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Water and temperature contribution to the structuration of starch matrices in the presence of flavour

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ABSTRACT

The effect of modulating the gelatinisation extent by hydration (50/50 and 80/20 water to starch ratio) and temperature (65 or 85 °C) on various properties of wheat starch in presence of flavours has been studied. The hydrothermal treatments resulted in samples with different properties. The lowest residual flavour content was found in samples treated at the highest hydration and temperature (85 °C) while the other treatment conditions led to samples with similar residual flavour content. Ethyl hexanoate significantly increased the characteristic pasting viscosities compared to starch ± 2-hexanone; suggesting a greater structuration with ethyl hexanoate. Heating starch in excess water caused amylopectin melting, but promoted an incomplete granular swelling as revealed by RVA. This study suggested that lowering the hydration upon treatment could limit both crystal melting (with a residual crystalline content up to 38% in the most extreme conditions) and granular swelling but increased granule organisation like following annealing.

1. Introduction

The structure and property of starch can be altered upon hydrothermal treatment induced in excess water, this phenomenon is well recognised as gelatinisation which is an irreversible order–disorder transition (Jenkins & Donald, 1998; Ratnayake, Jackson, & Steve, 2008, chap. 5; Tester & Debon, 2000). However, it is crucial to distinguish the types of hydrothermal treatments that can be applied to starch because their effects on starch structure depend on their temperature range, water-ratio and duration (Tester & Debon, 2000; Tester, Debon, & Karkalas, 1998). The term "heat–moisture treatment" is usually referred to high temperature (90–120 °C) processing and strictly applied at very low moisture content (10–30%) (Biliaderis, 2009; Tester & Debon, 2000; Zavareze & Dias, 2011). Another important phenomenon which may take place in heat-hydrated starch is "annealing." Annealing strongly associates with gelatinisation and affects gelatinisation properties (temperature and enthalpy). It refers to the application of a temperature treatment below gelatinisation temperature together with a hydration at intermediate up to excess level (40–55% to >60%) (Tester & Debon, 2000). Annealing is associated with partial gelatinisation and leads to an elevation of starch gelatinisation temperature (Tester & Debon, 2000).

Starch gelatinisation is defined as "the collapse (disruption of molecular order within the starch granule manifested in irreversible changes in properties such as granular swelling) native crystallite melting, loss of birefringence, and starch solubilisation" (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988). Wheat starch granules begin to swell at 45–50 °C and continue up to 85 °C, and then lose their birefringence. At 50–55 °C, the enthalpy changes attributed to dissociation of crystalline clusters dramatically decrease, while those attributed to double helices dissociation are observed at 55–60 °C (Tester & Morrison, 1990). The gelatinisation temperature is sensitive to the dry matter content of the starch suspensions: the higher the starch content, the higher the gelatinisation temperature (Rolée & Le Meste, 1999).

Although Atwell's definition (Atwell et al., 1988) limits "pasting" to "the phenomenon following gelatinisation in the dissolution of starch": through granular swelling, amylose leaching and granules disruption, the term "pasting" is usually associated with the general rheological behaviour of starch suspensions upon

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heating. The presence of partially or fully swollen starch granules is a crucial parameter for the rheological behaviour of the paste or resulting since it influences the final texture. The extent of starch swelling is strongly correlated with the leaching of polysaccharides which finally reflects the property of starch paste.

Considering flavour interactions in food, two types have been mainly extensively described in the literature as attractive and repulsive. Attraction is a binding of volatile compounds on a non-volatile substrate while repulsive is a release (Le Thanh, Thibeaudeau, Thibaut, & Voilley, 1992). There are three physical chemistry approaches to understand flavour interactions in food systems. The first one is the characterisation of flavour molecules partitioning between phases. The second is the analysis of the transport mechanisms where the flavours compounds are carried to food matrices via diffusion or other transport means. The last one is the study of flavour molecule binding to food component (Taylor, 1998).

The structure of starch allows it to have two different types of binding: flavour inclusion complexes and polar interactions (Arvisenet, Le Bail, Voilley, & Cayot, 2002; Boutboul, Giampaoli, Feigenbaum, & Ducruet, 2002; Conde-Petit, Escher, & Nuessli, 2006; Nuessli, Conde-Petit, Trommsdorff, & Escher, 1995). Conde-Petit et al. (2006) described flavour binding through two types: non-specific and specific binding. The interactions through sorption are of non-specific type whereas those through starch inclusion complex are specific. Aroma-starch adsorption occurs through hydrogen bonding which is strongly influenced by the polarity of flavour molecules (Boutboul et al., 2002). Viscosity and moisture content of starch matrices are proved to be factors affecting flavour binding and release (Le Thanh et al., 1992).

Various researches have been carried out in order to get a better understanding of starch–flavour interactions. However the experimental conditions vary with each work (type and quantity of starch and flavour, preparation and storage...), it thus remains difficult to have a general rule enabling one to understand the starch–flavours interactions as a whole. Among the key factors, the amount of water in the studied systems should also be considered. In the dry state, native starch granules physically adsorb flavour to their porous surface via hydrogen bonding (Escher, Nuessli, & Conde-Petit, 2000). Flavour retention and release in dry foods depend on the molecular mobility of flavour within the food matrix particularly, when starch is in the glassy state, they are controlled by hydration. The humidity of the system affects flavour release and retention as the latter are directly associated with phase partition (Boutboul et al., 2002) as well as molecular mobility. Boutboul et al. (2002) showed that flavour retention in any types of starch-based matrix increased with increasing flavour polarity. Indeed starch serves as a polar stationary phase and can form hydrogen bonds with those polar flavour molecules. The surface area has been shown to also play a key role (Boutboul et al., 2002; Hau, Gray, & Taylor, 1998): the higher the specific area, the greater the flavour retention. Moreover granular and native starches are less able to retain flavour since their structure in granular form limits accessibility for flavour (Boutboul et al., 2002).

Certain types of flavour interact via amylose–flavour inclusion complexes in heat-treated starchy matrix with high water content. The formation of flavour–inclusion complex is similar to an amylose–lipid complex, due to the structural similarity of certain flavour molecules with some fatty acids (Jouquand, Ducruet, & Le Bail, 2006). The inclusion complexes are formed during gelatinisation of starch (Biliaderis, 1992; Jang & Pyun, 1996) and their melting can be observed by DSC immediately after the onset of thermal events (gelatinisation and melting of starch crystallites).

There are few published works regarding flavour interactions under limiting water or in partially-gelatinised starch as well as on the influence of flavour on starch pasting properties. The existing literature (Blazek, Gilbert, & Copeland, 2011; Tang & Copeland, 2007) is in regard of the influence of amylose–lipid complex on pasting properties rather than the influence of flavour. It is still unclear how flavours interact and are retained in partially-gelatinised starch. The present study aimed at understanding interactions between starch and flavour upon moderate hydrothermal treatment and filling in the gap between interactions in native and fully gelatinised starches. Therefore, water content and heating temperature were varied in order to obtain samples at different gelatinisation degrees. Two flavours compounds were chosen according to their abilities to form (ethyl hexanoate) or not (2-hexanone) flavour–inclusion complex for a comparison study. The effects of residual crystallinity and flavours on pasting profile were further investigated.

2. Materials and methods

2.1. Starches and flavours

Native and starch pregelatinised wheat starch (Pregeflo® W-HV) were kindly provided by Roquette Frères (Lestrem, France). Ethyl hexanoate and 2-hexanone were obtained respectively from Sigma–Aldrich (Steinheim, Germany) and Acros (Geel, Belgium). Methyl heptanoate and ethyl octanoate produced by Sigma–Aldrich (Steinheim, Germany) were used as internal standards of flavour extraction and gas chromatography injection, respectively.

2.2. Sample preparation

The samples were prepared with a single flavour in order to compare the effect of flavour addition against no flavour addition separately. Two formulae were chosen according to weight ratios between native wheat starch and water: 20/80 (recipe A) and 50/50 (recipe C) g of starch per g of water. The native starch contained 11% of moisture content prior its mixing with water. The flavours were added directly onto starch prior to addition of water. The added quantity of ethyl hexanoate was 175 mg/100 g of starch–water mixture while 2-hexanone was 162 mg/100 g of starch–water mixture. Regarding the samples with flavour addition, the added ethyl hexanoate contents per gram of starch at dry basis were 9.6 mg in recipe A and 3.8 mg in recipe C. In case of 2-hexanone, the added contents were 8.9 mg in recipe A, while in recipe C was 3.6 g. The next steps were done in the same manner for samples with/without flavour. Samples were mixed in closed container and left standing on a magnetic stirrer (Variomag Multipoint, Thermo Scientific) at 800 rpm for one hour prior to heating treatment. The mixtures of starch and water were cooked in a double walled-vessel with manual agitation at 65, and 85 °C for 10 min. The vessel was equipped with circulating water connected to a temperature controlled bath. Once the samples cooled down to room temperature, they were subjected to Differential Scanning Calorimetry (DSC) and moisture content analysis. The cooked starch samples were kept in closed plastic containers at −30 °C prior to the flavour extraction and analysis.

The samples name derived from their formulae and heat treatment temperature, therefore they were denoted as A65, A85, C65 and C85.

2.3. Freeze-dried samples

Cooked starch samples were frozen immediately after their thermal treatment and stored at −30 °C before freeze-drying (Triad, Labconco, Kansas City, USA). The freeze-drying process was started from pre-freezing to −75 °C for 3 h then the