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Influence of lysophosphatidylcholine on the gelation of diluted wheat starch suspensions

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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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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