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STARCH-LIPID INTERACTIONS STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The amylose-lipid complex shows an endothermic transition around 100°C in excess water. Complexes were prepared by adding lipids to an amylose-solution, and the precipitated complex was studied in the DSC during a heating and cooling sequence. The thermal stability of the complex depends on the lipid part, and the reversibility during cooling depends on presence of excess lipids.

The influence of lipids on the gelatinization of starch was studied by adding lipids to wheat and potato starch, respectively, before the DSC-analysis. Depending on the lipid, an earlier as well as a delayed gelatinisation could be obtained.

INTRODUCTION

Amylose, the linear glucose polymer in starch, forms a helical inclusion complex with monoacyl lipids (ref.1). These complexes are of great importance in several food products as this type of lipids ("emulsifiers") is used to obtain suitable properties of starch based food products.

The inclusion complex is formed with the hydrocarbon chain of the monoacyl lipid inside the hydrophobic cavity of the amylose helix (Fig. 1). The helix is built up from three turns of amylose with six glucose residues in each turn (ref.2). Helices with seven and eight glucose residues per turn have also been suggested (ref.2). Moreover, it is uncertain to which extent the hydrocarbon chain is involved in the inclusion complex (ref.3). Complexes with somewhat different structures might thus exist.

The complex may exist in the native starch granule (e.g. in wheat starch) or be formed during gelatinization of starch in the presence of lipids (native occurring lipids or added emulsifiers). It is also possible to form the complex by adding lipids to an amylose solution, the complex will then precipitate out from solution.

The amylose-lipid complex exhibits a thermal transition around 100°C when heated in excess water (refs. 4 and 5). In the present investigation differential scanning calorimetry (DSC) was used to study this transition, as well as to study the effects of added emulsifiers on starch gelatinization.

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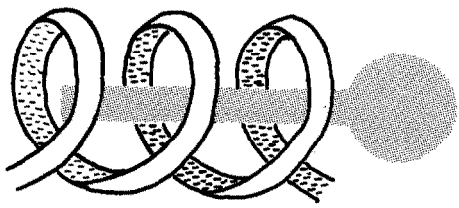

Fig. 1. Schematic illustration of an amylose-monoglyceride complex. The polar group is outside the amylose helix and the hydrocarbon chain is extended inside the helix.

MATERIAL AND METHODS

Amylose was a commercial preparation from potato starch (BDH Chemicals, England), the potato starch was a commercial sample (Stärkelsen, Kristianstad, Sweden), and the wheat starch was laboratory prepared (ref.5). Sodium stearoyl lactylate, SSL (Artodan SP 50) was from Grindsted Products, Brabrand, Denmark, and sodium dodecyl sulphate, SDS, was from BDH Chemicals, England. The monoglycerides used have been described elsewhere (ref.6).

The preparation of amylose-monoglyceride complexes was performed according to ref. 6. Starch gelatinization was studied at a water-to-starch ratio of 3:1, and SDS and SSL were added in amounts of 5% calculated on starch dry weight. SSL was added to the starch-suspension as a dispersion of the gel state (ref.7) and the SDS was added as a molecular solution. After further addition of water to give the proper water-to-starch ratio samples of these mixtures were weighed into DSC sample pans. The DSC used was a Perkin-Elmer DSC-2, and the conditions for the analysis was as follows (ref.6). The sample was heated from 23 to 117°C at a heating rate of 10°C, kept at 117°C until isothermal conditions were obtained (about two minutes), and then cooled at a cooling rate of 10°C/min. In some experiments a second and third heating/cooling cycle was performed. DuPont coated sample pans were used with an empty pan as a reference.

RESULTS AND DISCUSSION

Complexes precipitated from an amylose solution

When the amylose-lipid complex is heated in excess water an endothermic transition occurs at temperatures around 100°C (Fig. 2). This transition is reversible, at least partly, and during the conditions used here the exothermic transition occurred at a much lower temperature than the endothermic transition. In the example in Fig. 2 the temperature shift was about 20°C.

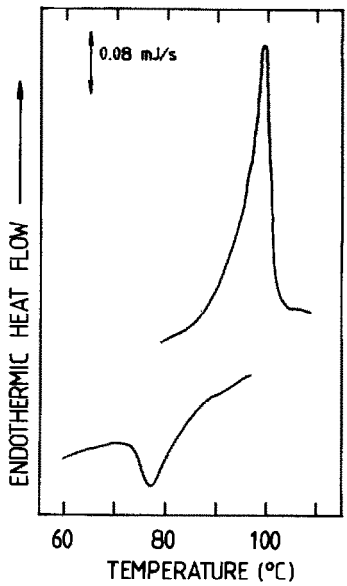

Fig. 2. The thermal transition of an amylose-monoglyceride complex during heating (upper curve) and cooling (lower curve). The scanning rate was 10^{0}C/min.

The endothermic transition has been interpreted as a dissociation of the complex (eg ref. 8), however, as will be discussed below, there are experimental findings which do not support this interpretation.

The enthalpy of the endothermic transition (ΔH_{endo}) depends on the amount of complex present (ref.4) and seems to be only slightly dependent on the lipid part of the complex (refs. 6 and 9). However, the transition temperature (T) seems to be very sensitive to the lipid part of the complex. The influence of chain length and unsaturation is illustrated in Table 1 for amylose-monoglyceride complexes (ref.6). It is seen that the longer and more saturated the hydrocarbon chain of the monoglyceride is the higher is T.

The exothermic transition depends not only on the lipid in the complex but also on the environment of the complex. This is expressed as % reversibility ($\Delta H_{exo}/\Delta H_{endo}$ x 100) in Table 2 for amylose-monoglyceride complexes which have been treated in different ways. If the endothermic transition is a dissociation of the complex the result in Table 2 could be interpreted as the amount of complex reformed during cooling. This was investigated further for amylose-glycerolmonopalmitate (GMP) complex in presence of uncomplexed monoglyceride. The uncomplexed GMP shows an endothermic transition at 53^{0}C due to melting of the hydrocarbon chain of the monoglyceride (ref.6), which

TABLE 1

The transition temperatures (T) of amylose-monoglyceride complexes.

Monoglyceride[a]	T (°C)	Monoglyceride[a]	T (°C)
12:0	85.1	18:1 trans	100.8
14:0	90.2	18:1 cis	97.0
16:0	98:5	18:2 cis, cis	90.3
18:0	103.5		

[a]Number of carbon atoms in the hydrocarbon chain of the monoglyceride:number of double bonds.

makes it possible to calculate the amount of uncomplexed monoglyceride present. When the amylose-GMP complex was given several heating and cooling cycles the enthalpy of the endotherm associated with the uncomplexed GMP did not change, whereas the enthalpy of the endotherm associated with the complex (ΔH_{endo}) decreased. During the second heating ΔH_{endo} was 15% of the initial value, and during the third heating only 3%. If these smaller ΔH_{endo}-values were due to a smaller amount of complex formed during cooling the amount of uncomplexed monoglyceride would be expected to increase. This was not the case, however, and the result does not support the interpretation of the thermal transitions of the amylose-lipid complex as simple dissociation and reformation of the complex. Alternatively, the transitions might involve complexes of different types.

Complexes formed during the gelatinisation of starch

When an emulsifier such as SSL or a surface active agent as SDS is added to starch two changes in the DSC-thermogram might be observed: a decrease of the gelatinisation endotherm and the appearance or increase of the amylose-lipid complex endotherm. The influence of the additives on the gelatinisation endotherm is illustrated in Fig. 3 as % gelatinisation versus temperature. It is seen that SDS seems to make the gelatinisation to occur earlier whereas SSL delays the gelatinisation. To a part this could be explained by an exothermic formation of the amylose-lipid complex. However, this should be expected to give a delay in the gelatinisation and not an earlier gelatinisation as in the case of SDS.

TABLE 2

The reversibility of the thermal transition of amylose-monoglyceride[a] complexes in different systems

System	Reversibility[b] (%)
Uncomplexed monoglyceride present	23
Uncomplexed monoglyceride extracted with chloroform	69
Extra monoglyceride added	16
Soybean oil added	53
In DMSO[c] solution	60

[a]The monoglyceride was a commercial sample composed of $C_{16:0}$ and $C_{18:0}$

[b]Reversibility = $\Delta H_{exo} / \Delta H_{endo} \times 100$

[c]DMSO = dimethylsulfoxide

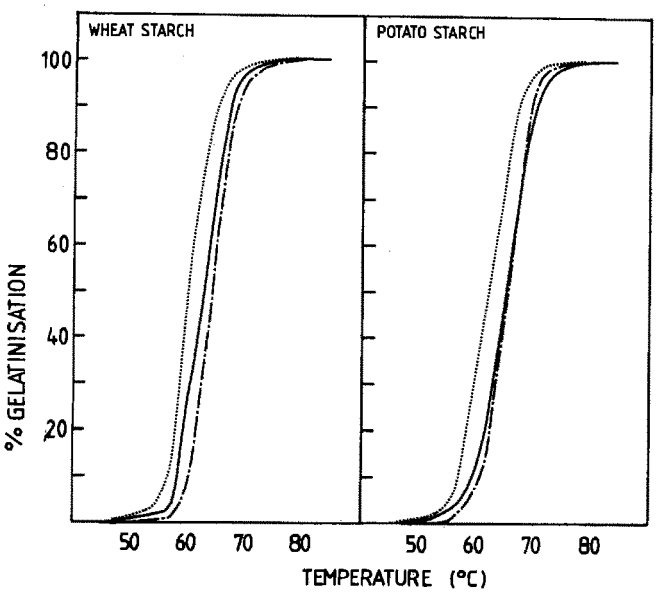

Fig. 3. % Gelatinisation versus temperature when wheat and potato starches are gelatinised in the presence of SDS and SSL, respectively. Water-to-starch ratio was 3:1, and the amount of additive was 5% calculated on starch dry weight.—— native starch; ------SDS; - - - SSL.

In all samples an increased endotherm of the amylose-lipid complex was observed (Table 3). However, the amount of complex formed during the gelatinisation seemed to depend on the type of starch as the ΔH_{endo}-value was greater for wheat starch (Table 3), i.e. even when the ΔH-value of the native wheat

starch was subtracted. The complex formation seems thus to occur more easily in wheat starch, which contain lipids in the native starch granule (ref.1) than in potato starch, which is lipid free. It is also seen in Table 3 that SSL gives more stable complexes than SDS.

TABLE 3

Transition temperature (T) and enthalpy (ΔH) of amylose-lipid complexes formed during gelatinisation of wheat and potato starch, respectively.

Additive	Wheat Starch		Potato starch	
	T (°C)	ΔH (J/g d.m.)	T (°C)	ΔH (J/g d.m.)
-	100.9	1.0	-	-
SDS	94.2	4.4	88.6	1.8
SSL	100.3	2.7	101.9	0.42

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