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Chemistry of gluten proteins

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Abstract

Gluten proteins play a key role in determining the unique baking quality of wheat by conferring water absorption capacity, cohesivity, viscosity and elasticity on dough. Gluten proteins can be divided into two main fractions according to their solubility in aqueous alcohols: the soluble gliadins and the insoluble glutenins. Both fractions consist of numerous, partially closely related protein components characterized by high glutamine and proline contents. Gliadins are mainly monomeric proteins with molecular weights (MWs) around 28,000–55,000 and can be classified according to their different primary structures into the α/β-, γ- and ω-type. Disulphide bonds are either absent or present as intrachain crosslinks. The glutenin fraction comprises aggregated proteins linked by interchain disulphide bonds; they have a varying size ranging from about 500,000 to more than 10 million. After reduction of disulphide bonds, the resulting glutenin subunits show a solubility in aqueous alcohols similar to gliadins. Based on primary structure, glutenin subunits have been divided into the high-molecular-weight (HMW) subunits (MW = 67,000–88,000) and low-molecular-weight (LMW) subunits (MW = 32,000–35,000). Each gluten protein type consists or two or three different structural domains; one of them contains unique repetitive sequences rich in glutamine and proline. Native glutenins are composed of a backbone formed by HMW subunit polymers and of LMW subunit polymers branched off from HMW subunits. Non-covalent bonds such as hydrogen bonds, ionic bonds and hydrophobic bonds are important for the aggregation of gliadins and glutenins and implicate structure and physical properties of dough.

Keywords: Gluten; Gliadins; Glutenins; Proline and glutamine

1. Gluten

Gluten can be defined as the rubbery mass that remains when wheat dough is washed to remove starch granules and water-soluble constituents. Depending on the thoroughness of washing, the dry solid contain 75–85% protein and 5–10% lipids; most of the remainder is starch and non-starch carbohydrates. In practice, the term 'gluten' refers to the proteins, because they play a key role in determining the unique baking quality of wheat by conferring water absorption capacity, cohesivity, viscosity and elasticity on dough. Gluten contains hundreds of protein components which are present either as monomers or, linked by interchain disulphide bonds, as oligo- and polymers (Wrigley and Bietz, 1988). They are unique in terms of their amino acid compositions, which are characterized by high contents of glutamine and proline and by low contents of amino acids with charged side groups. The molecular weights (MWs) of native proteins range from around 30,000 to more than 10 million. Traditionally, gluten proteins have been divided into roughly equal fractions according to their solubility in alcohol–water solutions of gluten (e.g. 60% ethanol): the solubles gliadins and the insoluble glutenins. Both fractions are important contributors to the rheological properties of dough, but their functions are divergent. Hydrated gliadins have little elasticity and are less cohesive than glutenins; they contribute mainly to the viscosity and extensibility of the dough system. In contrast, hydrated glutenins are both cohesive and elastic and are responsible for dough strength and elasticity. To simplify matters, gluten is a 'two-component glue', in which gliadins can be understood as a 'plasticizer' or 'solvent' for glutenins. A proper mixture of both fractions is essential to impart the viscoelastic properties of dough and the quality of the end product.

Though cysteine belongs to the minor amino acids of gluten proteins ($\approx$2%), it is extremely important for the structure and functionality of gluten (Grosch and Wieser,

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1999; Wieser, 2003). Most cysteines are present in an oxidized state and form either intrachain disulphide bonds within a protein or interchain disulphide bonds between proteins. These bonds are the main target for most redox reactions that occur during kernel maturation, milling, dough preparation and baking (Wieser, 2003). Additional covalent bonds formed during breakmaking are tyrosine–tyrosine crosslinks between gluten proteins (Tilley et al., 2001) and tyrosine–dehydroferulic acid crosslinks between gluten proteins and arabinoxylans (Piber and Koehler, 2005). The covalent structure of the gluten network is superimposed by non-covalent bonds (hydrogen bonds, ionic bonds, hydrophobic bonds). Though this class of chemical bonds is less energetic than covalent bonds, they are clearly implicated in gluten protein aggregation and dough structure (Wieser et al., 2006). Evidence for the presence of hydrogen bonds in gluten proteins are the dough weakening effect of hydrogen bond breaking agents (e.g. urea) and the dough strengthening effect of heavy water compared with that of ordinary water. The importance of ionic bonds can be demonstrated by the strengthening effect of NaCl or of bipolar ions such as amino acids or dicarboxylic acids. Hydrophobic bonds contribute significantly to the stabilization of gluten structure. They are different from other bonds, because their energy increases with increasing temperature; this can provide additional stability during the baking process.

2. Gliadins

Most gliadins are present as monomers; they were initially classified into four groups on the basis of mobility at low pH in gel electrophoresis (α-, β-, γ-, ω-gliadins in order of decreasing mobility). Later studies on amino acid sequences, however, have shown that the electrophoretic mobility does not always reflect the protein relationships and that α- and β-gliadins fall into one group (α/β-type). Modern methods such as two-dimensional electrophoresis or reversed-phase high-performance liquid chromatography (RP-HPLC) allow the separation of the gliadin fraction into more than hundred components. Based on the analysis of complete or partial amino acid sequences, amino acid compositions and MWs, they can be grouped into four different types: ω5-, ω1,2-, α/β- and γ-gliadins (Table 1) (Wieser, 1996). Within each type, structural differences are small due to substitution, deletion and insertion of single amino acid residues. ω-Gliadins are characterized by the highest contents of glutamine, proline and phenylalanine which together account for around 80% of the total composition. ω5-Gliadins have higher MWs (≈50,000) than ω1,2-gliadins (≈40,000). Most ω-gliadins lack cysteine, so that there is no possibility of disulphide crosslinks. These proteins consist almost entirely of repetitive sequences rich in glutamine and proline (e.g. PQQPFPQQ). α/β- and γ-gliadins have overlapping MWs (≈28,000–35,000) and proportions of glutamine and proline much lower than those of ω-gliadins (Table 1). They differ significantly in the contents of a few amino acids, e.g. tyrosine. Each of both types has two clearly different N- and C-terminal domains. The N-terminal domain (40–50% of total proteins) consists mostly of repetitive sequences rich in glutamine, proline, phenylalanine and tyrosine and is unique for each type (sequence Sections I and II, Fig. 1). The repetitive units of α/β-gliadins are dodecapeptides such as QPQPFPQQPYP which are usually repeated five times and modified by the substitution of single residues. The typical unit of γ-gliadins is QPQQPFP, which is repeated up to 16 times and interspersed by additional residues. Within the C-terminal domains, α/β- and γ-gliadins are homologous (sequence Sections III–V, Fig. 1). They present sequences which are non-repetitive, have less glutamine and proline than the N-terminal domain and possess are more usual composition. With a few exceptions, α/β-gliadins contain six and γ-gliadins eight cysteines located in the C-termional domain; they form three and four homologous intrachain crosslinks, respectively (Grosch and Wieser, 1999) (Fig. 1). Studies on the secondary structure have indicated that the N-terminal domains of α/β- and γ-gliadins are characterized by β-turn conformation, similar to ω-gliadins (Tatham and Shewry, 1985). The non-repetitive C-terminal domain contains considerable proportions of α-helix and β-sheet structures.

Though the distribution of total gliadins among the different types is strongly dependent on wheat variety (genotype) and growing conditions (soil, climate, fertilization), it can be generalized that α/β- and γ-gliadins are

Table 1
Characterisation of gluten protein types

Type	MW × 10^{-3}	Proportions[a] (%)	Partial amino acid composition (%)				
			Gln	Pro	Phe	Tyr	Gly
ω5-Gliadins	49–55	3–6	56	20	9	1	1
ω1,2-Gliadins	39–44	4–7	44	26	8	1	1
α/β-Gliadins	28–35	28–33	37	16	4	3	2
γ-Gliadins	31–35	23–31	35	17	5	1	3
x-HMW-GS	83–88	4–9	37	13	0	6	19
y-HMW-GS	67–74	3–4	36	11	0	5	18
LMW-GS	32–39	19–25	38	13	4	1	3

[a]According to total gluten proteins.