Fig. 1).

2. The amylose–lipid complex

2.1. Structure of the complex

Amylose–lipid complexes can be formed by gelatinizing starch in the presence of lipids; an example of heating starch in the presence of a polar lipid in the DSC pan is given in Fig. 1. The complex might also be formed by combining solutions of amylose and lipids. The complex then precipitates, and can be collected after centrifugation for DSC studies.

The structure of the amylose–lipid complex has been elucidated by X-ray diffraction and electron diffraction studies [12,14]. The complex is described as a helical inclusion complex with amylose forming a helix around the hydrophobic chain of the ligand. For complexes involving polar lipids, the helix around the monoacyl chain is usually composed of three turns, and each turn is composed of six glucosyl residues. When the ligand is bulky or branched, seven or even eight glucosyl residues might be required for one single turn of the helix [14]. Each monoacyl chain would thus require at least 18 glucosyl residues in the complex, causing saturation to be reached at lipid levels of around 10 g lipid per 100 g amylose for most of the relevant complex binders. Higher levels of added lipids result in free, uncomplexed lipid [24]. There are indications that less than three turns of the helix are really involved in the complex [20].

2.2. Transition temperature and enthalpy

The thermal transitions of the amylose–lipid complex during a heating–cooling–reheating sequence are illustrated in Fig. 2. The molecular events giving rise to the endothermic transition are not completely understood, but are thought to involve melting of the crystalline complex structure as well as dissociation of amylose and lipid [25]. On cooling, the complex forms again, and recrystallization occurs. The exothermic recrystallization peak is usually more sharp than the first melting endotherm, but located at a lower temperature. Considerable hysteresis effects have been observed between melting and recrystallization (see, for example, Refs. [3] and [25]).

The parameters most often used to characterize the transition are T_{cx}, the temperature at peak maximum, and ΔH_{cx}, the enthalpy of the transition. These values depend on the lipid in the complex as illustrated in Table 1. The longer the monoacyl chain, the higher the T_{cx} value will be, and with increasing degree of unsaturation in the monoacyl chain T_{cx} decreases. It should be noted that diacyl lipids (lecithin in Table 1) also form the complex, whereas no complex formation between amylose and triglycerides has been detected. The results in Table 1 are not

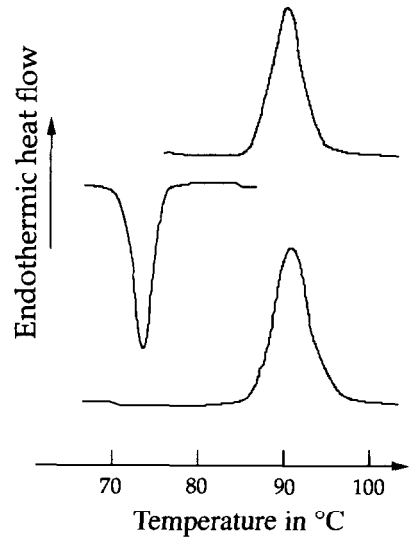

Fig. 2. Schematic melting (upper curve), cooling (middle curve) and reheating (lower curve) of an amylose–lipid complex. The thermogram is reconstructed from Ref. [3], and corresponds to the monomyristin–amylose complex.

unambiguous regarding the influence of charged ligands on T_{cx}. It has been suggested that the influence of the polar head might depend on the chain length of the ligand [30].

The ΔH_{cx} values differ considerably between different investigations (see Table 1). These discrepancies could be attributed to different ways of evaluating the transition endotherm in the DSC thermogram, to the composition of the complex, and to the preparation method.

The results given in Table 1 were obtained under conditions where the influence of the water content on the DSC parameters should be negligible (Fig. 3). If the water content is lowered below a certain value T_{cx} increases, an effect that could be interpreted as related to the plasticizing effect of water on the glass transition temperature and thus on the melting temperature of the crystals [31]. The appearance of the thermogram also changes when the water content decreases: double peaks are observed, and in some cases an exothermic transition can even be detected between them. This behaviour is attributed to melting and recrystallization during the time frame of the DSC experiment [31–33].

Different polymorphic forms of the amylose–lipid complex have been reported [16,24,30]. Depending on the ligand and temperature of complex formation, either a low-temperature melting form, a high-temperature melting form or a mixture of both, is formed (Table 2). The complex melting at the higher temperature was found to be crystalline when complexes of different forms were found [16].

Table 1
Transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) measured for amylose–lipid complexes formed either from solution or during gelatinization of starch

Lipid additive weight ratio lipid:starch (amylose) [a]	Conditions for complex formation [b]	T_{cx} in °C	ΔH_{cx} in (J per g dry matter)
SDS, 10:100 [c]	Solution	88.5 ± 1.1	18.9 ± 0.7
SDS, 5:100 [d]	Wheat	94.2 ± 0.5	4.4 ± 0.6
SDS, 5:100 [d]	Potato	88.6 ± 1.7	1.9 ± 0.1
GML, 10:100 [e]	Solution	85.1 ± 0.4	29.3 ± 1.3
Lauric acid, 0.040:1 [f,g]	Solution	94.1 ± 0.2	22.4 ± 1.8
		114.0 ± 0.2	6.0 ± 0.5
GMP, 20:100 [h]	Solution, 55°C	95.9 ± 1.1	17.2 ± 1.1
GMP, 10:100 [e]	Solution	98.5 ± 0.3	28.1 ± 1.7
GMP, 0.7 mM [i]	Potato	105	7.4
CTAB, 20:100 [j]	Solution	98.0 ± 0.4	17.9 ± 1.9
CTAB, 5:100 [d]	Wheat	92.8 ± 0.5	4.4 ± 0.2
CTAB, 5:100 [d]	Potato	91.9 ± 0.5	2.1 ± 0.2
CTAB, 10:100 [k]	Maize	98.6 ± 0.6	1.2 ± 0.3
CTAB, 10:100 [k]	Waxy maize	No endotherm	No endotherm
CTAB, 10:100 [k]	High-amylose maize	97.1 ± 1.1	3.5 ± 0.9
GMS, 20:100 [h]	Solution, 60°C	100.1 ± 1.2	22.2 ± 1.8
GMS, 20:100 [e]	Solution	103.5 ± 0.9	33.5 ± 3.4
Stearic acid, 0.031:1 [f,g]	Solution	98.3 ± 0.6	29.7 ± 1.8
GME, 20:100 [e]	Solution	100.8 ± 0.2	31.8 ± 0.8
GMO, 20:100 [e]	Solution	97.0 ± 0.4	29.3 ± 2.1
Oleic acid [l]	Solution	109	25
GMLi, 20:100 [e]	Solution	90.3 ± 0.9	23.5 ± 1.7
Lysolecithin, 20:100 [h]	Solution, 55°C	103.1 ± 1.0	21.5 ± 1.1
Lysolecithin, 20:100 [c]	Solution	104.7 ± 1.2	23.0 ± 1.6
Lysolecithin, 5:100 [d]	Wheat	104.6 ± 0.3	6.4 ± 0.6
Lysolecithin, 5:100 [d]	Potato	109.7 ± 0.5	5.9 ± 0.3
Lecithin, 20:100 [c]	Solution	95.8 ± 0.3	11.1 ± 0.7
Lecithin, 5:100 [d]	Wheat	96.9 ± 1.9	0.88 ± 0.13

[a] SDS, sodium dodecyl sulphate; GML, glycerol monolaurin; GMP, glycerol monopalmitin; CTAB, cetyltrimethylammonium bromide; GMS, glycerol monostearin; GMO, glycerol monoolein; GMLi, glycerol monolinolein. [b] Solution means that the complex has been formed by precipitation from solution. The name of a starch indicates that the complex has been formed when starch and lipid were heated together in the DSC. The water content in the DSC analysis is >75%. [c] Unpublished data. [d] Data from Ref. [26]. [e] Data from Ref. [3]. [f] Molar ratio, ΔH_{cx} expressed in J per g amylose. [g] Data from Ref. [24]. [h] Data from Ref. [16]. [i] Data from Ref. [15]. [j] Data from Ref. [27]. [k] Data from Ref. [28]. [l] Data from Ref. [29].

2.3. Complex formation between starch and lipids

For complexes formed between starch, i.e. amylose present as a starch granule, and lipids, ΔH_{cx} depends on the amount of lipid added, and eventually the amylose in the starch will be saturated (Fig. 4). This is different from the situation where complexes are precipitated. For such complexes, ΔH_{cx} as well as T_{cx} are indepen-

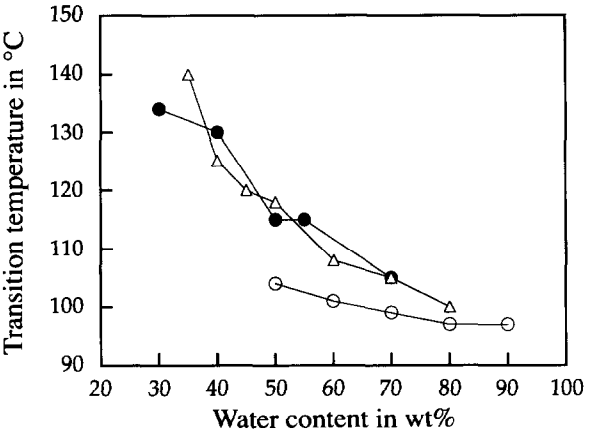

Fig. 3. The influence of water content on the transition temperature of amylose–lipid complexes; ○, amylose–monopalmitin (only the low temperature form is shown, data from Ref. [31]); ●, potato starch–monopalmitin complex (data from Ref. [15]); △, the amylose–lipid complex of wheat starch (data from Ref. [21]).

Table 2
Thermal transition temperature (T_{cx}) and X-ray diffraction patterns of polymorphic forms of the amylose–lipid complex

Ligand	Conditions for complex formation	T_{cx1} in °C	T_{cx2} in °C	X-ray pattern of sample
1-Decanol [a]	Heating in the DSC to 150°C			
	(a) Cooling, 150 → 20°C	82		
	(b) Cooling, 150 → 80°C	106		
Lauric acid [b]	Crystallization at 50°C	93.3 ± 1.0	111.5 ± 0.5	
	Crystallization at 70°C	94.5 ± 0.5	111.0 ± 0.2	
Monomyristin [c]	Crystallization at 60°C	90.8 ± 0.9		Amorphous
	Crystallization at 90°C	91.3 ± 0.8	112.5 ± 1.1	V-pattern
Monopalmitin [c]	Crystallization at 60°C	96.2 ± 0.6		Amorphous
	Crystallization at 90°C	95.0 ± 0.8	112.9 ± 1.0	V-pattern
Monostearin [c]	Crystallization at 60°C	100.1 ± 1.2		Amorphous
	Crystallization at 90°C	114.3 ± 0.8		V-pattern
Lysolecithin [c]	Crystallization at 60°C	102.3 ± 0.4		
	Crystallization at 90°C	102.2 ± 0.9		

[a] Data from Ref. [30]. [b] Data from Ref. [24]. [c] Data from Ref. [16].

dent of the amount of lipid added, indicating that it is the saturated complex that precipitates [24]. For solution-grown complexes (fatty acids and monoglycerides), saturation was achieved around 10 g/100 g amylose [24]. A higher level of lipid is required for saturating amylose in starch. The saturation was reached in the ligand/starch ratio range of 0.05–0.08 (w/w) for SDS (sodium dodecyl sulphate), SSL (sodium stearoyl lactylate), CTAB (cetyltrimethylammonium bromide) and

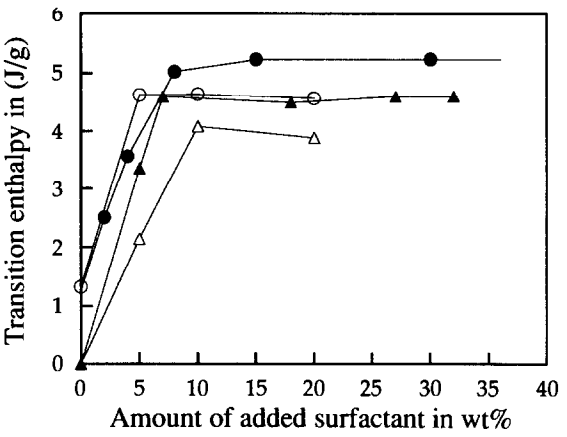

Fig. 4. The dependence of ΔH_{cx} of the amylose–lipid complex on the amount of lipid added to starch; ○, wheat starch and CTAB (data from Ref. [26]); △, potato starch and CTAB (data from Ref. [26]); ●, wheat starch and SDS (data from Ref. [34]); ▲, potato starch and SDS (data from Ref. [34]).

potato starch [34], but below 0.05 for wheat starch and CTAB [26]. These values correspond to about 20 g lipid per 100 g amylose.

If a starch–lipid sample is heated, cooled and then reheated in the DSC, higher enthalpy values are often obtained during the second scan (Table 3). For a complex precipitated from solution (amylose–CTAB), no change in ΔH_{cx} was observed with a second or third heating [27], as expected for a fully saturated complex [24]. When amylose and lecithin were mixed with water in the DSC pan, ΔH_{cx} during the second scan was about double that during the first scan [35]. The increased ΔH_{cx} values during the second scan are probably due to better conditions for complex formation after the first heating. In the case of starch, amylose leaking occurs at temperatures above the starch gelatinization temperature range. Sievert and Holm [36] recently showed that ΔH_{cx} during the second scan of a lysolecithin–amylose complex depends on the final heating temperature during the first scan. The melting temperature of amylose crystals is well above 100°C [37–40].

ΔH_{cx} values obtained for different types of starch are given in Table 1. To some extent the differences are due to the level of amylose, but the location of the amylose in the starch granule as well as its chemical properties must be of importance. It has been suggested that amylose is more intimately in contact with amylopectin in potato starch than in, for example, wheat starch [41], and this could explain the lower complexing ability of potato starch, i.e. the low ΔH_{cx} values compared with wheat and maize (Table 3). It has also been suggested that intermediate material could explain the differences between wheat and potato starches in complex-forming ability [35].

The thermal properties of complexes formed between chemically modified starches and lipids are illustrated in Table 4. For these starches, T_{cx} and ΔH_{cx} values were lower for the modified starch, indicating that less stable complexes were

Table 3
Transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) of amylose–lipid complexes during heating and reheating in the DSC

Sample	Scan no.	T_{cx} in °C	ΔH_{cx} in (J per g dry matter)
Potato starch and lysolecithin [a]	I	104.9 ± 0.2	5.1 ± 0.1
	II	106.9 ± 0.2	5.9 ± 0.3
Potato starch and CTAB [b,c]	I	95.1 ± 1.8	3.6 ± 0.1
	II	98.1 ± 1.8	5.3 ± 0.2
Wheat starch and lysolecithin [a]	I	103.4 ± 0.2	5.7 ± 0.2
	II	107.1 ± 0.3	9.1 ± 0.1
Wheat starch and CTAB [b,c]	I	94.7 ± 1.9	4.2 ± 0.3
	II	98.1 ± 1.3	6.8 ± 0.2
Maize starch [d]	I	98.6 ± 0.6	1.2 ± 0.3
	II	96.8 ± 1.4	2.5 ± 0.5
Maize starch and lysolecithin [a]	I	103.5 ± 0.4	6.0 ± 0.1
	II	107.4 ± 0.6	8.1 ± 0.3
Maize starch and CTAB [b,d]	I	94.4 ± 1.4	4.2 ± 0.3
	II	98.1 ± 2.1	6.7 ± 0.1
Amylomaize starch [d]	I	97.1 ± 1.1	3.5 ± 0.9
	II	97.8 ± 0.7	2.7 ± 1.0
Amylomaize and lysolecithin [a]	I	106.0 ± 0.3	9.6 ± 0.5
	II	107.1 ± 0.1	16.0 ± 0.3
Amylomaize starch and CTAB [c,d]	I	93.6 ± 2.4	4.9 ± 0.6
	II	97.6 ± 0.6	12.6 ± 1.4

[a] Data from Ref. [35]. [b] CTAB, cetyltrimethylammonium bromide. [c] Unpublished results. [d] Data from Ref. [28].

Table 4
Transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) of amylose–lipid complexes formed with chemically modified starches

Starch [a]	Ligand [b]	T_{cx} in °C	ΔH_{cx} in (J per g dry matter)
Cross-linked waxy maize starch [c]	CTAB	No endotherm	No endotherm
High-amylose maize starch (reheated) [c]	—	97.8 ± 0.7	2.7 ± 1.0
High-amylose maize starch (reheated) [c]	CTAB	97.6 ± 0.6	12.6 ± 1.4
Acetylated high-amylose maize starch (reheated) [c]	—	93.1 ± 0.4	2.1 ± 0.1
Acetylated high-amylose maize starch (reheated) [c]	CTAB	90.3 ± 1.8	3.4 ± 1.0
Potato starch [d]	Monomyristin	92.5 ± 0.7	6.4 ± 0.4
Hydroxy-propylated potato starch [d,e]	Monomyristin	77.3 ± 0.4	1.6 ± 0.3
Hydroxy-propylated potato starch [d,f]	Monomyristin	No endotherm	No endotherm

[a] The water content was 75% in all samples. [b] CTAB, cetyltrimethylammonium bromide. [c] Data from Ref. [28]. [d] Data from Ref. [8]. [e] Molar substitution = 0.045. [f] Molar substitution = 0.125.

Table 5
Transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) of amylose–lipid complexes formed during processing of wheat grain or flour

Sample and treatment before DSC analysis	T_{cx} in °C	ΔH_{cx} in (J per g dry matter)
Wheat flour, 10 g water per g flour [a]	91.9 ± 0.2	1.1 ± 0.3
Suspension above boiled for 20 min on a water bath [a]	100.9 ± 0.7	2.3 ± 0.4
Drum-dried flour [a]	97.1 ± 0.1	5.0 ± 0.7
(a) Reheated in the DSC [a]	93.6 ± 2.3	2.3 ± 0.4
(b) Homogenized before DSC analysis [a]	96.1 ± 0.4	2.3 ± 0.7
Whole grain flour [b]	90.3 ± 0.7	1.52 ± 0.0
Whole grain flour, dried autoclaved [b]	91.8 ± 0.7	0.53 ± 0.09
Whole grain flour, steam flaked [b]	91.3 ± 0.0	1.26 ± 0.09
Flour, 80% extraction rate [c]	90.8 ± 0.0	1.95 ± 0.07
Flour, 80% extraction rate, extruded [c]	87.6 ± 1.3	1.77 ± 0.27
Flour, 80% extraction rate, extruded with 2% soya oil [c]	85.6 ± 1.3	0.44 ± 0.23
Flour, 80% extraction rate, extruded with 1% linoleic acid [c]	84.1 ± 1.7	0.34 ± 0.10

[a] Data from Ref. [43]. [b] Data from Ref. [44]. [c] Data from Ref. [45].

formed, and probably also lower amounts. A high degree of modification even prevented the complex formation [8].

The processes used for heat treatment of flour and starch in the food industry are quite different from the situation in the DSC pan; pressure, shearing, heating time, heating rate and temperature might all affect the complex formation. The conditions during a food process will greatly influence the complex formation [42]. The results in Table 5 show that very different kinds of complexes might be formed [43–45]. Unfortunately, the X-ray diffraction patterns for these complexes are not known. It is thus not possible to tell if they represent different polymorphic forms (as in Table 2), more perfect crystals, or simply a larger amount of complexes formed.

3. The amylopectin–lipid complex

As discussed above, at most 18–24 glucosyl residues are required for one helical inclusion complex to form. With an average chain length of 23–44 glucosyl residues for amylopectin [46], it might then be possible for at least the outer branches to take part in complex formation. Indirect data from DSC, as discussed below, indicate that amylopectin–lipid complexes are formed during the gelatinization. Other indirect methods also support the existence of an amylopectin–lipid complex [8,11,34,47].

Neither X-ray diffractometry nor DSC can give direct evidence of an amylopectin–lipid complex, at least not after a simple heating (see below) [35,47]. The reasons for this are probably the same as for the lack of any proof indicating the

presence of amylose–lipid complexes in native starch. To detect crystallinity by X-ray diffractometry, a minimum size of crystalline domains is required. Probably neither the amylose–lipid complexes in native starch nor the amylopectin–lipid complexes form crystallites of the proper size. For a transition to be detected in the DSC, there has to be enough co-operativity in the process, which is probably not achieved under most circumstances for an amylopectin–lipid complex. The formation (and melting) of such a complex will probably occur over a broad temperature interval, without causing any distinct peaks in the DSC thermogram. In the native starch, the complexes could be too well-separated for a co-operative melting process.

An endotherm due to a crystalline amylopectin–lipid complex was observed during reheating of a waxy maize–SSL mixture that had first been heated to 120°C, and then stored at 4°C [48]. DSC endotherms at temperatures around 110°C were reported for mixtures of amylopectin and CTAB (water content 50%) that had been first heated and then stored for two days [49].

4. Lipids

For the same amylose or the same starch, the properties of the complex depend on the lipid (Table 1). However, the importance of the lipid is not only revealed in the properties of the complex; how much of the lipid forms the complex is also important. There are good possibilities to promote or restrict complex formation from the choice of lipid. This is not only because long and saturated monoacyl chains form more stable complexes — the phase behaviour of the lipid has also to be taken into account. It is often stated that unsaturated monoglycerides have poor complex-forming ability [50], and this is true if the monoglyceride is added as an aqueous dispersion at room temperature. Because the complex formation is a molecular process, it is favourable with a high monomer concentration, both of lipid and of starch (amylose). When lipids are dispersed in water, liquid-crystalline phases are formed, and they are in equilibrium with a very low monomer concentration, i.e. $\approx 10^{-6}$ M [51]. When unsaturated monoglycerides are dispersed in water at room temperature, the cubic phase is formed [52], and heating to 60°C does not change the phase behaviour. Saturated monoglycerides, however, form the lamellar liquid-crystalline phase when heated to 60°C. The monomer concentration of this phase is about the same as for the cubic phase, but the lamellar phase is more effectively dispersed in an aqueous system. If the phase behaviour of the unsaturated monoglyceride is changed, e.g. transformation to the lamellar phase (liposomes) with the aid of the cholate, these monoglycerides are as effective in complex formation as their saturated counterparts [52].

As illustrated in Fig. 1 (peaks I_a and I_b), the lipids might show up in the DSC thermogram. Saturated monoglycerides that are not complexed give a chain melting endotherm. Such an endotherm makes it possible to calculate the amount of lipid in the complex. The enthalpy of the transition due to the chain melting is high, 150–200 J g^{-1}, compared with 10–20 J g^{-1} for the gelatinization of starch [3]. If

free, uncomplexed lipids are present, there might also be endotherms due to phase transitions of the lipid. The enthalpies of such transitions, however, are quite small (0.4–1.3 J g^{-1}) [3]. The use of SDS and CTAB as complex-binders is based on their favourable phase behaviour; they form micellar solutions (cmc for SDS is 8.3 mM, and for CTAB 0.9 mM) [53]. The use of ligands such as SDS and CTAB will of course introduce charges into the complex.

If the uncomplexed lipids are not extracted, the chain melting endotherm may overlap with other peaks in the DSC thermogram (the peaks are not always as well separated as in Fig. 1). It can then be a good idea to use an unsaturated lipid with a low chain melting temperature as a model substance. To ensure high complex formation, the lipid has to be added as a liposomal dispersion [47,52].

The presence of uncomplexed lipid seems to influence the transition of the amylose–lipid complex, especially the reversibility, i.e. $\Delta H_{exo}/\Delta H_{cx} \times 100$. This was found to be 23% when the complex was analysed as precipitated from solution, 69% when excess monoglyceride was extracted with chloroform, and 16% when extra monglyceride was added [54]. For complexes formed from micellar solutions (SDS, CTAB, lysolecithin), the reversibility is always high (80–90%). The addition of lecithin (5%) to wheat starch caused ΔH_{cx} to decrease from 1.33 J g^{-1} in native starch to 0.88 J g^{-1} in the starch with lecithin [26]. From Table 5, it is evident that the presence of soya oil affected the melting behaviour of the complex formed in extruded wheat flours.

5. Influence of lipids on the gelatinization of starch

Values of the gelatinization enthalpy of starch (ΔH_g, i.e. peak II in Fig. 1) in the presence of lipids are reported to be unchanged, decreased or increased compared to the value without an additive. An increased ΔH_g value could be due to the sum of gelatinization and chain melting of an added lipid (see above). A decrease in the ΔH_g value is frequently observed, and is explained as the exothermic complex formation occurring at the same time as the endothermic gelatinization. When ΔH_g in the presence of a lipid and ΔH_{cx} are added, it is found that the sum is lower than ΔH_g without an additive [26,34]. This has been observed for several starches, including wheat starch as well as waxy maize starch. The difference could be explained by complex formation occurring between amylopectin and lipid.

The influence of added lipids on the gelatinization temperature range depends on the additive. A decrease in T_o (the onset temperature of gelatinization) might be due to a chain melting endotherm, but this is not the reason for the effect of SDS. A decrease in both T_o and T_m (temperature at peak maximum) has been observed when SDS is added to starch [26,55,56]. T_m was observed to decrease by 1.2°C for wheat starch, 2.9°C for potato starch [26], 3.5°C for rice starch, 3.9°C for defatted rice starch, and 4.4°C for pea starch [56]. Moreover, the influence of SDS is not due to the charge, as CTAB had almost no effect, or an increasing one. Emulsifiers like monoglycerides, SSL, and DATEM (diacetyl tartaric acid ester of monoglyceride) are usually found to increase slightly T_o and T_m; an increase of 1–3°C is often reported [26,56].

6. Influence of lipids on the retrogradation of starch

Only a few words will be said about the influence of lipids on retrogradation, as the study of retrogradation by DSC is covered in another paper in this volume [61].

Reheating a stored starch gel in the DSC causes melting of the recrystallized amylopectin [38,57]. The enthalpy of this endotherm (ΔH_c) increases with storage time, and when an emulsifier is added the increase in ΔH_c is lower. This is also the case for a waxy maize starch, an observation that gives further indirect evidence for the existence of an amylopectin–lipid complex [47]. The effectiveness in delaying ΔH_c for a waxy maize starch was found to be CTAB > monoglyceride > lecithin > triglyceride, i.e. the same order as found for complex-forming ability with amylose.

The amylose–lipid complex itself does not influence the development of ΔH_c [58]. Added amylose–lipid complexes influenced the retrogradation of waxy maize starch only when they had been heated above their transition temperature together with the starch. The lipid evidently must be available for interaction with the amylopectin. Judging from the values of T_{cx} and ΔH_{cx}, which remain unchanged during storage, the amylose–lipid complex does not undergo changes with time [59].

The level of additive used for keeping bread soft is usually in the range 0.5–1.0% (on flour basis). If the addition is increased above this, a further decrease in ΔH_c has been noted; ΔH_c also continued to decrease when there was no further increase in ΔH_{cx} [59].

7. Conclusions

The use of DSC to study starch–lipid interactions has greatly increased our knowledge of this kind of interaction, especially the amylose–lipid complex. The DSC technique has indicated that amylopectin also forms a kind of complex. However, other methods need to be used to give direct evidence about the nature of this complex.

A logical next step in studies of starch–lipid interactions would be to follow the rheological properties, e.g. gel formation, of the complexes in a detailed way. Such measurements, together with X-ray diffractometry, should be able to reveal more information about the nature of the different complexes formed. It might be questioned if the formation of a molecular complex is the only way in which starch and lipids interact. Polymers and surfactants in general interact through, for example, electrostatic interactions, and through the influence of polymers on micelle formation of surfactants [60]. Similar mechanisms would also be expected for starch–lipid interactions.

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