Carbohydrate Polymers 93 (2013) 224–231

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Influence of lysophosphatidylcholine on the gelation of diluted wheat starch suspensions

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ARTICLE INFO

Article history:
Received 14 November 2011
Received in revised form 27 April 2012
Accepted 4 May 2012
Available online 11 May 2012

Keywords:
Amylose inclusion complex
Lysophosphatidylcholine
Gelatinization
Wheat starch granular structure
Water ingression
Thermal transition

ABSTRACT

Starch is an omnipresent constituent which is used for its nutritional and structuring properties. Recently concerns have been raised since starch is a source of readily available glucose which is tightly correlated with diabetes type II and obesity. For this reason, the possibilities for modulating the digestibility of starch while preserving its functional properties were investigated; therefore the focus of this paper is on starch gelatinization and the effect of lysophosphatidylcholine (LPC) on the structuring properties of wheat starch. The effect of LPC on thermal properties and viscosity behavior of starch suspensions was studied using DSC and RVA, respectively. The influence on granular structure was observed by light microscopy. The RVA profile demonstrated no viscosity increase at high LPC concentrations which proves intact granular structure after gelatinization. LPC in intermediate concentrations resulted in a notable delay of pasting; however the peak and end viscosities were influenced as well. Lower LPC concentrations demonstrated a higher peak viscosity as compared with pure starch suspensions. DSC results imply that inclusion complexes of amylose–LPC might be formed during pasting time. Since the viscosity profiles are changed by LPC addition, swelling power and solubility of starch granules are influenced as well. LPC hinders swelling power and solubility of starch granules which are stimulated by heating.

1. Introduction

Starch is the largest source of carbohydrates in human food. Starch is a key component of staple foods, such as wheat, rice and potato. Starch and starchy food products can be classified according to their digestibility, which is generally characterized by the rate and the duration of glycemic response (Singh, Dartois, & Kaur, 2010). The starch in staple foods has been implicated in the complications related to obesity and type II diabetes. It is specially the rate of enzymatic digestion of starch that is considered important. A fast rate leads to a rapid increase in postprandial blood glucose levels which is considered negative and a slow rate is recognized positive since this leads to lower metabolic stress. Predicting and controlling postprandial blood glucose levels is therefore of great interest in the context of worldwide health concerns.

Guraya, Kadan, and Champagne (1997) showed the higher resistance of amylose–lipid complexes to breakdown by human α-amylase. They were able to reduce digestibility by 41.6% after amylose–emulsifier complexation in non-waxy starch. Within another study by Holm, Björck, Ostrowska, and Eliasson (1983), the complexed amylose with lysolecithin was exposed to pancreatic α-amylase that displayed a substantially reduced susceptibility to α-amylase *in vitro* digestion. Their *in vivo* study demonstrated slower rate of amylose digestion after inclusion complexation. At the same time, starch is widely used in food products for its structure forming properties. Putseys, Lamberts, and Delcour (2010) demonstrated the impact of different concentrations of emulsifiers on pasting and gelation of starch. They assume that emulsifiers are absorbed by starch granules at the surface and water ingression is suppressed which results in less viscosity growth. This prompted us to study if starch digestibility can be decoupled from its structure forming properties. This study represents a first step to investigate if and how functional and structuring properties of wheat starch can be combined with a slower digestibility after amylose inclusion complexation.

Three events occur during conventional time-temperature processing of starch: swelling, gelatinization as well as retrogradation which the last occurs after processing. All are results of starch–water interactions (Ito, Hasegawa, Adachi, Kojima, & Yamada, 2004). As starch molecules are associated by hydrogen bonding, water penetrates inside the starch granules while heating, driven by differences in osmotic pressure, leading to disruption

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http://dx.doi.org/10.1016/j.carbpol.2012.05.020

of the intra-chain and inter-chain hydrogen bonds. In the more amorphous areas, in which the molecules are not as closely associated, progressive hydration and swelling will occur more rapidly. In addition, linear amylose molecules are released into solution (Christianson, Hodge, Osborne, & Detroy, 1981). Hydrogen bonding forces in wheat starch granules weaken at two stages of swelling. The first stage occurs at 55–77 °C. At 55 °C pasting starts and between 60 and 65 °C the granules lose their crystallinity so that they swell more. In the second stage, the first large increase in viscosity is observed when gelatinization occurs. Gelatinization is an irreversible physical change. At this stage, amylose is leached from the granules and enters the aqueous phase (Svensson & Eliasson, 1995). On cooling, the starch chains (mainly amylose) in the gelatinized paste tend to associate, leading to the formation of a more ordered structure which is termed retrogradation (Hoover, 1995).

Amylose in a helical conformation has the ability to form inclusion complexes with components like fatty acids and phospholipids (Putseys et al., 2010). This so-called V-complex is formed between the aliphatic chains of lipids and the amylose.

Lysophosphatidylcholine (LPC) is widely used in food products as surfactant to improve the functional properties of foods; e.g. in starch containing foods it complexes with the amylose helix and retards retrogradation. The formation of an amylose–LPC inclusion complex causes a transition in the amylose molecular structure from coil to helix which results in an increase in the order of the molecular structure of amylose (visible as the V-type X-ray diffraction pattern) as well as less amylose leakage during processing (Toro-Vazquez et al., 2003). The length of the fatty acid chains of LPC is an influencing factor on amylose inclusion complexation. Shorter fatty acid chains suppress amylose leaching more effectively, due to better accommodation into the amylose helix (Siswoyo & Morita, 2003a, 2003b).

In addition, the complexed amylose with LPC is hardly hydrolyzed by α-amylase (Siswoyo & Morita, 2003a, 2003b). Frei, Siddhuraju, and Becker (2003) reported the lower glycemic response of high amylose rice cultivars after addition of phospholipids that was attributed to reduced enzyme susceptibility after the formation of complexes between amylose and phospholipids upon heating.

Previous studies have demonstrated the complex formation of LPC and amylose (Toro-Vazquez et al., 2003), although the effect on the functional properties of starch has not been adequately discussed. In addition, inclusion of LPC into the amylose helix can delay enzymatic degradation. The current study evaluates the influence of LPC on the structuring properties of wheat starch and aims to benefit from the amylose–LPC complexation while preserving these properties. For this reason, several methodologies were employed to relate the functionality of LPC in several concentrations to the alteration of structuring properties of the wheat starch. This is a precise look to figure out the formation of amylose inclusion complexes with LPC, while LPC is added at the starting point of the process, to allow the complexation at each possible point of time and thermal condition. That propels the applicability of the study in the practical fields. In this paper, the focus is on the temperature that induces changes in starch and how amylose–LPC inclusion complexation influences the physical and technologically relevant functionality of wheat starch such as viscosity.

2. Materials and methods

2.1. Materials

Egg yolk L-α-lysophosphatidylcholine (LPC), type XVI-E, lyophilized powder, purity >99% and fatty acid content of 16:0 69%, 18:0 27% and 18:1 3%, from Sigma Chemical Company (St. Louis, MO, USA) was used.

Unmodified wheat starch with a purity of 99%, a moisture content of 12.98%, a total lipid content of 0.4% and 2.8% damaged granules was obtained from Sigma Chemical Company as well.

LPC was kept at −20 °C and wheat starch at room temperature under dark and dry conditions.

Lugol, as iodine solution to stain starch granules was purchased from Sigma Chemical Company.

GOPOD (glucose oxidase peroxidase) was purchased from Megazyme. The kit includes reagent buffer (potassium phosphate buffer, p-hydroxybenzoic acid and sodium azide), reagent enzyme (glucose oxidase plus peroxidase and 4-aminoantipyrine) and D-glucose standard solution (in benzoic acid).

All other used reagents were of analytical grade or better.

2.2. Viscosity measurement

A RVA-4 Newport Scientific (NSW, Australia) Rapid Visco Analyzer was employed to study the temperature-viscosity profile of the starch suspensions used in this study.

A series of 9% (w/w) wheat starch suspensions in deionized water was prepared by mixing starch with 0.1%, 0.3%, 0.5%, 1% and 5% LPC (based on dry matter (DM) wheat starch). The suspensions were kept 10 min at room temperature to equilibrate. The temperature of each suspension was first equilibrated at 50 °C for 60 s, increased to 95 °C at a rate of 6 °C/min, and held at 95 °C for 300 s, decreased to 50 °C at the same rate and finally held at 50 °C for 120 s. The reference (pure starch) was subjected to the same temperature gradient.

2.3. Light microscopy observation

0.1%, 0.3%, 0.5% and 1% LPC (based on DM wheat starch) was added to 9% (w/w) wheat starch suspension in deionized water. Each suspension was processed by RVA to create the same temperature profile as described earlier. At 50 °C, 60 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, 90 °C, 95 °C as well as at the end of the temperature profile (50 °C) samples were taken, diluted with distilled water to obtain 0.5% suspension and stained with 50 μL iodine solution. Starch granules were observed under bright-field illumination with a Nikon light microscope (Nikon, Eclipse 400, NY, USA) using 10× objective lens. Images were captured with a high resolution color camera (Nikon, COOLPIX 4500, MDC Lens, Japan).

Any changes in starch crystallinity at 50 °C, 60 °C and 65 °C were observed by light microscopy under polarized light.

2.4. Swelling power

Swelling power was determined in duplicate (according to Steeneken and Woortman (2009) with some modifications) using 0.5%, 1%, 2%, 3% and 5% LPC (based on DM starch) in diluted starch suspensions. A series of 8 mL wheat starch suspensions in deionized water (3–8%, w/w, depending on starch weight and LPC concentration) were prepared and heated at 70 °C, 80 °C, 90 °C and 95 °C in a ventilation oven for 45 min while rotating. Then the mixture was separated by 15 min centrifugation at 1000 rpm. The supernatant height was measured in mm where the Q (Swelling Power based on the volume of precipitated particles) was determined.

2.5. Soluble starch measurement

During swelling and gelatinization, especially linear amylose becomes soluble and may leak from the granules. This was followed by measuring the amount of soluble starch (SS). SS was determined (Megazyme Resistant Starch Assay Procedure, K-RSTAR

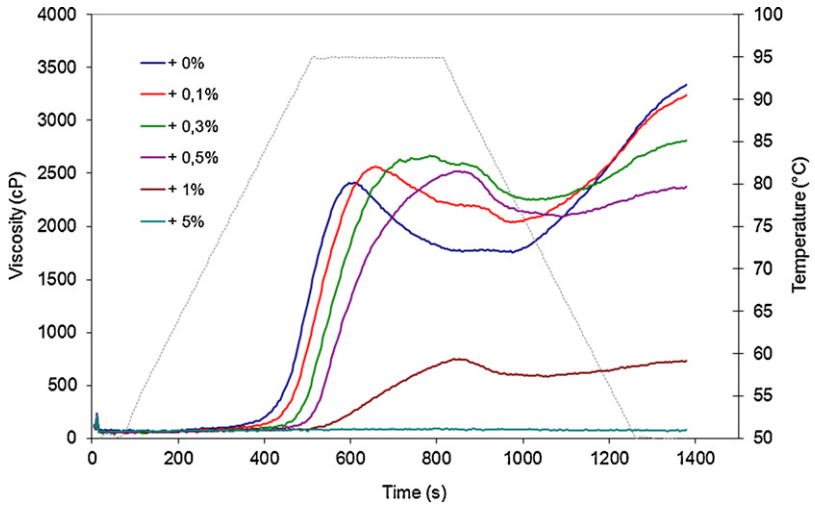

Fig. 1. Effect of different concentrations of LPC on pasting time and viscosity behavior of 9% wheat starch suspension. Viscosity is plotted on the left axis against time. The temperature profile is represented by the dotted line. Different colors represent different LPC additions (see insert).

08/05, based on AACC Method 32-40) in duplicate using 0.5%, 1%, 2%, 3% and 5% LPC (based on DM starch) in diluted starch suspensions. A series of 8 mL wheat starch suspensions in deionized water (1.5–4%, w/w, depending on starch weight and LPC concentration) were prepared and heated at 70 °C, 80 °C, 90 °C and 95 °C in a ventilation oven for 45 min while rotating. The mixture was separated into the supernatant and the precipitate by centrifugation at 1000 rpm for 15 min. The supernatant was centrifuged for 15 min at 16,000 rpm. 1 mL diluted amyloglucosidase (AMG) was added to 1 mL of the supernatant to convert amylose into glucose. After 16 h of incubation at 55 °C, the enzyme was inactivated by heating the mixture to 100 °C for 30 min. Then, 3 mL glucose oxidase peroxidase (GOPOD) was added to 100 μL of sample and incubated for 20 min in a water bath at 50 °C to stain the glucose. The absorbance was read at 510 nm using a Spectramax spectrophotometer (Spectramax M2 Dual Mode C, Molecular Devices, Virginia, USA). 100 μL D-glucose standard was mixed with 3 mL GOPOD and used as a reference. A diluted wheat starch suspension without LPC was taken as a blank sample. Absorbance values were corrected for the absorbance of the enzyme solution. Finally, solubility was calculated from the carbohydrate concentration of the known amount of the supernatant solution, as measured by the swelling power method with GOPOD, after centrifugation at 16,000 rpm. Soluble starch is expressed as a weight fraction on a dry basis.

2.6. Thermal analysis

A series of 20% (w/w) wheat starch suspensions in deionized water was prepared by mixing starch with 0%, 0.5%, 1%, 2%, 3% and 5% LPC (based on DM wheat starch). Samples were rotated an hour at 50 rpm at ambient temperature. The suspension was pipetted into stainless steel pans (Perkin Elmer, Norwalk, CT, USA) which were sealed afterwards. Samples were analyzed by Perkin Elmer Pyris 1 DSC (Norwalk, CT, USA) previously calibrated with indium (melting temperature = 156.6 °C, melting heat = 28.45 J/g). The baseline from 20 °C to 120 °C was obtained with an empty pan as reference as well as sample pan. The heating rate was 10 °C/min. The onset (T_o), peak (T_p) and ending (T_e) temperatures for the different transitions were determined and calculated by DSC software. Enthalpy (ΔH, J/g of sample) for the different transitions was calculated based on the endothermic peaks. The samples were compared with a wheat starch reference suspension. All samples were measured in duplicate.

3. Results

3.1. Effect of LPC on pasting time and viscosity

The RVA measurements show that LPC alters the viscosity behavior of starch suspensions depending on its concentrations. At 5% LPC, the viscosity profile is linear and no increase was observed (see Fig. 1).

At lower LPC additions, the effect is less pronounced. At 1% LPC, viscosity increases slightly and at 0.5% and lower, swelling is just delayed but not hindered as at the higher concentrations. Pasting temperatures were registered at 350 s, 400 s and 450 s for 0.1%, 0.3% and 0.5% LPC concentration, respectively, comparing with the reference at 300 s. Starch suspensions with 1% LPC demonstrated an onset temperature at 500 s and a very low peak viscosity (750 cP), compared to the lower concentrations.

Addition of LPC in different concentrations also resulted in markedly lower end viscosities, in comparison with the reference.

3.2. Swelling power

The swelling power of starch depends on the water-holding capacity of starch molecules by hydrogen bonding (Sasaki & Matsuki, 1998).

Swelling power of 9% starch suspensions were measured after addition of 0.5%, 1%, 2%, 3% and 5% LPC in starch suspensions heated to 70 °C, 80 °C, 90 °C and 95 °C.

Without addition of LPC, starch swelling clearly increases with temperature (see Fig. 2). It becomes obvious that addition of LPC limits swelling. Lower values were observed at higher concentrations of LPC but in none of the studied LPC concentrations swelling is inhibited completely. The influence of LPC is clearly depended to the added amount. No further increase in inhibition at concentration higher than 3% was found.

3.3. Soluble starch measurement

The amount of water soluble starch, expressed as the amount of leached amylose, is an index to indicate the solubility of the macromolecular starch components. The influence of temperature and the addition of 0.5%, 1%, 2%, 3% and 5% LPC on the solubility index of wheat starch at 70 °C up to 95 °C were studied. The results were compared with the reference.

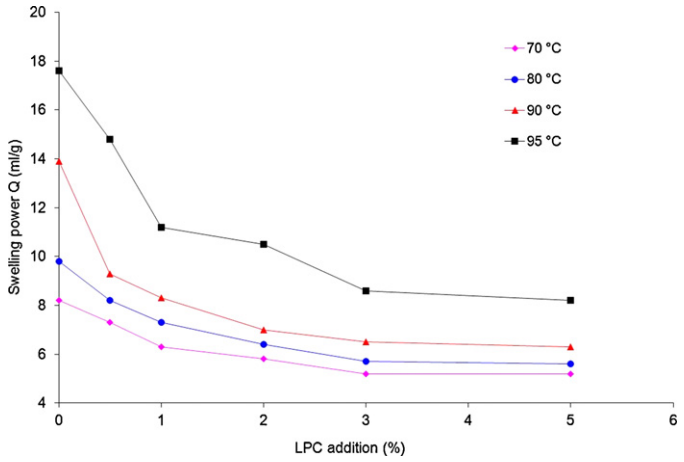

Fig. 2. Swelling power alteration of wheat starch at 70–95 °C while increasing LPC concentration. Q represents swelling power that is plotted on the left axis. Different colors represent different temperatures.

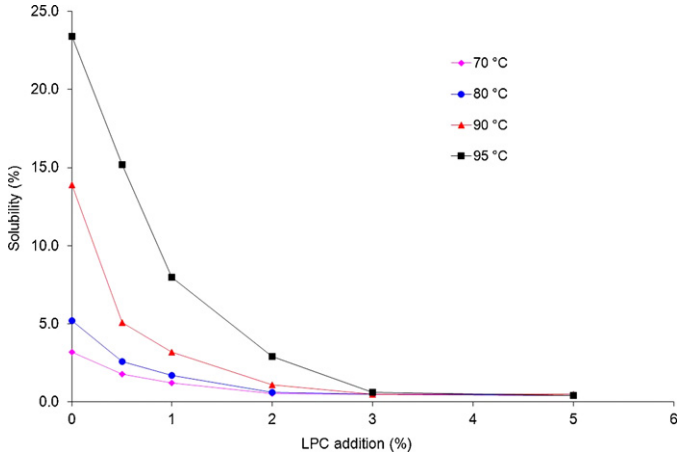

Fig. 3. Solubility values in wheat starch suspension at 70–95 °C while increasing LPC concentration. Solubility is plotted on the left axis based on percentage. Different colors represent different temperatures.

Both amylose and amylopectin are insoluble in cold water. Fig. 3 clearly shows that in the absence of LPC the solubility increases when starch suspensions are heated. It becomes clear that the leakage is suppressed by addition of LPC although starch suspensions were subjected to high temperatures. The highest effect was observed while addition of highest concentration of LPC. As in the case of swelling power (see above), addition of 3% and 5% LPC resulted in about the same effect; indicating that the maximal effect is reached at 3%.

3.4. Light microscopy

3.4.1. Iodine staining

Starch granules typically swell upon heating in the presence of water, leading to a loss of granule integrity. The effect of LPC addition on granular shape at different temperatures was studied. The starch granules were observed by light microscopy after iodine staining. Light microscopy images of wheat starch granules after addition of 0.3%, 0.5% and 1% LPC heated at 50–95 °C as well as 50 °C (the end point of RVA profile) are depicted in Fig. 4. Images at 50 °C are not shown since the granules have quite similar appearance and in all cases appear unchanged compared to the control.

In pure starch suspension, gelatinization starts at 60 °C (see Fig. 4). At about 70 °C, amylose begins to leach out, therefore some starch fragments, due to amylose leaching, are observed. Blue color, as an indicator, mainly appears due to amylose–iodine complexation. Less blue color indicates a high amount of leached amylose. The process continues with swelling and change of granular shape at 80 °C. The granules clearly become fragmented above 90 °C in which blue color is rarely seen.

The influence of LPC on granular shape is very much pronounced at high concentrations. After addition of 1% LPC, intact granules can be observed even at the end of RVA profile (see Fig. 4, fourth row). Fig. 4 at second and third rows demonstrates the influence of LPC after addition at moderate concentrations which results in low granular collapse and limited rupture. The influence of LPC on granular shape is not very pronounced at lower concentrations (0.3% and 0.5%) as amylose leakage was to some extent hindered. It can be seen also by the results which were presented above in swelling power measurement.

3.4.2. Loss of birefringence

Starch granules display birefringence upon exposure to polarized light, thus indicating the presence of crystalline regions within the starch granular matrix. Upon heating birefringence is lost due to the melting of these regions (Riley, Wheatley, & Asemota, 2006).

To study the effect of LPC on the crystalline region of starch granules, we therefore studied the birefringence loss of starch granules by polarized light (light microscopy).

Fig. 5 shows the light microscopic images of starch granules without and with 0.5% and 2% LPC demonstrating the effect of LPC on changes in starch crystallinity. It is clearly shown that the birefringence has disappeared at 65 °C. Interestingly this behavior is not affected by the addition of LPC.

3.5. Effect of LPC on thermal transition of starch

Heating starch suspension in DSC leads to two transitions (see Fig. 6); the first is related to the loss of the internal starch structure and the second is related to the presence and melting of amylose–LPC complexes (existing in starch granules or formed by the added LPC: 0.5%, 1%, 2%, 3% and 5%).

For pure starch, the first transition starts at 60 °C (Fig. 6) and results in an enthalpy of 17.6 J/g and the second transition starts at 100 °C and results in an enthalpy of 1.8 J/g.

Addition of LPC does not affect the initial transition temperatures, however the peak height and enthalpy of the second transition (melting of the amylose–LPC inclusion complex) increases with addition of LPC (see Fig. 6 and Table 1). Higher amounts of LPC lead to lower enthalpy of the first transition and higher peak height and enthalpy of the second transition.

4. Discussion

Starch is omnipresent in foods for two reasons. Starch is a main source of carbohydrates and is also an efficient structure builder. From a nutritional point of view, it is of interest to slow down the rate of starch digestion. This can be achieved by the addition of LPC, forming amylose V complexes that are reported to be more difficult to digest (Guraya et al., 1997; Holm et al., 1983). It is not known, however, to what extent this can be used without harming the structuring properties of starch. For this reason, the focus of this research was to systematically study the effect of LPC on the thermal transition of starch and resulting properties. To this end, different levels of LPC for complex with amylose were induced. The results show that the complex formation is dependent on LPC concentration and leads to alteration of viscosity profile in the RVA, less swelling and better preservation of granule integrity due to less amylose leakage.

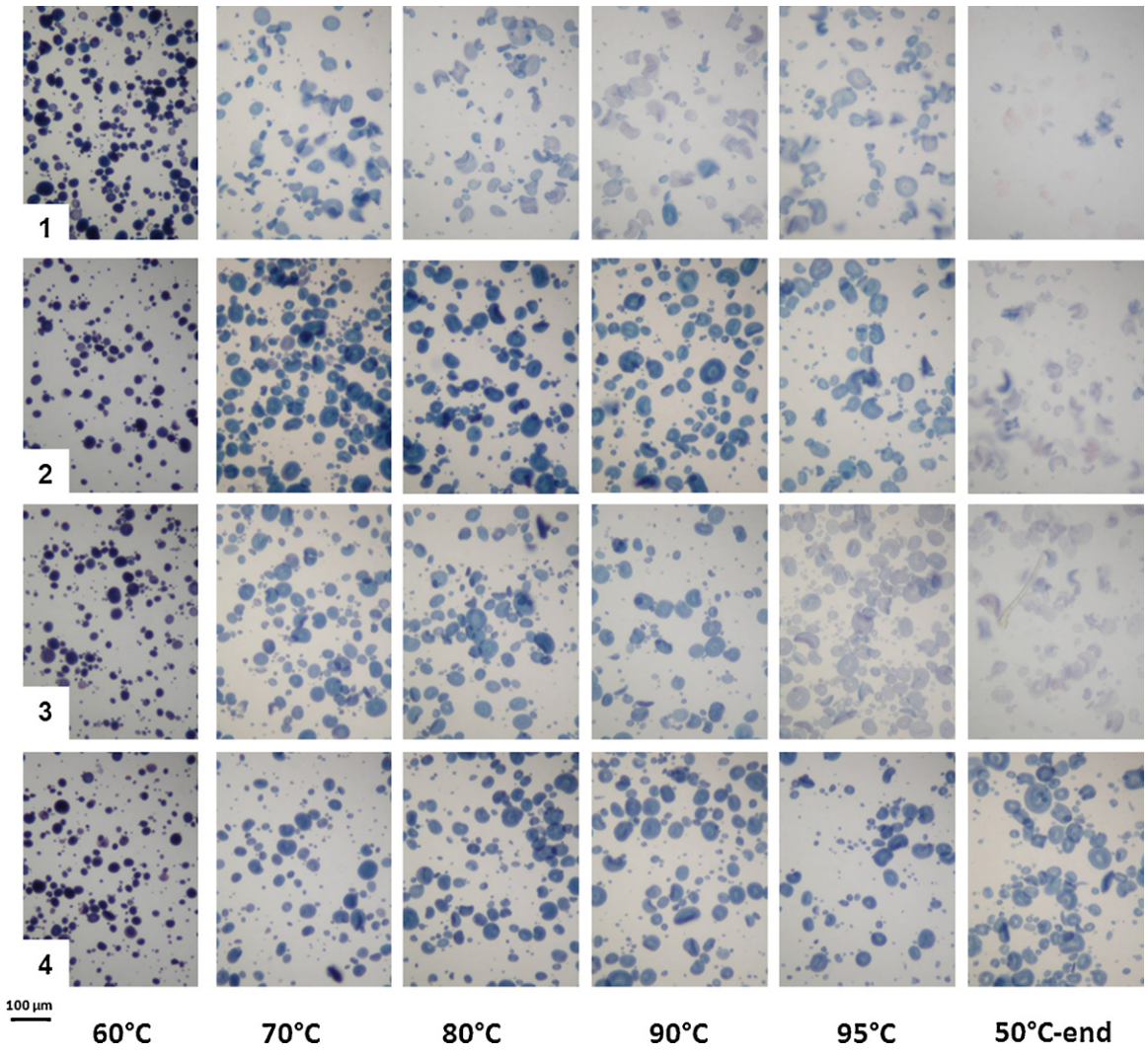

Fig. 4. Stained wheat starch (WS) granules with iodine under light microscope at temperatures between 60 °C and 95 °C as well as 50 °C at end of viscosity profile. Row "1": WS (reference), Row "2": WS + 0.3% LPC, Row "3": WS + 0.5% LPC, Row "4": WS + 1% LPC. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

Studying the influence of LPC at different thermal transitions of starch gives an insight into the mechanisms that occur during processing and result in alterations in the physical and functional properties of starch.

LPC addition at high concentration prevents viscosity increase during RVA measurement, indicating limitation of water absorption by starch granules and therefore swelling is restricted. When water absorption is limited, granular dimensions remain almost with no change; therefore a viscosity increase is not observed.

At lower LPC concentrations, water ingression is less influenced by LPC. 1% LPC blocks only part of the starch to swell. At 0.5% LPC and lower, water absorption and swelling accordingly are delayed but not hindered as was observed at higher concentrations.

Addition of LPC at different concentrations also resulted in lower final viscosity compared with the reference. More LPC leads to lower end viscosity. This is in agreement with the results obtained by Putseys, Lamberts, et al. (2010). They reported that the presence of emulsifier resulted in a weaker and less structured network in the early cooling phase that is less shear resistant than the control. Moreover, the leached amylose chains are involved in complex formation with emulsifier and only small amylose fractions can form amylose double helices. Therefore, network formation occurs to a lesser extent than in the absence of emulsifier. Conde-Petit and Escher (1995) also reported the formation of junction zones (as physical cross-link) in a network between granules due to leached amylose inclusion complexation with emulsifiers.

During swelling, amylose leaches from the granules. This is one of the processes involved in gelatinization (BeMiller & Whistler, 2009, chap. 6). Upon further heating, water uptake and swelling continue, the viscosity of starch suspension further increases until a maximum of viscosity (T_p). At this point granules rupture and break down into starch fragments which results in a viscosity decrease. The shear forces throughout the RVA process disrupt the formed starch gel. In the third phase, viscosity increases again upon cooling which marks the beginning of amylose retrogradation. Therefore, our results show that LPC is absorbed by the granules before reaching the gelatinization temperature and forms rather stable inclusion complexes with amylose inside the granule. This complexation successively hinders water uptake, represses amylose leaching and therefore swelling is limited. Hence, alteration in viscosity behavior depends on the degree of inclusion complex formation that correlates with the ratio of ligand to the existing amylose helices.

We think that starch granules become too rigid to swell when LPC is present at high concentration in the suspension and the amylose leakage is less accordingly, as was already discussed by Putseys et al. (2010).

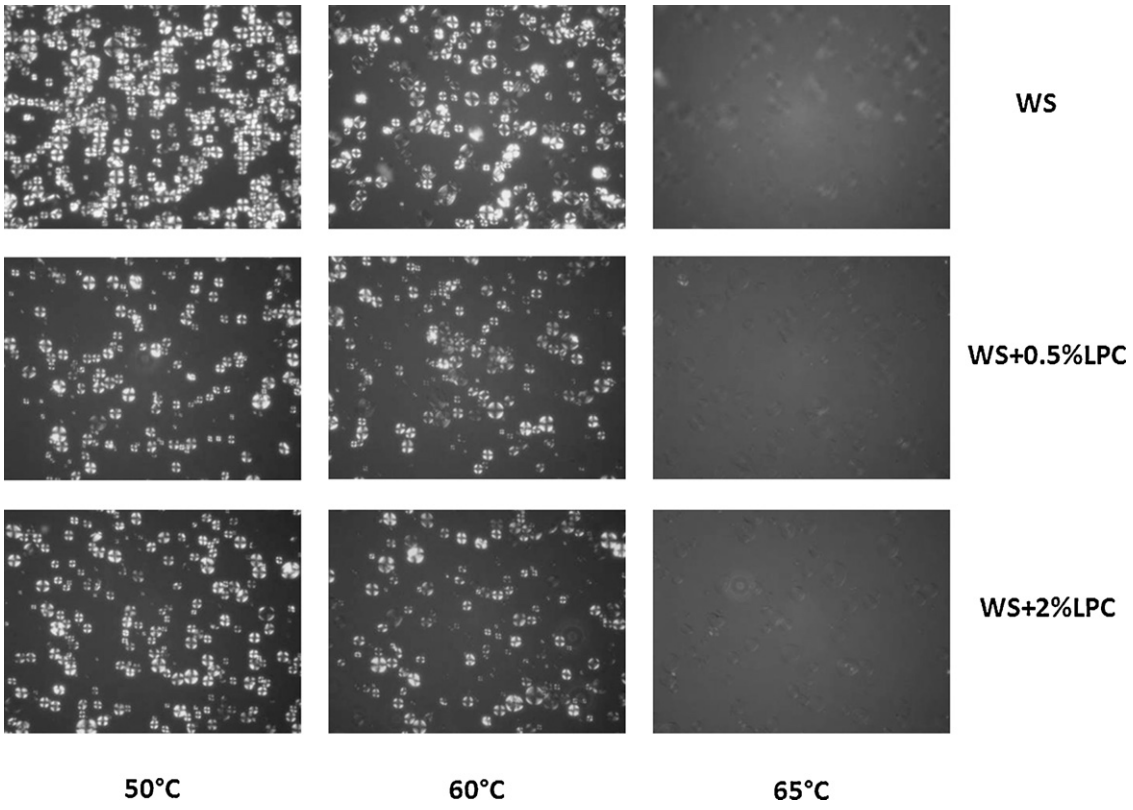

Fig. 5. Polarized light microscope images showing loss of birefringence at 50–65 °C in 9% wheat starch (WS) suspension. First row presents the reference, second: WS + 0.5% LPC, third: WS + 2% LPC.

The efficient role of LPC in preventing swelling was also illustrated by our microscopy images. This effect is more prominent at higher LPC concentrations. We observed no rupture after addition of 1% LPC, even at 60 °C.

Richardson, Langton, Bark, and Hermansson (2003) observed a non-stained bright area around some of the granules by CLSM while addition of emulsifiers at high concentrations and low temperatures. The layer acts as a protective layer around the granules to slow down water transportation. In addition, Putseys, Lamberts, et al. (2010) reported that the lipids form a layer surrounding the granules which results in less amylose leakage. Eliasson, Larsson, and Miezis (1981) also observed a lower degree of disruption of starch granules when the amount of lipids present on the surface increases.

We observed no alteration in the temperature of birefringence loss. LPC even at high concentrations does not prevent the crystallinity loss. It becomes obvious that LPC does not interfere with the change in crystallinity order within the starch granules. The DSC results also show that the crystalline regions of the starch granules are not affected by the addition of LPC; as no difference in the onset of the first endotherm in comparison with the reference was observed.

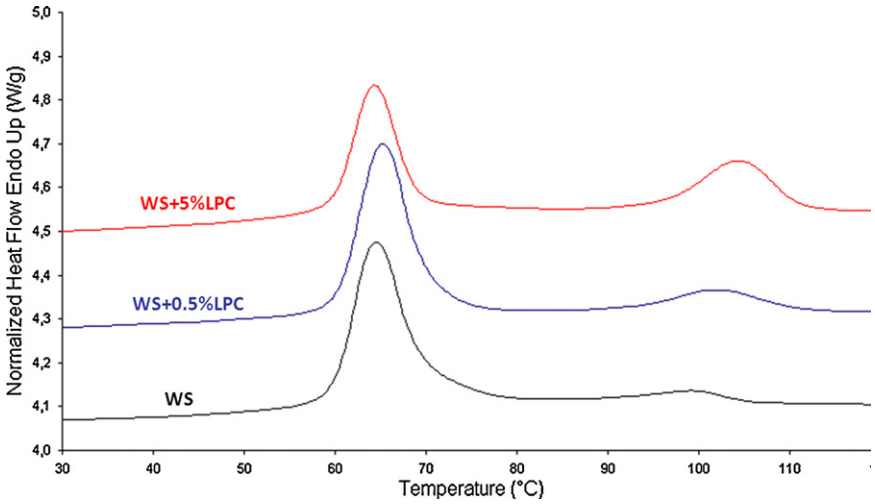

Fig. 6. DSC thermograms showing thermal properties of 20% wheat starch suspension and effect of 0.5% and 5% LPC (based on wheat starch) on the thermal transition. Heat flow is plotted on the left axis. Different colors represent the wheat starch suspensions with different LPC addition comparing to the reference. WS stands for wheat starch and LPC for lysophosphatidylcholine.

Table 1
Thermal analysis of 20% wheat starch–LPC suspension with different LPC concentrations (based on starch) comparing with the reference. WS stands for wheat starch and LPC for lysophosphatidylcholine.

Samples	Starch				Amylose-LPC		
	Onset (°C)	Peak (°C)	ΔH (J/g)	ΔY (W/g)	Peak (°C)	ΔH (J/g)	ΔY (W/g)
WS suspension	59.7	64.6	17.6	0.42	100.0	1.8	0.03
WS + 0.5% LPC	60.3	65.4	16.7	0.38	101.9	3.2	0.05
WS + 1% LPC	59.7	64.6	16.4	0.36	102.6	4.3	0.06
WS + 2% LPC	60.0	64.8	14.0	0.31	103.8	5.7	0.08
WS + 3% LPC	59.7	64.4	13.6	0.30	104.5	6.4	0.10
WS + 5% LPC	59.8	64.4	12.2	0.30	104.4	6.6	0.11

LPC addition resulted in a lower enthalpy of the first endotherm and a higher enthalpy of the second endotherm in DSC scan. The second endotherm is a direct indication that inclusion complexes with amylose are formed. A higher enthalpy of the second endotherm upon LPC addition clearly proves that more inclusion complexes are formed with a higher amount of LPC. As the complex formation is an exothermic transition, this also results in a lower enthalpy of the first endotherm. Our results are in accordance with Biliaderis and Tonogai (1991) who have observed the reduction of the enthalpy in the first endotherm due to complex formation of amylose with LPC as well. They have also stated that not only amylose but also the longer linear chains of amylopectin interact with LPC. These endothermic transitions were furthermore reported by Yamashita et al. (2001) in complexation of wheat starch and lysophospholipid and by Siswoyo and Morita (2003a, 2003b) in complexation of defatted wheat starch with mono and diacyl-*sn*-glycerophosphatidylcholine as well.

Water content and the amount of present ligand influence the rate of amylose inclusion complexation. Eliasson (1980) stated that the onset temperature and enthalpy of the first endotherm vary with water content and later on, Eliasson et al. (1981) reported that at low water content, the gelatinization enthalpy and the gelatinization temperature are not influenced by the presence of lipids. Jovanovich, Zamponi, Lupano, and Anon (1992) demonstrated that at water content of 36–64%, lower moisture results in lower enthalpy and higher onset temperature of the first endotherm; therefore amylose–lipid inclusion complexation forms later.

Our starch suspensions were scanned with different amount of LPC at high water content (above 80%). We did not observe any shift in onset temperature of the first endotherm influenced by the amount of LPC at high water content.

We suppose that LPC has no influence on water ingression before the crystallinity loss but later in the process, amylose helices have more liberty to move and contribute in the complex formation with LPC. A difference in osmotic pressure leads to water ingression which is a function of the number of soluble molecules. This number would decrease when amylose–LPC complexes are formed. We hypothesize that a reduction in osmotic pressure is driven by this phenomenon and consequently that reduction of water uptake suppresses amylose leakage and swelling. Hernandez-Hernandez et al. (2011) stated that during the starch gelatinization, amylose tends to leach as consequence of osmotic pressure and water ingression; therefore approaches the external layers of the granule that there meets LPC that exists in the water phase. A protective barrier is constituted by the formed complexes which prevents rapid granule hydration. They believed that this barrier increases thermal stability of the granules and allows the granular morphology to remain intact even above gelatinization temperatures. Putseys et al. (2010) also reported a layer formation around the granules, after amylose–lipid inclusion complexation that diminishes the entry of water. However, in situ complexation between amylose and lipids, either at the surface or inside the granules, lessens amylose leaching (Putseys, Lamberts, et al., 2010).

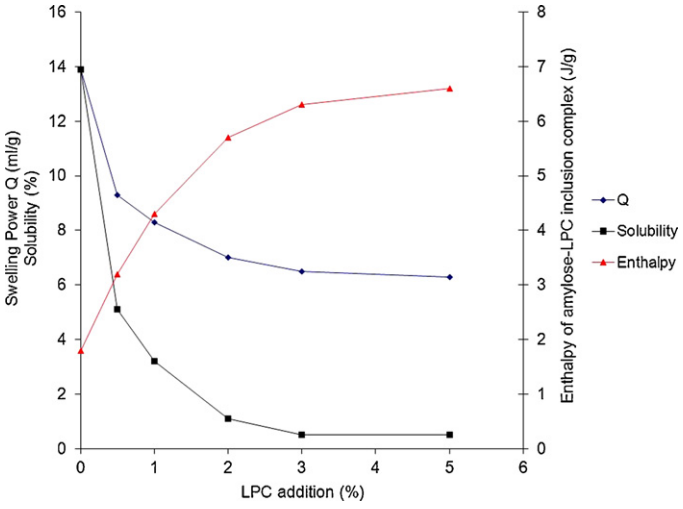

Fig. 7. Swelling power and solubility alteration at 90 °C while enthalpy increase in the second transition (due to amylose–LPC inclusion complexes). Swelling power and solubility are plotted on the left axis against enthalpy. Different points represent different LPC additions.

The swelling power of starch granules and the amount of water soluble starch were substantially inhibited by addition of LPC. Heating enhances water penetration into the granules and amylose leakage into the solution accordingly. The dynamic role of temperature is well-known in weakening the intragranular binding forces of starch to accelerate leaching of amylose, which leads to an increase in solubility. By addition of LPC to starch suspensions and formation of amylose–LPC inclusion complexes, amylose does not easily leach out. In addition the crystalline arrangement of amylopectin prevents the easy penetration of water into the granules by contributing its longer chains in inclusion complexation (Putseys et al., 2010). These two phenomena limit solubility due to less amylose leakage and swelling, as a consequence of less water absorption by amylopectin. The observed decreased swelling and solubility by a higher amount of LPC is therefore again a direct indication for the enhanced amylose–LPC complex formation.

Fig. 7 combines the discussed results on the influence of LPC on granular properties of wheat starch at 90 °C. It is clear higher amounts of LPC result in less solubility and swelling power and a higher enthalpy of the second endotherm (melting of the amylose–LPC inclusion complexes). These results suggest that with a higher amount of LPC more amylose–LPC inclusion complexes are formed.

Our results clearly indicate the influence of LPC on swelling power and solubility based on amylose–LPC complex formation. LPC slips into the amylose helices and forms inclusion complexation. Furthermore, amylose–LPC inclusion complexation on the granule surface reduces water mobility inside granule hence results in swelling reduction.

5. Conclusion

This study describes the effects of LPC at different concentrations on pasting time, gelatinization, granular structure, amylose leakage and thermal transition of wheat starch.

Amylose–LPC complexation has an extensive influence on structuring properties of wheat starch. No viscosity increase due to less swelling, reduced rupture and thus limited amylose leakage was reported as consequences of LPC addition at high concentrations to a diluted wheat starch suspension.

At lower concentrations, its influences are moderate while retaining the starch functionalities.

From the structuring point of view, concentrations higher than 1% are unacceptable. At these levels, starch can no longer be used as a structure builder. However at LPC concentrations of around 0.5%, amylose–LPC complexes form and amylose leakage is largely prevented leading to less granular rupture.

Low digestibility of amylose–LPC complexes by enzymes comparing with amorphous amylose can be regarded as slow starch; however the effect on amylopectin is still unclear. The effect on starch digestibility will be subject of our future study.

Acknowledgments

This study was funded by the Top Institute of Food & Nutrition and the University of Groningen. We thank TNO Quality of life for granting us access to the RVA instrument.

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