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Functional Replacements for Gluten

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Abstract

Celiac disease (CD) is an immune-mediated disease triggered in genetically susceptible individuals by ingested gluten from wheat, rye, barley, and other closely related cereal grains. Currently, the only therapy able to normalize the clinical and histological manifestation of the disease is a strict and life-long gluten-free (GF) diet. The replacement of gluten presents a significant technological challenge, as it is an essential structure-building protein, which is necessary for formulating high-quality baked goods. The objective of this paper is to review some basics about CD, its current prevalence, and the recent advances in the preparation of high-quality GF breads using GF flours, starches, hydrocolloids, gums, and novel functional ingredients and technologies.

INTRODUCTION

Celiac disease (CD) was once thought to be quite rare but has recently been shown to be one of the most common immune-mediated disorders in Western countries. Currently, Western countries show an estimated prevalence of CD of approximately 1% of the population (Catassi et al. 2010, Mustalahti et al. 2010). This change in the perception of its incidence moved gluten-free (GF) foods from a small niche product into mainstream grocery stores and onto chain restaurant menus. This spurred a quest for improved product quality, as poor-quality, expensive products were the norm (Hager et al. 2011).

GF products are welcomed by those diagnosed with gluten intolerance and wheat allergy. However, GF foods have also become popular because of the media attention brought on by books, websites, and emotive testimonials that suggest that elimination of gluten improves a variety of autoimmune conditions, promotes weight loss, and enhances general well-being. However, proof that GF diets can ameliorate or improve any of these conditions is lacking.

The first part of the paper introduces some basics about the disease and the need for GF products. The latter part of the paper focuses on the challenges, techniques, and alternate grains, gluten replacers and enzyme technologies being used to improve GF products.

WHY THE NEED FOR FUNCTIONAL REPLACEMENTS? CELIAC, GLUTEN INTOLERANCE, AND GLUTEN SENSITIVITY DEFINED

CD, also called gluten enteropathy and celiac sprue, is an autoimmune disease occurring in genetically sensitive individuals. CD is a severe form of a continuum of disorders called gluten sensitivity (GS). Several components are necessary: the genetic markers, a physiological or emotional stressor, and the presence of the offending amino acid sequence (Ciccocioppo et al. 2005) in the gliadin portion of the gluten protein complex of grains related to wheat, rye, and barley.

The inappropriate T cell–mediated immune response to gluten ingestion in those with CD results in impairment of the villi of the small intestine. This, in turn, impairs nutrient absorption, which impacts many body systems (Tjon et al. 2010).

PREVALENCE OF CELIAC DISEASE: SYMPTOMS AND DIAGNOSIS

CD was originally thought to be a rare, childhood food intolerance, characterized by severe malabsorption and always showed gut involvement. It is now known to occur at any age (the median age at diagnosis is approximately 50 years), may not involve the gut, and manifests with a wide range of symptoms (Rashtak & Murray 2009).

Clinical manifestations of CD vary according to age group: adults present diarrhea and silent manifestations, such as anemia, osteoporosis, and neurological symptoms, whereas infants and young children who develop CD not only present diarrhea, but also abdominal distension and failure to thrive (Fasano 2005, Green & Cellier 2007).

CD has emerged to encompass a broad spectrum of clinical manifestations (Farrell & Kelly 2002, Fasano & Catassi 2001, Feighery 1999, Murray 1999), which are associated with a large variety of changes in the mucosa of the small intestine (Kaukinen et al. 2001, Wahab et al. 2001). The incidence in the United States is approximately 1 in 100; worldwide, it is 1 in 266. However, the true prevalence of CD is difficult to ascertain because of often unclear clinical symptoms manifestation (Farrell & Kelly 2002) and the diversity and/or sensibility of the diagnostic criteria used to support the diagnosis of CD (Biagi et al. 2010).

DIAGNOSIS AND NUTRITIONAL PROBLEMS

Antibody techniques, specifically IgA tissue transglutaminase (TGase) and antiendomysial and IgG antideamidated gliadin peptide antibodies, have improved screening for CD (da Silva Neves et al. 2010). These antibody measures not only correlate with intestinal damage but also help further understanding of how people with mild or nongut symptoms suffer from GS.

CD, GS, and wheat allergy are reasons that some consumers choose GF products. Other consumers choose this particular diet because they believe that such a diet may mitigate conditions ranging from neurological conditions, including attention-deficit/hyperactivity disorder, autism, and multiple sclerosis, to digestive disorders, such as irritable bowel syndrome, and other autoimmune disorders, such as arthritis. Some use the GF diet as a way to control calories, and some because they view it as a healthier diet. Some adopt it because it is the diet du jour (O'Neill 2010). In the 2011 market analysis entitled *Gluten-Free Foods and Beverages in the US* (Euromonitor 2011), it states that only 8 to 12 percent of GF consumers reported purchasing GF products because they or a member of their household has CD.

Total life-long avoidance of gluten ingestion remains the cornerstone treatment for CD. The diet requires ongoing education of patients and their families by both doctors and dietitians. Compliance with a strict GF diet is not easy because (*a*) harmful gluten may contaminate food during processing steps, (*b*) it is socially limiting, (*c*) GF products are generally not widely available, are more expensive, and have lower palatability than those of conventional products (Arendt et al. 2008b), and (*d*) it may lead to nutritional deficiencies of B vitamins, minerals (especially calcium and iron), and fiber (Hopman et al. 2006). Thus, the production of high-quality GF products has become a very important socioeconomic issue (Berghofer & Schonlechner 2009, Gallagher et al. 2004). Moreover, GF products are commonly of lower quality and have poor mouth-feel and off-flavors (Hager et al. 2011). This review shows the many advances that are being made in the search for GF products of high sensory and nutritional quality.

FUNCTIONAL REPLACEMENTS FOR GLUTEN

Gluten's unique properties in bakery products, particularly yeast-leavened ones, are due to its ability to form thin gas-retaining films and its ability to aggregate into a stretchable, extensible, coagulable, protein-starch matrix (Gallagher et al. 2004). Its presence determines the overall appearance and textural properties of cereal-based products.

The crumb in wheat breads is a solid matrix of a continuous phase of gelatinized starch (Durrenberger et al. 2001) and a continuous gluten network that encloses the starch granules and fiber fragments (**Figure 1**). GF breads lack a protein network that can both hold water and form the matrix to embed the starch. The net result is a batter rather than a dough and a bread with numerous quality defects.

The Formulation of Gluten-Free Bakery Products

The development of GF bakery products has involved the use of (*a*) GF flours, such as rice, sorghum, oats, buckwheat, amaranth, quinoa, teff, and corn, (*b*) starches, (*c*) dairy products, (*d*) protein supplementation, (*e*) gums and hydrocolloids, (*f*) functional ingredients, and (*g*) alternative technologies, such as sourdough fermentation, enzymatic processing, and high hydrostatic pressure (HHP) processing. Recent scientific approaches are reviewed below.

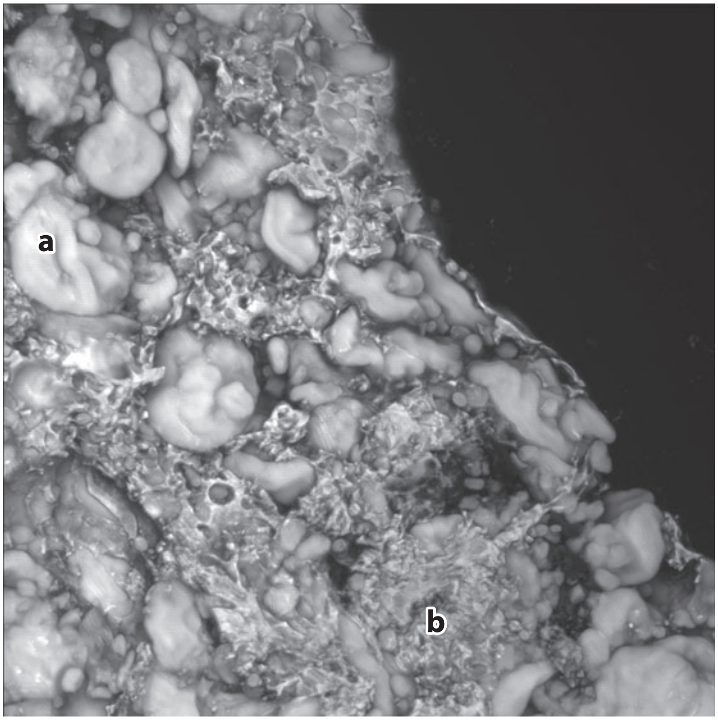

Figure 1

Confocal laser scanning microscope image of wheat bread crumb showing the gluten-starch matrix: (*a*) gelatinized starch granules; (*b*) embedded in the gluten network (40 × magnification) (Renzetti 2009).

Nongluten-Containing Grains and Pseudocereals

Historically, corn and rice were used in GF foods, but now alternate grains, legumes, seeds, and nut flours increase variety, nutritional quality, and palatability of GF products. These are listed in **Table 1**.

Corn

Corn (*Zea mays* L. ssp. *mays*) (**Figure 2**) and cornstarch (corn flour) have been used for GF products using xanthan gum as the networking component. The resulting bread has good specific volume but shows a coarse crumb structure and lack of flavor (Christianson et al. 1974). Ács (1996a,b) substituted xanthan, guar gum, locust bean gum, and traganceth for gluten in GF bread formulations based on cornstarch to increase loaf volume and soften crumb structure. A mixture of 72.4% cornstarch 17.2% rice flour, 8.6% cassava starch, and 0.5% soy flour resulted in GF bread with better volume and crumb structure (Sanchez et al. 2002).

Rice

Rice (*Orzyza sativa*) flour (**Figure 2**) is considered highly suitable for preparing GF products because it is bland and colorless, easily digested, and hypoallergenic (Kadan et al. 2001). It is also low in sodium, fat, and fiber (Gujral & Rosell 2004a,b). However, for baking applications, proteins in rice lack the elastic, plastic properties of wheat gluten (Juliano 1985) necessary to retain gas

Table 1 Grain and seed sources in the gluten-free diet

Gluten-containing grains	Gluten-free grains
Wheat (*Triticum* spp., including spelt, emmer, farro, einkorn, kamut, dickel, durums)	Amaranth[a]
Rye (*Secale*)	Buckwheat[a]
Triticale (a *Triticum* × *Secale* cross)	Corn
Barley (*Hordein*)	Millet
Oat[b]	Quinoa[a]
	Rice
	Sorghum[a]
	Soy[a]
	Legumes[a]
	Teff

[a]These sources contain higher levels of fiber, protein, calcium, and iron.
[b]Most oats have been grown, stored, transported, or processed with the gluten-containing grains and are therefore contaminated with gluten.

produced during fermentation. Also, rice starch, especially if substituted at more than 10% of the formulation, influences the texture of a product (Bean & Nishita 1985). This limits the use of rice flour in GF breadmaking (Gujral & Rosell 2004a,b).

The variety and the resulting amylose content of the rice flour also influence the quality of GF bread. Nishita et al. (1976) showed that rice varieties with low amylose contents and low gelatinization temperatures give superior crumb properties. Kadan et al. (2001) found that substituting 10% short grain rice for long grain rice in a white-rice bread formula improved texture and slowed retrogradation compared with breads made of 100% long grain rice.

Other dough additions have improved the quality of GF rice bread. Gums, such as hydroxypropyl methylcellulose (HPMC) (Sivaramakrishnan et al. 2004), guar gum, carboxylmethylcellulose (CMC) (Cato et al. 2004), xanthan gum (Lee & Lee 2006), and locust bean gum, have been

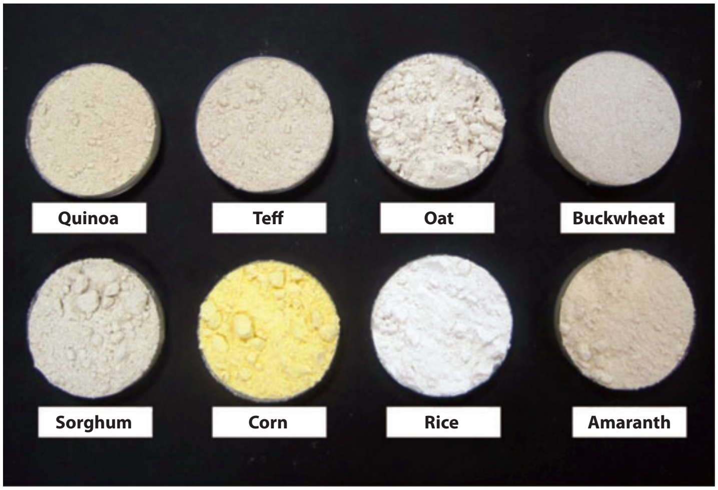

Figure 2
Images of gluten-free (GF) flours widely used for the production of GF bakery products.

shown to increase the batter viscosity and improve bread quality (Demirkesen et al. 2010). The emulsifier diacetyltartatic ester of monoglycerides (DATEM) (0.5%) improved GF bread volume and sensory scores (Demirkesen et al. 2010). Protein-crosslinking enzymes, such as TGase (Renzetti et al. 2008), and lipid protein–linking enzymes, such as cyclodextrin glycosyl transferase, help form viscoelastic complexes that improve performance of the batters (Gujral et al. 2003). The resulting gluten-like network improves texture of GF rice breads.

Sorghum

Sorghum (*Sorghum vulgare*) is often recommended as a safe food for celiac patients because it is more closely related to maize than to wheat, rye, and barley (Kasarda 2001). As with other cereal grains, the primary component of sorghum is starch (Rooney & Waniska 2000). Sorghum is similar to maize but may have a slightly lower protein and starch digestibility (Bean et al. 2006). However, some physicochemical properties of sorghum flour (**Figure 2**) negatively affect breadmaking performance. Specifically, its tendency to form coarse grits causes not only a sandy mouth-feel but also, when heated, allows formation of web-like structures that interfere with the starch gel, resulting in problems like a flat top of the bread and a large hole in the crumb. Moreover, sorghum's high gelatinization temperature (Schober 2009) may result in inadequate gelatinization during baking.

The quality of GF sorghum bread can be improved by adding proteins (Cauvain 1998), hydrocolloids (Satin 1988), emulsifiers, starches (Onyango et al. 2010, Schober et al. 2007), rye pentosans (Casier et al. 1977), or sourdough starter cultures (Galle et al. 2010b, Schober 2009a, Schober 2009b).

Starch has a pivotal role in GF sorghum-based bread. The addition of starches that gelatinize more readily completely facilitates development of a cohesive crumb network that traps gas bubbles and prevents loss of carbon dioxide and crust collapse. The additional starch also dilutes particles of endosperm and bran in sorghum flour that disrupt the liquid films around the gas cells and starch gel uniformity (Taylor et al. 2006). Additionally, Onyango and colleagues (2010) showed that a 50:50 blend of cassava starch and sorghum flour produced a better overall crumb than sorghum breads made from maize, potato, or rice starch. How specific properties of cassava starch influence the quality of sorghum breads needs further elucidation.

The variety of sorghum also matters (Schober et al. 2005) in the development of GF bread. Although breads differ little in volume, height, bake loss, and water activity, there are significant differences in size and number of pores as well as crumb hardness. Both differences in kernel hardness and damaged starch are key elements that determine suitability of sorghum hybrids for GF breadmaking.

Enzymes can also improve GF sorghum breads. Recently, glucose oxidase (EC1.1.3.4) addition to sorghum GF-bread formulations increased specific volume and maintained loaf shape (Renzetti & Arendt 2009). Improvements were thought to relate to protein polymerization that enhanced continuity of the protein phase and elastic-like behavior of sorghum batter.

Teff

Teff (*Eragrostis tef*) is only distantly related to cereals such as wheat, barley, rye, and oats, and lacks gluten-like prolamins that cause problems for CD patients (Tatham et al. 1996). Teff flour (**Figure 2**) is traditionally used in Ethiopia and Eritrea to produce a spongy pancake-like bread called injera. Teff flour is mixed with water in a 50:50 ratio to produce a batter that is then fermented. However, approximately 20% of the batter is removed and cooked to give a viscous paste called absit. The functionality of absit in the injera flatbread can be described as that of hydrocolloids in GF breads, providing the batter with a better gas-holding capacity because of increased viscosity.

Teff contains 3% fat, 9%–11% protein, and 80% starch, of which amylose makes up 25%–30% of the starch (Bultosa et al. 2002). Teff flour nutritional contents are similar to wheat flour and can be used for many of the same purposes. However, reports on the use of teff in GF bread production are lacking. However, its use for production of injera may stimulate research in the development of GF bread based on teff flour.

Pseudocereals

Pseudocereals, unlike monocotyledonae cereals, are dicotyledonae, but their starch-rich seeds can be used like cereals. The three best-known pseudocereal crops are grain amaranth (*Amaranthus caudatus*, *Amaranthus cruentus*, *Amaranthus hypochondriacus*), quinoa (*Chenopodium quinoa* subsp. *quinoa*; *Chenopodiaceae*), and buckwheat (*Fagopyrum esculentum*; *Polygonaceae*). These pseudocereals are being sought as alternatives to gluten-containing grains in the GF diet because of their nutritional contribution to the diet of persons with CD (Kupper 2005).

Amaranth

Amaranth (*Amaranthus* spp.) is a good choice for a GF patient because of its favorable nutrition profile. It offers high-quality oils (including squalene) and proteins with an amino acid composition close to that of egg (Yanez et al. 1994) (**Figure 2**).

The starch in amaranth has some unusual qualities, including excellent freeze-thaw and retrogradation stability, high gelatinization temperature, high viscosity, high water-binding capacity, high swelling power, and enzyme susceptibility. However, these same qualities may impair baking quality, which is regarded as poor with amaranth (Baker & Rayas-Duarte 1998, Hunjai et al. 2004). Amaranth loaves have improperly formed crumbs and small volumes (Aufhammer 2000). Recent application of sourdough technology has made amaranth doughs with a viscoelasticity similar to wheat. This is thought to be due to the lactic acid bacteria (LAB) and the enhanced flour enzyme activity in the acid environment developed during sourdough fermentation (Houben et al. 2010). However, the influences of sourdough fermentation on the rheological characteristics of the final products remain to be investigated.

Amaranth as part of a GF formulation has been investigated by Gambus et al. (2002). Replacement of 10% of cornstarch with amaranth not only increased protein and fiber levels by 32% and 152%, respectively, but also retained sensory quality, indicating that amaranth flour can be used to enhance the protein and fiber contents of GF breads.

Buckwheat

Common buckwheat (*Fagopyrum esculentum* Moench) is not taxonomically related to wheat. Protein content (11%–15%) is also similar to cereal grains, but with 55% starch the grain is lower in total starch than cereals (Bonafaccia et al. 2003). Buckwheat starch contains 24% amylose and 76% amylopectin (Aufhammer 2000), which is similar to that found in cereal starches.

Buckwheat addition can improve the nutritional quality of GF bread (Alvarez-Jubete et al. 2009, 2010). Buckwheat flour in GF breads increased protein, fiber, calcium, iron, and vitamin E, as well as their polyphenolic compounds and antioxidant activity.

Some technological limitations arise with buckwheat addition. GF breads containing 8.5% buckwheat flour (**Figure 2**) were brittle after two days of storage (Moore et al. 2004). Torbica et al. (2010) showed that GF breads made with different ratios of rice and unhusked or husked buckwheat flour achieved optimal crumb texture with a rice flour/buckwheat flour ratio equal to 70:30. However, high amounts of buckwheat flour impaired the protein network. This caused cracked crust surfaces. Moreover, increasing the amount of husked buckwheat flour from 10% to 20% increased taste intensity. Unhusked buckwheat flour has a bitter taste (Luthar 1992). In the process of milling, the husk is removed, leaving a pleasant flavor (Torbica et al. 2010).

Hydrocolloids, such as propylene glycol alginate (PGA), in a GF dough allow the addition of up to 40% buckwheat flour without any deleterious effect in terms of specific volume, crumb firmness, and crumb structure (Peressini et al. 2011). The effect of PGA [0.5% on fwb (flour weight basis)] improved batter viscosity by enabling the formation of elastic films at the gas-liquid interface, which helped gas retention (Baeza et al. 2004).

Quinoa

Quinoa (*Chenopodium quinoa* Willd) is a seed crop that originated in the Andes. The protein content of quinoa (13%–14%) is significantly higher than that of wheat (Repo-Carrasco et al. 2003). Quinoa is emerging as a healthy alternative to gluten-containing grains in the GF diet because it is a grain high in protein and offers a wide range of nutrients (Kupper 2005). Bread with added quinoa flour (**Figure 2**) reduced the volume, partly related to properties of the starch (Chauhan et al. 1992). However, GF breads were improved by replacing 50% of the potato starch with quinoa in the formulation that also contained rice flour (Alvarez-Jubete et al. 2009). The substitution increased the protein and fiber contents significantly to help meet nutritional recommendations for celiac patients. Moreover, the presence of vitamins and other bioactive compounds, such as phytosterols, further improve the nutritional quality of GF breads containing quinoa. However, more studies are needed on this promising GF alternative.

Oats

Oats (*Avena sativa*) have nutritional advantages that have been noted in recent years, including unsaturated fatty acids, vitamins, minerals and unusual phytochemicals, as well as fibers, especially the viscous β-glucan (Flander et al. 2007, U.S. Food and Drug Administration 2008, Pulido et al. 2009, Ryan et al. 2007). The latter has been shown to lower cholesterol and help control blood glucose. Both are important to many consumers, especially those on GF diets, which are often low in fiber and some microconstituents (Malandrino et al. 2008). Moreover, oats make possible a variety of palatable food choices in a restrictive diet (Janatuinen et al. 2002). Hüttner et al. (2010b) investigated the rheological properties and breadmaking performance of three commercial whole oat flours (**Figure 2**). Whole oat flours with coarse particles, limited starch damage, and low protein content resulted in a bread with good quality, nice volume, and soft crumb structure (Hüttner et al. 2010b).

FUNCTIONAL INGREDIENTS USED FOR THE PRODUCTION OF GLUTEN-FREE BREADS

Dairy, egg, soy, and maize have long been used in baking, so replacing gluten with these is a logical approach for GF foods to improve both their nutritional and functional qualities.

Dairy Proteins

In a baked product, dairy ingredients form networks that enhance flavor and crust color, improve texture, reduce staling, and increase water absorption, and therefore enhance the handling properties of batters (Arendt et al. 2008a). GF wheat starch breads prepared with sodium caseinate and milk protein isolate have improved shape and volume, a firmer crumb, an appealing white color, and better sensory scores. However, batters and breads containing whey protein were poor by most metrics (Gallagher et al. 2003). In contrast, Nunes et al. (2009) showed that the inclusion of whey protein in GF bread induced a higher volume than did sodium caseinate in systems that also contained gums. Gums exert relevant differences in water availability in the batter that, in turn, influences crumb structure. Moore et al. (2004) noted that GF formulations that contain dairy fared better after two days storage than other GF formulations. Micrographs of the bread crumb of the GF breads with added dairy showed network structures more closely resembling those of traditional wheat bread.

Despite the functional improvements seen with the use of dairy in GF formulations, this protein source has a significant drawback for use in GF products. The damage that CD causes to the intestinal villi leaves some intolerant to lactose (Bodé & Gudmand-Høyer 1988). Therefore, lactose may limit acceptance of GF products with dairy ingredients.

Egg Proteins

Egg proteins form strong cohesive viscoelastic films, which are essential for stable foaming (Ibanoglu & Ercelebi 2007) and improved gas retention (Jonagh et al. 1968). Egg albumen in combination with methylcellulose and gum arabic improves GF breads' crumb, first bite hardness, adhesiveness, masticatory hardness, and cohesiveness (Toufeili et al. 1994). Thus, it improves overall quality.

GF breads utilizing both egg proteins (egg powder) and the enzyme TGase increase the water-holding capacity of the GF bread and form a protein network similar to that found in wheat bread. The resulting bread shows lower baking losses and increased crumb moisture, fineness, lightness, and homogeneity (Moore et al. 2006). Thus, egg can be a structure builder in GF products and can add much needed nutritional enhancement.

Soybean

Soy has long been used to add the needed amino acids to complement grain proteins and to improve nutritional quality. It also improves mechanical behavior of dough and textural quality of the final bread during storage (Ribotta et al. 2004, Sanchez et al. 2004).

Soy flours and protein concentrates added to GF wheat starch–based breads transform crumb and texture from a rough, crumbly, open interior to a more tender and close-grain structure (Ranhorta et al. 1975). However, high levels of soy severely decrease GF bread quality. A small amount of soy (0.5%) added to a corn starch, cassava starch, and rice flour formulation increases the loaf volume and gives the crumb a more even texture and improved sensory scores (Sanchez et al. 2002).

Enzyme-active soybean flour improves the volume and structure of GF bread over flours with inactivated enzymes, so the effect is due to both structural proteins and enzymatic activity (Ribotta et al. 2004). Moreover, the particle size and concentration of the soybean flours also affect bread quality. In conclusion, soy proteins are suitable for GF formulations as they can overcome problems related to crumb.

Corn Protein (Zein)

Zein from corn has recently been found to be suitable for GF bread production (Schober et al. 2008). The maize prolamin (zein) combined with starch and water can form viscoelastic doughs closely resembling wheat dough, provided (*a*) they are mixed above room temperature (Lawton 1992), (*b*) hydrocolloids, such as HPMC, are added so the bread will have adeqaute volume (Andersson et al. 2011, Schober et al. 2008), and (*c*) the surface of the zein particles is defatted. This improves their ability to aggregate by not impairing water absorption and enabling protein-interactions between zein particles. The combination of defatted zein with HPMC in a cornstarch GF formulation yielded a bread with markedly improved volume and shape (Schober et al. 2010). Modifications of zein through development of new recipes or different processing conditions may possibly improve dough rheology and baking performance even further and reduce the cost of this type of GF bread.

Starches

Starches are widely used by the food industry to gel, thicken, retain moisture, emulsify, form films, and texturize. In dough, they absorb water and significantly contribute to texture, appearance, and overall acceptability of baked goods (Miyazaki et al. 2006, Ward & Andon 2002). In terms of structure, they may act as inert filler in the continuous matrix of the dough (Bloksma 1990) or be part of a bicontinuous network of protein and starch (Eliasson & Larsson 1993). During bread baking, starch granules gelatinize, i.e., they swell and are partially solubilized, but still maintain their granular identity (Hug-Iten et al. 2001). Starch gelatinization could play an important role in GF formulation because of the ability of starch pastes to trap air bubbles that aid the gas-holding capacity of batter. Thus, gel-forming starches, such as pregelatinized starches, and air cell stabilizers, such as gums, have been suggested as a means to hold gas (Gallagher 2009). Moreover, the addition of starch in GF formulas could (*a*) improve batter consistency during mixing, (*b*) enhance the softness of the crumb, and (*c*) control starch gelatinization during the baking process (Gallagher 2009).

Starch from corn, cassava, sweet potato, potato, sorghum, barley, and rice can be used in GF products. Isolated wheat starch is not recommended because many celiac patients are sensitive to even traces of gliadins (Lohiniemi et al. 2000). Rice starch is a basic ingredient in GF bread because of its low sodium content and high digestibility (Gallagher et al. 2002). Corn and tapioca starches may impart unusual tastes to bread (Sànchez et al. 1996). Further studies are required to better understand the impact of different starch types and their functional properties in GF products.

Hydrocolloids

The viscoelastic properties provided by the gluten network are largely responsible for the important rheological characteristics of dough, such as elasticity, extensibility, resistance to stretch, mixing tolerance, and gas-holding ability (Gan et al. 1989). The replacement of gluten in GF products presents major challenges because GF batters have a liquid consistency due to an inadequate gluten network (Cauvain 1998). Thus, polymeric substances that create viscoelastic properties are required for development of GF breads (**Table 2**) to improve structure, mouth-feel, acceptability, and shelf life of GF baked goods (Toufeili et al. 1994).

Hydrocolloids or gums are hydrophilic long-chain, high molecular weight polysaccharides extracted from plant, seaweed, and microbial sources, as well as gums derived from plant exudates

Table 2 Hydrocolloid used in gluten-free breadmaking

Hydrocolloid	Gelling properties[a]	Effect on gluten-free bread	References
Agarose	Forms gels upon heating	Increased loaf volume Decreased uniformity of crumb (large gas cells)	Lazaridou et al. 2007
Guar gum	Highly viscous solutions, no gelling properties	Even cell size distribution in crumb, retarded bread staling	Schwarzlaff et al. (1996)
Locust bean gum	Slightly soluble in cold water, dissolves in water at 85°C Forms gels with κ-type carrageenans and xanthan	Increased height of the bread loaves, retarded bread staling	Schwarzlaff et al. (1996)
Hydroxypropyl-methyl-cellulose	Forms gels upon heating Some interfacial activity and ability to form films	Increased specific volume Improved gas retention and water absorption	Kang et al. (1997) Gan et al. (1989), Kadan et al. (2001)
Pectin	Low-methoxyl pectins form gels in presence of calcium ions	Increased crumb porosity	Lazaridou et al. (2007)
Xanthan gum	High viscosity, pseudoplastic solutions (unaffected by temparature, pH, salt conditions). Forms gels with agarose, κ-type carrageenans, locust bean gum, konjac gum	Good crumb structure Decreased loaf volume and increased crumb firmness	Christiansson et al. (1974) Lazaridou et al. (2007), Schober et al. (2005)

[a]Source: Hüttner & Arendt 2010.

and modified biopolymers prepared by chemical treatment of cellulose (Dickinson 2003). They usually have colloidal properties and are capable of producing gels in water systems (Hoefler 2004).

All types of hydrocolloids have been considered as gluten replacers in GF breads (Gallagher et al. 2004, Gujral & Rosell 2004b, Lazaridou et al. 2007, Lee & Lee 2006, Schober et al. 2008, Toufeili et al. 1994). Generally, hydrocolloids enhance texture and appearance and improve loaf volume. However, hydrocolloid functionality was dependent on the source and extraction process, the chemical structure and any modification to it, the dose used, and the interaction with other food polymers and ingredients (Anton & Artfield 2008, El-Sayed 2009, Hüttner & Arendt 2010). HPMC and xanthan gum are most used because they most successfully replace gluten in GF breads, regardless of the formula used (Anton & Artfield 2008).

Water

Water impacts the rheological behavior of GF batters and quality of GF breads (Arendt et al. 2008b). Dough expansion and gas retention during proofing require elasticity. If the proportion of water is too low, the dough becomes brittle and inconsistent and exhibits a marked crust effect due to rapid dehydration at the surface. If water proportion is too high, the batter viscosity is low, resulting in little or no resistance to deformation, thus no extensibility and development (Arendt et al. 2008b). Starch gelatinization and other reactions occurring during baking are affected by water. Thus, water governs softness of crumb, crispness of the crust, shelf-life, and other textural properties (Wagner et al. 2007). GF formulations with 10%–20% additional water result in higher loaf volume and softer crust and crumb texture (Gallagher et al. 2003, McCarthy et al. 2005). Schober et al. (2005) studied the rheological and crumb properties of sorghum batter and bread, respectively, by varying the water content (95%–120% fwb) while maintaining a constant starch content (30% cornstarch). High water formulations gave pancake-like batters, whereas low water formulations gave doughs that lacked elasticity. Batters higher in water yielded breads with higher volumes than those with low water contents.

The amount of water and the amount of gum impacts texture. HPMC (2.2%) and 79% water yielded good-quality GF bread (Bárcenas & Rosell 2005). Hydrocolloids limit both the diffusion and the loss of water from bread crumb. According to Davidou et al. (1996), HPMC in wheat bread decreased the hardening rate and retarded amylopectin retrogradation, which, in turn, delayed bread staling. Thus, water content and mobility may be key factors controlling loaf volume and crumb firmness in bread.

NOVEL APPROACHES IN GLUTEN-FREE BREADMAKING

Sourdough Technology

Sourdough, a mixture of flour and water fermented with LAB and yeasts (Hammes & Gänzle 1998), improves flavor and structure of bread (Arendt et al. 2007) by enhancing (*a*) gas retention, (*b*) textural quality, (*c*) flavor, (*d*) nutritional value in terms of mineral bioavailability, starch digestibility, and concentration of bioactive compounds, and (*e*) shelf life by retarding staling and by protecting bread from spoilage (De Vuyst & Vancanneyt 2007, Gobbetti 1998, Poutanen et al. 2009). Doughs are improved through lactic acid fermentation, proteolysis, exopolysaccharide production, and synthesis of volatile and antimicrobial compounds (Arendt et al. 2007, Corsetti & Settanni 2007). Thus, sourdough technology appears to be a natural and efficient way to improve the quality of GF bread (Moroni et al. 2009).

Cultures for GF sourdough must foster beneficial fermentations and inhibit the growth of contaminants (De Vuyst et al. 2009, Minervini et al. 2010). So far, commercial starters are not suitable for the fermentation of GF materials and need to be developed (Moroni et al. 2010, Vogelmann et al. 2009). Strains not commonly isolated in traditional sourdoughs but found in GF ones might work as starters in GF systems (Edema & Sanni 2008, Meroth et al. 2004, Moroni et al. 2010, Sterr et al. 2009, Vogelmann et al. 2009).

Sourdough fermentation improved crumb structure of GF sorghum bread (Schober et al. 2007). Similarly, GF bread prepared with *Lactobacillus plantarum* FST 1.7 as sourdough starter culture showed not only softer crumb but also reduced mold growth (Moore et al. 2008). Furthermore, Hüttner et al. (2010a) found that sourdough with species isolated from oats increased loaf volume and improved crumb structure and oat bread quality. Such results suggest sourdough technology can be successfully applied for improving the quality of GF bread (Galle et al. 2010a, Moore et al. 2007, Moroni et al. 2010, Sterr et al. 2009, Vogelmann et al. 2009).

High Hydrostatic Pressure Technology

HHP technology, which consists of submitting foods to pressures between 100 and 1000 MPa, may be a useful technology for GF foods because it creates new structures and textures by modifying functional properties of proteins and starches (Ahmed et al. 2007, Gomes et al. 1998, Kieffer et al. 2007). With HHP, starch swells and is gelatinized without the disruption of granule integrity that occurs with heating (Gomes et al. 1998, Vallons & Arendt 2009). In general, the extent of swelling highly depends on the applied pressure, treatment time and temperature, and concentration and type of starch (Stolt et al. 2000).

Protein is also affected by HHP treatment. In wheat, the formation of disulphide bonds enhances the need to form a strong protein network (Kieffer et al. 2007). When HHP is applied to wheat dough, reduction of specific volume, uneven cell gas distribution, and increased crumb hardness are observed (Bárcenas et al. 2010), but different results occur when HHP is applied to GF batters. In HHP basmati rice slurries, there is complete gelatinization of starch and denaturation of protein and increased mechanical strength (Ahmed et al. 2007). In HHP-treated buckwheat, white rice, and teff batters, there are (*a*) changes in the microstructure of the batters, (*b*) starch gelatinization, and (*c*) protein polymerization by thiol/disulphide-interchange reactions in white rice and teff batters (Vallons et al. 2010). For buckwheat proteins with no free sulfhydryls, no protein crosslinking is observed. HHP treatment of oat batters causes pregelatinization of starch, which resulted in higher batter viscosity and elasticity that, in turn, increased gas retention of the batters and improved texture and volume of the bread (Hüttner et al. 2010a). Thus, HHP processing seems to be a promising tool for the improvement of GF bread.

Enzyme Technology

Enzymes are commonly applied in the baking industry and are being successfully applied to GF systems. Crosslinking enzymes, particularly TGase, promote protein networks needed to increase dough elasticity and reduce dough deformation in GF foods (Gujral & Rosell 2004a, Renzetti et al. 2008). However, the improved batter properties do not always translate into increased bread volume (Renzetti et al. 2008, Marco & Rosell 2008). Beneficial effects of TGase were seen in breads from buckwheat, rice, and corn flour, but not from oat, teff, and sorghum flours (Renzetti et al. 2008).

The enzyme glucose oxidase (GO) also promotes protein networks in some GF batters. Gujral & Rosell (2004b) used GO and obtained GF rice breads with increased volume and decreased crumb hardness. GO combined with 2% HPMC improved the bread even more. GO treatment of sorghum and corn also improved the breads, whereas no improvement was observed with buckwheat, teff, and oat breads (Renzetti & Arendt 2009, Renzetti et al. 2010).

Enzymes that cause depolymerization (proteases) have also been used in GF formulations. Protease-treated oat and brown rice batters had lower batter consistency and viscosity, allowing greater expansion and bread volume and reducing crumb hardness and chewiness (Renzetti 2009, Renzetti & Arendt 2009, Renzetti et al. 2010). Both peptidases and glutathione disrupt disulfide-linked proteins, present (or formed) in making rice breads. Because highly linked proteins inhibit starch swelling (Derycke et al. 2005), less agglomerated proteins enhance starch phase continuity and improve bread quality.

Enzyme and other technologies are in their infancy but are offering great promise in the search for bread products that are GF.

CONCLUSION

CD has emerged as a common food intolerance worldwide. The only currently available and safe treatment for CD is the dietary exclusion of grains containing gluten along with supportive nutritional care to address mineral and vitamin deficiencies (Hopman et al. 2006).

Products for a GF diet are often expensive and of poor quality. This is not surprising because gluten forms the basic structure necessary for the appearance, texture, structure, and flavor of many baked products, especially yeast bread. Replacing gluten in GF bread requires employing a mix of allowed flours, proteins, hydrocolloids, and technologies in an attempt to replace gluten's many roles. Ingredients must help form a basic structure, a viscoelastic network to hold gas and form cell structure, bind water, allow expansion and volume development, and improve the overall structure of the bread. Optimizing GF bread formulas with the correct amount of water and ingredient mixture is the challenge. Xanthan gum and HPMC are the most suitable hydrocolloids identified so far. Egg protein and specially-treated corn protein are promising structural ingredients. Technologies such as enzyme, HHP, and sourdough fermentation appear to offer promise to improve GF bread quality. Even if the research on GF products is still in its infancy, researchers have been able to create products that are superior to the ones currently on the market and that celiac patients might soon be able to see available in the stores.

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