LWT - Food Science and Technology 84 (2017) 212–221

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Understanding the interaction between wheat starch and *Mesona chinensis* polysaccharide

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ARTICLE INFO

Article history:
Received 26 March 2017
Received in revised form
25 May 2017
Accepted 25 May 2017
Available online 26 May 2017

Keywords:
Anionic polysaccharide
Gelatinisation
Gelation
Granule swelling
Amylose leaching

ABSTRACT

In order to elucidate the mechanism of interaction between *Mesona chinensis* polysaccharide (MCP) and wheat starch, the granular swelling, amylose leaching, and gelatinisation properties of 20 mg wheat starch/g suspension were studied in the presence of increasing concentrations of MCP. At room temperature, the presence of MCP (0.2–15.8 mg/g suspension) induced shear-reversible starch aggregation. Heating of starch-MCP suspension resulted in an earlier onset of viscosity that was characterised by a peak "M". This was also accompanied by delayed granular swelling and a 40% reduction in amylose leaching when 11.3 mg MCP/g suspension was present. An interaction was thought to occur when amylose leaches out of wheat starch granules forming an MCP-amylose barrier, increasing the apparent size of the granules. The final G′ of starch gel (~1 Pa) increased during cooling in the presence of increasing concentrations of MCP up to 20 Pa with 11.3 mg MCP/g suspension, indicative of a 3D network comprising of amylose, MCP and starch granules. The final gel properties were dependent on the concentration of MCP present whereby an extensive MCP-amylose network was required to stabilise the starch granule aggregates despite a reduction in the amount of amylose leached.

1. Introduction

Polysaccharides such as xanthan, guar, carrageenan, and cellulose are commonly added into food products for improved functionality. Polysaccharides have various roles in food products, such as providing mouthfeel and texture, increasing viscosity, forming gels and delaying starch retrogradation. These functionalities are determined by the interactions between polysaccharides and many food ingredients and generally include various types of interactions including electrostatic bonding and physical entanglement. The interaction between polysaccharides and starches, a major component of many food products, has been widely studied over the last decade. However, the results of these studies have not clearly elucidated the complex interactions involved, partially because of the wide range of starch and polysaccharide types that have been used (BeMiller, 2011). Typically, interactions between starches and polysaccharides are characterised by changes in the pasting properties of the starches including pasting temperature and paste viscosities along with their amylose leaching behaviour. In wheat starch for instance, the peak viscosity increases in the presence of guar, tara, locust bean and konjac gums (Funami et al., 2005) but decreases in the presence of gum arabic and soluble polysaccharides from soybean (SSPS) (Funami et al., 2008). Interactions between polysaccharides (guar, tara, locust bean, and konjac) and wheat starch molecules are thought to play a role in increasing the peak viscosity of wheat starch suspension (Shi & BeMiller, 2002) but the mechanisms behind these interactions have never been clearly explained. On the other hand, in the case of gum arabic and SSPS, it was proposed that the polysaccharides adsorb onto starch granules to create a coat that prevents polymer leaching, which led to a decrease in peak viscosity (Funami et al., 2008). The ability of polysaccharides to coat starch granules has also been observed for xanthan gum (Gonera & Cornillon, 2002; Mandala & Bayas, 2004), for which the coat was thought to increase the rigidity of starch granules (Mandala & Bayas, 2004), hence increasing the viscosity of the starch paste due to less granule disintegration (Achayuthakan & Suphantharika, 2008). The specificity of starch and polysaccharide interactions is further demonstrated by the ability of gum arabic and xanthan to decrease and increase the amount of amylose leached respectively (Funami et al., 2008; Mandala & Bayas, 2004). In order to explain the

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http://dx.doi.org/10.1016/j.lwt.2017.05.066
0023-6438/

variations in the pasting properties of wheat starch-polysaccharide systems, several mechanisms have been previously proposed: (1) thermodynamic incompatibility which leads to an increase in the effective starch concentration in the continuous phase (Alloncle & Doublier, 1991; Funami et al., 2005), (2) interactions between starch and polysaccharides resulting in polysaccharide adhesion on granule surface (Abdulmola, Hember, Richardson, & Morris, 1996) and (3) interactions between leached starch polymers (especially amylose) and polysaccharides resulting in an increase in viscosity (Shi & BeMiller, 2002).

The polysaccharide fraction from the herb *Mesona chinensis* (denoted as MCP) is among the less common polysaccharides that seems to show an interesting interaction with starches. *Mesona chinensis* is a herb of the mint family that is used in Asia to make a gel dessert known as Grass Jelly. The extract of this herb has been used as traditional medicine to treat diseases such as diabetes, hypertension, heatstroke, and muscle joint pain (Feng, Ye, Zhuang, Fang, & Chen, 2012). The health benefits associated with *Mesona chinensis* and its unique taste make the dessert gel popular in many Asian countries. Studies on MCP have suggested its use as a fat-substitute in sausages (Feng et al., 2013), salad dressings (Lai & Lin, 2004), and in extruded rice formulations (Zhuang et al., 2010). The extract of *Mesona chinensis* is black in colour, has low viscosity and does not form a gel on its own when heated and cooled. In order to make Grass Jelly, the extract of this herb needs to be heated with starch to a high temperature and then cooled. The gel formed from this mixture is more brittle and stronger in comparison to gels formed by starch alone. Such strong gels have only been reported to form when the extract is cooked with non-waxy starches (Lii & Chen, 1980). The ability of the extract to form strong gels with starches has been attributed to the presence of an anionic polysaccharide found in the extract. This polysaccharide has been reported to contain galactose, glucose, mannose, xylose, arabinose, rhamnose and galacturonic acid (Feng, Gu, Jin, & Zhuang, 2008). The structure of MCP is made up of α-(1 → 4)-galacturonan backbone with insertions of α-1,2-Rha*p* residues on which all of the other sugars are attached to (Feng et al., 2008). The interaction between wheat starch and MCP has been reported as synergistic resulting in an increased viscosity and formation of a strong gel (Feng, Gu, Jin, & Zhuang, 2010a). However, the nature of this interaction has not been established.

The high viscosity imparted by the addition of MCP to starch systems can be used to modify texture and stability. Increasing the viscosity of a system is also considered to reduce the hydrolysis of starch due to limitations of enzymes accessibility (Brennan, Suter, Luethi, Matia-Merino, & Qvortrup, 2008). This means that MCP may be used to formulate starch based food products with lower digestibility. In order to use MCP as an ingredient in food formulations, there is a need to understand how MCP interacts with starch when they are processed i.e. heated and cooled. While the synergism between MCP and starches has been reported, the interaction between the two has not been studied in detail. With the exception of pasting curves generated from the Rapid Visco Analyser, the majority of studies carried out on starches and MCP focus on the final gel properties (rheology and microstructure of the gel) rather than the gel properties during its formation. Since the interaction between starches and MCP is thought to take place during heating and cooling, this study will follow the events (amylose leaching, granular swelling and development of G′ during cooling) that occur during gelatinisation and gelation, which are not available in the current literature. This will provide a novel understanding on the interaction between wheat starch and MCP as the mixture is heated into a paste and cooled to form a gel. Therefore, this paper aimed to better understand the mechanism of interaction between MCP and wheat starch by looking at the rheological, gelatinisation, granular swelling and amylose leaching properties of wheat starch in the presence of increasing concentrations of MCP.

2. Materials and methods

2.1. Mesona chinensis polysaccharide

Dried crude *Mesona chinensis* powder was purchased from Xi'an Hua Rui Bio-Engineering Co. Ltd. (Xi'an, China). The composition of the extract was analysed by an accredited chemical laboratory (Massey University Nutritional laboratory, Palmerston North, New Zealand). Protein, fat, dry matter, ash and starch contents were measured using the DUMAS combustion method (AOAC 991.36), convection oven method (AOAC 930.15, 925.10), ashing at 600 °C (AOAC 942.05), and amyloglucosidase-α-amylase method (AOAC 996.11) respectively. The total sugars were measured using the phenol-sulphuric acid method (Hall, Hoover, Jennings, & Webster, 1999). Total carbohydrate content of the extract was calculated based on 100% - (Moisture + Ash + Protein + Fat) %. Non-starch polysaccharide content was calculated by difference [total carbohydrate % − (Starch + Free sugar) %].

2.2. Starch-MCP suspension preparation

Briefly, *Mesona chinensis* solution was prepared by weight by dissolving *Mesona chinensis* powder in MilliQ (Millipore, Billerica, MA, USA) water on a dry weight basis and left to hydrate for at least 8 h under constant stirring using a magnetic stirrer. A range of mesona powder concentrations (1, 5, 10, 20, 30, 50 and 70 mg mesona powder/g solution) was selected to determine the concentration at which MCP and wheat starch interact to increase the viscosity of the suspension. The solution was centrifuged at 4000 g for 30 min to remove all insoluble materials. The insoluble materials were then oven dried and the total soluble solids in the supernatant were determined to be 0.9, 4.5, 8.9, 17.9, 26.9, 44.8, 60.3 mg/g solution. The total carbohydrate of the supernatant was measured using the phenol sulphuric acid method. The free sugar present in the solution was obtained by precipitating NSP overnight from the water extract using ethanol. The ethanolic extract was then centrifuged and free sugar in the supernatant was measured using the phenol sulphuric acid method. The total soluble NSP (MCP concentrations) was then calculated by difference (total carbohydrate − free sugar) and this was determined to be 0.2, 1.1, 2.3, 4.5, 6.8, 11.3 and 15.8 mg MCP/g suspension. Wheat starch was purchased from Penford (Sydney, NSW, Australia) and its moisture content was determined by oven drying method. All starch suspensions were prepared by weight on a dry weight basis. MCP solutions were mixed with wheat starch to obtain suspensions containing 20 or 100 mg starch/g suspension.

2.3. Rheological measurements

Rheological measurements were carried out using a controlled-stress rheometer (MCR302, Anton Paar Physica, Graz, Austria) fitted with a starch cell (C-ETD160/ST) and spindle (ST24-2D/2V/2V-30). Based on preliminary trials, stirring conditions were selected to prevent starch granule sedimentation. Twenty millilitres of the wheat starch/MCP suspensions were added into the rheometer cup and the sample was thoroughly mixed by rotation at a shear rate of 800 s^{-1} for 3 min at 20 °C. The shear rate was then reduced to 100 s^{-1} for 2 min while maintaining the temperature at 20 °C to equilibrate the system. The temperature was then increased to 95 °C at 2 °C/min and held at 95 °C for 5 min. At this point, the rheometer was switched to small strain oscillation mode using a