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Influence of purified konjac glucomannan on the gelatinisation and retrogradation properties of maize and potato starches

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Abstract

The effects of purified konjac glucomannan (PKG) on the gelatinisation and retrogradation properties of different starches was investigated by differential scanning calorimetry (DSC) and α-amylase digestion. It was established that when moisture was progressively restricted in starch–water or starch–konjac polysaccharide–water systems, the conclusion temperature by DSC (T_c) increased progressively with the concentration of PKG in the system. This increase in T_c was directly related to the volume fraction of water (as modelled by the modified Flory–Huggins equation) and was considered to be the result of the hydrocolloid limiting water availability for gelatinisation and swelling. In addition, the PKG was extremely effective at retarding 'long-term' retrogradation of starch during low temperature storage (reflected in the enthalpy of dissociation by DSC and amount of starch digested by α-amylase). In this context, the konjac hydrocolloid may (a) act as a physical barrier to prevent amylopectin chain association during storage, (b) restrict enzyme–substrate contact and (c) exert a viscosity effect that affects mobility within the stored system.

Keywords: Starch; Konjac glucomannan; Gelatinisation; Retrogradation; α-Amylase digestion

1. Introduction

Starch is a major storage energy reserve in plants where it exists as insoluble granules. These are extracted commercially from many botanical sources including potato, maize, wheat and rice to produce a wide variety of industrial products (Tester & Karkalas, 2002). The granules are composed mainly of two different glucose polymers: essentially linear amylose molecules and highly branched amylopectin (Cura, Jansson, & Krisman, 1995; Hizukuri, 1986). Starches (normal) generally contain around 25% amylose and 75% amylopectin, although waxy genotypes contain considerably higher amounts of amylopectin whist high amylose genotypes are amylose rich (Hizukuri, 1986; Suzuki, Hizukuri, & Takeda, 1981).

When starches are subjected to high temperatures, (typically greater than 50 °C) in the presence of water, the granules swell and rupture due to disruption of amylopectin double helices (hydrogen bonds dissociation), while amylose preferentially leaches out of the swollen granules (Tester, 1989). These events, collectively known as 'gelatinisation', are accompanied by a dramatic increase in the systems viscosity as granule structure is progressively ruptured (Yang & Rao, 1997). When gelatinised starch is stored, particularly at low temperature (Jang & Pyun, 1997), it undergoes 'retrogradation' (or staling in baked goods) caused by re-crystallisation of the polymer (dispersed amylose and amylopectin) chains. Starch retrogradation occurs in two stages. Initially, over the first two days post-processing, the amylose component associates rapidly (Miles, Morris, Orford, & Ring, 1985; Miles, Morris, & Ring, 1985), which is followed by a slower re-crystallisation of the amylopectin fraction (Ring et al., 1987), a process that may proceed for several weeks.

The gelatinisation parameters (onset, T_o; peak, T_p and; conclusion, T_c temperatures and enthalpy, ΔH) as determined by differential scanning calorimetry (DSC) are

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characteristic of different starches (Tester, 1989). The gelatinisation parameters and extent of starch retrogradation are influenced by the starch composition and architecture (Fredriksson, Silvero, Andersson, Eliasson, & Aman, 1998; Ring et al., 1987; Sasaki, Yasui, & Matsuki, 2000); moisture content during both gelatinisation (Donavan, 1979; Eliasson, 1980; Svensson & Eliasson, 1995) and storage (Jang & Pyun, 1997; Liu & Thompson, 1998); storage temperatures (Jang & Pyun, 1997; Kim, Kim, & Shin, 1997) and; presence of non-starch polysaccharides (Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997; Ferrero, Martino, & Zaritsky, 1996; Rojas, Rosell, & Benidito de Barber, 1999; Sommerville, 1999). Considering the industrial and nutritional importance of such effects, the interaction of different industrial hydrocolloids with various types of starch has received little attention. In particular, research concerning interactions between konjac glucomannan and starch during processing is sparse.

In an age where consumption of 'ready-meals' or pre-cooked chilled food is rapidly increasing, there is a need to understand how undesirable changes during storage of starch-based foods can be controlled. As well as being responsible for deterioration of textural quality, retrogradation can also reduce the digestibility of starchy foods (Botham, Morris, Noel, & Ring, 1996; Brennan, Blake, Ellis, & Schofield, 1996; Fredriksson et al., 2000).

Konjac glucomannan has been introduced into Europe (E425) and the USA as a food additive due to its gelling and emulsifying properties. It is an essentially linear polysaccharide composed of blocks of β-1,4-linked mannose and glucose residues in the ratio of ~1.6:1, with acetylation around every 19-sugar residues (Gidley, McArthur, & Underwood, 1991; Kato & Matsuda, 1969). In Japan, konjac flour is extracted from the root tuber of the *Amorphaphallus konjac* plant and has traditionally been used in Japanese cookery for centuries. The effect of konjac flour on gelatinisation and retrogradation of maize starch (Yoshimura, Takaya, & Nishinari, 1996), and its effects on the rheological properties of maize starch gels (Bahnassey & Breene, 1994; Fanta & Christianson, 1996; Shelso, 1990; Yoshimura, Takaya, & Nishinari, 1998) have received the most attention to date. No study has been conducted on the effects of purified konjac glucomannan on the gelatinisation and retrogradation of starches with different ratios of amylose and amylopectin and at different moisture contents to reflect real food systems. Hence, the following study was undertaken using waxy, normal and high amylose maize starches plus potato starch to model these interactions.

2. Materials and methods

2.1. Materials

Samples of 'SFJ' (pet food grade) konjac flour were supplied by Kalys (Roubaix and Grenoble, France). Commercially available normal (C*03402), high amylose (C*03003) and waxy maize (C*04201) starches were obtained from Cerestar, Vilvoorde, Belgium and normal potato starch (S/7920/60) was obtained from Fisher Scientific, UK Ltd.

2.2. Purification and characterisation of konjac polymer

Purification of konjac flour was conducted according to a slightly modified procedure of Prosky et al. (1984) for determination of dietary fibre as shown in Fig. 1. A sodium metabisulphite pre-steep was introduced to ensure maximum removal of tightly associated protein (followed by dialysis, incubation with α-amylase, protease and amyloglucosidase). The polysaccharide was precipitated in ethanol, filtered, rinsed and dialysed for 36 h before being lyophilised, ground to a fine powder then sieved. The moisture content of the purified polysaccharide was determined by weight loss after oven drying at 130 °C for 2 h, starch content was determined according to Karkalas (1985), and protein, lipid and ash were determined by standard Kjeldahl (protein equals nitrogen × 6.25) and acid hydrolysis methodology (1 g boiled in nine volumes 6 M HCl followed by triplicate extraction with 10 ml petroleum ether, and quantification of solids in the solvent gravimetrically after evaporation), and by weight loss after dry ashing in a muffle oven (550 °C, 16 h), respectively. Neutral sugars were determined by gas–liquid chromatography according to the method of Englyst and Cummings (1988) as modified by Karkalas (1994), and the degree of acetylation was determined according to Hestrim (1949).

2.3. Characterisation of starches

Moisture, starch, lipid, protein and ash were determined as for the konjac polymer (2.2). Total (lipid extracted) amylose was determined according to the iodine binding method of Morrison and Laignelet (1983). The amylopectin content was calculated by subtracting the amylose content from the total starch content of the native starches.

2.4. Measurement of the effects of purified konjac glucomannan on the gelatinisation and retrogradation of starch in excess, intermediate and restricted moisture by DSC

Each starch was weighed into a 10 ml screw cap tube with purified konjac glucomannan (PKG) powder in ratios of 100:0, 198:2, 99:1, 95:5 and 90:10 by weight and tubes were vortex mixed thoroughly. For the determination of gelatinisation parameters in excess moisture, triplicate samples (3–3.5 mg) of each starch or starch–PKG mixture were weighed into 40 μl aluminium DSC pans and 15 μl degassed deionised water containing 0.02% sodium azide (NaN_3) was added by micro-syringe and the contents were