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EFFECTS OF HYDROCOLLOIDS AND CAROB BEAN FLOUR ON RHEOLOGICAL PROPERTIES OF BATTER AND CAKE QUALITY

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ABSTRACT
Carob bean flour which contains significant amount of dietary fiber, amino acid and minerals can be an alternative flour to enrich nutritional value of gluten free cakes. The objective of this study was to determine the effects of partial replacement of rice flour by carob bean flour at different concentrations (10%, 20%, 30%) and addition of different types of gums (xanthan gum, and guar gum), on specific gravity and rheological properties of gluten free cake batters. In addition, quality of cakes (weight loss, porosity, specific volume, hardness) were investigated. All cake batters showed shear thinning behavior. Gum containing batters exhibited higher apparent viscosities. Xanthan gum added batters had lower hardness but higher specific volumes. Guar gum addition had a negative effect on all cake quality parameters except moisture loss. Cakes containing 20% carob bean flour achieved generally the best quality parameters. Therefore, cakes with 20% carob bean flour and xanthan gum can be recommended to be used in gluten free cakes for celiac patients.
Keywords: Carob bean flour, hydrocolloids, gluten free cake, rheology, cake quality

HİDROKOLLOİDLERİN VE KEÇİBOYNUZU UNUNUN HAMURUN REOLOJİK ÖZELLİKLERİ VE KEKİN KALİTESİNE OLAN ETKİSİ

ÖZ
Keçiboynuzu unu önemli miktarda diyet lif, amino asit ve mineral içerdiği için besin değeri artırılmış glutensiz kekler için alternatif bir un olarak kullanılabilir. Bu çalışmanın amacı, pirinç ununun kısmı olarak değişik oranlarda (%10, %20 ve %30) keçiboynuzu unu ile yer değiştirilerek hazırlanan ve farklı zamk türleri (ksantan ve guar zamkları) kullanılan glutensiz kek hamurlarının özgül ağırlığının ve reolojik özelliklerinin araştırılmasıdır. Bunun yanında kek kalitesi de (nem kaybı, gözeneklilik, özgül hacim ve sertlik) araştırılmıştır. Bütün kek hamurları kaymayla incelen davranış göstermiştir. Zamk içeren tüm hamurlar ayrıca daha yüksek görünür vizkoziteye sahip olmuşlardır. Ksantan zamkı eklenen kekler daha düşük sertlik ama yüksek özgül hacime sahip olmuşlardır. Guar zamkı nem kaybı dışında hiç bir kek kalitesini olumlu olarak etkilelememiştir. Keçiboynuzu unu konsantrasyonu %20 olan kekler genellikle en iyi kalite parametrelerine sahip olmuşlardır. Bu nedenle ksantan zamkı ve %20 konsantrasyonda keçiboynuzu unu kullanılarak hazırlanan glutensiz kekler çölyak hastaları için önerilebilinir.
Anahtar kelimeler: Keçiboynuzu unu, hidrokolloid, glutensiz kek, reoloji, kek kalitesi

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INTRODUCTION

An auto immune system disorder and permanent intolerance to ingestion of gluten or other prolamines throughout the life is called celiac disease (Giménez-Bastida et al., 2015). Prolamines present in barley, rye and wheat which are hordein, secalin and gliadin, respectively are responsible from stimulating and initiating immunological reactions (Pietzak, 2012). Celiac disease causes damage to absorptive surface area of small intestine. This leads to imbalanced absorption of nutrients briefly folic acid, B12 vitamin, iron and fat soluble vitamins, and reduction in digestive enzymes. Consequently, all these result in bloating, abdominal pain and weight loss (Rubio-Tapia et al., 2013). People suffering from celiac disease have to exclude any food containing gluten from their diet.

A large quantity of proteins present in seed have role in either structural or metabolic function. Some of these proteins are responsible from storage of high amount of amino acids and rest is in charge of seedling growth. Furthermore, these storage proteins have role in not only total protein content but also quality of end product (Shewry et al. 1995). Since gliadins and glutenin have high levels of glutamine and proline amino acids, they are called as storage proteins (Veraverbeke and Delcour, 2010). Cysteine residues has an importance for both gliadin and glutenin since they make disulfide bonds between either different polypeptides (inter chain disulfide bond) or the same polypeptides (intra-chain disulfide bond) (Veraverbeke and Delcour, 2010). These disulfide bonds formed by sulfhydryl groups have important effect on stabilizing ability and functional property of dough (Shewry & Tatham, 1997). Glutenin gives elasticity to dough due to mostly hydrogen bonds, non-covalent interaction (van der Walls', hydrophobic and electrostatic) and disulfide bonds within and between glutenin proteins. Moreover, gliadin behaves as a plasticizer that moderate bond strength which glutenin forms. Therefore, proportion between polymeric glutenin and monomeric gliadin molecules regulate balance between dough elasticity and viscosity (Veraverbeke & Delcour, 2010; Shewry & Tatham, 1997). Therefore, storage proteins clearly affect the rheological properties of dough.

Carob (*Ceratonia siliqua L.*) is mainly cultivated coastal zone in southwest Asia and Mediterranean basin. It is composed of two main parts, 90% by weight is pulp and the rest is seed. Carob pulp contains high amount of sugar (48-56%) predominantly maltose, fructose, glucose and sucrose. Cellulose and semi- cellulose amount in pulp was also recorded as 18%. In addition, ripe pulp comprises high amount of condensed tannins. Furthermore, embryo, endosperm, and seed coat are the main components of carob seed. Endosperm of carob bean seeds is composed of galactomannan which is a polysaccharide formed by combination of galactose and mannose units. Carob bean seeds are used in food industry as gum which is known as locust bean gum (E410), a thickening or stabilizing agent (Karababa and Coşkuner, 2013).

Carob bean seeds contain a protein called caroubin that shows similar rheological properties with wheat gluten but their chemical compositions are different (Tsatsaragkou et al., 2012). This makes carob flour a favorite replacer of gluten for celiac patients. Carob germ flour includes gallotannins, polyphenols, and proanthocyanidins which prevent formation of reactive oxygen species and free radicals. These promotes development of diseases such as cancer and Alzeheimer (Custodio et al., 2011).

Disruption in cell wall formation, low porosity, volume, and hard texture are the main difficulties faced with gluten free product due to absence of gluten. Hydrophilic biopolymers with high molecular weight are commonly named as hydrocolloids. They improve cohesive forces between starch granules, stabilizers, and pre-gelatinized starches and are widely used in food industry to mimic gluten behavior. Thus, hydrocolloids are used in gluten free products for thickening gelling, and texture improvement purposes (Naji-Tabasi and Mohebbi, 2014).

Xanthan gum has strong ability to increase batter stability, and gas entrapment. Moreover, it can increase water holding capacity. This may be explained by hydroxyl groups which increases the number of hydrogen bonds leading to more interaction with water. In addition to that, xanthan has pseudoplastic characteristics and shows synergistic effect with some polysaccharides like glucomannas and galactomannans. They can improve more gelation and viscoelastic ability (Mohammadi et al, 2014, Burešová et al, 2016).

Guar gum is one of the naturally occurring, water soluble, non-ionic and nontoxic polysaccharide having very high molecular weight. It is the seed of cluster bean (*Cyamopsis tetragonolobus L.*) which consists of many layers from inside to outside endosperm (34-40%), the germ (43-46%), and outer shell (16-18%). Although the germ part is composed of mainly protein, endosperm portion is predominantly galactomannan that is constituted by galactose and mannose units. Mannose to galactose ratio in guar gum is generally 2:1 (Sandhu et al, 2015). The effect of guar gum on viscosity mainly depends on molecular weight of galactomannan. Guar gum has good dissolving or swelling ability in polar solvents due to strong hydrogen bonds (Moser et al, 2013).

The effect of combination of rice and carob bean flour on porosity, and firmness of bread has been analyzed and optimum ratios (carob bean flour/ water amount) were recorded as 10/110, 15/ 130, 15/140. It was stated that porosity value was affected by both water and carob flour amount. It was stated that although increasing water content increased porosity, increasing carob flour amount decreased that value. Both increasing water and carob flour amount decreased firmness (Tsatsaragkou et al., 2012).

In literature, there is no research that analyze the effects of xanthan gum and guar gum on quality of gluten free cake containing carob bean flour. The objective of the study was to investigate effect of carob bean flour concentration and hydrocolloid type on gluten free cake batter and final cake quality in terms of moisture loss, porosity, hardness and specific volume.

MATERIALS AND METHODS

Materials

Rice flour and carob bean flour were obtained from Basak Flour (Ankara, Turkey), and Havancızade (Istanbul, Turkey), respectively. Salt (Billur Tuz, İzmir, Turkey), shortening (Sana, Unilever, Istanbul, Turkey), sugar (Bal Küpü, Aksaray, Turkey), and baking powder (Dr. Oetker, Izmir, Turkey) were purchased from local markets in Ankara. Egg white powder and emulsifier (Monoglyceride and polyglycerol esters of fatty acid) were obtained from ETI Food Industry Co. Inc. (Eskişehir, Turkey). Xanthan gum and guar gum were bought from Sigma-Aldrich (Steinheim, Germany and St. Louis, MO, USA).

Experimental

Preparation and analysis of cake batter

Cake batter formulation contained 5% baking powder, 3% salt, 100% sugar, 9% egg white powder, 25% shortening, 3% emulsifier, and 90% water in terms of flour basis. Carob bean flour at different concentrations (10, 20, and 30%) was added to the formulation by replacing rice flour. In order to see the effect of gum, 1% xanthan gum or guar gum was used interchangeably. Carob bean flour containing cakes without the addition of gum was used as control for each concentration.

The first step of preparation of cake batter was mixing. Dry ingredients were mixed for 2 min at 85 rpm with a mixer (Kitchen Aid5K45SS, USA). Gum was dispersed in water by high speed homogenizer at 7200 rpm for 5 min (IKA T18Ultra-Turrax, Staufen, Germany). Melted shortening and gum suspension were added to the mixture and mixed further at 85 rpm for 5 min. Rheological analysis and specific gravity measurement were carried out in cake batter.
Rheological behavior of cake batter was examined using a parallel plate rheometer (Kinexus dynamic rheometer, Malvern, Worcestershire, UK). The gap between the plates was fixed to 1 mm. To understand the flow behavior of batter, shear rate between 1-10 s^{-1} was applied and the corresponding shear stress data was obtained.

For specific gravity measurement, certain volume of cake batter was weighed and divided by the weight of water with the same volume (Turabi et al., 2008)

Baking and analysis of cakes

For baking of cakes, an electrical oven (9411FT, Arçelik Inc. Co., Istanbul, Turkey) was used. Oven temperature was preheated to 175°C and four glass cups each containing 100 g batter were placed into the hot oven. Baking operation took 28 min. Then, weight loss, porosity, specific volume, and texture of cakes were measured.

Weight loss was determined by using the equation (1);

$$\text{Weight loss} = [(W_{initial} - W_{final})/W_{initial}] \times 100 \quad (1)$$

where $W_{initial}$ refers to weight of batter before baking, W_{final} represents the weight of cake after baking.

Porosity of cakes was measured by compression method (Turabi et al., 2008). After baking process, cake was cut into a cylindrical shape using mould with 3 cm × 3 cm (D x H), then initial volume of cake was calculated using these dimensions ($V_{initial}$, cm^3). After applying 25N load on to cake sample for 2 min, final volume was calculated (V_{final}, cm^3). Then, porosity of sample was estimated by using equation (2)

$$\text{Porosity} = (V_{initial} - V_{final}) / V_{initial} \quad (2)$$

To measure the specific volume, rape seed displacement method was used (AACC, 1990).

For texture analysis, cakes were cut into cubic shape having dimensions of 3cm x 3cm x 3cm after being cooled down for 1 hour. To measure the hardness value of cakes, texture analyzer with a cylindrical probe having diameter of 1 cm and load cell of 50 N (TA Plus Lloyd Ins., UK) was used. Force required to compress 25% of initial height of the sample with a compression speed of 55mm/min was measured.

Statistical analysis

To decide whether there is a significant difference between percent replacement of rice flour by carob bean flour and the type of hydrocolloids used, analysis of variance (ANOVA) was carried out using MINITAB (Version 16). If significant difference was determined, Tukey multiple comparison test was used for comparison ($P \leq 0.05$). Baking was replicated twice for each cake formulation. The correlation coefficient between specific gravity, specific volume and hardness of cakes was expressed by Pearson correlation with 95% confidence level ($\alpha=0.05$).

RESULTS AND DISCUSSION

Rheological analysis of cake batter

All formulations of cake batters with or without hydrocolloids was fitted to Power Law Model

$$\tau = K\gamma^{n} \quad (3)$$

where 'K' indicates consistency index ($Pa.s^n$) and 'n' refers to flow behavior index. Consistency index of batters changed from 40.69 1.06 to 186.33±8.46 $Pa.s^n$ (Table 1) and flow behavior index values were in between 0.28±0.01 and 0.44±0.04.

Table 1. Power Law constants and specific gravity results of carob bean flour added cake batter formulations at 25ºC.

Carob bean flour concentration	Gum type	n	K($Pa.s^n$)	R^2	Specific gravity
10	Control	0.44±0.04[a]	40.69±1.06[f]	0.98	0.94±0.03[cd]
10	Xanthan gum	0.32±0.06[bc]	173.52±0.83[ab]	0.99	0.93±0.06[d]
10	Guar gum	0.34±0.03[bc]	131.67±0.34[d]	0.99	1.01±0.09[b]
20	Control	0.39±0.03[ab]	46.08±3.90[f]	0.99	0.96±0.01[cd]
20	Xanthan gum	0.28±0.01[c]	186.33±5.98[a]	0.99	0.93±0.04[d]
20	Guar gum	0.33±0.01[bc]	144.35±3.79[cd]	0.98	1.03±0.00[b]
30	Control	0.38±0.07[ab]	74.50±0.73[e]	0.99	1.03±0.05[b]
30	Xanthan gum	0.33±0.01[bc]	159.17±0.20[bc]	0.99	0.97±0.01[c]
30	Guar gum	0.32±0.05[bc]	155.6±4.47[c]	0.99	1.07±0.05[a]

Since all flow behavior index values were lower than 1, it could be interpreted as all batter had shear thinning -pseudo plastic- behavior which resulted in macromolecular network deformation due to applied shear stress. Flow behavior index is an indication of degree of pseudo plasticity. While 'n' value decreases, shear thinning behavior becomes more dominant. As can be seen from Table 1, xanthan and guar gum added batters with 10% carob bean flour had significantly lower flow behavior index than control, which meant that hydrocolloid addition enhanced pseudo plasticity. On the other hand, consistency index could be used to decide thickening of batter. Addition of gum always increased consistency index value. While consistency index increases, apparent viscosity of batter increases at the same time. Although gum added samples had significantly higher viscosities, due to more dominant pseudo plasticity characteristics (lower n value), macromolecular structure of cake batter including hydrocolloid could more easily be affected and broken under the shear (Zhang et al, 2005).

Apparent viscosity of cake batters containing 20% carob bean flour concentration was shown in Figure 1. Similar behavior was observed for both 10% and 30% carob bean flour added cakes.

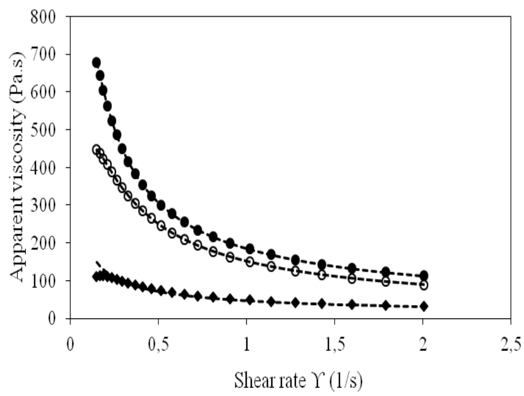

Figure 1. Apparent viscosity of 20% carob bean flour containing batters with different gums; xanthan gum (●), guar gum (○), control (♦), model (---)

As seen, xanthan gum added formulations had the highest consistency index values which were significantly different than guar gum containing batters and control samples formulations containing for 10% and 20% carob bean flour. This might be due to unique and rod- like structure of xanthan. This characteristic structure is more easily affected applied shear than other conformations i.e. randomcoil which guar gum has (Torres et al., 2014). Therefore, more responsive characteristics of xanthan gum led to higher consistency index (Ashwini et al, 2009).

Increasing carob bean flour concentration from 10% to 30% in formulation resulted significant difference between consistency index values. This might be due to high amount of crude fiber in carob which varies between 9% -13% (Salinas et al, 2015).

Specific gravity of cake batter

Specific gravity is an indication of how much air is incorporated into batter during mixing. Table 1 represents specific gravity values of carob bean flour added cake batters prepared with gums. According to two-way ANOVA results, xanthan added formulations had the lowest specific gravity. This meant that xanthan addition helped aeration of batter and improved specific gravity. This result was also supported by other studies. For example, a research carried out in 2014 stated that xanthan gum could enhance gas entrapment and stability. This might lead to higher air incorporation (Mohammadi et al., 2014). Contrary to xanthan, guar gum had negative influence on specific gravity. This different outcomes of different hydrocolloids might be explained by two ways. The first one is that guar gum added formulations had higher consistency index than xanthan gum added ones. Increasing consistency index may help air incorporation up to some extend but excess increase may undermine the aeration process. The second one is that some physicochemical characteristics of cake batter such as surface tension depended on the formulation (Manisha et al, 2012). Therefore, guar gum might have an adverse effect on these characteristics.

Weight loss of cake

Baking is a process that involves both heat and mass transfer. While heat is transferred through the cake, it leads to vaporization of moisture from the surface, which results in weight loss of samples. Since moisture loss increases the hardness of cakes, flour with high fiber, starch content and hydrocolloids can be added to cake formulations to decrease moisture loss. For example, cakes prepared with different hydrocolloids including sodium alginate, pectin, locust bean gum, xanthan gum and guar gum had less moisture loss than control during baking process (Gómez et al, 2007). Weight loss of cakes containing different concentrations of carob bean flour was shown in Table 2. According to ANOVA results, moisture loss affected both presence and type of the hydrocolloids since due to hydroxyl (-OH) group in the structures, which could bind water molecules.

Table 2. Weight loss, porosity, specific volume and hardness of cakes prepared with carob bean flour at different ratios and containing different gums

Carob bean flour concentration	Gum type	Moisture loss (%)	Porosity	Specific volume (ml/g)	Hardness (N)
10	Control	4.2±0.05^{ab}	0.32±0.02^{b}	1.62±0.02^{bcd}	3.83±0.15^{bc}
10	Xanthan gum	4.11±0.11^{abc}	0.41±0.02^{a}	1.75±0.01^{ab}	1.95±0.08^{f}
10	Guar gum	3.47±0.05^{d}	0.31±0.01^{b}	1.49±0.02^{cd}	4.65±0.08^{a}
20	Control	4.38±.08^{a}	0.31±0.03^{b}	1.65±0.01^{abc}	2.17±0.03^{ef}
20	Xanthan gum	3.79±0.03^{bcd}	0.38±0.03^{ab}	1.72±0.07^{ab}	3.49±0.10^{c}
20	Guar gum	3.52±0.2^{d}	0.22±0.02^{c}	1.52±0.01^{cd}	4.14±0.01^{b}
30	Control	4.32±0.02^{a}	0.37±0.03^{ab}	1.81±0.03^{a}	2.7±0.02^{d}
30	Xanthan gum	3.63±0.03^{cd}	0.34±0.04^{ab}	1.74±0.01^{ab}	2.54±0.10^{de}
30	Guar gum	3.43±0.03^{d}	0.22±0.06^{c}	1.47±0.03^{d}	5.08±0.00^{a}

Although xanthan gum addition decreased the moisture loss, the lowest value was obtained in guar gum added formulations. This might be due to different water retention capacities of hydrocolloids which was strongly related to chemical structure (Gómez et al, 2007). It was also stated that moisture retention of hydrocolloids depends on their interaction with other ingredients in the cake formulation.

Porosity

Air incorporation during mixing and entrapment of carbon dioxide bubbles during baking are mainly responsible from the cake porosity. Specific gravity and apparent viscosity of cake batter are the two important parameters that affect incorporation and entrapment of gas bubbles. While specific gravity becomes important physical property to decide how much air is incorporated in cake batter, the latter one gains importance to prevent escaping, carbon dioxide produced by baking powder (Turabi et al, 2010). The correlation coefficient between specific gravity and porosity was determined as -0.717 (P=0.001).

The most crucial role of gums in gluten free systems is that they can mimic the gluten behavior, increase viscosity, give viscoelastic property to batter, and prevent rising of gas bubbles through the surface during baking (Turabi et al, 2010). This leads to higher porosities of cakes, as can be seen in Table 2. In general xanthan addition to formulation ended up with relatively higher porosity results which might be the effect of both lowest specific gravity of xanthan added formulations and highest consistency index values. Similar supportive results for this hypothesis have been revealed (Turabi et al, 2010). It was concluded that cakes prepared with xanthan and xanthan-guar blend had higher porosity than cakes containing other gums which was related to higher apparent viscosities of these cake batters (Turabi et al, 2010). Furthermore, it was revealed that addition of hydrocolloids in the formulation increased apparent viscosity and gas retention capacity (Kondakci et al, 2015) This might enhance stability of gas bubbles by preventing coalescence. Therefore, more stable matrix led to increasing of porosity. Although guar gum was used for the same purpose with xanthan gum, it did not have the same impact on porosity as xanthan gum did. Guar gum added formulations had lower porosity than control cakes. This might be explained by specific gravity. Specific gravities of guar gum containing batters were higher than xanthan gum containing ones since aeration of air in cake batter during mixing process was not successful. Moreover, increasing carob bean flour concentration did not have any effect on porosity.

Specific volume

One of the most critical quality parameter for consumer is volume of cakes which is shown in Table 2. Porosity can also be used as critical quality parameter since the correlation coefficient between specific volume and porosity was determined as 0.795 (p= 0.000). Therefore, as expected from the porosity results, xanthan gum added formulations resulted in relatively higher specific volumes but this increase did not make a significant difference in control cakes. During baking process, viscoelastic cake batter can be converted to the porous solid structure due to simultaneous reactions of gelatinization of starch and coagulation of protein. These two physico-chemical changes strongly depend on type and origin of both protein and starch. Sugar, protein and other ingredients including gums are the factors affecting starch gelatinization. For example, xanthan may increase gelatinization temperature and delay gelatinization of starch, since gums decreases water activity or available water for gelatinization. While the bound water amount increases, gelatinization temperature also increases (Spies and Hoseney, 1982). If the required temperature for gelatinization is achieved later, the transition of batter from viscoelastic to solid structure occurs later. This allows more time for forming of CO_2 and obtaining more porous structure and higher volume (Majzoobi et al,2014). This might be reason of relatively higher volume of xanthan added cakes. On the other hand, guar gum containing cakes had always the lowest volumes. According to a study conducted in 2007, changing in pasting temperature might be related to interaction between hydroxyl groups of gums and starches (Gómez et al., 2007). Due to these different interactions, guar and xanthan gum added formulations had distinct volumes. Furthermore, according to ANOVA results replacing rice flour with carob bean flour did not make any difference in terms of volume.

Hardness

Textural analysis of cakes was evaluated in terms of hardness. As can be seen from Table 2, the concentration of flour and gum types had significant influences on this quality parameter. Hardness results were found to be correlated with specific volume results. Correlation coefficient between hardness and specific volume was -0.832 (P=0.000). Specific gravity of guar gum added cake batters were the lowest. The cakes obtained from this batter had the lowest volume and highest hardness. On the other hand, xanthan gum addition to the formulation enhanced texture profile and decreased hardness of cakes. The reason of different textural profiles between hydrocolloid added cakes might be the lower batter density, and higher foaming characteristics of xanthan added cakes (Shao et al, 2015). Furthermore, the similar results have been found and it was stated that guar gum added formulation achieved always the highest hardness value (Sumnu et al, 2010).

Furthermore; while 10% and 30% concentration led to increasing hardness, 20% carob bean flour containing cakes had the softest texture. A similar pattern; decreasing and increasing tendency with respect to increasing chestnut flour concentration; was also attained in a study (Demirkesen et al, 2010). This result was associated with the fiber content. It was stated that fiber and water content had a critical importance on quality parameters of baked products. While optimum fiber amount enhanced volume and textural properties, excess amount of fiber led to less volume and unacceptable textural properties. Therefore, fiber content in 10% carob flour content might be less to improve quality, but 30% carob flour might be too high to get optimum hardness.

Conclusion

All formulations obeyed power law model and shear thinning behavior. Moreover, addition of any hydrocolloid to the formulation increased consistency index of cake batters. Air incorporation to the cake batter was more successful in xanthan gum containing samples which was reflected in specific gravity results. Batter containing carob bean flour at a concentration of 30% had the highest specific gravity which might be due to increasing fiber content. Higher fiber amount might obstruct aeration of air. While gum addition to the formulation significantly decreased weight loss of cakes, higher carob bean flour in cake did not affect moisture retention. On the other hand, increasing carob bean flour concentration from 10% to 30 % had a negative influence on porosity. Xanthan gum added formulations had higher porosity values. Therefore, lowest specific volume was observed in guar gum containing cakes which might led to higher hardness values. As a result, xanthan gum can be recommended to be used in gluten free cakes.

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