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Functionality of the storage proteins in gluten-free cereals and pseudocereals in dough systems

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ABSTRACT

The dough functionality of the storage proteins in "gluten-free" grains has been studied for almost 25 years. Zein, maize prolamin, when isolated as α-zein can form a wheat gluten-like visco-elastic dough when mixed with water above its glass transition temperature. There is good evidence that its dough-forming properties are related to a change in protein conformation from α-helix to β-sheet and association of the molecules into fibrils. Stabilisation of β-sheet structure and visco-elasticity can be enhanced by inclusion of a co-protein. No other isolated cereal or pseudocereal storage protein has been shown to form a visco-elastic dough. Many treatments have been applied to improve "gluten-free" storage protein functionality, including acid/base, deamidation, cross-linking by oxidising agents and transglutaminase, proteolysis, disulphide bond reduction and high pressure treatment. Such treatments have some limited positive benefits on batter-type dough functionality, but none is universally effective and the effects seem to be dependent on the composition and structure of the particular storage protein. Research into mutants where prolamin synthesis is altered appears to be promising in terms of improved dough functionality and scientific understanding. Research into how treatments affect the functionality and structure of isolated storage proteins from "gluten-free" grains other than maize is required.

1. Introduction

Excellent progress has been made in the development of technology to produce gluten-free breads and other dough-based products with the aid of hydrocolloids and gums to improve dough visco-elasticity and gas-holding (Anton et al., 2008; Sciarini et al., 2010). An alternative approach involving improving the visco-elasticity and gas-holding properties of the storage proteins of gluten-free cereals has also been the subject of considerable research since the early 1990s (Lawton, 1992), but progress has been much slower (Erickson et al., 2012).

This approach of using the storage proteins of gluten-free cereals to support the creation of a stable, expanded leavened dough is nevertheless highly desirable. Many gluten-free bread products have poor nutritional quality in terms of proteins, micronutrients and dietary fibre due to them consisting primarily of purified carbohydrates (Matos and Rosell, 2015). Gluten-free dough-based products are generally also disproportionately costly (Singh and Whelan, 2011). Further, there is also a need for non-wheat and low-wheat (as opposed to gluten-free) bread. This is particularly the case in the developing countries of Asia and Africa where there is a huge increase in demand for bread and other Western-type foods, due to continuing high population growth and rapid urbanisation (Pingali, 2007). Cultivation of wheat and barley, which are temperate cereals, is not generally economically viable in these countries which lie in the tropics and semi-arid sub-tropics. Scientific developments in non-wheat dough systems, which parallel those that have taken place in brewing where cereals such as sorghum are now used extensively (Taylor et al., 2013b), would be highly beneficial to both persons who are intolerant to gluten and consumers in developing countries.

This review will focus on research being undertaken to improve the functionality of the storage proteins of maize, sorghum, the millets, oats, rice and the pseudocereals (buckwheat, amaranth and quinoa) in dough systems. Firstly, the composition and structural

Abbreviations: CLSM, confocal laser scanning microscopy; G′, shear storage modulus; G″, shear loss modulus; HMW-GS, high molecular weight-glutenin subunits; SEM, scanning electron microscopy; SAOS, small amplitude oscillatory test; T_g, glass transition temperature.

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chemistry of these proteins in relation to those of wheat glutenin with respect to visco-elasticity will be briefly examined. Next, research into the dough functionality of the "gluten-free" storage proteins as isolated proteins will be reviewed. Then, the major section will review research into improvement of their dough functionality through chemical and physical modifications. After which, improvement through genetic modification of the proteins will be examined. Lastly, possible directions regarding practical application of the findings in bread-making and ongoing research will be considered.

2. Composition and structure of the storage proteins of non-wheat cereals and pseudocereals

To mimic the functional properties of gluten in non-gluten dough systems it is useful to understand how the storage proteins of non-wheat cereals and pseudocereals differ from wheat gluten in composition and structure. The functionality of gluten in wheat dough systems is complex, as recently reviewed by Juhász et al. (2015). As is well-known, gluten comprises monomeric gliadins which are responsible for dough viscosity and extensibility and polymeric glutenins, which critically are responsible for elasticity and strengthening the dough. In particular, the high molecular weight glutenin subunits (HMW-GS) are important in determining gluten elasticity (Shewry et al., 2002).

There are several valuable reviews concerning non-wheat grain storage proteins, including Shewry and Halford (2002), Lawton (2002) and Belton et al. (2006). Table 1 compares the composition and structure of the wheat high molecular weight glutenins with those of the prolamins of the tropical C4 cereals: maize sorghum, pearl millet and teff. The prolamins of maize and sorghum, zein and kafirin, respectively, like the wheat prolamins, are composed of a number of sub-classes (Shull et al., 1991). The polypeptide monomers are, however, all much smaller in size than the wheat HMW-GS, but like the HMW-GS they polymerise through disulphide cross-linking, due to the high cysteine content of the β- and γ-sub-classes. The secondary structures of zein and kafirin are predominately α-helical and tightly folded into a hairpin or rod-like structure, rather than consisting of more open spirals of β-turnslike HMW-GS (Belton et al., 2006). Also, both zein and kafirin are considerably more hydrophobic than gluten. Presumably as a consequence of their greater hydrophobicity and different secondary structure, zein and kafirin have a higher glass transition temperature (T_g) than gluten (Taylor et al., 2013a). The prolamins of pearl millet, pennisetin, whilst less studied, are considered to be similar to α-zein in structure (Bugs et al., 2004).

Table 2 summarises the properties of the storage proteins of rice and oats, and of the pseudocereals amaranth, quinoa and buckwheat. The major storage proteins of rice and oats are globulins, similar to those of legumes, and account for some 70–80% of the endosperm storage proteins (Shewry and Halford, 2002). Both are related to the 11–12S legumin type globulins. The rice glutelins comprise acidic and basic polypeptide chains linked by a single disulphide bond (Shotwell et al., 1990) and share similarities with HMW glutenins (Shewry and Halford, 2002). The oat globulins, like the legumins, form hexameric structures. The major storage proteins of pseudocereals are also similar to the legume proteins. They contain 2S albumin and 11S globulin storage proteins, with 7S globulins present in buckwheat and amaranth. Those of amaranth have predominantly β-sheet structure with β-barrel conformation (Tandang-Silvas et al., 2012). The 11S type globulins of oats, rice and the pseudocereals polymerise by disulphide bonding.

It is clear that whilst the composition and structure of these storage proteins share some similarities with glutenin, in particular the extensive disulphide bonded polymerisation of zein and kafirin, there are important differences in terms of amino acid composition, sequence and secondary, tertiary and quaternary structure.

3. Dough forming properties of non-wheat storage proteins

3.1. Isolation in protein bodies

Zein, kafirin and pennisetin prolamins, presumably as a result of their relative hydrophobicity and disulphide bond cross-linking (Shewry, 2002; Belton et al., 2006), are isolated in protein bodies in the starchy endosperm cells of the mature grain (Adams et al., 1976). Likewise, the rice prolamins are isolated in Type I protein bodies (Saito et al., 2012) and the glutelins are isolated in Type II protein bodies (Yamagata et al., 1982) and in oats the globulin and prolamin storage proteins are co-located in the same protein bodies (reviewed by Shewry and Halford, 2002). The albumin and globulin storage proteins of the pseudocereals, amaranth (Coimbra and Salema, 1994), buckwheat (Elpidina et al., 1990) and quinoa (Prego et al., 1998) are also isolated in protein bodies. The localisation of storage proteins in discrete protein bodies in these "gluten-free" grains is unlike the situation in wheat where the glutenin and gliadin proteins form a continuous matrix around the starch granules within the cells of the mature starchy endosperm (reviewed by Shewry and Halford, 2002).

3.2. Dough formation

For zein, kafirin, pennisetin and the rice storage proteins to be functional in doughs, it is presumably necessary for the protein bodies to be disrupted during dough mixing and the proteins freed. However, disruption of the protein bodies has only been observed to happen in maize under conditions when high mechanical energy (specific mechanical energy of ≥100 kJ/kg) was applied using extrusion cooking (Batterman-Azcona et al., 1999) or roller flaking (Batterman-Azcona and Hamaker, 1998). Transmission electron microscopy indicated that the freed α-zein may have formed fibrils (Batterman-Azcona et al., 1999). With oats and pseudocereals, the storage proteins are presumably readily freed from the protein bodies during dough-making due to their aqueous soluble nature (Schoenlechner et al., 2008).

Lawton (1992) in seminal research showed that commercial zein, which is essentially only α-zein (Lawton, 2002; Oom et al., 2008), formed a visco-elastic wheat flour-like dough when mixed with maize starch and the inclusion of dibutyl tartrate (as a plasticizer) at 25 °C and above, and at 35 °C in the absence of dibutyl tartrate. A visco-elastic dough could not be formed below 25 °C and visco-elasticity was lost if the doughs were cooled below 25 °C. These temperatures were shown to relate closely to the T_g of zein as a function of moisture content. It was further observed by scanning electron microscopy (SEM) that zein had formed an extensive network of fibres (fibrils). The author concluded that the visco-elasticity of zein was governed by its T_g and that fibre formation was apparently responsible for the visco-elasticity of the zein-starch doughs. Such zein-starch doughs can also expand and hold gas (Sly et al., 2014; Berta et al., 2015). Dough viscosity has been found to be the major factor affecting gas bubble structure formation (Berta et al., 2015).

Oom et al. (2008) showed that kafirin (comprising α- and γ-kafirin) plus starch in water mixtures would not form visco-elastic doughs, even at the elevated temperature of 55 °C and with addition of lactic acid as a plasticizer. However, a "dough" could be formed with kafirin by plasticizing kafirin (which had been hydrated in water) into a resin using oleic acid in a 2:1 ratio (kafirin:oleic acid). At 22 °C, kafirin and commercial zein-oleic acid resins showed similar extensional viscosity and strain hardening as a