Flour Modification for the Development of Gluten Free Bread

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1 Introduction

The trend of Gluten Free (GF) products has emerged globally in the past few years owing to updated consumer awareness about wheat allergy, gluten sensitivity and intolerance or a widely spread belief that GF products are healthier (Golley et al., 2015). Gluten sensitivity is the major driving force for the scientists to explore opportunities to develop technologies developing high quality gluten free breads. In particular, gluten sensitivity may arise as a result of celiac disease, non-celiac gluten sensitivity and wheat allergy. It has been estimated that about 1% of the world population has encountered with celiac disease and the only treatment available till date is strict exclusion of gluten containing ingredients from diet (Ronda & Roos, 2011). Although GF breads are available in the market, improvement in their quality to enhance acceptability is still challenging. In case of breadmaking, it is essential to mimic the textural properties obtained when prepared with wheat dough. Gluten proteins are critical components of wheat giving bread a unique body and texture due to their visco-elastic properties (elasticity by glutenins and viscosity by gliadins). Formation of gas cells and their stability provide excellent loaf volume and crumb texture to wheat-based breads. Absence of gluten hinders the dough rheology and production process of breadmaking. Gluten free dough is very sticky and difficult to handle due to its low elasticity and cohesiveness, which is a crucial property for breadmaking (Matos & Rosell, 2015).

Major ingredients avoided in production of gluten free products are wheat, rye and barley. Several other nutritional ingredients such as maize, rice, millets, quinoa, soya etc. have been evaluated for their potential as GF bread ingredients. There are number of challenges in development of gluten free products specially bread

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including poor texture, undesirable taste and flavor, reduced expansion and inferior crust and crumb characteristics. Several approaches have experimented to overcome these issues. Functionality of sourdough fermentation in gluten free bread making has been positively correlated to improvement in quality attributes such as sensory properties, nutritional profile and shelf stability (Moroni et al., 2009). Similarly, incorporation of certain additives such as starches, flours, gums, hydrocolloids, emulsifiers, and proteins has also been reported to influence the quality of GF bread (Houben et al., 2012). Role of each additive and ingredient and their impact on GF bread quality is detailed in the coming sections. Presently, there are certain novel technologies being evaluated in manufacturing of high-quality GF bread such as enzymatic treatment, high pressure processing, and extrusion technology. This chapter deals with the recent trends of modification of flour to develop gluten free bread.

2 What Is Gluten?

Gluten is a complex protein composed of gliadin and glutenins, which plays a very important role in the bakery industry by offering a wide range of techno-functional properties *viz.*, water holding capacity, elasticity, cohesivity and viscosity to the dough (Fig. 1). When wheat dough is washed thoroughly with water, starch

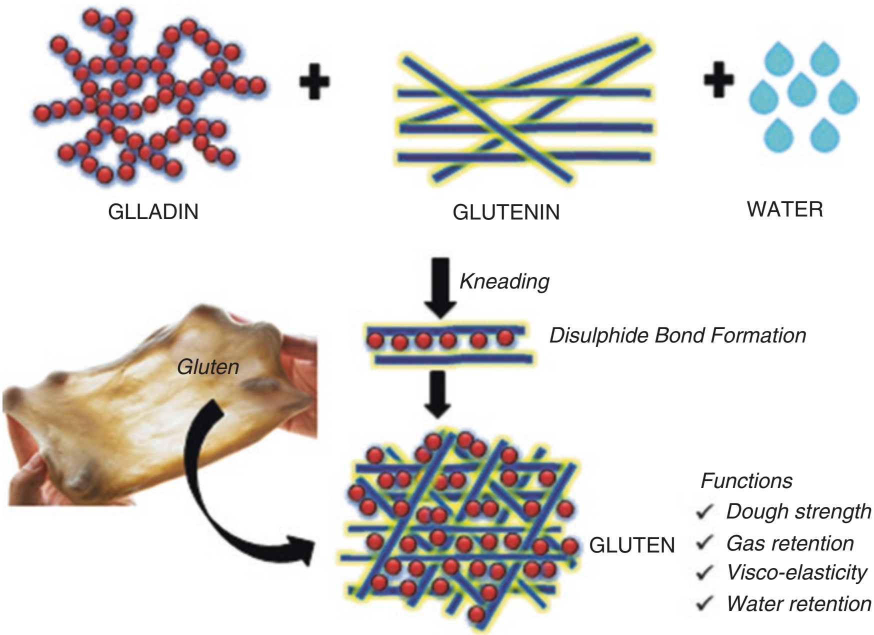

Fig. 1 Gluten formation and its functions

granules and water-soluble constituents are removed leaving behind rubbery mass known as “Gluten”. On dry basis, gluten contains protein content ranging from 75% to 85% depending upon the extent of washing and 5–10% lipids, remaining are carbohydrates including starch. Cereals containing gluten are wheat, rye, barley, einkorn, kumut, triticale and spelt. Gluten has a wide range of variability in chemical composition and size because of the difference in genotype, growth pattern and some other technical aspects.

Gluten proteins have been fractionated into two components depending upon their solubility in alcohol-water solution, for instance 60% ethanol; gliadins and glutenins being soluble and insoluble respectively. Gluten proteins have been classified on different basis such as variation in the molecular weight and sulfur content. Another way of classification divides gluten protein on the basis of their primary structures as α, β, γ, and ω gliadins (Shewry & Lookhart, 2003). Most important amino acid affecting the structure and functionality of gluten is cysteine which is present in very little amount (about 2%). Most of the cysteine molecules are oxidized and are responsible for the formation of disulphide bonds within the protein or between separate protein molecules. These disulphide bonds are utmost important sites for redox reactions taking place during milling, dough formation and processing treatments such as baking.

The structure of gluten matrix is maintained by a series of covalent and non-covalent bonds involving ionic bonds, hydrophobic bonds and hydrogen bonds. The gluten matrix corresponds to the quality of dough which further impacts the final product quality such as bread and other bakery products. Gluten is a potential additive used to impart flavor and texture, helps in retention of water due to extending and binding properties. Modification of gluten is also done in accordance to its end product use (Biesiekierski, 2017).

3 Gluten Sensitivity or Gluten Intolerance

“Gluten Sensitivity” or “Gluten Intolerance” is a broader term integrating three major gluten related sensitive conditions *viz*. Celiac Disease (CD), Non-Celiac Gluten Sensitivity (NCGS) and Wheat Allergy (WA) (Fig. 2). Although these three disorders share some common symptoms including upset stomach, diarrhoea and vomiting on consumption of gluten products, they have remarkable variation in terms of causes, laboratory markers and histopathological intestinal conditions. Gluten proteins, a mixture of prolamins resist hydrolysis in the gastrointestinal tract with the action of proteases resulting in the occurrence of pathogenic protein subunits or peptides which are able to cause celiac disease and wheat allergy (Balakireva & Zamyatnin, 2016).

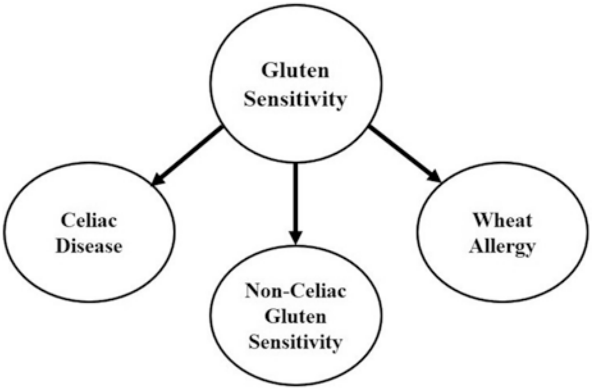

Fig. 2 Different forms of gluten sensitivity

3.1 Celiac Disease (CD)

Celiac Disease is a chronic condition influenced by immunological response triggered by ingestion of gluten and related proteinaceous compounds. CD has been reported in 1% of the total population worldwide with most of the cases undiagnosed. There has been four to five times increase in the prevalence of CD in past 50 years, however, the reason for such upsurge is not clearly known. This disorder is observed in inherently predisposed individuals and better understood as action by certain autoantibodies against transglutaminase-2 (tissue), deaminated peptides (gliadin) and endomysium (Ludvigsson et al., 2013).

CD is a result of incomplete digestion of gluten protein leaving behind peptides containing about 33 amino acid units which in the intestinal tract pass through the epithelial cells barrier to enter lamina propria either via paracellular or transcellular pathway. There occurs an adaptive immune response reaction when CD4 positive cells recognize gliadin peptides through antigen presenting cells leading to the emergence of proinflammatory cytokines, specifically interferon-γ (Sollid, 2002). In addition to adaptive response, innate immune responsive reaction is also activated which is detected by the action of enterocytes as enhanced expression of interleukin-15 causing the stimulation of intraepithelial lymphocytes cells triggering occurrence of receptor NK-G2D recognized as the natural cell killing expression (Mention et al., 2003). These receptor cells impart cytotoxicity by damaging enterocytes by a similar mechanism noted in case of infection due to expression of a cell surface antigen emerged out of stress (Meresse et al., 2004; Green & Cellier, 2007). Although the actual mechanism for such interactions in the lamina and epithelium has not been systematically explained, recent reports suggest non gluten proteins also initiate cell damage in innate epithelial (Junker et al., 2012). Impact of CD on nutrient absorption is illustrated in Fig. 3.

Genetic factors have been seen to play a significant role in occurrence of CD. This condition does not arise unless any individual has HLA gene products encoding for

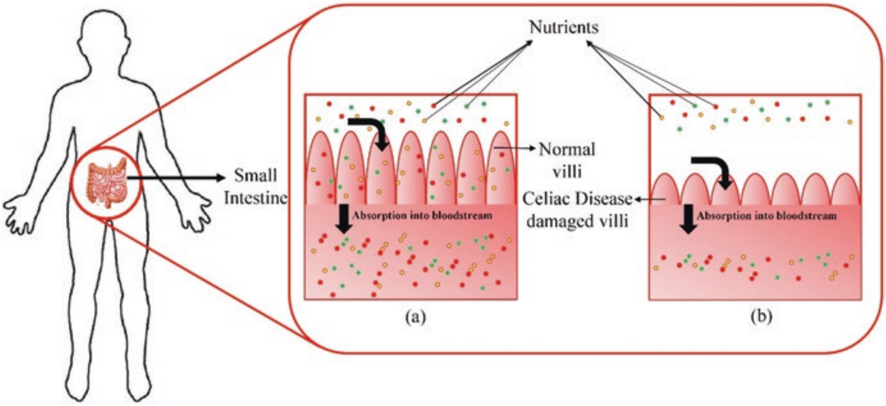

Fig. 3 (**a**): Absorption of nutrients through normal villi and (**b**) Poor absorption of nutrients through CD damaged villi

HLA-DQ8 or HLA-DQ2 kinds of proteins (Sollid & Lie, 2005). These two alleles are considered crucial for the identification of CD in an individual since their presence in general population is about 30–40%. In case of CD positive patients, HLA-DQ2is present in more than 90% cases and remaining patients are found positive for HLA-DQ8. Therefore, absence of these genes confirms the negative results for CD. However, a non-HLA class of genes has also been identified to have a role in CD, but their impact has not been confirmed.

In relation to environmental effects, it has been observed that introduction of gluten to weaning foods and breast feeding are two very critical factors. Infants below the age of 4 months administrated with feed containing gluten are at higher risk to adapt to CD (Norris et al., 2005). Moreover, certain drugs and proton pump inhibitors have also been reported to cause onset of CD, but this impact is inconclusive since there is possibility of undiagnosed CD in such case rather than its origin. Gastrointestinal discomforts including disorders relating to pancreas and liver have also been documented with the development of CD severity ranging from enhanced level of transaminases in serum to deadly liver failure and cancer. However, relation of CD to cardio-vascular diseases is contradictory.

3.2 Non-Celiac Gluten Sensitivity (NCGS)

The term NCGS refers to the condition triggered by ingestion of food containing gluten presenting intestinal and extra intestinal symptoms in patients tested negative for CD. This gluten related disorder has been proposed to be more frequent in comparison to CD, however, data for exact frequency is limited due to lack of absolute biomarkers. Such condition disappears on withdrawal of gluten from diet within hours and immediate symptoms are observed again with introduction of gluten in diet (Leonard et al., 2017). The extraintestinal impact of this disorder is characterized in terms of foggy brain, which is expressed by symptoms of muscle pain, weakness, dermatitis, numbness (arm/leg), headache along with neurological impacts such as decline in alertness level, memory interruption and slow thinking. Another impact of gastrointestinal disorder appears in terms of diarrhoea, constipation, stomach or abdominal pain, bowel irregularity and bloating.

The pathophysiology details of Non-Celiac Gluten Sensitivity are imprecise and not conclusive. Adaptive immune response and enhanced interferon γ response are the underlying evidences in few reports studying the gluten challenge. The differentiation of CD from NCGS is known due to lack CD specific antibody biomarkers but in certain cases, antibodies in reference to gliadin proteins are observed which are having lower specificity for CD and such antibodies -disappear with the onset of GF(GF) diet, for example IgG (Caio et al., 2014). Gluten proteins have been reported for certain intrinsic biological properties altering the morphology of the cells leading to motility, and organizational setup of cytoskeleton due to constricted junction proteins (Roncoroni et al., 2013; Casella et al., 2018). Binding of TLR2 receptors cells with gliadin protein subunits has been reported to enhance the production of Interleukin 1 (proinflammatory cytokine) via intermediation of Myd88, which is a known compound for the release of zonulin upon consumption of gluten to increase the permeability of the mucosal cells (Palová-Jelínková et al., 2013).

Certain reports argued that the term "non-celiac wheat sensitivity" better describes the condition as the actual reason for underlying disorder may be the other constituents present in wheat. However, NCGS has been suggested as the most common gluten related disorder with the absence of diagnostic biomarkers. In addition to gluten, believed possible components responsible for such condition are FODMAPs (fermentable sugars such as mono-, di- and polysaccharides), sugar alcohols and anti-nutrients like amylase-trypsin inhibitors (ATIs). Intake of FODMAPs has been correlated with the positive symptoms of NCGS; and the diet limited in FODMAPs for 2 weeks resulted in self-reported NCGS improved symptoms in a recent study. ATIs have also been reported to have significant impact in NCGS, although they represent only 4% of the total protein present in wheat. They are also responsible for activation of innate immune response in small intestine and colon inflammation as reported in both *in vitro* and *in vivo* studies and thereby triggering the expression of myeloid cells of mesenteric lymph node and activate Toll-like receptor-4 due to ATIs being resistant to heat and proteases enzymes (Zevallos et al., 2017; Barbaro et al., 2018).

3.3 Wheat Allergy (WA)

One of the most general reasons of food allergies related to consumption (inhalation or ingestion) is wheat and some of the proteins out of many present in wheat (more than 100) are considered responsible for allergies. Wheat proteins have been classified as albumins, globulins, gliadins and glutenins on the basis of their extraction in different solvent systems. Majorly, the wheat allergy has been reported to be seen with glutenin fractions (low and high molecular weight compounds) along with globulins (α, β, γ, and ω fractions). Certain components of albumins and globulins such as proteinases inhibitors, α-amylase inhibitors, β-amylase, puroindolines, lipid transfer proteins (LTPs) and other surface-active protein moieties. Since wheat belongs to family Poaceae and is a grass, allergens like lipid transfer proteins and α-amylase cross react with other pollen allergens of grass. The most common allergies observed in case of wheat are wheat-dependent exercise-induced anaphylaxis (WDEIA), anaphylaxis and Baker's asthma owing to heat resistant allergens including trypsin and α-amylase inhibitors (Ricci et al., 2019).

Wheat allergen belonging to the class of nsLTP (Tri a 14) is a significant candidate to cause allergy through IgE-mediated foods along with Baker's asthma and WDEIA. Similarly, water insoluble Tri a 19 (ω-5-gliadin) has also been categorized as one of the potential allergens in reference to WEDIA. Presence of antibodies against mechanism of Tri a 37 (highly resistant to digestion and high temperature, a plant defensive protein) in an individual is a great risk to develop allergy upon consumption of wheat (Cianferoni, 2016). WA is generally attributed to outcome of IgE-mediated reactions showing the impact characterized by nausea, bronchial obstruction, urticaria, abdominal pain, angioedema or anaphylaxis within 2 h of ingestion of wheat product.

Pathogenesis of WA has been explained as the clinical indications of WA are attributed to the release of mediators from basophils and mast cells (such as leukotrienes, histamine and platelets activator factor). Contact of any particular allergen with specific IgE antibodies at their receptor point accelerates the cross linking IgE receptor (FcεRI) to trigger the activity of basophils and mast cells. Such release of antibodies due to wheat are a result of Th2-biased immune dysregulation and oral tolerance. Intrinsic profile of wheat allergens also determines the whether specific allergen induces immune response or not. Generally, food allergies are caused due to glycoproteins which are comparatively resistant to acid, temperature and proteases digestion (Lee & Burks, 2006; Lack, 2008; Radauer & Breiteneder, 2007).

Derivative allergies are also important in case of wheat. With the actions of enzymes, proteolysis occurs cutting the protein molecules into simpler units with addition of water molecules at the site and the process is also known as enzymatic hydrolysis yielding polypeptides, peptides and protein hydrolysates. Such hydrolysates are also of allergic nature which was earlier not present in wheat. During the generation of simpler units from proteins such as polypeptides, exposure of buried regions to the surface is observed and these sites are believed to be antigenic. These allergens are not present in wheat as an ingredient in any food, however protein hydrolysates are used as additives in many food commodities (Akiyama et al., 2007; Pasha et al., 2016).

4 Role of Gluten in Bread Making

The proteins belonging to the gluten complex in wheat are of great importance in reference to bread making. Many *in vivo* and *in vitro* investigations have proposed protein structural-functional relationship as critical parameter of functionality in food processing. The major protein of wheat is gluten, which is a mixture of many distinct but related proteins fractions mainly comprising of glutenin and gliadin. Functionality of gluten is known in terms of its heat stability, its potential as binding agent, retention of moisture, and being an additive, it is used to improve the flavor and texture of the bakery products (Biesiekierski, 2017).

The unique rheological behaviour of gluten is the crucial factor for its suitability in many food products. The unusual functional characteristics of gluten are attributed to the ratio of glutenin to gliadin leading to the changes in the interactions. Viscoelastic properties and quality of the bread depend upon the gluten proteins. The strength and elasticity to the dough are imparted by glutenins while dough extensibility and viscosity are contributed by hydrated gliadins molecules. Both the quality and quantity of proteins are vital in breadmaking. The variation in the bread quality from different wheat cultivars is due to the qualitative and compositional differences. For good quality bread, disulphide bonds in linking the subunits of glutenins are of utmost importance.

It is very well known and documented for many years that higher the protein content of wheat, better is the bread quality. The functional properties of gluten including elasticity, viscosity and extensibility leads to the entrapment of carbon dioxide in the dough, released by yeast during fermentation. The gluten network is altered with porous structure which becomes permanent during high temperature treatment (baking). As mentioned earlier, the balance between glutenin and gliadin is critical because high glutenin level will increase the elasticity limiting the expansion of the loaf while retention of carbon dioxide is affected poor elasticity due to lower proportion of glutenin (Shewry et al., 1995).

The first step of gluten development in bread making is the hydration of wheat flour followed by kneading which gives mechanical energy to the system and dough with elastic nature is formed. Dough formation in breadmaking is considered poor or good depending upon the quality and volume of the loaf. A good loaf volume and silky crumb is the desirable feature of the bread. The quality of the final product is determined in terms of:

(a) Retention of carbon dioxide and to develop porous small gas cells,
(b) Balance between elasticity and viscosity for adequate expansion and retention of shape.

The contact of wheat proteins with oxygen is also equally important for development of gluten network in dough. There occurs the formation of intermolecular disulphide bonds with interactions between the protein fractions of the wheat leading to the resultant three-dimensional matrix of the dough. Blending is also critical to allow complete hydration and to supply mechanical energy required for rearrangement of gluten proteins. Mixing is a complex process favouring mechanical as well as chemical alterations during the formation of dough. Oxidation of sulfhydryl groups of proteins leads to the formation of disulphide bonds. Although these bonds are low in number, they provide significant difference in the quality of the resultant dough (Sluková et al., 2017). Gluten proteins are hydrated and developed with the aim of inclusion of air into the dough control on the number and size of gas cells during mixing.

5 Challenges in Gluten Free (GF) Bread Making

Since strict GF diet is the only way to combat CD, NCGS and WA, it is important to find alternatives for baking industry. Wheat, rye and barley are the major cereals to be avoided for GF food formulations. Gluten is a complex protein matrix giving wheat unique functional properties which are difficult to replicate with other cereal crops. Commercially available GF food products are incomparable with those made from wheat due to lack of excellent functionality in terms of texture, organoleptic profile and visual appeal. GF breads give poor texture and volume to crumb and crust along with undesirable mouth feel and taste due to added additives. Starch is the primary structural ingredient in GF bread and thereby such products are low at nutritional value and undergo staling readily by retrogradation. Also, expansion and gas retention in GF breads are poor since gluten is the only matrix to hold these unique properties. Consistency of dough from non-gluten ingredients is more likely to that of batter resulting in loss of baking quality by producing crumbly texture of the bread. Yazynina et al. (2008) reported that elimination of gluten from bread is associated with loss of iron, folate and vitamin B complex along with reduced level of minerals and fibre. Fat content has been reported as double as that of gluten containing bread (Pellegrini & Agostoni, 2015). Lysine content of commercially available GF breads is lower while fat and carbohydrate content is high (Naqash et al., 2017). Although many ingredients such as teff, sorghum, oats, buckwheat, rice and maize have been used with the incorporation of additives like starches, proteins, hydrocolloids, emulsifiers and in certain cases gluten has been removed from traditional recipe, the texture and aroma due to production of unique volatile compounds have not been replicated to date (Pacyński et al., 2015).

Water binding capacity of gluten is attributed to high content of glutamine and hydroxyl amino acids which almost represent 10% of the gluten and hydrogen bonding between these fractions give rise to cohesion and adhesion characteristics. Cysteine fractions, contributing to 2–3% of total amino acids help in the formation of dough due to interchange reactions between sulfhydryl-disulfide giving gluten matrix an extensive polymerization. Gliadin fraction of gluten imparts desirable viscosity and extensibility to the wheat dough. Therefore, due to unique structural orientation and excellent functional properties of gluten protein complex, it is technologically an extreme challenge to mimic the rheological and sensory profile of wheat bread using gluten-free ingredients and additives to replicate desired properties (Arendt et al., 2008).

6 Gluten Free Bread Formulations

Owing to the challenges like CD, NCGS and WA, cereal technologists are working in the direction to cater the need of GF food products. Considering the knowledge available at present scenario, strict GF diet is the only solution to this sensitivity as the symptoms immediately disappear upon withdrawal of gluten. Scientists and technologists worldwide have tried their best to overcome this challenge by incorporating alternatives to wheat in bread either with addition of nutritional ingredients and additives or by technological modification of GF flour. An overview of challenges and opportunities of GF (GF) bread formulations is demonstrated in Fig. 4. Addition of hydrocolloids have resulted in the viscoelastic properties of the dough and at the same time, bio-functional ingredients such as buckwheat, nutri-cereals, teff and brown rice produced highly nutritious product (Moroni et al., 2009). Recipe of GF breads is heterogeneous in nature being a combination of different cereals such as maize, rice, nutri-cereals, super grains along with additives to impart techno-functional properties including starches, non-gluten proteins, fats, enzymes and hydrocolloids.

In the absence of gluten, it becomes very important to add such additive which can mimic the role of gluten in forming dough and imparting good texture and volume to the crumb without affecting the organoleptic and functional properties of the bread. Milk proteins are potential ingredients in the ability to form gluten like matrix in the bread giving improved crumb texture and prevent staling for a significant timing. Use of proteases enzymes from microbiological origin such as *Aspergillus oryzae* and *Bacillus stearothermophilus* and transglutaminase have been reported to improve the rheological properties of the bread by promoting network formation (Mohammadi et al., 2015).

7 Additives in Gluten Free Breads

Since no ingredient other than gluten can yield final product with excellent textural properties as obtained with use of wheat, it becomes essential to incorporate certain additives in dough making to achieve similarity to wheat-based bread as maximum as possible. In past few years, it has been found that addition of additives like starches, hydrocolloids, emulsifiers and proteins at specific levels to non-gluten ingredients yield breads mimicking the structure and visco-elastic profile of conventional bread dough.

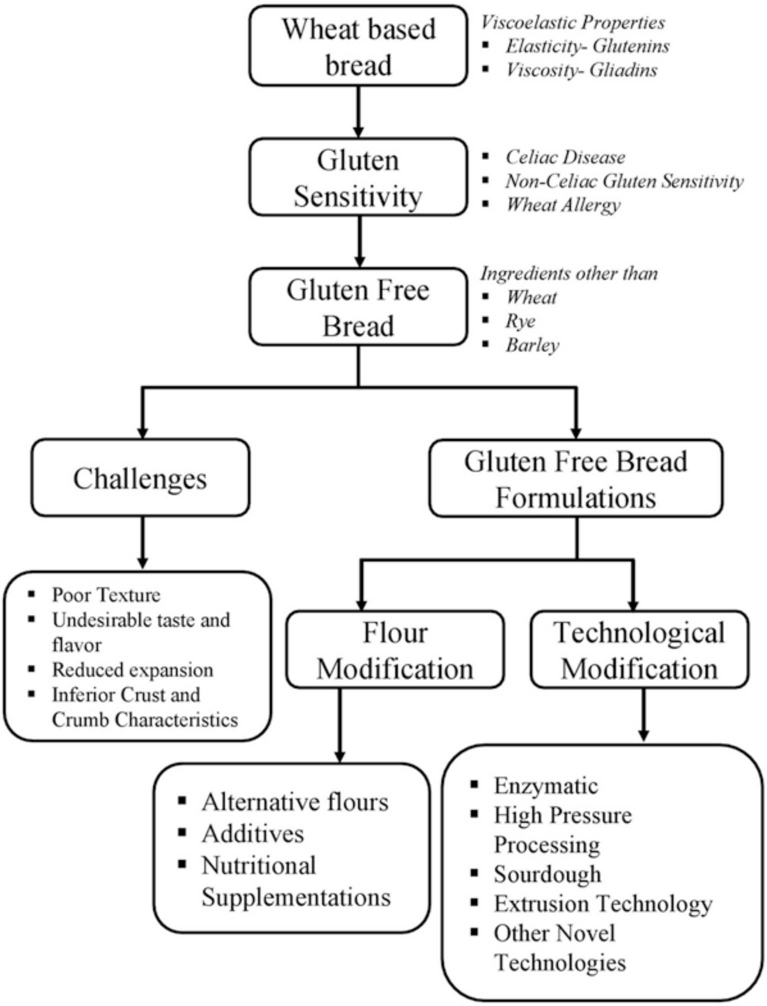

Fig. 4 An overview of challenges and opportunities of Gluten Free (GF) bread formulations

7.1 Starch as Additive

In GF bread formulations, starch is responsible for primary texture and structure of the bread; added in both native and modified forms such as resistant starches, chemically modified and maltodextrins. Maltodextrins having varying degree of dextrose equivalents (DE) has been examined for quality and stability of GF bread. Chemical modification of starches has been studied for improving the volume of the loaf and elasticity of the crumb structure. Chemically modified starches like acetylated di-starch adipate and hydroxypropyl di-starch phosphate when used for preparation of

GF bread, resulted in elastic crumb and decreased value for hardness and chewiness (Ziobro et al., 2012).

A physically modified starch such as pre-gelatinized tapioca starch has also improved the crumb volume and softness. Resistant starches not only improved the nutritional quality of the bread, but also the rheological profile of the bread in terms of improvement in the elasticity and reduction in the hardness of the crumb. The property of resistant starch as elastifying agent in rice-based products has also been reported (Naqash et al., 2017). Starch functionality of gelatinization and retrogradation plays important role in the formation of dough as it absorbs about 45% water and act as continuous filler in dough matrix. On heating in the presence of moisture during baking process, starch molecules gelatinize but still maintain their granular behaviour.

7.2 Proteins as Additive

To mimic the role of gluten in GF bread, proteins from animal origin such as casein and egg proteins and of plant origin involving soya and other legumes can also be added. Milk proteins have similar chemical structure to one of the gluten proteins, giving GF bread desired shape and texture. Functionality of milk proteins is dependent on the constituent protein fractions. For instance, caseinate fraction acts as good emulsifier and provide stability to the batter; good water binding capacity is attributed by skimmed milk powder and whey proteins are excellent in forming gels (Houben et al., 2012).

Performance of egg in GF bread is mainly due to albumin providing stabilization to foam to retain gas and to give better structure to loaf in absence of gluten (Deora et al., 2015). Plant proteins such as isolated pea and soya proteins also have remarkable water holding properties improving mechanical properties of the dough. Plant proteins have illustrated enhancement in the specific volume, sensory profile along with decline in the retrogradation. They also make the final product more softer and elastic by improving the viscoelastic properties of the dough (Matos et al., 2014; Ziobro et al., 2016).

7.3 Hydrocolloids as Additives

Hydrocolloids are class of water-soluble polysaccharides, commonly known as gums having the property to control texture and rheology of food systems and also capable of stabilizing the emulsions, gels, foams and suspensions. They provide variety of functional properties making them potential additives in food processing (Naqash et al., 2017).

These are added to mimic the formation of gluten network in absence of wheat proteins. Xanthan gums and carboxymethyl cellulose (CMC) are two important hydrocolloids to improve the size of gas cells resulting in improvement of the crumb porosity. Korus et al. (2015) examined the linseed mucilage as alternative to the hydrocolloids to form structure of the dough and found improvement in the sensory and textural properties of the bread along with rheological profile of the dough.

Hydrocolloids such as xanthan gum, locust bean gum, guar gum and tragant have been evaluated for activity as binding agents and found favourable results for bread volume and firmness. According to FAO/WHO Expert Committee on Food Additives, the daily intake of certain hydrocolloids such as pectin, guar gum, carrageenan, xanthan, CMC and locust bean gum is 'not specified' which means that these ingredients do not possess any hazard to health at levels necessary to impart desirable impact on the final product (Anton & Artfield, 2008).

Among several hydrocolloids studied for their application in GF bread formulations, xanthan gum and hydroxypropylmethylcellulose (HPMC) are best suited for mimicking the functionality of gluten. Xanthan gum, an exocellular carbohydrate obtained from microorganisms, improves the rheological profile of GF dough. The possible mechanism has been described on the basis of chain conformation and molecular structure of the gum resulting in the intermolecular interactions of the chain. At lower shear rates, xanthan gum exhibited better elasticity among other hydrocolloids, reason may be its weak gelation and higher viscosity (Lazaridou et al., 2007).

7.4 Emulsifier as Additive

Emulsifiers, also known as surface active agents and surfactants are often considered as dough improvers. They are functional additives in bakery products enhancing strength of the dough and crumb softness which is mainly due to amphiphilic nature. They are active at interfacial sites of two phases and forms dispersion (Stampfli & Nersten, 1995). Emulsifiers are important ingredients of bakery industry owing to their ability to have interaction with various dough ingredients and flour components giving rise to desirable texture of the final product (Demirkesen et al., 2010).

Emulsifiers, when added to GF bread, have contributed in improving the stability of breadmaking thermodynamically lesser stable system (Gómez et al., 2004). They have been reported to positively impact the dough structure with decreased crumb firmness (Onyango et al., 2009). Properties like antifarming and dough improvement by emulsifiers are generally attributed to their ability to reduce repulsive charges between protein fractions, thereby leading to their aggregation. They have also been reported to delay or retard retrogradation by limiting the water movement within starch molecules (Stauffer, 2000). Another important property of emulsifiers is generation of liquid films around gas cells providing them protection and stabilization. Most common emulsifiers used to functional additives in GF breadmaking are diacetyl tartaric acid esters of monodiglycerides, Sodium stearoyl-2-lactylate, polyglycerol esters of fatty acids, distilled monoglyceride and lecithin (Eduardo et al., 2014).

8 Nutritional Enrichment of Gluten Free Bread

Number of cereals, legumes and pseudocereals flour has been used in the development of GF breads. These flours are added to breads to improve the nutritional quality since they possess bio-functional properties. GF bread formulation constituting quinoa, amaranth and alternative sweeteners yielded product of similar quality to that of control wheat bread. In a similar study with quinoa and buckwheat, increased crumb volume was observed along with enhanced cohesiveness and springiness. Pseudocereals have also been reported to better withstand high temperature and shear in comparison to rice flour.

Dietary fibre is an important food component owing to its unique functionality and excellent nutritional characteristics. Consumers have shown inclination towards fibre enriched bakery products even with reduced functionality, for instance, reduction of loaf volume and hardness of the crumb with particular flavour. Addition of both soluble and insoluble fibres has been evaluated in GF breads. Dietary fibre from cereal sample (oat and maize) when added in GF bread gave rise to improved loaf volume and texture in comparison to control GF bread. Oats are rich source of β-glucan (soluble dietary fibre) which is associated with several health promoting properties like reduction in low density lipoproteins, attenuation of insulin level and post prandial blood glucose.

Proteins are added to GF breads with double objective of enhancing the nutritional and functional profile since they improve flavor, texture and amino acid content. Proteins from different sources such as dairy, legumes, eggs and cereals have been added to GF bread formulations.

Houben et al. (2012) suggested that eggs create improved crumb structure due to their emulsifying and foaming properties. These properties promote the retention of gas during baking and build desirable structure. For nutritional enhancement of GF breads, fruits and vegetables in dried and native forms have been added such as green kiwifruit puree, strawberry seeds, raisin juice, orange pomace and banana flour (Capriles & Arêas, 2014).

9 Technological Modification for the Development of Gluten Free Bread

Gluten Free bread is gaining popularity these days due to the upsurge cases of gluten intolerance. But, development of GF bread is itself a challenge due to the absence of gluten, which is well known as a heart of bread. Additives can be added to overcome these challenges but again, due to their chemical origin, their use is limited. To overcome such issue and to maintain the acceptability of GF bread among consumers technological modifications are carried out in the food processing industry by various techniques/technology like enzymatic modification, high pressure (HP) processing, sourdough fermentation, extrusion technology, germination, heat treatment, hydrothermal treatment etc. which are discussed below (Table 1):

10 Enzyme Modification

Enzyme modification is a natural way of modifying GF flour because they are substrate specific therefore can modify specific properties according to its applicability. Enzymes are generally recognized as safe (GRAS), so they do not have any negative health implication as that of chemicals (Rosell, 2009). Recent past studies, have been done to improve the rheological properties of GF dough by oxidation, hydrolysis or protein cross-linking. Enzymes like transglutaminase (TGase), glucose oxidase (GO), amylases, cyclodextrin glycosyltransferases, protein cross-linking enzymes and many more are used in GF formulation to improve its rheological and sensory properties (Fig. 5).

Enzymes are added to improve the functionality of GF bread to produce desirable loaf texture and transglutaminase (TGase) is one of the best candidates for improving cross-linking to impart characteristic texture. Mechanism of TGase has been reported in three terms as deamination, crosslinking and amine incorporation. Intermolecular and intramolecular iso-peptide bond interactions are induced due to cross linking when ε-amino group in lysine work as acyl receptor. TGase also plays important role to link different proteins such as caseins, soya proteins, wheat proteins and albumins. Modification of proteins by amine incorporation occurs when primary amines are absent in the bread formulation and thus water acts as acyl acceptor for the deamination of glutamine units (Motoki & Kumazawa, 2000).

Studies reported that TGase increased the protein cross-linking in oat and rice dough, respectively, causes improvement in viscoelastic and gas retention properties of dough. TGase can also catalyse deamination and acyl transfer reactions. TGase reported to improve the dough handling properties of brown rice batter and quality of GF bread prepared from it. These changes in properties are mainly attributed to the formation of highly polymerised structure from large protein complex and stronger hydrophobic interactions among proteins in presence of TGase (Renzetti et al., 2012; Deora et al., 2014). Hatta et al. (2015) examined improvement in bread properties like gas retention and textural parameters with rice protein due to action of proteases by degrading α- and β-glutelin in rice. TGase in addition with hydrocolloids such as guar gum has been reported to improve the bread quality; however, at higher concentration of TGase, increase in the hardness of the crumb was observed (Mohammadi et al., 2015). Use of pre-gelatinized starch along with TGase can potentially be used to produce good quality GF bread. In sorghum batter,

Table 1 Technological modification in the flour in the development of Gluten free Bread

S.No.	Flour treatment	Treatment	Improvement	Reference
1	Enzymatic modification	Pre-gelatinized tapioca starch (30%) and transglutaminase in the preparation of gluten free jasmine rice bread	Decreased dough elasticity Increased resistance to deformation Better expansion of gas cells Specific volume increased to 2.4 $cm^{3/g}$	Pongjaruvat et al. (2014)
		Tyrosinase and laccase in the oat bread development	Firmness of bread treated with tyrosinase increased in comparison to laccase due to cross-linking of oat globulins. Specific volume increased Combination of both enzyme increased the softness of bread	Flander et al. (2011)
		Tranglutaminase and quinoa flour	Overall acceptability of the bread improved with increased softness of bread	Romano et al. (2018)
2.	High Pressure Processing (HPP)	Sorghum dough is treated at 200 and 600 MPa and added to untreated dough @ 2% and 10%	Delayed staling of bread containing 2%, 600 MPa treated sorghum flour. No difference in specific volume.	Vallons et al. (2010)
		Composite dough (oat, millet, sorghum bread) treated at 200, 350, 500 MPa for 10 min.	Excellent nutritional and anti-radical properties. No significant change in specific volume is observed. Little change in staling	Angioloni and Collar (2012)
		Corn starch and rice flour are treated at 600 MPa for 5 min at 40 °C	No significant different was observed in specific volume of bread before and after treatment. Delayed staling was observed.	Cappa et al. (2016)
3.	Sourdough Fermentation	Lactobacillus plantarum AL30 (Amaranth dough)	Visco-elastic properties of dough were similar as that of wheat dough	Houben et al. (2010)
		Lactobacillus amylovorus DSM19280 as starter in quinoa bread preparation	Increase in the firmness of bread Delayed staling Higher specific volume	Axel et al. (2015)
		Lactic acid bacteria and yeast in the preparation of chest flour bread	Higher Specific volume than control Gas retention improved Crumb softness increases	Aguilar et al. (2016)

(continued)

Table 1 (continued)

S.No.	Flour treatment	Treatment	Improvement	Reference
4.	Extrusion Technology	Acidic extruded rice flour bread	Improvement in color and texture of bread	Pedrosa Silva Clerici et al. (2009)
		Composite flour (Buckwheat, rice, maize and extruded maize) bread	Develops regular porosity in the bread crumb No significant change in specific volume Softer crumb than the bread containing without extruded maize flour	Ozola et al. (2011)
		Extrusion effect on rice bread	Improved dough consistency Increase in specific volume Delayed staling	Mario et al. (2014)
5.	Germination	Germinated quinoa and oat bread preparation	Improvement of specific volume Improvement of crumb texture Germinated quinoa only adds to the flavour and nutritional properties of the bread.	Makinen et al. (2013)
		Amaranth, Millet, Corn, Lentil, Lupin, Pea and quinoa were sprouted and added @5%	Good specific volume and reduced hardness in comparison with control. Amaranth based bread was found to have the highest specific volume.	Horstmann et al. (2019)
6.	Heat treatment	Heat treated flour	Increased elasticity of dough Increased specific volume	Gêlinas et al. (2001)
		Heat treated (125 °C for 30 min) sorghum based bread	Improved dough handling properties Increased specific volume	Marston et al. (2016)

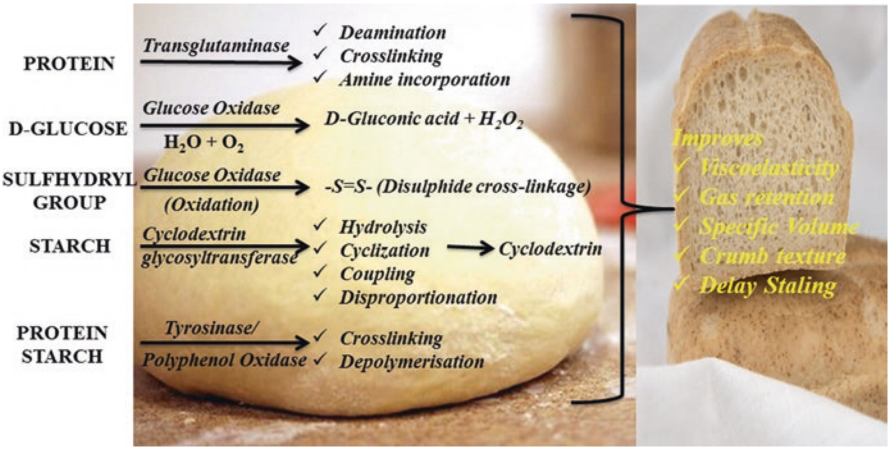

Fig. 5 Action of enzymes on macromolecules during the development of GF bread

dough handling properties were found to be significantly increased by incorporation of pre-gelatinized cassava starch followed by modification using microbial transglutaminase (MTGase). MTGase decreased the resistance to compliances and deformation while increased the zero shear viscosity and elastic recovery in sorghum based batter (Onyango et al., 2010).

Glucose oxidase (GO) is the charm of bakery industry, it carries out the oxidation of β-D glucose into D-gluconic acid and a molecule of hydrogen peroxide. GO also promotes the oxidation of free sulfhydryl into disulphide cross linking, thereby results in moderating the rheological properties of GF dough. Moreover, hydrogen dioxide produced during oxidation also plays a role in modulating textural characteristics. Gujral and Rosell (2004), reported improved elasticity of rice flour dough due to the disulphide cross-bridge formation in the presence of GO. Another study confirms the enhancement of elastic behaviour of sorghum and corn flour dough, author correlates the improved dough handling properties with aggregation of protein structure and polymerization of sulfhydryl groups into disulphide cross-bridges (Renzetti & Arendt, 2009).

$$\beta-\mathrm{D}-\mathrm{Glucose}+\mathrm{H_2O}+\mathrm{O_2} \xrightarrow{\text{Glucose oxidase}} \mathrm{D}-\mathrm{Gluconic\,acid}+\mathrm{H_2O_2}$$

$$-\mathrm{SH}+-\mathrm{SH} \xrightarrow{\text{Glucose oxidase}} -\mathrm{S}=\mathrm{S}-\ (\mathrm{Disulphide\,cross}-\mathrm{linking})$$

Cyclodextringlycosyltransferase (CGTase) is another enzyme used widely in bakery industry with the capacity to hydrolyze α-1,4 glycosidic linkages in starch molecule and linking reducing and non-reducing end to produce cyclic molecule. CGTase improve the pasting properties of GF flour by cyclization of starch and glucose into cyclodextrins. Cyclodextrins are the amphiphillic molecule having hydrophilic outer part and hydrophobic internal cavity. Rice proteins are hydrophobic in nature, so traditionally addition of conditioner and improver into flour was of no use in improving textural properties of rice bread, but incorporation of CGTase cause improvement in loaf volume, crumb texture and delaying the bread staling (Gujral et al., 2003). This Antistaling property of CGTase is due to the formation of complexes with protein and lipid.

Tyrosinase and polyphenol oxidase are oxidative enzymes with the capacity to catalyze crosslinking of macromolecules by their phenol moiety, which causes improvement in viscoelastic properties of gluten-free dough. It has been reported that tyrosinase and polyphenol oxidase strengthen the oat dough by promoting intermolecular covalent bonding or cross-linking of oat protein (Buchert et al., 2010; Mattinen et al., 2005). Renzetti et al. (2010) reported improvement in the specific volume of oat bread due to the depolymerisation of β-glucan and polymerisation of protein.

Thermoase, a protease enzyme obtained from *Bacillus stearothermophilus* when evaluated for development of GF rice breads resulted in improvement of visual properties, loaf volume and texture. Positive impact of thermoase in relation to staling of the bread was also noted. (Kawamura-Konishi et al., 2013). With the application of enzymes, it has also been observed that gelatinization temperature is decreased. Enzymes are also useful in mimicking the perforated structural organization of wheat-based breads in GF breads with smooth surface appearance as revealed in microstructural evaluation (Naqash et al., 2017). Therefore, application of enzymes in GF bread formulations is a promising approach to improve the quality.

11 High Pressure Processing

High Pressure (HP) processing is a "non-thermal technology" in which food is subjected to elevated pressures, to achieve the microbial inactivation while retaining sensory characteristics and nutritional value of the food products. At the present time, HP is gaining considerable attention in flour modifications as well. HP results in remarkable change in the macromolecular structure which enhances the functionality of the flour leading to the development of newer product with desirable sensory characteristics. HP treatment majorly affects the starch and protein structure through starch gelatinization and disruption in protein structure (Ahmed et al., 2007).

HP can be used as one of the promising technique with the potential area in food texture engineering (Deora et al., 2014). Pressure used for modification varies from 100–1000 MPa. The application of HP causes swelling and gelatinization of starch without disturbing the granule integrity. Extent of swelling and gelatinization depends upon the applied pressure, duration, temperature, type and concentration of starch (Stolt et al., 2000; Vallons & Arendt, 2009). Starch is one of the key ingredient in the development of the GF products. It is demonstrated that application of HP lowers the gelatinization temperature of starch and form paste with creamy texture. These altered properties can be directed to improve the consistency of GF batter, used to develop products with properties similar as that of wheat-based product (Stolt et al., 2000; Liu et al., 2008; Deora et al., 2014).

Studies have been conducted to investigate the effect of HP of 200, 400 and 600 MPa for 10 min on the viscoelastic properties of GF flour. The result of the investigation confirmed that HP treatment improves the functionality of GF flours by prompting the protein cross-linking and starch gelatinization, which indirectly reflects the improvement in viscoelastic properties of teff, white rice and buckwheat (Vallons et al., 2011). Huttner et al. (2009), applied the pressure of 200, 300, 350, 400 and 500 MPa for 10 min on oat batter, observed increased viscosity of batter at 300 MPa but at 350 MPa, the elastic component was predominant. These changes attributed to the starch gelatinization and formation of disulphide bonds or urea-insoluble complexes in the oat batter. Vallons and Arendt (2009) also reported elasticity in the sorghum batter above 300 MPa. Huttner et al. (2010) treated oat dough at 200, 350 and 500 MPa for 10 min, and replaced untreated oat dough with treated oat flour @ 10%, 20% and 40%. They reported 10% oat dough treated at 200 MPa was best in improving the crumb volume, appearance and reduced the bread staling rate. Vallons et al. (2010) treated sorghum dough at 200 and 600 MPa, and added HP treated sorghum to untreated sorghum @ 2% and 10%. They reported delayed staling of bread containing 2% of sorghum treated at 600 MPa due to the inactivation of enzymes responsible for bread staling while 10% resulted in poor bread quality because of low specific volume. They found no difference in bread containing sorghum treated at 200 MPa with that of control bread. Therefore, with above studies, it can be concluded that when GF flours are subjected to HP, there is an improvement in the viscoelastic properties which is a major challenge of GF bread and these flours with altered functionalities can be directed to make GF product. To realise the potential of HP processing in GF flour modification, more research is required to improve the specific properties like dough expansion, structure and gas retention of the dough as well as shelf life and cost for the development of GF bread.

12 Sourdough Fermentation

Sourdough fermentation is one of the oldest biotechnological process to leaven baked good, and it is known to improve texture, appearance, volume, aroma and shelf life of the bakery products. Sourdough is a blend of flour, water and other ingredient which is spontaneously fermented by lactic acid bacteria (LAB) or yeast under controlled condition. Fermentation enhances the dough handling properties as well as improves the textural, sensorial and nutritional properties of the GF bread. During fermentation due to various metabolic processes different exopolysaacharides (EPS), organic acids, antimicrobials and antifungal agents are produced (Moroni et al., 2009).

Fermentation process triggers the naturally occurring enzyme in the grain. These enzymes increased the bioavailability of the nutrients. Starch gets hydrolysed into simple sugars and disaccharide due to the increased amylolytic activity resulting in maltodextrin, maltose and glucose. Specific sourdough bacteria breaks sucrose and produce exopolysaccharide which leads to improvement in the techno-functional properties of GF breads by increasing the water binding capacity of flour. Increase in fiber content lowers the glycemic index of GF bread and does not cause rapid rise in blood sugar. Production of organic acid like lactate, formate, succinate, acetate and citrate improves the sensory property of bread. Antimicrobial and antifungal agents produced extend the shelf life of dough during storage. Carbon dioxide produced during heterofermentation by LAB and yeast affects the leavening process of final dough and indirectly improves the bread softening. Moreover, Sourdough bacteria breaks the anti-nutritional compounds during proofing process which inturn improves the bioavailability of the nutrients especially minerals like Ca, Mg, Fe, Zn, K and Mn. Incorporating sourdough in GF bread can potentially replace the chemical preservative (Carbo et al., 2020).

Fonio based bread was found to be with improved dough strength and gas holding capacity due to increased water absorption capacity (Edema et al., 2013). Sorghum based GF bread was prepared, sourdough fermentation, they reported EPS formed masked the organic acid effect and led to softer crumb of bread. In addition, modification in the macromolecules resulting from metabolic processes (Galle et al., 2012). Bread prepared from GF flour including quinoa, buckwheat, sorghum and teff, employed with sourdough fermentation by *Weissellacibaria* MG1, leads to acidification causing increased crumb porosity which inturn decreased hardness. Furthermore, staling of bread was significantly reduced (Wolter et al., 2014). Bender et al. (2017) studied the effect of selected *lactobacilli* on the functional properties of and stability of GF sourdough bread. They suggested *Lb. sanfranciscencis* strain was able to enhance the all the functional properties of millet and buckwheat based GF bread. Sourdough fermentation leads to the improvement of the elasticity and delayed the process of staling, this may be attributed to the breakdown of starch and non-gluten proteins by LAB. Therefore, sourdough fermentation of GF bread is a promising approach to improve the quality, but still lot of research is required in microorganism optimization.

13 Extrusion Cooking

Extrusion cooking is one of the processing techniques to modify the functional properties of the GF flour. It involves mixing of different ingredient that are forced through a small opening of specific shape and are cut into specific size by blade. Extrusion bring gelatinization of starch, denaturation of proteins, structural changes in lipid and decrease in anti-nutritional factors content leading to the overall change in the GF flour. In GF product, the main textural properties depend upon starch. During extrusion gelatinisation of starch occurs that enhances the water binding capacity of flour and extruded flour make abundant hydrogen bonds with water that ultimately ease the dough development.

Pedrosa Silva Clerici et al. (2009) develops the GF bread by addition of acidic extruded rice flour with improved color and texture of bread. Alongside, extruded maize flour is also used to make GF bread and reported to have excellent physicochemical properties (Ozola et al., 2011). Defloor and Delcour (1999) noticed addition of extruded starches improved the specific volume of bread made with tapioca and soya flour, this was due to the partial gelatinization of starch and increased consistency of dough which improves the gas retention properties of dough. Due to the complex formation between amylose and lipids there is a delay in staling of bread. Mario et al. (2014) reported extruded rice flour improved dough consistency and effect was more noticeable when percentage of extruded flour was higher. Bread obtained is of higher specific volume and water requirement to make same consistency of dough was higher than the control and staling of bread was less noticeable till 72 h with a large particle size of extruded rice flour.

Enzyme liquefaction can be accompanied with extrusion technology to speed up the process. This method can be used to concentrate protein which can be utilised as gluten substitute in GF formulation. In this processing, flour is first extruded through which starch is gelatinized which more prone to enzymatic activity, thereby liquefying enzyme break all the starch and concentrate protein in the remaining mixture. Sorghum proteins are capable of contributing to the viscoelastic properties to the GF dough, so sorghum protein can be concentrated by extrusion-enzyme liquefaction technology and can be further added to the GF formulation in the development improved quality bread with good digestibility (De-Mesa et al., 2009; De Mesa Stonestreet et al., 2012). Mario et al. (2014) reported addition of lipase in extruded rice flour positively affected the bread volume, this was may be due to the fact that lipases hydrolysed the lipids in dough that acts as emulsifier which results in increase the volume of GF bread. Enzyme treated dough have higher capacity to incorporate air and prevent coalescence phenomenon (Sahi & Alava, 2003).

14 Others Technologies

The Inclusion of germinated flour in the cereal products has been one of the upcoming trends in the market. Germination is natural and inexpensive way of modifying GF flour. During germination enzymes gets triggered cause hydrolysis of the macromolecules and results in enhancement of nutritional bioavailability, digestibility, antioxidant and functional properties of the flour. Therefore, germinated grain with full of enzymatic activity can be used as functional food ingredient in the prepared of GF product. Makinen et al. (2013) studied the potential of germinated oat and quinoa in bread preparation. They reported germinated oat at a concentration of <1% results in improvement of specific volume and crumb texture whereas germinated quinoa only adds to the flavour and nutritional properties of the bread. In oat bread improved sensory properties was due to increased water absorption capacity of germinated oat flour. GF bread prepared from germinated soy was found to have good specific volume then heat treated soy flour (Shin et al., 2013). Horstmann et al. (2019) conducted comparative study of GF sprouts (amaranth, millet, corn, lentil, lupin, pea, quinoa) at 5% w/w concentration in the development of GF bread. They reported all the breads with germinated flour have good specific volume and reduced hardness in comparison with control and among all amaranth bread were having highest specific volume and this is assumed because of the increased α-amylases activity that causes decrease in viscosity which allows greater gas cell expansion.

Heat treatment is one of the methods used to improve the bread quality in weak, poor or GF flour. Heat causes unfolding of protein, partial gelatinization of starch and inactivation of enzymes in the flour while improving volume expansion. In recent past study, it has been reported that bread prepared from heat treated flour showed increased elasticity of dough with positive effect on specific volume (Gêlinas et al., 2001). Marston et al. (2016) reported increase in specific volume of heat treated sorghum based bread. Heat treatment of 125 °C for 30 min was found to be optimum, and this increase in specific volume was because of the oxidation of the free sulfhydryl group to disulphide cross-link Bridge as a result stronger dough will form with resistance to mechanical stress. Hydrothermal pre-treatment to GF flour leads to the partial gelatinization of starch which results in excellent thickening properties and high water absorption capacity and can potentially replace hydrocolloids as additive (Hormdok & Noomhorm, 2007).

15 Conclusion

Gluten is a complex protein composed of gliadin and glutenin. Gliadin is responsible for strength and elasticity of dough while glutenin relates with the extensibility and viscosity of dough. Gluten plays a key role in the rheological properties. However, people with gluten intolerance are not able to digest gluten based products. Thereby, GF flour comes into play with a major challenge to mimic the viscoelastic properties of gluten. GF flours can either be supplemented with additives or can be employed with different technological modification. Although, it appears from the above discussion that technological modifications are showing positive impact on the textural properties of bread. But, still the commercial applicability to improve the GF flour is at its infancy stage. Extensive research is required in this area to increase the usability of these techniques in flour modification that can be aimed to make GF bread or other related products.

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