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Amylose–Lipid Complexes as Controlled Lipid Release Agents during Starch Gelatinization and Pasting

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The effect of amylose–lipid (AM-L) complexes consisting of amylose populations with different peak degrees of polymerization (DP) and complexed with glyceryl monostearate (GMS) or docosanoic acid (C22) on the pasting properties of wheat and rice starches was evaluated with a rapid visco analyzer (RVA). AM-L complexes were formed by both (i) addition of lipids to amylose fractions with peak DP 20, 60, 400, or 950 at 60 °C or (ii) potato phosphorylase-catalyzed amylose synthesis in the presence of lipids. All AM-L complexes affected pasting properties in line with their dissociation characteristics. AM-L complexes therefore have potential as “controlled lipid release agents” with effects markedly different from those observable with emulsifier addition in starch pasting. More in particular, short chain AM-L complexes resulted in a starch pasting behavior comparable to that of cross-linked starch, as evidenced by reduced granule swelling, good viscosity stability in conditions of high temperature and shear, and a stable cold paste viscosity.

KEYWORDS: Amylose–lipid complex; rapid visco analyzer (RVA); lipid; starch swelling; potato phosphorylase

INTRODUCTION

The use of food grade emulsifiers in starch-based foods (bakery products, pasta foods, processed potatoes, etc.) has become common practice because of their ability to affect food structure (e.g., crumb softness) and to prevent retrogradation (1). In addition, emulsifiers also influence starch swelling properties and the viscosity of starch in foods that are heated during processing (2). Literature explains these effects as complex formation between (partly) leached amylose and emulsifiers that delay starch swelling (3, 4). Retrogradation is subsequently affected by the in situ-formed amylose–lipid (AM-L) complexes, either directly by preventing the amylose molecules from crystallizing or indirectly by changing the water distribution (5).

Researchers today agree that the swelling delay is due to emulsifier complexation with amylose although there is some doubt about the “location” of this AM-L complex formation. Eliasson (4) reported that complexation between (partly) leached amylose and glyceryl monostearate (GMS) leads to formation of an insoluble layer on the granule surface, which delays water transport into the granules, preventing further leaching of amylose and therefore delays starch swelling. On the other hand, surfactant molecules are small enough to diffuse into swollen starch granules (6). Ghiasi and co-workers (3) therefore believe that the emulsifier molecules enter the starch granules and complex with intragranular amylose, delaying the release of

solubles, and the deformation and collapse of the starch granules. Furthermore, complex formation results in a more rigid structure and stabilizes the swollen granules against breakdown and decrease in viscosity (2).

In contrast to emulsifiers, the effect of fatty acids on starch pasting behavior has been less studied. In one study (7), the effect of 1-monolaurin and potassium laurate on potato starch pasting was compared. As expected, inhibition of potato starch swelling by 1-monolaurin was observed. After the potato starch lipid suspension was heated to 70 °C, birefringent granules were still detected. This indicated that not even partial gelatinization had occurred in the presence of 1-monolaurin, which formed liposomes and had a high monomer concentration in the reported thermal gelatinization conditions. The same experiment with a micellar solution of potassium laurate did not have this drastic inhibition effect on starch gelatinization. Larsson (7) explained this by the preference of these amphiphilic molecules to be in the micellar form as compared to the amylose inclusion complex. Larsson (7) concluded that the effect of lipids on starch gelatinization is mainly related to the physical state of the lipids (with liposomes as the preferred state), the lipid monomer concentration, and how fast amylose leaches from the starch granules.

The addition of AM-L complexes *as such* to starch instead of emulsifiers or fatty acids has—to the best of our knowledge—not been studied. The aim of this work was, therefore, to reveal the influence of AM-L complexes and their constituent lipid and amylose populations on starch pasting properties. To that end, wheat and rice starches, supplemented with AM-L com-

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Table 1. Wheat and Rice Starch Characteristics

characteristic	starch	
	wheat	rice
moisture (%) ^a	12.2	13.2
gelatinization T_m (T range) (°C) ^b	58.5 (11.1)	63.1 (11.5)
gelatinization enthalpy (J/g dm)	12.9 ± 1.3	14.5 ± 0.1
endogenous AM-L complex T_m (°C)	98.5	96.6
endogenous AM-L complex enthalpy (J/g dm)	2.1 ± 0.5	2.7 ± 0.9
close packing concentration (%) ^c	5.5	3.9

^a Moisture content determined as described in the Materials and Methods.

^b Gelatinization and AM-L complex dissociation determined by DSC as described in the Materials and Methods. ^c Close packing concentration determined as described in the Materials and Methods.

plexes, lipid, or amylose fractions, were analyzed with the rapid visco analyzer (RVA). AM-L complexes with different (dissociation) characteristics were prepared from GMS and docosanoic acid (C22), and amylose populations with peak degrees of polymerization (DP) 20, 60, 400, and 950 (8). Moreover, short chain AM-L complexes were prepared by the potato phosphorylase-catalyzed amylose synthesis in the presence of GMS and C22 (9). We here report on the outcome of this work.

MATERIALS AND METHODS

Materials. *Starch.* Wheat and rice starches were kindly donated by Tate & Lyle (Aalst, Belgium) and Remy Industries (Wijgmaal, Belgium), respectively. The moisture content was determined by weight loss at 130 °C for 2 h of ca. 1.0 g of accurately weighed starch. Gelatinization and endogenous AM-L complex dissociation were determined with differential scanning calorimetry (DSC) as described below. The close packing concentration was determined as described by Eerlingen and co-workers (10). The obtained starch characteristics are listed in **Table 1**.

Amylose. Amylose populations with peak DP 20, 60, 400, and 950 were prepared from several defatted starch sources as previously described (8).

Lipids. Lipids used were C22 (purity > 85%), purchased from Acros Organics (Geel, Belgium), and Dimodan PVP (GMS) (purity > 90%), kindly donated by Danisco (Brabrand, Denmark). GMS used in the potato phosphorylase-catalyzed synthesis of AM-L complexes was from Sigma-Aldrich (Bornem, Belgium) and had a purity of 99%.

AM-L Complexation. Complexes with different dissociation characteristics were obtained by varying amylose DP and lipid class. Amylose populations (peak DP 20, 60, 400, and 950) were complexed with C22 and GMS (Dimodan) at 60 °C by a conventional complexation procedure (11). Amylose was dissolved in hot dimethyl sulfoxide and diluted with boiling water. After boiling (30 min) and equilibration at 60 °C, lipid (dissolved in hot ethanol) was slowly added under vigorous mixing and kept for 4 h at 60 °C. The complexes, labeled with the following information bearing codes “peak DP of amylose fraction—lipid” (e.g., DP950-GMS), were recovered by centrifugation, washing and freeze drying. Experimental details have been previously described (8).

For the semienzymic synthesis of short chain AM-L complexes, potato phosphorylase was isolated from Nicola cultivar potatoes and added to a buffer containing glucose-1-phosphate, maltohexaose, and C22 or GMS (Sigma). In the presence of lipids, the amylose synthesis continued until AM-L complexes precipitated. Synthesized complexes obtained with C22 or GMS are labeled as AM-C22 and AM-GMS, respectively. More experimental details are elsewhere described (9).

DSC. DSC was performed with a Seiko DSC 120 (Kawasaki Kanagawa, Japan). Samples (2–4 mg) were accurately weighed into aluminum sample pans, and water was added (1:3 w/w sample dry matter (dm)/water). The pans were sealed, weighed, and equilibrated overnight at room temperature to distribute the water evenly in the sample. After the pan weight was checked for possible moisture loss,

the sample pan and an empty reference pan were heated from 25 to 135 °C at 4 °C/min. Calibration was with indium and tin. Onset (T_o), peak (T_m), and conclusion (T_c) (dissociation) temperatures and enthalpies (ΔH) of starch were determined with Seiko software. ΔH was expressed as J/g dm starch, and temperatures were expressed in °C. Results were averages of at least three measurements. The coefficient of variation, defined as the ratio of the standard deviation and the mean of the obtained results, was less than 1.5% for T_o , T_m , and T_c . For ΔH values, respective standard deviations are given in **Table 1**.

Starch Pasting and Gelation Properties. Starch pasting and gelation properties were determined with a RVA (model RVA-4D; Newport Scientific, Sydney, Australia). Starch suspensions (11% dm), with or without addition of amylose of variable peak DP (5%), lipid (1%), or AM-L complexes (5%) (calculated on starch dm weight), were mixed in a RVA canister. Water was then added to reach a total weight of 25.00 g. Suspensions were equilibrated for 1 min at 40 °C, heated to 95 °C in 13 min, held at 95 °C for 5 min, cooled to 50 °C in 8 min, and held at 50 °C for 23 min [RVA temperature (T) – time (t) profile]. The rotor speed was 160 rpm. Viscosity is expressed in centiPoise (cP). Parameters were determined as follows: peak viscosity (PV), i.e., the maximum viscosity during pasting, and the corresponding peak time (PT); hot (HPV) and cold (CPV) paste viscosity, i.e., the viscosity at the end of holding at 95 °C (19 min) and at the end of the run (50 min), respectively; setback viscosity, i.e., the difference between the CPV and the HPV; breakdown, i.e., the difference between the PV and the HPV; and finally, the percentage breakdown, i.e., the breakdown divided by the PV and multiplied by 100. The reproducibility of the RVA method was investigated by analyzing wheat starch eight times at the same concentration (11% dm). Standard deviations (expressed in %) for PV, HPV, and CPV were 1.2, 0.6, and 0.7%, respectively.

RESULTS

Material Characteristics. **Table 1** lists the characteristics of the wheat and rice starches. Wheat starch had a lower gelatinization T_m than rice starch. DSC runs revealed that both starches had AM-L complexes, which were either endogenously present or formed by complexing the endogenous lipids during the DSC scan. Close packing concentrations were well below the 11% dm applied in the RVA experiments. **Figure 1** represents the pasting profiles of wheat and rice starch controls. Wheat (**Figure 1A**) and rice (**Figure 1B**) starch had a similar PT and breakdown, but wheat starch had a higher PV and setback than rice starch (**Tables 2 and 3**). As expected, the RVA runs were excellently repeatable as verified by eight individual measurements of the wheat starch sample with standard deviations (expressed in %) of the main parameters of 0.6–1.2%. These values are similar to the standard deviations reported by others (12).

AM-L complexes, prepared by the conventional complexation method, were characterized in detail elsewhere (8). In this paper, only DSC characteristics of the complexes formed at 60 °C are discussed and presented in **Figure 2**. Potato phosphorylase-synthesized AM-L complexes were also characterized in detail in previous work (9).

For this work, AM-GMS and AM-C22 were prepared on a larger scale. The peak DP of AM-GMS and AM-C22 obtained was about 70 and 85, respectively. **Figure 2** presents DSC results of both complexes. AM-C22 and AM-GMS had an enthalpic transition around 67 and 75 °C, respectively, representing noncomplexed lipid. In contrast to the conventional AM-L complexes, semienzymically synthesized AM-L complexes were not washed with chloroform to remove non-complexed lipids. As shown previously (8, 9), dissociation temperatures increase with increasing amylose chain length and with lipid chain length as longer lipids necessitate longer amylose helices. Moreover, longer amylose chains result in more complexed lipids per chain and thus larger crystallite size.

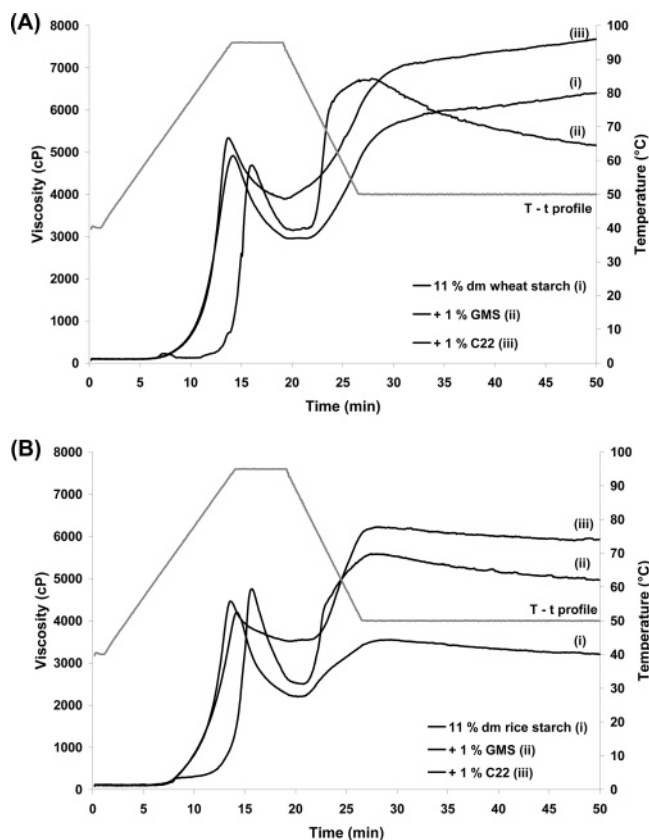


Figure 1. Pasting profiles of (i) wheat (A) and rice (B) starches supplemented with (ii) 1% GMS or (iii) C22.

Table 2. Pasting Properties of Wheat Starch (11% dm) with or without Addition of Amylose Populations (5%), Lipids (1%), or AM-L Complexes (5%)^a

wheat starch (11% dm) supplemented with	PV (cP)	PT (min)	breakdown cP	%	CPV (cP)	setback (cP)
+ 1% GMS (Dimodan)	4915	14.2	1920	39.1	6400	3405
+ 1% C22	4690	16.0	1450	30.9	5160	1920
+ 1% GMS (Sigma)	5340	13.7	1440	27.0	7675	3775
+ 5% DP20	5075	18.7	25	0.5	5460	410
+ 5% DP60	4860	14.1	1860	38.3	6540	3540
+ 5% DP400	5270	14.1	2120	40.2	6410	3260
+ 5% DP950	5560	14.0	2490	44.8	7200	4130
+ 5% DP20-GMS	5210	14.1	2210	42.4	6810	3810
+ 5% DP60-GMS	4565	15.5	1205	26.4	6345	2985
+ 5% DP400-GMS	4600	15.5	1285	27.9	6470	3155
+ 5% DP950-GMS	4795	15.0	1630	34.0	7965	4800
+ 5% DP60-C22	5000	14.7	1890	37.8	6680	3570
+ 5% DP400-C22	5525	19.1	5	0.1	5890	370
+ 5% DP950-C22	6030	15.2	650	10.8	8540	3160
+ 5% AM-GMS	5680	16.1	485	8.5	7960	2765
+ 5% AM-C22	5220	17.1	315	6.0	6450	1545
+ 5% AM-C22	3425	19.1	-15	-0.4	3060	-380

^a The pasting parameters were determined as follows: the PV, i.e., the maximum viscosity during pasting, and the corresponding PT; the HPV and CPV, i.e., the viscosity at the end of holding at 95 °C (19 min) and at the end of the run (50 min), respectively; the breakdown, i.e., the difference between the PV and the HPV; the percentage breakdown, i.e., the breakdown divided by the PV and multiplied by 100; and finally, the setback viscosity, i.e., the difference between the CPV and the HPV. Standard deviations of wheat starch pasting parameters were 0.6–1.2% ($n = 8$).

Overall, the AM-L complexes used in the RVA experiments clearly had different dissociation characteristics, with T_m ranging from 85.9 to 106.9 °C and T_o ranging from 75 to 92.5 °C (Figure 2). Therefore, a different influence on starch pasting

Table 3. Pasting Properties of Rice Starch (11% dm) with or without Addition of Amylose Populations (5%), Lipids (1%), or AM-L Complexes (5%)^a

rice starch (11% dm) supplemented with	PV (cP)	PT (min)	breakdown cP	%	CPV (cP)	setback (cP)
	4200	14.2	1935	46.1	3205	940
+ 1% GMS (Dimodan)	4750	15.7	2105	44.3	4960	2315
+ 1% C22	4460	13.5	940	21.1	5930	2410
+ 1% GMS (Sigma)	5045	16.9	855	16.9	5385	1195
+ 5% DP20	4070	14.2	1810	44.5	3060	800
+ 5% DP60	4420	14.1	2050	46.4	3140	770
+ 5% DP400	4550	14.1	2190	48.1	3130	770
+ 5% DP950	4585	14.2	2255	49.2	2870	540
+ 5% DP20-GMS	4220	14.9	1780	42.2	3535	1095
+ 5% DP60-GMS	4250	15.1	1740	40.9	3800	1290
+ 5% DP400-GMS	4310	14.6	1850	42.9	3695	1235
+ 5% DP950-GMS	4480	14.5	2050	45.8	3560	1130
+ 5% DP60-C22	4475	17.3	120	2.7	5840	1485
+ 5% DP400-C22	5155	14.6	1395	27.1	4720	960
+ 5% DP950-C22	4840	14.7	1040	21.5	4980	1180
+ 5% AM-GMS	4300	18.3	15	0.3	5205	920
+ 5% AM-C22	3680	18.9	0	0.0	4170	490

^a The pasting parameters were determined as follows: the PV, i.e., the maximum viscosity during pasting, and the corresponding PT; the HPV and CPV, i.e., the viscosity at the end of holding at 95 °C (19 min) and at the end of the run (50 min), respectively; the breakdown, i.e., the difference between the PV and the HPV; the percentage breakdown, i.e., the breakdown divided by the PV and multiplied by 100; and finally, the setback viscosity, i.e., the difference between the CPV and the HPV. Standard deviations of wheat starch pasting parameters were 0.6–1.2% ($n = 8$).

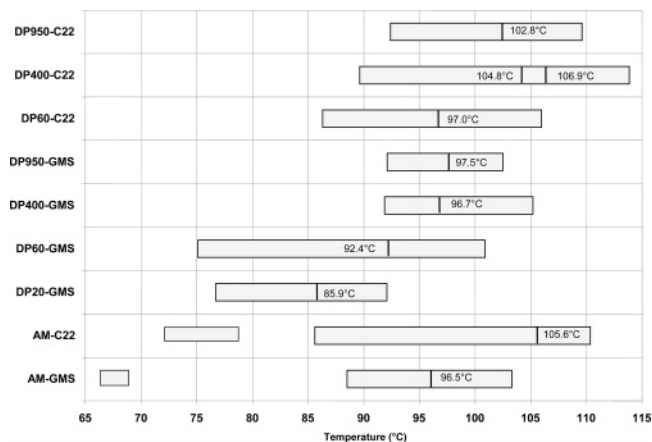


Figure 2. Schematic representation of dissociation characteristics of the different AM-L complexes determined with DSC. Start and end points of the bars represent onset and conclusion dissociation temperatures, respectively. Vertical lines with accompanying °C represent the peak dissociation temperature of the AM-L complexes.

behavior was expected for the different supplemented AM-L complexes.

Rheological Behavior of Starch in the Presence of Amylose Populations or Lipids. In conventional AM-L complexation, a saturating weight ratio of one part lipid to five parts amylose is often used as was also the case in this experimental setup. We therefore added 5% amylose fraction or 1% lipid, calculated on the starch dm weight, in the RVA experiments as reference.

Amylose Populations. Tables 2 and 3 list the pasting properties of wheat and rice starches supplemented with 5% amylose populations, respectively. DP20 had the smallest effect on the pasting properties of both starch samples. It contributed little to the overall viscosity and did not interfere with leaching amylose, resulting in a more or less similar PV and CPV. In general, viscosity increases with increasing DP of a polymer.

The observed slightly higher PV for DP60, DP400, and DP950 added to wheat and rice starches therefore needs not be surprising. For wheat starch, a higher CPV was obtained, especially for the longest amylose fractions. This can be explained by interaction of the DP400 or DP950 chains with the leached amylose, resulting in a stronger amylose network and increased CPV. This was, however, not the case for rice starch.

In literature, the effect of sugars or the ratio of amylose to amylopectin on the pasting behavior of starch has been reported more than once (13–15). However, the rheological behavior of starch supplemented with amylose fractions, differing in DP, has, to the best of our knowledge, not been described. It can be concluded from this study that the addition of amylose, differing in DP, had a rather limited impact on the starch RVA parameters, with the exception of wheat starch supplemented with long (DP > 400) amylose chains for which a higher CPV was observed.

Lipids. The addition of 1% lipid (in powder form), mixed with starch prior to suspending in water, had a different impact on the pasting properties than the amylose fractions. **Figure 1A,B** represents the effect of 1% GMS and 1% C22 on wheat and rice starches, respectively. GMS addition for both starch samples resulted in postponement of swelling. It was clearly noticeable that viscosity started to increase at the same time as for the control starch. However, the increase was then abruptly restricted by the action of GMS. The addition of the same type of emulsifier to different starches may result in different rheological responses (16) as evidenced by the GMS effect on the CPV of wheat and rice starches.

The effect of the fatty acid C22 on starch pasting behavior was totally different from that of GMS and included a slight increase in PV and a small decrease in PT. In addition, the breakdown was reduced and the highest CPV was obtained for C22 supplementation.

GMS is an emulsifier commonly used in starch-based food products (17, 18). C22 has a fairly high melting temperature. C14 and C18 (with a melting temperature in the range of that of GMS) were also added to wheat starch, and the mixtures were analyzed by RVA (results not shown). However, none of the fatty acids tested resulted in an effect similar to that observed for GMS and thus did not delay wheat starch swelling. The observed differences are discussed in more detail in the Discussion section.

Rheological Behavior of Starch in the Presence of Conventionally Obtained AM-L Complexes. **Figure 3A** shows pasting profiles of wheat starch (11% dm) supplemented with 5% of the different GMS complexes or 1% GMS. Pasting profiles of wheat starch in the presence of 5% GMS complexes in general shifted gradually toward the 1% GMS addition pasting profile with decreasing amylose DP. This behavior can be explained by the dissociation characteristics of these complexes (**Figure 2**). However, it should first be stressed that DSC dissociation characteristics were obtained at a sample:water ratio of 1:3 whereas RVA results were obtained in a ca. 1:7 ratio. DSC data do not exactly indicate when these complexes dissociate in the RVA canister and have therefore only a predictive value. As the temperature in RVA does not exceed 95 °C, it could be foreseen from **Figure 2** that DP400 and DP950 complexes are probably less dissociated than DP20, DP60, or synthesized AM-L complexes. Moreover, because of their lower T_0 values, DP20-GMS and DP60-GMS release GMS earlier during heating than DP400-GMS and DP950-GMS. The released GMS complexes the

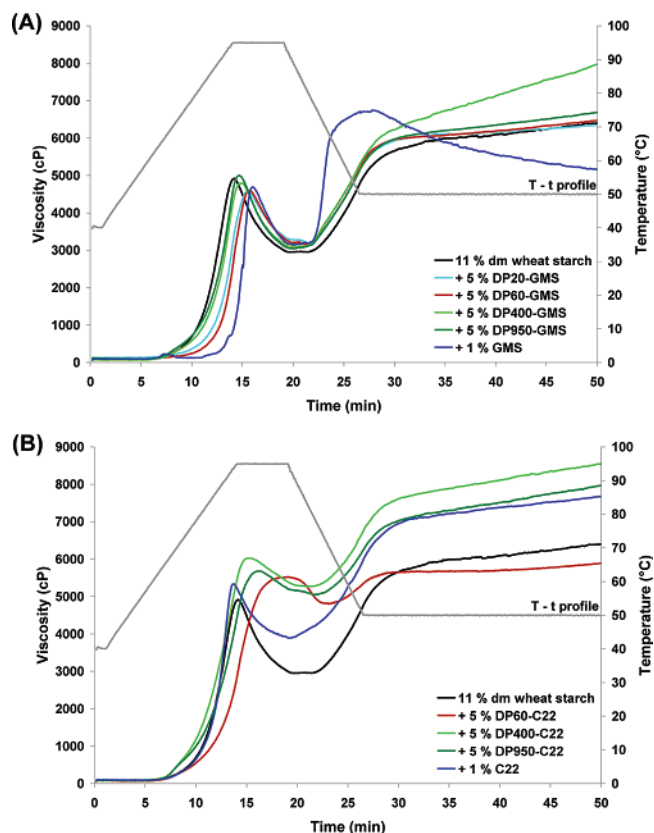


Figure 3. Pasting profiles of wheat starch (11% dm) supplemented with 5% GMS complexes (A) differing in amylose chain length or with 5% C22 complexes (B) differing in amylose chain length.

leaching amylose causing a similar—although slightly smaller—delay in swelling. PV (except for DP950-GMS) and breakdown were decreased by the GMS complexes (**Table 2**). The percentage breakdown decreased with decreasing amylose DP of the GMS complexes (**Table 2**). Cooling caused a similar rate of viscosity increase as in the wheat starch control in contrast to the steep viscosity increase for the 1% GMS addition. CPV was approximately the same as for the control, except for DP400-GMS. The freed DP400 chains, after partly releasing GMS at 95 °C, seem to interact strongly with native amylose resulting in a strong and stable amylose network. To what extent released GMS recomplexes with the original amylose (DP 20, 60, 400, or 950) chains or the longer, native amylose chains could not be determined.

PT data in **Table 3** indicate that rice starch pasting profiles in the presence of 5% added GMS complexes were intermediate between the profiles of the control starch and the profiles of the 1% GMS-supplemented starch. In addition, it could be noted that the higher the DP of the amylose used for complexation, the more the profiles inclined toward that of the control starch. PV was slightly increased by the GMS complexes and percentage breakdown decreased. For all samples supplemented with GMS complexes, CPV was higher than that of the rice starch control but lower than the CPV of rice starch to which 1% GMS was added. Setback values of GMS complex supplemented samples were also between setback values for the rice starch control and 1% GMS addition.

C22 Complexes. **Figure 3B** represents the wheat starch control (11% dm) supplemented with 5% of the different C22 complexes or 1% C22. **Table 3** lists the results for rice starch. Surprisingly, addition of 5% DP950-C22 and DP400-C22 to wheat starch accelerated starch swelling and resulted in a higher

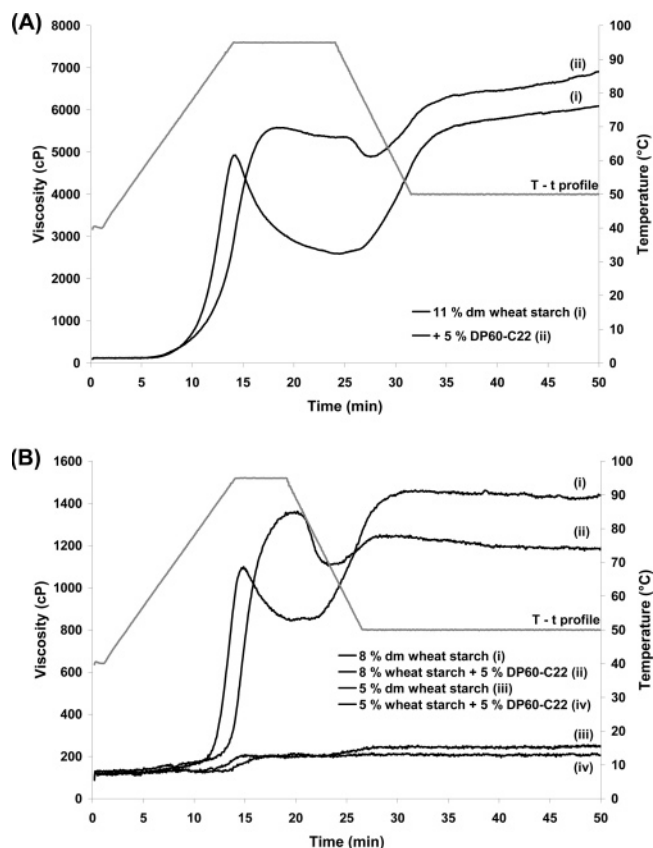


Figure 4. Pasting profiles of (i) wheat starch (11% dm) supplemented with (ii) 5% DP60-C22 complex and subjected to a RVA temperature–time profile with 5 min longer holding phase at 95 °C (A). Pasting profile of wheat starch [8% dm (i) and 5% dm (iii)] supplemented with 5% DP60-C22 (B).

PT and PV. Breakdown was reduced, and the CPV exceeded the CPV of the 1% C22-supplemented wheat starch. DP60-C22, with the lowest dissociation temperature of the three C22 complexes, delayed the starch swelling somewhat, while PV and PT increased. However, the most surprising observation upon DP60-C22 addition was the broad plateau pasting “peak” as demonstrated by the minimal percentage breakdown (0.1%) in Table 2. Wheat starch granules, in the presence of DP60-C22 complex, appear to be extremely rigid as they do not rupture while subject to shear at 95 °C. Viscosity dropped as cooling started. In the case of addition of DP950-C22 and DP400-C22, viscosity already decreased during the holding phase at 95 °C. The DP60-C22 complex resulted in a stable CPV, which was lower than the wheat starch control CPV.

For rice starch (Table 3), similar results as for wheat starch were observed. In particular, the DP60-C22 complex once again resulted in a broad pasting peak. Viscosity dropped as soon as cooling started. Consequently, the percentage breakdown was minimal (2.7%).

Because pasting profiles of wheat and rice starches were so surprisingly affected by the DP60-C22 complex, more experiments were performed with DP60-C22 and with other short chain AM-L complexes.

Rheological Behavior of Starch in the Presence of Short Chain AM-L Complexes. Figure 4 represents additional RVA experiments performed with the DP60-C22 complex to confirm its starch stabilizing behavior under high heat and shear conditions. When the shearing time at 95 °C was doubled, the pasting peak of wheat starch supplemented with 5% DP60-C22 broadened as well. The percentage breakdown was only 4.3%

(not shown), and viscosity dropped again from the moment cooling started (Figure 4A). To examine whether this effect was caused by the physicochemical and/or structural properties of an AM-L complex, 4% DP60 and 1% C22 were mixed together and added to a wheat starch control. The resulting pasting profile (not shown) was nearly a superimposition of the DP60 (5%) and C22 (1%) effects. Lower concentrations (5 and 8% dm) of wheat starch were also tested, as pasting profiles are much affected by the starch suspension’s concentration (19). The 5% dm concentration was just below the close packing concentration (Table 1). Even at these lower starch concentrations, 5% DP60-C22 resulted in similar stabilizing effects (Figure 4B).

Preparation of amylose populations with rather low DP, followed by complexation, is quite time-consuming; therefore, AM-L complexes, namely, AM-GMS and AM-C22, were obtained by potato phosphorylase-catalyzed amylose synthesis in the presence of the respective lipids (cf. Materials and Methods). Their peak DPs were comparable to the peak DP of conventionally obtained DP60 complexes.

Figure 5A presents RVA profiles of wheat starch supplemented with 5% AM-GMS or 1% GMS (Sigma). PT was somewhat lower for AM-GMS-supplemented wheat starch, but PV somewhat higher than with GMS addition. In contrast to GMS, 5% AM-GMS induced a stable and higher CPV. AM-GMS, with a peak DP of 70, resulted in a similar effect as DP60-GMS, but the pasting peak was broader, and the percentage breakdown was lower (6.0 vs 27.9%) and, therefore, more comparable to the effect of DP60-C22 addition. In the case of rice starch (Figure 5B), addition of AM-GMS resulted in similar effects as DP60-C22 complex supplementation, i.e., a broad pasting peak, little if any breakdown, and stable CPV.

Figure 5C,D shows the effect of 5% AM-C22 on wheat and rice starch pasting. PT was similar as for the DP60-C22 complex supplemented in wheat starch, although higher than for the rice starch DP60-C22 supplementation. Although higher PV and CPV were expected for AM-C22 addition, the overall effect of AM-C22 was comparable to that of DP60-C22.

DISCUSSION

AM-L complex addition clearly affected starch pasting. As the resulting RVA profiles are not a simple superimposition of the constituent lipid and amylose fraction supplementation RVA profiles, the dissociation behavior of the AM-L complexes seems a predominant factor in determining their functionality.

Literature has—to the best of our knowledge—not yet reported about AM-L complex supplementation *as such* to starch. In contrast, the effect of emulsifiers, such as GMS, on starch pasting properties has frequently been discussed (cf. Introduction) and allows comparison with our results. GMS delays starch swelling and subsequently causes PT to increase. This was also the case in the present work. However, contradictory influences of GMS on PV have been reported. Krog (2) reported for wheat starch an increase in PV when distilled monoacyl glycerols were added. The here-described data, as well as those from Ghiasi and co-workers (3) and Azizi and Rao (20), show a decreased PV for wheat starch when GMS was added. Several authors (1, 2, 21, 22) already stressed that the physical state in which the emulsifier is added in a starch pasting or breadmaking process is predominant and may be different in the stated studies.

GMS complexes altered in a similar manner the pasting behavior of both starches studied here. We believe that this effect is easily explained based on controlled release of GMS from the GMS complexes at their dissociation temperature. The

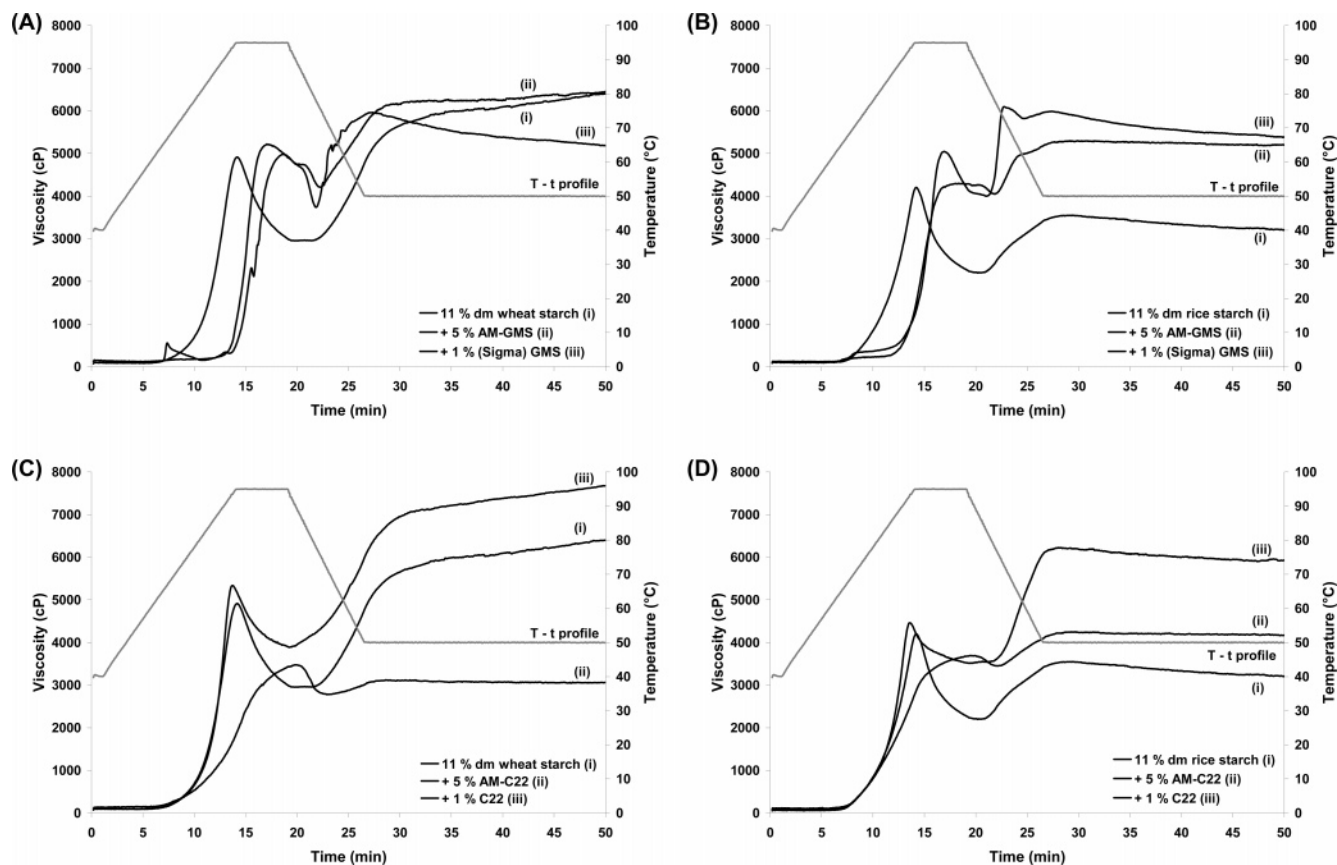


Figure 5. Wheat (A) and rice (B) starch pasting profiles when supplemented with (5%) semienzymically synthesized GMS complexes and the corresponding profiles when supplemented with (5%) semienzymically synthesized C22 complexes (wheat starch, C; rice starch, D).

liberated GMS subsequently complexes the leached amylose and delays swelling, although to a lesser extent due to its postponed release. In the case of C22 complexes, a similar controlled release of C22 is envisaged, in agreement with the complex dissociation temperature. However, we believe that C22 is released from the C22 complexes in a more easily “complexable physical state” as compared to the state in which C22 was added “as such” (cf. Rheological Behavior in the Presence of Lipids). Addition of C22 complexes increased PV and PT in comparison to the 1% C22 addition. Especially, the DP60-C22 complex had a remarkable effect on the viscosity of the wheat and rice starch pastes while stirring at 95 °C. Moreover, addition of potato phosphorylase-synthesized short chain AM-L complexes, namely, AM-GMS and AM-C22, resulted in effects on starch pasting similar to those observed for the DP60-C22 complex. The pasting profile of wheat and rice starches, supplemented in DP60-C22, AM-GMS, or AM-C22, resembles the pasting behavior of cross-linked starch. Cross-linking retards breakdown, and high levels of cross-linking inhibit granule swelling and reduce viscosity (23).

One factor that is expected to contribute to the difference in effects noted upon addition of either free lipid or AM-L complex addition is the higher probability to form type II AM-L complexes. Indeed, when only GMS is added, it melts at about the same temperature needed for amylose leaching from wheat or rice starch granules used in this study. A rapid complexation, yielding presumably type I AM-L complexes, occurs from roughly 55 to 65 °C onward. The formed complexes dissociate when higher temperatures (~95 °C) are reached and recomplex by cooling. When GMS captured in an AM-L complex is added, it is released at a much higher temperature, determined by the amylose DP. The liberated GMS may be able to form AM-L

complexes, but now, the probability to form type II AM-L complexes is larger as the temperature conditions are more favorable for type II complex formation. These complexes theoretically do not dissociate below 95 °C and, under the conditions of the RVA run, once formed, are permanently present in the paste. Apart from the formed (type II) AM-L complexes, amylose, liberated and noncomplexed lipid, non-dissociated originally added AM-L complexes, and starch granule remnants will be present in the starch paste at 95 °C. It can be hypothesized that the viscosity drop (upon cooling) is due to further complexation of the amylose and lipid and subsequent precipitation (Hoseney, personal communication).

As for C22, we believe that, in addition to the above-exposed hypothesis, the “physical state” of C22 is the predominant factor. It seems that, for C22 supplementation in these experimental conditions, the fatty acid is not in a favorable phase (at the right time) for complex formation. By addition of C22 in complex form, C22 is (while heating) released and apparently in a more favorable condition to form AM-L complexes than when added in its noncomplexed form. Because short chain AM-L complexes release proportionally more lipid and sooner, their effect is more striking. This is particularly in the case for DP60-C22, AM-GMS, and AM-C22.

Potato phosphorylase-catalyzed synthesis of AM-L complexes is a good alternative for preparation of large amounts of short chain AM-L complexes and study of their functionality in real food systems (e.g., breadmaking, pasta production, potato processing, etc.) to which nowadays emulsifiers are already added.

In conclusion, addition of AM-L complexes to wheat and rice starches markedly impacted starch pasting behavior. The pasting profiles could not be obtained by superimposing the

pasting profiles obtained for lipid (1%) and amylose fraction (5%) addition. This indicates the importance of the AM-L complex structure and properties. Indeed, it can be concluded that AM-L complexes release their “captured” lipids in a controlled way, in agreement with their dissociation temperature, and affect starch pasting from that moment on. In general, GMS complexes gradually delayed starch swelling as the dissociation temperature of the GMS complexes decreased. In the case of C22 complex addition, it was observed that C22 was—once the complex dissociation temperature was reached—released in a form that is easier to complex with the leaching amylose. In contrast, C22 addition as such to starch had little effect on starch swelling, PV, and PT. Short chain AM-L complexes stabilized the starch paste in high temperature and high shear conditions more than longer amylose complexes did. The pasting behavior for short chain AM-L complex additions resembled the pasting profile of (chemically) cross-linked starch. Potato phosphorylase-synthesized short chain AM-L complexes, namely, AM-GMS and AM-C22, resulted in similar effects, i.e., granule swelling was reduced, good viscosity stability in conditions of high temperature and shear (indicated by a broad pasting peak), and a stable CPV was obtained.

ABBREVIATIONS USED

AM-L, amylose–lipid; RVA, rapid visco analyzer; GMS, glyceryl monostearate; C22, docosanoic acid; DP, degree of polymerization; DSC, differential scanning calorimetry; PV, peak viscosity; PT, peak time; HPV, hot paste viscosity; CPV, cold paste viscosity.

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