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RESEARCH ARTICLE

Influence of hydrocolloids on rheological properties of gluten-free dough based on corn flour

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ABSTRACT

The production of high quality bread made from ingredients other than wheat flour represents a major technological challenge, due to the absence of the viscoelastic gluten compound. To tackle this problem, hydrocolloids such as CMC (Carboxymethyl cellulose), Tragacanth and quince seed mucilage were incorporated into gluten-free formulations. The rheological characteristics of gluten-free doughs and their effect on the quality of bread were studied based on corn flour. CMC increased the viscoelasticity and temperature stability of the dough and also higher concentrations of CMC proved more productive. Tragacanth improved only the elasticity of the dough sample and made it more stiff and rigid. Effect of quince seed mucilage was complex without much improving the rheological properties of the dough. The results showed that incorporation of hydrocolloids improved the sensory scores of gluten free breads.

Key words: Corn; hydrocolloids; dough rheology; carboxymethyl cellulose

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INTRODUCTION

Celiac disease or gluten sensitive enteropathy is an autoimmune disease of small intestines caused by the ingestion of gluten, a storage protein found in wheat, barley and rye (Rosell et al., 2014). It is related to the inflammation of the small intestine leading to mal-absorption of several important nutrients and intestinal mucosal damage and in a longer period of time results in a damage of small intestine villi (Cureton and Fasano, 2009). Celiac disease is one of the most common lifelong disorders and can lead to long term complications such as osteoporosis, cancer, and infertility (Hill et al., 2005). The effective treatment for celiac disease is a strict adherence to a gluten-free diet throughout the patient's lifetime, which in time results in clinical and mucosal recovery (Gallagher et al., 2004).

The replacement of gluten presents a major technological challenge, as it is an essential structure-building protein imparting viscoelasticity, film forming ability, thermosetting properties and high water absorption capacity to baked products. To overcome this challenge, gluten-free bread formulations involving diverse approaches, such as the use of different naturally gluten free flours (rice, maize, sorghum) (Mancebo et al., 2015; Sciarini et al 2010) and ingredients such as hydrocolloids,

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emulsifiers or combinations as alternatives to gluten, to improve their technological and sensory properties (Demirkesen et al., 2014; Mir et al., 2016). Hydrocolloid is one of the classes of additives which are widely used to improve bread quality in gluten-free bread formulations as a replacement to the viscoelastic and gas-binding properties of gluten. In addition they also interfere with the swelling, gelatinization, gelling properties of the dough and the retrogradation of the starch (Arendt et al., 2006).

The rheological characterisation of gluten-free doughs is usually related to quality indicators of bread and provides important information for food technologists, allowing the appropriate selection of ingredients to optimise the final product (Lazaridou and Biliaderis, 2009). The type and dosage of hydrocolloids have significant effects on functional performance of the dough and subsequent bread quality. Cato et al. (2004) reported that the carboxymethyl cellulose was the best in regards to dough viscoelastic properties of gluten-free dough. The rheological characteristics of gluten-free doughs and their effect on the quality of biologically leavened bread were studied in amaranth, chickpea, corn and rice flour (Mir, et al., 2016 and Buresova et al., 2014). The rheological characteristics including resistance to extension, extensibility, stress at the moment of dough rupture were observed by uniaxial dough deformation. The dough exhibiting stronger resistance to extension, greater extensibility and higher stress at the moment of sample rupture had better bread baking quality.

The current work was designed to study the production and evaluation of some experimental gluten free doughs containing different levels of Carboxymethyl cellulose (CMC), Tragacanth and Quince. CMC have been, in particular, the subject of intense investigation due to their ability to display enhanced swelling capacity (Maswal et al., 2015) which improves the flavour quality and texture structure of bread (including texture degree, central structure, taste, etc.) and has been widely used to improve bread quality (Lazaridou et al., 2007; Angioloni et al., 2005) . The hydrophilic groups of CMC absorb water and swell in the process of dough making thereby increasing the gas-holding capacity, conducive to maintain CO_2 in the bread proofing and baking process. Tragacanth is a viscous, odorless, tasteless, water soluble mixture of polysaccharides obtained from sap drained from the root and is used in foods as an emulsifier, thickener, stabilizer, and texture additive (Moreira et al., 2013) while quince seeds are high in pectin used to make jam, jelly and quince pudding (Abbastabar et al., 2015). The main objective of this study was to create and explore a dough system composed of corn flour and different hydrocolloids that would be able to reproduce the rheological properties of wheat gluten in bread making. This is the first report to investigate the structural diversity and hence the variation in properties of composite baked products of corn flour with different percentages of CMC, Tragacanth and quince seeds using rheology. Further, the properties of synthesized baked products with different hydrocolloids were compared and explained. The effect of temperature and applied frequency on the baked products was studied and also the results were explained in light of various rheological models.

MATERIALS AND METHODS

Materials

CMC (Carboxymethyl cellulose) was obtained from Loba chemicals. Tragacanth and Quince seed mucilage of highly quality were obtained from natural sources were utilized. All the materials including corn flour were procured form local market and stored in air tight plastic containers at room temperature for further use.

Methods

Preparation of bread

Basic bread formulation consisted of 100g corn flour, 50g sugar, 3g salt, 2g of baking powder, and 75ml of water (except in breads with hydrocolloid addition, where 50 ml of water are used). Hydrocolloids viz CMC , Tragacanth both at levels 2, 4 and 6 wt% and quince seed mucilage at level 5, 7.5 and 10 wt% were used in the development of corn bread. All the ingredients including hydrocolloids were put together and mixed in a planetary mixer (Model SM-25, SINMAG Japan) for 2 min at 214 rpm. The dough was then placed in non-sticky pans and baken in in baking oven (Model SM 601T, SINMAG, and Japan) at 225ºC for 30-35 min. The pan bread were taken out, cooled and stored at room temperature.

Rheological studies

Rheometric experiments were performed with an oscillatory rheometer (Anton Par, Physica- MCR 101). Plate-plate geometry (diameter = 25 mm) were used for the measurements. Frequency sweep (0.05% strain) was carried out to study the viscoelastic performance over a wide range of frequencies (1 to 100 Hz) at a temperature of 20ºC, 25ºC and 30ºC for all prepared samples. For residual stress relaxation dough was allowed to rest for 15 minutes.

Sensory properties of gluten-free bread

Sensory properties of the product were conducted based on crust colour, crumb appearance, texture, flavour and overall acceptability. A panel of 15 members was selected to evaluate the sensory properties of crackers. The sensory evaluation was performed in laboratory with clean sensory cabinets containing fresh water. The panellists were instructed to evaluate the above attributes of the samples and to rate each attribute. A nine point hedonic scale with 1 (dislike extremely), 5 (neither like nor dislike), 9 (like extremely) was used for the study.

Statistical analysis

The data were analysed statistically using SPSS 18.0 (SPSS Inc., Chicago, USA,) and the means were separated using the Duncan multiple range test ($p<0.05$). All the data are presented as the mean with the standard deviation.

RESULTS AND DISCUSSION

Rheological observations

The rheological properties viz elastic modulus (G′), storage modulus (G″), and tan δ (G′/G″) of dough depicts the good and poor bread making flours and have been used to characterize bread samples (Ziobro et al., 2013). More particularly, dynamic oscillatory testing measures the elastic and viscous component to assess the frequency dependent properties of dough sample that provides important parameters of the behaviour of food material. In the present study the frequency sweep was explored as a function of type and concentration of hydrocolloids and also as a function of temperature. G′ was more than G″ in all the studied samples indicating the prevalence of elastic features over viscous and also both the moduli increased with increase in angular frequency characteristic of weak gels observed for a number of gluten-free dough products (Korus et al., 2009). As the hydrocolloids used include compounds with completely different chemical structures, they are therefore expected to have different effects on the dough and bread properties.

Effect of CMC

The variation of G′ and G″ with angular frequency as a function of concentration of CMC is given in Fig 1. G′ and G″ increases by adding CMC to the dough sample indicating the increase in cross-linking density and thereby elasticity of the sampledue to favourable starch-CMC interactions.Similar results were reported in the gluten-free dough formulations with addition of hydrocolloids (Lazaridou et al., 2007) and in rice dough with HPMC (Sivaramakrishnan, et al., 2004). The increase in CMC content increased both of the moduli with the exception in sample with 6wt% CMC where G″ is slightly decreased. CMC being hydrophilic polymer has high water absorption and retention capacity therebyincreases the water solubility and swellibility of dough. The increase in swelling leads to the formation of a three-dimensional network of swollen granules fills the entire available volume of the system and hence increases elasticity of the dough sample. Due to CMC water is retained in the baked and unbaked product and also released veryslowly which stabilizes the texture of the bread sample. CMC improves the elasticity resulting in lessshrinkage and makes the bread sample resistant to mechanical forces.The yieldcan be increasedas the improved dough stability bringsless breakage and also the dough is lesssticky so that the cleaning times can be reduced.

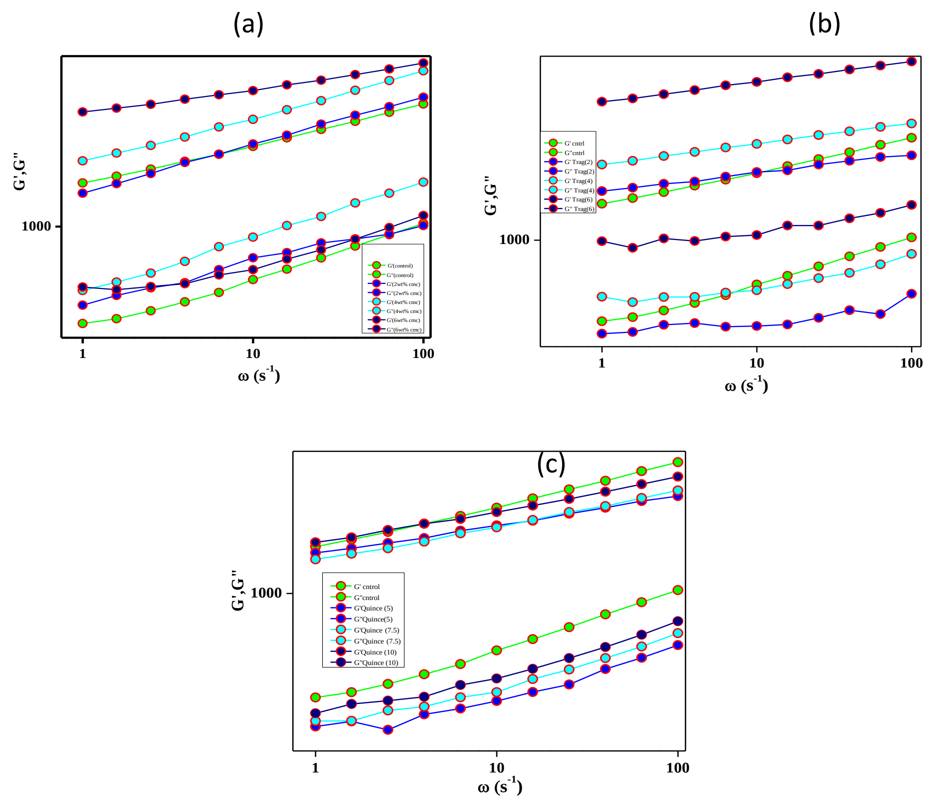


Fig.1. Plots showing variations in G' and $G''$with angular frequency for a range of a) CMC b) Tragacanth c) Quince concentrations.

Effect of Tragacanth

The variation of G′ and G″ with angular frequency as a function of concentration of Tragacanth is given in Fig 1. Tragacanth affected the dynamic rheological properties of dough in different manner, while G′ was increased regularly with increase in Tragacanth concentration, G″ decreasedexcept for 6wt% Tragacanth where slight increase is observed. The results infer that while there is increase in strong interactions like dipole-dipole, covalent bonding which impart elasticity to the sample, the forces like hydrogen-bonding prevailing in the system has lesser magnitude which leads to decrease in the viscous contribution. So the bread sample with Tragacanth additive has lesser extensibility and more stiff rigid solid-like behaviour. The elasticity improving effect of Tragacanth seems to be related to their effect in reducing the repulsive charge interactions within the starch granules and hence helping them to aggregate but at the same time has poor hydrogen bonding capability with complex starch granules thereby exhibiting less viscosity.

Fig.2. Plot showing comparative effect of variations in G' and G'' with angular frequency on addition of different hydrocolloids.

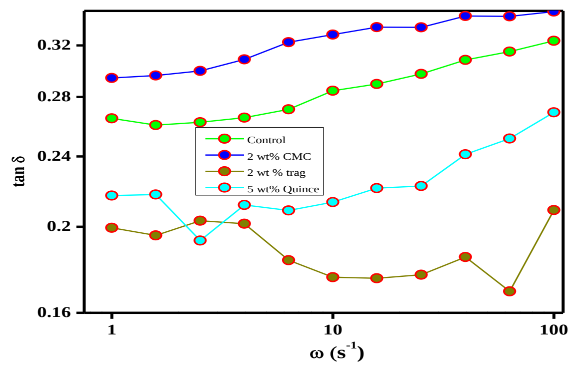


Fig.3. Plot showing variations in Phase angle with angular frequency for different hydrocolloids.

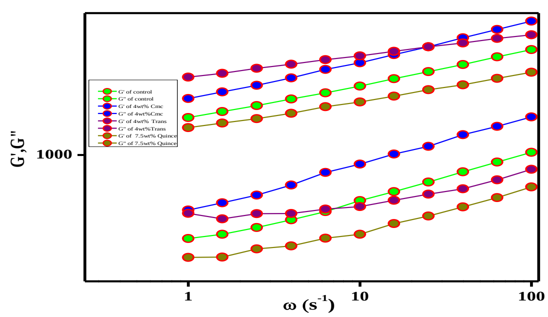
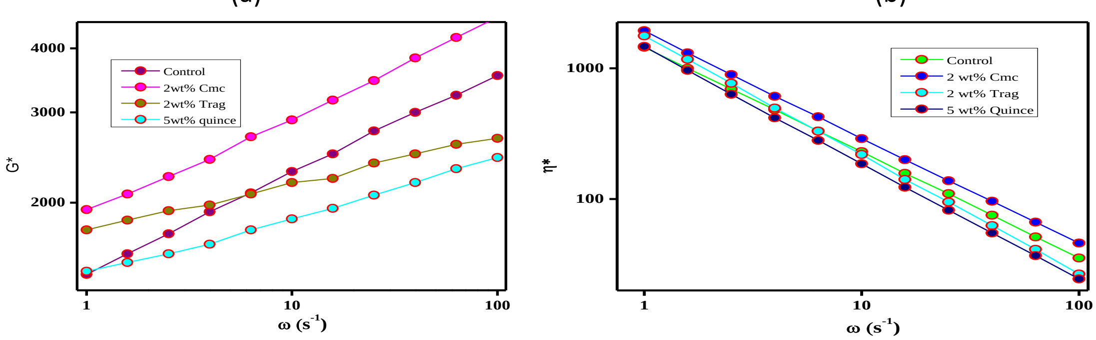


Fig.4. Plot showing variations in a) G* and b) η* with angular frequency for different hydrocolloids.

(a) (b)



Effect of quince seed mucilage

Effect of quince seed mucilage on the rheology of dough is complex given in Fig. 1. Both G′ and G″ first decreases with addition of quince seed mucilage and then increases with further additions. The results suggest that there is not much favourable interaction between the quince and starch granules. There occurs segregation of starch granules by dilution with quince seed mucilage which reduces the viscoelasticity of the bread sample. The interaction between the pectin moieties at higher concentrations of quince seems to impart some of the lost viscoelasticityto the bread sample.

Comparative effect of hydrocolloids on the rheology of gluten-free bread

The relative effect of hydrocolloids on the G′ and G″ of gluten-free bread is given in Fig 2. CMC and Tragacanth increases G′ of the dough sample thereby increasing its elasticity while quince decreases the elasticity of the sample. The value of G″ and hence the viscosity is increased by CMC only while it is decreased both in Tragacanth and quince. The results predict that out of the three hydrocolloids used, CMC proves efficient and could be widely exploited in food processing industries as a replacement for gluten owing to its viscoelasticity and high water absorption capacity. Tragacanth is capable of only increasing the rigidity and mechanical properties of the bread at the cost of extensibility and softness so could not be used for commercial purpose of bread making. However, quince seed mucilage cannot impart the desirable viscoelasticity to the gluten-free bread sample.

Material damping is measured by phase shift tangent$(\tan(\delta) = (G''/G'))$. The values of phase shift tangent in the present study varied in the range 0.1< tan (δ) < 0.5 characteristic for weak gels which is in agreement with the earlier reports regarding the viscoelastic properties of gluten-free dough (Korus et al., 2009; Witczak et al., 2012).The variation of tan (δ) with angular frequency for the samples with CMC, Tragacanth and quince seeds is given in Fig. 3. The addition of CMC resulted in significant increase while Tragacanth and quince decreased tan (δ) value of gluten-free dough sample. Increase in G′ and consequent increase in tan (δ) by CMC makes this hydrocolloid capable of producing doughs with balanced tensile and elastic properties much required to ensure optimal baking performance. This type of behaviour is in agreement with earlier observations regarding viscoelastic properties of gluten-free dough with different additives (Korus et al., 2009). An increase of storage modulus accompanied by the drop in phase shift tangent was observed for the dough sample supplemented with Tragacanth hydrocolloid shifting its properties toward values typical for strong gels. Such structure forming activity was earlier also reported for soy protein isolate (Crockett et al., 2011). Addition of quince decreased tan (δ) and viscoelasticity of the dough sample but shows slightly higher values of tan (δ) than the dough sample with Tragacanth. So the dough with quince is less rigid and stiff and more moist and slack than that Tragacanth.

Complex viscosity

The variation of complex viscosity with angular frequency for dough with different hydrocolloids is given in Fig. 4a. The complex viscosity decreases with increase in angular velocity for all the samples due to rupture of the swollen granules of dough at higher frequencies. The zero shear viscosity and complex viscosity was higher for the sample with CMC probably due to enormous granule swelling as CMC possesses remarkable swelling ability (Maswal et al., 2015). CMC forms physically crosslinked hydrogel with the dough whose three-dimensional structure is stabilised mainly by multiple inter- and intrachain hydrogen bonds like that of β-glucan (Lazaridou et al., 2009) and stabilisation of a three-dimensional network bysecondary forces explainsits higher viscosity. Tragacanth shows higher complex viscosity at lower ω values which decreases more sharply with increase in angular velocity. The results indicate that the molecular associations like H-bonding which imparts viscosity to the system are weaker for Tragacanth in agreement with the results provided in above sections. The decrease in complex viscosity in comparison to thecontrol for quince seed mucilage containing dough sample seems to be probably because ofsegregation of starch aggregates and hence decreasein molecular level interactions by quince seed mucilage explained earlier.

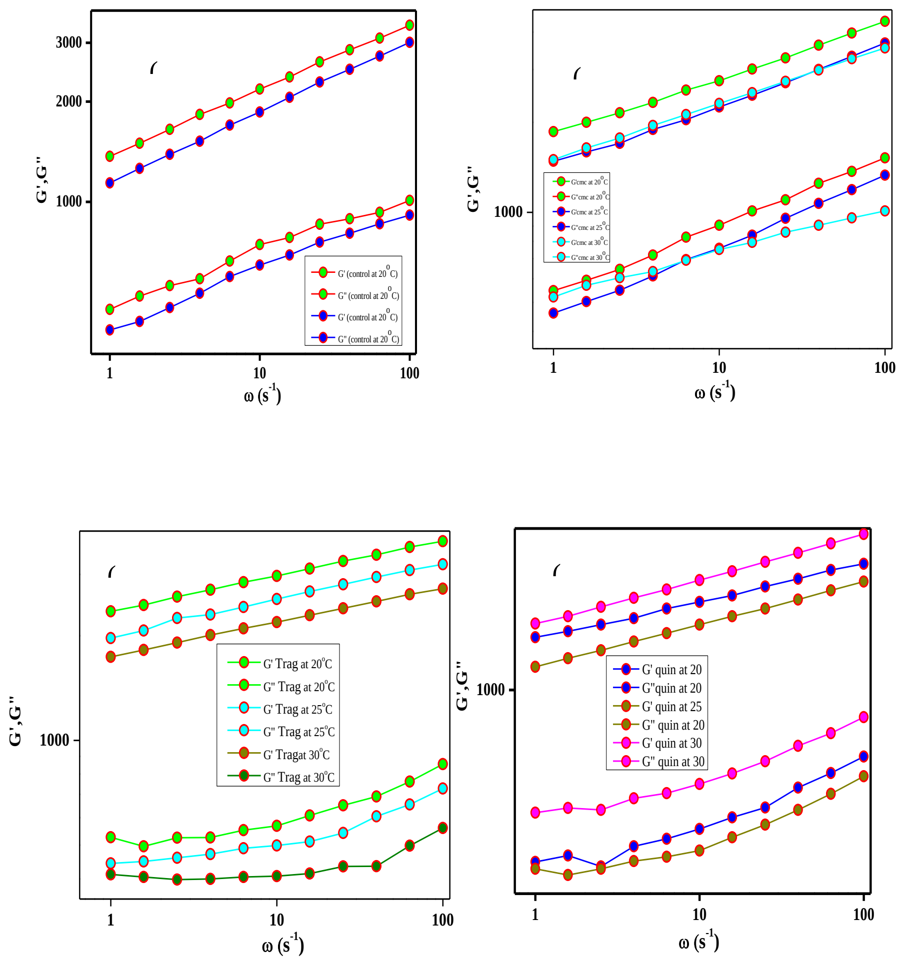


Fig.5. Plot showing variations in G' and G'' with temperature a) in control b) CMC c) tragacanth d) quince seed mucilage.

Complex modulus

It is the measure of materials overall resistance to deformation. It is higher at all ω values for CMC containing dough while the sample with Tragacanth shows higher values of G* at lower angular frequency region only (Fig. 4b). The increase in resistance to deformation of the dough containing CMC is likely due to the increased swelling ability of modified starches that fill the spaces and change the consistency of dough as major factor reported for the growth of G* is water hydration capacity (Witczak et al., 2012). Tragacanth increases G* values of dough only at lower ω values, while at higher frequency it is unable to retain the elasticity of the sample due to poor molecular level interactions. Quince seed mucilage is unable to improve the mechanical properties of dough sample and is showing the negative results.So the results obtained confirm that the increase in swelling capacity of starch by favourable interactions significantly affects the efficiency and properties of the dough.

Fluid models

To quantify the rheological response of dough samples prepared with different types and dosage of hydrocolloids different yield stress fluid models were applied.

Shear rate versus apparent viscosity data of the present study follows a power law (Mitsoulis et al., 2007) with a good regression given in Table 1. According to the law

$$\eta = K\dot{\gamma}^{n-1} \qquad (1)$$

K is the consistency index, a measure of average viscosity of the fluid, and n is the power law index, a measure of its deviation from Newtonian behaviour. Both K&n, included in Table 1, are important for a sample; once they are known the apparent viscosity can be calculated at any desired shear rate. Dough sample with CMC has higher average viscosity (K) and is also significantly more shear thickening (higher n values). The model confirms the experimental observation that the dough sample with CMC are much harder to pour at low shear and also offer higher resistance at higher shear rates which is desirable quality in bread industry. Tragacanth decreases the average viscosity of the sample and also makes it to flow freely at higher shear rate which decreases its commercial appeal. Quince seed mucilage also shows poor results as replacement of gluten as it decreases the elasticity and also average viscosity of the sample.

Table 1: Parameters and regression coefficient (r^2) of various flow models in shear rate-shear stress curve used in this study.

Model	Parameters	Control	CMC	Tragacanth	Quince Seed mucilage
Power law	K	3.2265	4.0167	1.8092	2.1016
	n	0.1042	0.1905	0.0954	0.1291
	r^2	0.9944	0.9987	0.9946	0.9952
Herschel-Bulkley	σ_o	0.2232	0.3073	0.0454	0.1524
	K	2.7727	4.1341	1.7711	1.9866
	n	0.2097	0.2429	0.0995	0.2279
	r^2	0.9993	0.9998	0.9946	0.9996

We also tried yield stress model of Herschel-Bulkley (Herschel et al., 1928) defined by the equation:

$$\sigma = \sigma_o + K\dot{\gamma}^{n} \qquad (2)$$

Where σ_{HB0} is Herschel-Bulkley yield stress. This model describes non-Newtonian behavior after yielding and is basically a power law model with a yield stress term.

All the studied samples exhibit yield flow behaviour. Below the yield stress (σ_o) the sample deforms elastically (like stretching a spring) and above the yield stress it flows like a liquid. Dough sample with CMC exhibit higher yield stress probably due to more tightly ordered packing of the dispersed phase exhibiting solid like behaviour at low shear rate followed by the control. The values of K and n as per this model (Table 1) show that for the yielded samples the consistency and index exhibits the same trend as yield stress, i.e., highest for the sample with highest yield stress.

Effect of temperature

During mixing, fermenting, baking and storing dough is subjected to different temperature. So the study of temperature stability of dough is very important. For this purpose the effect of temperature on the moduli (G′ and G″) of the samples at a range of frequencies is given in Fig 5. At low temperature inter and intra molecular interactions like H-bonding gets strengthen so the viscoelasticity of the dough samples is more. However, with increase in temperature the vibrational and rotational degree of freedom overtakes the systemization of molecular level interactions thereby favouring chaos in the system. Fig. 5 depicts that in all the samples studied the viscoelasticity of the dough samples were decreased as a function of temperature. The sample with CMC is having the highest water retaining capability as explained earlier shows minimum decrease when compared to all other samples confirming its temperature stability and hence its viability in bread making. Both Tragacanth and quince seed mucilage although affected the rheology of dough but are unable to impart it the desired temperature stability much anticipated in food technology and industries. In case of Tragacanth both the moduli decreases constantly with increase in temperature probably due to breaking of molecular linkages which are functions of temperature while quince seed mucilage shows sort of thermosetting behaviour at higher temperatures (Fig. 5).

Sensory properties of gluten-free bread

Sensory properties of gluten-free breads incorporated with various levels of hydrocolloids were evaluated based on colour, texture, appearance flavor and overall acceptability (Table 2). Non-significant difference is observed in the colour parameter with the highest found in 4% CMC followed by 4% Tragacanth and 7.5% quince seed mucilage, while lowest mean score for colour was observed in control bread. The crumb appearance also showed the variation with the highest value observed in CMC 4%. Mean score for texture revealed that the 4% CMC, 4% Trgacanth and 7.5% quince seed had highest score, while lowest mean score for texture was noticed in 2% Tragacanth. The control bread differs significantly from rest of the treatments. Results revealed that the bread incorporated with different hydrocolloids were softer than the control and softness increased as the level of hydrocolloids increased. These results are similar to that of Mir et al. (2016).

The quality score in response to flavor of breads depicted that the maximum score was obtained by both 4% CMC and 4% Tragacanth followed by 7.5% quince seed , while lowest mean score for flavor was observed in 6% CMC and 6% Tragacanth. Higher the level of hydrocolloids added in the bread samples resulted is the undesirable flavor. This might be due to the bland flavor of hydrocolloids. These results are parallel to the findings of Gupta et al. (2011). The data in the table outlines that the majority of panelists accepted the breads made from 4% CMC, 4% Tragacanth and 7.5% quince seed mucilage. These results are in agreement with the studies of Mahmoud et al (2013).

Table 2: Sensory mean scores of gluten-free breads

Parameter	Control	CMC			Tragacanth			Quince seed mucilage		
		2%	4%	6%	2%	4%	6%	5%	7.5%	10%
Crust colour	7.40b	8.10ab	8.35a	7.85ab	7.80ab	8.00ab	7.80ab	7.75ab	7.70ab	7.50b
Crumb appearance	6.85e	7.60abc	7..85a	6.95de	7.50abcd	7.75ab	7.25bcde	7.65abc	7.60abc	7.15cde
Texture	6.65b	7.65a	7.80a	7.35ab	6.75ab	7.75a	7.35ab	7.30ab	7.75a	7.30ab
Flavour	7.50abc	7.70ab	8.05a	6.75d	6.80d	8.00a	6.75d	6.90cd	7.90a	7.25bcd
OAA	6.60d	7.60ab	7.75ab	6.80cd	7.15bcd	8.05a	6.80cd	7.15bcd	7.65ab	7.30bc

Values are expressed as mean. Mean values with different superscripts in the same row for each cultivar were significantly different ($p<0.05$)

CONCLUSION

The present study concludes that hydrocolloids modified the viscoelastic properties of gluten-free dough in a variety of ways. The addition of CMC shows strong molecular interactions with the starch granules thereby enhanced the viscoelastic properties of the dough to the greatest extent. Tragacanth was able to only improve the elasticity of the dough sample and because of the poor interactions was effective at only lower shear rates. Quince seed mucilage decreased the molecular aggregation of starch granules and hence affects the viscoelasticity of the dough samples. The results presented confer that while higher concentrations of CMC could be beneficial for the mechanical properties of the gluten-free dough while Tragacanth makes the dough more stiff and rigid.

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