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Self-structuring foods based on acid-sensitive low and high acyl mixed gellan systems to impact on satiety

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A B S T R A C T

This study investigated the *in vitro* acid-induced gelation of mixed systems of two biopolymers; low acyl and high acyl gellan gum. Rheological and texture analysis showed that these mixed gels displayed textures that lay between the material properties exhibited for the low and high acyl variants. DSC analysis showed that mixtures of the low acyl and high acyl forms exhibit two separate conformational transitions at temperatures coincident with each of the individual biopolymers.

Various metabolically relevant pH environments and hydrocolloid concentrations were investigated. These resulted in very different acid gelled structures, which were characterised by texture analysis. The structures of the acid gels were shown to depend upon the pH, hydrocolloid concentration and proportion of each biopolymer used during their production.

A selection of these mixed gellan structures were assessed post-production in terms of their response to prolonged exposure to an acidic (pH 1), stomach-like, environment. This resulted in a significant increase in the gel strength, regardless of the biopolymer proportions. The high acyl gellan was less acid-sensitive, and subsequently no evidence of acid gelation was observed with high acyl gellan at a proportion greater than 60% of the total biopolymer.

The findings presented here demonstrate that structuring as well as de-structuring of mixed gellan acid gels can be controlled in acidic environments similar to those that are present in the stomach after food consumption.

1. Introduction

Before the 20th century, obesity was rare (Haslam, 2007). In 1997 however, the World Health Organization (*WHO*) formally recognized obesity as a global epidemic (Caballero, 2007). As of 2008 the *WHO* estimated that globally at least 500 million adults are obese, with higher rates among women than men. Once considered a problem only of high-income countries, obesity rates are rising worldwide and affecting both the developed and developing world (Tsigosa et al., 2008).

One way of tackling the high and rising levels of morbid obesity in today's society is to control the consumer's energy intake from foods. One problem is that foods have become softer, more easily digestible and therefore less satiating. This leads to the individual feeling hungry more quickly and subsequently wanting to eat again, often between meals. Therefore, there is a requirement to find ways to control the rate of food digestion without impacting on the enjoyment of the food. This needs to be both in terms of its digestive properties and the sensory aspects it delivers during consumption. In addition, this needs to be achieved in such a way that the food is stable during storage and distribution (Norton, Fryer, & Moore, 2006; Norton, Moore, & Fryer, 2007).

One approach, that could impact on people's appetite and can be delivered in liquid or soft solid products without an adverse effect on consumer response, is the use of hydrocolloids that respond to the pH conditions experienced inside the stomach. Once in contact with low pH conditions these hydrocolloids self-structure to form gels. It is well known that alginate gels as its pH is lowered (Draget, Skjåk-Bræk, & Stokke, 2006), and previous studies have investigated the ability of alginate to structure the stomach contents (Hoad et al., 2004; Norton, Frith, & Ablett, 2006). These studies showed that some structuring occurred within the stomach, as measured by NMR imaging, and that satiation was prolonged as a result. Their findings highlight the need for further study, as it was reported that acid gels were produced too quickly after entering the stomach and thus gave less than optimal structuring of the stomach

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contents. In addition, the alginate used was sensitive to calcium ions and so would prove to be very difficult to incorporate into foods.

One alternative hydrocolloid that forms acid gels is gellan gum (Yamamoto & Cunha, 2007). This has received little attention and has only been widely investigated under slow acid release from Glucono-Delta-Lactone (GDL), with just a few exceptions that have studied acid gelation by direct addition of acid, which is more relevant to digestion (Norton, Cox, & Spyropoulos, 2011). Gellan gum is a carboxylated extracellular polysaccharide secreted by the organism *Sphingomonas elodea*during aerobic fermentation (Kang & Veeder, 1982). The gellan polymer consists of monosaccharides β-D-glucose, β-D-glucuronic acid and α-L-rhamnose in molar ratios of 2:1:1 (Sanderson, 1990) linked together to form a primary linear structure. The biopolymer is produced with two acyl substituents present on the 3-linked glucose, L-glycerol positioned at O(2) and acetyl at O(6). Direct recovery of the polysaccharide from the fermentation broth yields the high acyl form whereas deacylation by alkali treatment results in the low acyl variant. Gellan gum is currently commercially available in both the high acyl and the low acyl form. When hot solutions of gellan gum are cooled in the presence of gel-promoting cations, gels of various textures can be formed, principally through cation-mediated helix–helix aggregation (Gibson & Sanderson, 1997). Intermediate mechanical properties between those of the individual components are seen when combining low acyl gellan with high acyl gellan to form mixed gels (Sanderson, 1988).

The aim of this work was to investigate the acid gelation of gellan in order to gain an insight into the gel structures that can be produced by direct addition of acid, as well as investigating the effect of mixing the two variants of gellan to control the mechanical properties of the acid gel. Both the effects of total polymer concentration and the ratio of low to high acyl gellan on the mechanical properties of the mixed gellan gels were investigated. The structure of the produced acidified mixed gels was studied by means of texture analysis, rheology and differential scanning calorimetry. Mixed gellan gels were assessed post-production in terms of their response to a prolonged exposure to an acidic environment that simulates the conditions found in the stomach after ingestion.

2. Experimental

2.1. Materials

Low acyl gellan gum and high acyl gellan gum (Kelcogel F and Kelcogel LT100), provided by CPKelco (UK). The water used was filtered through a reverse osmosis milli-Q water system. HCl acid (38% wt./wt.) was purchased from Fisher Scientific (Loughborough, UK), and diluted to form a 0.5% (0.137 mol/dm^3) stock solution, which was used for the direct acidification of all the produced acid gel structures. All materials were used with no further purification or modification of their properties.

2.2. Methods

2.2.1. Preparation of mixed gels

Aqueous mixed hydrocolloid solutions of the two gellan variants with total concentrations between 0.5 and 3 wt.% were prepared by dissolving the required amounts of each hydrocolloid in distilled water at 80 °C. The natural pH of the gellan solutions was measured as 5.4, which was not dependent on concentration. The pH of the mixed gellan solutions was adjusted by drop wise addition of 0.5 wt.% (0.137 mol/dm^3) HCl (also at 80 °C) and these acidified solutions were then poured into cylindrical moulds (22.5 mm internal diameter and 50 mm height), which were stored at room temperature for 24 h to allow for gel formation. Texture analysis of all mixed acid gel samples was carried out immediately after the 24 h setting period.

2.2.2. Texture analysis

The structure of the prepared mixed acid gels was assessed by performing compression tests using a TA XT plus Texture Analyser (Stable Micro Systems Ltd., UK), with a 40-mm diameter cylindrical aluminium probe. All samples had a diameter of 22.5 mm and their length when measured was 10 mm. All measurements were carried out in triplicate with a compression rate of 1 mm/s.

The force/distance data, as obtained directly from the texture analyser, was converted into true strain (ε_H) and true stress (σ_T) data using the following equations (Moresi & Bruno, 2007):

$$\varepsilon_E = \frac{H_0 - h}{H_0} \tag{1}$$

$$\varepsilon_H = \ln(1 + \varepsilon_E) \tag{2}$$

$$\sigma_E = \frac{F}{A_0} \tag{3}$$

$$\sigma_T = \sigma_E(1 + \varepsilon_E) \tag{4}$$

where ε_E and ε_H are the engineering and true (Hencky) strain, σ_H and σ_T are the engineering and true stress, H_0 and $A_0$are the initial height and cross-sectional area of each sample and F and h are the compression force applied and height of each sample as recorded during the compression tests.

From the obtained true stress/true strain curves, the slope of the initial linear region (up to strain values of 0.05%) can be used to calculate the Young's modulus (Smidsrød, Haug, & Lian, 1972) while the slope of the second linear region (for strain values over ~0.1%), leading to the subsequent structure failure can be used to calculate the bulk modulus (Nussinovitch, 2004). These calculated moduli provide information regarding the two deformation mechanisms associated with each of the two linear regions. When the samples are initially loaded the connections between the hydrocolloid molecules within the gel network are deformed, as a result of the applied stress. During this initial compression stage the gel matrix exhibits elastic behaviour, the measure of which is given by the calculated Young's modulus. When a critical stress is reached the connections in the hydrocolloid network break where the process of deformation enters a second much steeper linear region. During this compression stage the exhibited behaviour is non-elastic and the slope of the linear region in the true stress/true strain curve, thus the calculated bulk modulus, relates to the stiffness/deformability of the gel matrix, until structure failure occurs.

Finally the total work to failure (Kaletunc, Normand, Nussinovitch, & Peleg, 1991) is the total work (given as work per unit area in this study) that is required in order for the structure to fail and this is determined from the area, up to the point of failure, under the true stress/true strain curve. Fig. 1 shows a typical true stress/true strain curve and also how the data in the plot is interpreted to give the Young's modulus, bulk modulus and total work to failure for the acid gel structures.

2.2.3. Post-production exposure to an acidic environment

The 3 wt.% mixed gellan gels were exposed to an acidic environment by placing the 10 mm samples into an acid solution (pH 1) for periods of time of up to 3 h 3 h was an exposure time chosen as an average gastric residence time although residence times as short