The recent development of gluten-free bread quality using hydrocolloids

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Abstract. The development of gluten-free bread production has drawn massive attention to decrease the number of wheat imports in some developing countries and fulfilled the needs of people with celiac and other diseases related to gluten components. Since the gluten component in wheat flours has taken a major role to form an extensible structure in the bread dough, its removal has emerged considerable issues in gluten-free bread production. Hydrocolloids are a food additive which able to form a gel with water and have demonstrated positive functional properties in the overall quality of gluten-free bread. The impact of hydrocolloid on the dough and final product depends on its chemical structure, concentration, and main ingredients used. This study will explore the effects of hydrocolloids as gluten-replacer that capable to mimic the viscoelastic properties of gluten through enhancing dough viscosity that can lead to the stabilization of different ingredients. Several hydrocolloids that released positive effects in gluten-free bread making are xanthan gum, hydroxypropyl methyl cellulose (HPMC), psyllium gum and even a mixture of hydrocolloids. Different types of hydrocolloids affect different mechanisms to stabilize dough foam and the final quality of the bread. This paper focuses on the reported applications of hydrocolloids in the development of gluten-free breadmaking and reviews different mechanisms of hydrocolloids in a way to assist foam formation and stabilization. Regarding the overall review, HPMC and xanthan gum are the most suitable gums to add in gluten-free bread making with characteristics that HPMC can produce higher volume and softer crumbs compare to xanthan gum.

1. Introduction

Bread typically made from wheat has been one of the most consumed staple foods due to its characteristics of ready to eat food and rich in carbohydrates. Lifestyle changes have promoted shifting in food consumption patterns, in which several developing countries have shown a rising trend of bread consumption [1, 2]. However, critical issues remain as those countries are highly dependent on wheat imports to fulfill its market demand. Besides, people who have gluten intolerance and are indicated to have celiac diseases are eliminating products containing gluten in their diet [3-5]. Consequently, both economic and health issues have encouraged many researchers to develop the quality of gluten-free bread using various approaches.

The main challenge in gluten-free bread development is the absence of gluten that particularly impart viscoelastic properties in dough which function to retain gas during proofing and baking stages.
Consideration of gluten-free bread formulation has been made to achieve desired quality through diverse gluten-free flours (rice, sorghum, maize, legume) [6-10] and starches (potato, cassava and corn) [11, 12] utilization. The addition of other ingredients such as hydrocolloids, shortening, enzymes and emulsifiers have been done to enhance bread quality in terms of physical, chemical and sensory characteristics resemble bread made from wheat flour [13].

Hydrocolloids remain as one of the most potential options to replace gluten, which is known as water-soluble polysaccharides that have hydrophilic-chain, capable to bind water and frequently has colloidal properties, in which in the water-based system it can produce gels and capable to mimic gluten viscoelastic properties [14-16]. Water retention properties are beneficial to increase bread texture, prevent syneresis and reduce staling rate. Hydrocolloids have different functional properties depend on the chemical structure from their natural sources such as animals, microorganisms, plant extracts, seeds and seaweed [17]. They have ability to control dough rheology through increasing viscosity, assist foam formation and stabilizing foams, emulsions and suspensions [15, 18].

Some potential hydrocolloids which are regularly used and capable to improve crumb properties, bread volume and achieve good consumer acceptance are xanthan gum and cellulose derivatives gums which are hydroxypropyl methyl cellulose (HPMC) and carboxymethylcellulose (CMC) [17]. Those types of gums have a different mechanism to substitute gluten regarding its chemical structures and multiple interactions among ingredients used. Also, the combination of xanthan and cellulose derivatives gums have been reported to generate good gluten-free bread features [7, 19]. This paper is aim to review recent findings on the application of hydrocolloids in upgrading gluten-free bread quality to expand opportunity which supports further development.

2. Hydrocolloids

Numerous researches have been reported hydrocolloids as a promising solution in improving gluten-free bread quality. The incorporation of hydrocolloids was known to retard starch retrogradation, improve water holding capacity, further extend the shelf life of the bread [16, 20]. Hydrocolloids’ nature, concentration and properties affect the stabilization of dough foam through several mechanisms such as enhancing viscosity, avoid coalescence and flocculation and strengthening the liquid film which trapped gas bubbles [21]. Besides, the single or mixture of types of flour and starch will mainly influence the quality of the final product. Table 1 displayed the recent development of gluten-free bread using hydrocolloids and each research discussed below.

| Types of flour or starches | Hydrocolloid       | References |
|----------------------------|--------------------|------------|
| Rice flour, corn starch    | CMC, xanthan gum   | [7]        |
| Hom nil rice flour         | CMC, xanthan gum   | [22]       |
| Rice flour                 | HPMC               | [23]       |
| Rice, maize and quinoa     | Xanthan gum        | [24]       |
| Rice flour and cassava     | Psyllium gum       | [25]       |
| starch                     |                    |            |
| Corn and potato starch     | HPMC               | [26]       |
| Rice, maize and white      | Xanthan gum, guar  | [27]       |
| quinoa flour               | gum, HPMC          |            |

Mohammadi [7] reported the impact of CMC and xanthan gum (5-20 g/kg) application on quality attributes of bread made from rice flour and corn starch. Addition 15g/kg xanthan gum showed moisture increased, while the combination of 10g/kg CMC and 10g/kg xanthan gum resulted in lowest hardness of bread among the others and received the largest acceptability score. CMC created bigger gas cells
and demonstrated better crumb porosity but xanthan gum proved as the best gums which enhanced gluten-free bread quality regarding low hardness and high elasticity.

Wongkhol [22] investigated gluten-free bread quality based on Hom Nil rice flour through evaluation of several parameters such as dough development characteristics, texture profile, staling rate, and sensory acceptability. The research utilized CMC and xanthan gum which take the role to replace gluten in which the result showed that the ratio of xanthan gum and CMC 3:0 respectively gained the highest sensory acceptability score among other treatments, particularly on the overall acceptability parameter. However, bread with the lowest hardness is achieved by the addition of xanthan gum and CMC with a ratio of 2:1.

Morreale [23] conducted a study to assess hydrocolloids’ vary viscosity that influence gluten-free bread quality using a range of HPMC with similar backbone properties and the ratio of hydroxypropyl and methoxyl residues but still retain the main chemical structure, the viscosity value consisted of 100 mPa.s, 4000 mPa.s and 15,000 mPas. The research used viscosity of HPMC as a quantitative independent factor using a multilevel factorial model with different levels of HPMC ranging from 1%-3% and hydration level 90%-110%. The research confirmed that the hydration level is essential to determine the viscoelastic properties of gluten-free batter and its rheology. HPMC viscosity and its addition level would define batter consistency and several crumb textural characteristics such as hardness, cohesiveness and resilience. Overall research reported that based on desirability index calculation, the optimum bread achieved through incorporation of 2.2% HPMC 15,000 cP and hydration level of 110%.

Encina-Zelada [24] studied the effect of xanthan gum on gluten-free bread and batter that used rice, maize and quinoa flours as main raw materials. The addition of a high level of xanthan gum with a constant amount of water showed a tendency to maintain more water that led to less sticky batters, enhanced index of consistency and viscosity and higher hardness level. However, higher water amount produced low firmness, consistency and more springy and cohesive bread due to less viscous and stickier batter. Formulation of 1.5-2.5% xanthan gum and 110% water generated good appearance loaves in regards to reduce crumb hardness, high specific volume, high springiness level and open grain visual texture.

Addition of dietary fibre like psyllium gum should be considered properly as it was known that gluten-free product for celiac disease patient is commonly related to diabetes mellitus, specifically type 1. Fratelli [25] investigated the capability of psyllium gum that can influence gluten-free bread quality not only towards its physical characteristics and sensory acceptability but also enhancing dietary fibre content and glycemic response. Psyllium gum was applied ranged from 2.86% to 17.14% and water levels 82.14% to 117.86 using flour basis. Results showed that psyllium gum able to increase bread quality by producing a softer crumb texture, better loaf volume, enhanced bread appearance and sensory acceptability level. Supplementation of 2.86% psyllium gum and 82.14% water levels considered as the optimum formulation that can improved dietary fibre content from 2.5% to 4.0% and received the highest sensory acceptability score among other treatments.

Berta [26] reported the impact of HPMC and zein protein on bread volume and crumb texture. HPMC proved to affect viscoelastic properties of dough, play a key role in improving the volume and also stabilize bubbles in the dough by acting as an emulsifier. On the other hand, the zein protein primarily affected gluten-free bread texture by improving dough elasticity. Eventually, the researchers concluded that the optimized formulation of HPMC and zein protein produced similar texture and staling behaviour to wheat bread.

Encina-Zelada [27] also investigated the mixture and even separated effects of xanthan gum, guar gum and hydroxypropyl methylcellulose using a D-optimal mixture design. Bread specific volume, softness and mean cell density are increased through guar in interaction with xanthan, and HPMC in interaction with guar gum. On the other hand, denser crumb appearance produced through xanthan and HPMC interaction as it led to decreased crumb cohesiveness and resilience, stickiness and mean cell density. However, the design showed optimum hydrocolloid combination was achieved with a mixture
of 0.60% guar gum, 0.24% xanthan gum and 3.16% HPMC with properties of high specific volume, low hardness, mean cell density and crust luminosity value.

2.1. Carboxymethyl cellulose (CMC)
Carboxymethyl cellulose (CMC) or sodium CMC is produced by reacting cellulose with sodium hydroxide and monochloroacetic acid, further released by-product in form of sodium chloride and sodium glycolate. Subsequently, it was purified using water and undergo a milling process to yield CMC. CMC is a linear, anionic polymer which is soluble in hot and cold water. The polymer comprises of β-anhydroglucose units which contain three hydroxyl groups. Stability and solubility are influenced by some factors such as salt, temperature, amount of free water, shear stress and presence of other polysaccharides and protein [28, 29]. CMC could form clumps with swollen skin surround the hydrated substances if it doesn’t dissolve appropriately. In order to achieve good CMC solution, it should be incorporated in a slow rate into water. Several recommended techniques to prevent clump formation are adding water miscible nonsolvent such as sorbitol, glycerin or propylene glycol, dry mixing in sugar and dispersion in oil and the mixture that include an emulsifier to an aqueous system afterwards. Generally, application of CMC in food product required degree of substitution (DS) of 0.7-0.8 [30]. CMC solution with DS ranging from 0.9 to 1.2 is categorized as non-Newtonian fluid, specifically shear thinning types or pseudoplastic, while DS 0.4-0.7 demonstrated thixothropic properties [29]. CMC generated high viscosity but decreased at low pH and inclusion of electrolyte [28].

2.2. Hydroxypropyl methyl cellulose
The manufacturing of hydroxypropyl methyl cellulose (HPMC) is done through simultaneous incorporation of methylene chloride and low amounts of propylene oxide, further purified and go through a grinding process to gain HPMC. This cellulose derivative backbone is comprised of β-D-glucose units with 1,4 linkage with methyl groups that partially etherified three hydroxyl groups. HPMC is soluble in cold water with wide range of viscosity rely upon the degree of substitution and degree of polymerization. Compare to pure methylcellulose, HPMC with medium to high DS (1.5-2.0) have high solubility in cold water (0-30°C) and its hydration perform at higher temperature (25-30°C). Temperature increase above incipient gel temperature (63-80°C) will affect gelling and indicated as reversible gels on cooling [31].

2.3. Xanthan gum
Xanthan gum is a polysaccharide produced by microorganism Xanthomonas campestris, consisted of a 1,4-linked β-D-glucose backbone and side chains of one glucuronic acid and two mannoses. It is soluble in cold and hot water and demonstrated high pseudoplastic properties. Xanthan gum has a viscosity that stable at a wide range of temperature and pH. The gradual reduction in viscosity happens when pH below 4.0. To achieve optimum functional properties, it must be well dispersed with high shear mixing, otherwise, it forms clump. This polymer shows synergistic interaction by increased viscosity with galactomannans such as tara gum, locust bean, cassia and glucomannans such as konjac mannan [28].

3. Mechanism of Foam Film Formation and Stabilisation in Bread Dough
Foam is generated during the agitation in the mixing process where air bubbles are introduced into the liquid phase. Unique structures of liquid foam are achieved by combining two different kinds of low viscosity fluid (e.g. water and air) that can create a structure with improved viscoelastic characteristics. Foams' structures are internally unstable, thus require surface-active substances to generate a film surround bubbles in order to stabilise them over coalescence. Therefore, foam stabilisation occurs as the main challenge of manufacturing gluten-free bread as the absence of gluten led to the inability to retain numerous amounts of carbon dioxide released from the fermentation process. Gas cell formation and stability are two essential factors that affect the final product and sensory properties of bread. This section will further explain the role of surface-active molecules in foam formation and stabilisation during bread making.
The mixing stage is aimed to break apart existing air bubbles, further reduce its size and multiply number of bubbles as mixing time increases. The size of bubbles is crucial as it can affect its growing phase along the proving stage and the final product. There are three major factors which underlie gas bubbles sizes such as energy input during mixing, the viscosity of continuous phase and surface tension. Hydrocolloids mainly take a role in the rheology aspect by increasing continuous phase viscosity. Higher mixing speed will lead to higher energy release and form a greater shear field, further capable to generate smaller gas bubbles lead to smaller bubbles size. In this case, the viscosity of the continuous phase plays an important role to maintain the formation of small gas bubbles related to the amount of energy input of the system. Small bubbles require to create foam in the dough, which results to rise in the interfacial area within the system. The interfacial tension should be decreased in order to form a stable foam, thus surface-active molecules are needed as it has a hydrophilic and hydrophobic site to lower surface tension effectively. When the bubble gas cells have been formed, it functions as nucleation sites for released carbon dioxide during fermentation which may expand and affect to dough rising.

After foam formation, foam stabilization is another important stage to consider as each gas cell must stay separately to prevent some instability mechanism such as foam drainage, coalescence and disproportionation. High viscosity will reduce foam drainage tendency by decreasing fluid flow among bubbles and prevent movement towards gravity. Stable foam is developed when protective and adsorbed layer of molecules is presented around gas bubbles. The surface properties of this layer are important to avoid coalescence among bubbles. Coalescence takes place when thin film in the surfaces among bubbles present adjacent to each other to cause rupture of bubbles. Accordingly, repulsive forces are necessary to prevent close contact of bubbles, but common electrostatic or steric forces are no more effective. In this case, there are two different main foam stability mechanism occur and it is present in Figure 1.

![Figure 1](image_url)

**Figure 1.** Mechanism of foam film stabilisation by protein and surfactants (a) Viscoelastic mechanism by proteins (b) Gibbs-Marangoni mechanism by surfactants. Sources: Adopted from [18].
a. The viscoelastic mechanism
Figure 1 (a) visualised the viscoelastic mechanism in which the process involves stabilisation of lamellae by great interfacial elasticity by adsorbed layers. Polymers or proteins create an adsorbed layer in form of a two-dimensional gel at the surface but have equal viscoelastic properties to a three-dimensional gel. The adsorbed layer was formed by protein or polymers. When deformation takes place in lamella, the adsorbed layer with elastic properties stretches and deforms. The lamella will remain intact when the deformation forces present in the elastic limit and further the two adsorbed layers will restore to their initial position. Moreover, they formed a physical barrier between gas cells which able to avoid coalescence.

b. The Gibbs-Marangoni mechanism
Figure 1 (b) visualised the Gibbs-Marangoni mechanism which counts on substances such as a surfactant, emulsifier, or detergent. When deformation takes place, lamella will experience local thinning and drain concentration of local surfactant. In order to reduce the concentration gradient, molecules will move to the depleted region. Surfactants flow will attract interlamellar fluid to the thinner area, further affect to return to its initial thickness.

4. Different Effects of Xanthan Gum and HPMC in Starch Bread
As it was found that xanthan gum and HPMC are the two most common hydrocolloids which utilize in producing gluten-free bread, both gums have different effects throughout the process and result in different properties in the final product. During bread making, there are two primary different stages which are before and after starch gelatinization. The first stage involves the suspension of some ingredients such as salt, sugar, yeast cells and starch granules in water. Bubbles are suspended in the mixing process and further expanded during fermentation. In order to prevent coalescence and other instability mechanisms that may encourage bubbles rising and settling of the starch, the addition of hydrocolloid is required to increase the viscosity of the liquid phase and homogenize the system during fermentation and baking [17].

![Figure 2](image)

**Figure 2.** Starch breads model. (a) No hydrocolloid addition (b) Viscosity increase by hydrocolloid addition (e.g xanthan gum). (c) Addition of surface-active hydrocolloids like HPMC Sources: Adopted from [17].

Figure 2(a) represented a condition when no hydrocolloid is added and affect to the settling of molecules within the system as it doesn’t mix homogeneously. Xanthan gum has been proved to release beneficial effects in gluten-free bread in which it can maintains stable viscosity during heating, unlike the other hydrocolloids such as locust bean gum, guar gum and gum tragacanth that decrease viscosity [14, 17]. The effect of xanthan gum is visualized in Figure 2 (b). On the other hand, HPMC as hydrocolloid is also indicated as surface-active molecules. It is characterized as having hydrophilic and
hydrophobic groups (hydroxy propyl groups and methyl ether groups). Surface-active molecules are able to stabilize foams by avoiding coalescence, aid to disperse air and generate small bubbles regarding to its structure. Figure 2 (c) visualized the effect of surface-active hydrocolloids in starch bread where smaller bubbles are generated. Therefore, HPMC capable to both increasing viscosity, stabilising the gas bubbles through decreasing gas liquid interface tension. Furthermore, HPMC will produce bread with higher volume and very soft crumb texture [17].

5. Conclusions
Hydrocolloids are one of the most potential additives which can be utilized to improve bread quality in terms of physical properties and sensory acceptability. Several types of hydrocolloids have been reported to have a beneficial effect in gluten-free production in terms of physical quality, sensory acceptability and even improving nutritional quality. The combination of different kinds of hydrocolloids may result in a positive interaction depend on the types of hydrocolloids associate with their structures. Hydrocolloids are capable to increase the viscosity of continuous phases within the system, assist gas bubbles formation and prevent some instability mechanisms during foam stability such as coalescence and foam drainage. Different kinds of hydrocolloids effect its mechanisms in dough foam stabilization and the final quality of the bread.

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