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IMPACT OF LOCUST BEAN GUM / XANTHAN GUM ADDITION ON NEW GENERATION SNACK DESIGN FROM CAROB FRUIT BYPRODUCTS

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ABSTRACT
Carob products are good sources of bioactive compound/dietary fiber having beneficial effects on cardiovascular and gastrointestinal diseases. Other energy sources like tahini also improves physicochemical properties of foods. This study demonstrated the possibility for 50% replacement of cocoa powder by carob flour and the effect of Locust Bean Gum (LBG) and Xanthan Gum (XN) on consumer acceptability and physical properties of carob-based snacks. All formulations composed of carob syrup and tahini were combined with LBG and XN at different doses (1% and 2%) or together at equal combinations, as well. As LBG increased hardness up to some extent, XN influenced adhesiveness with a huge increase. Synergistic interaction of XN and LBG showing higher results on physicochemical properties than their single use was mostly observed in fresh samples under room temperature conditions. This study promoted acceptable new generation snack products with carob flour and gum addition after optimizations.
Keywords: Food hydrocolloids, carob fruit, cocoa powder, texture, sensory analysis

KEÇİBOYNUZU GAMI / KSANTAN GAMI İLAVESİNİN KEÇİBOYNUZU MEYVESİ YAN ÜRÜNLERİNDEN ELDE EDİLMİŞ YENİ NESİL ATIŞTIRMALIK TASARIMINA ETKİSİ

ÖZ
Keçiboynuzu ürünleri, kardiyovasküler ve gastrointestinal hastalıklar üzerinde faydalı etkileri olan iyi biyoaktif bileşik/diyet lifi kaynaklarıdır. Tahin gibi diğer enerji kaynakları da gıdaların fizikokimyasal özelliklerini iyileştirmektedir. Bu çalışma, kakao tozunun keçiboynuzu unu ile %50 oranda ikame edilme olasılığını ve keçiboynuzu bazlı atıştırmalıklarda Keçiboynuzu Gamı (LBG) ve Ksantan Gamının (XN) tüketici kabul edilebilirliğine ve fiziksel özelliklere etkisini incelenmiştir. Keçiboynuzu şurubu ve tahinden oluşan tüm formülasyonlara farklı dozlarda (%1 ve %2) veya eşit oranlardaki LBG ve XN gamları ilave edilmiştir LBG sertliği bir dereceye kadar arttırırken, XN gamı yapışkanlığı büyük bir artışla etkilemiştir. Tek başlarına kullanımlarına kıyasla fizikokimyasal analizlerde daha yüksek sonuçlar vererek sinerjistik etkilerini gösteren XN ve LBG, özellikle bu etkilerini oda sıcaklığındaki

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taze numunelerde göstermişlerdir. Bu çalışma, optimizasyon çalışmaları ile keçiboynuzu unu ve gam ilavesi yapılan yeni nesil keçiboynuzu bazlı atıştırmalık ürünlerin geliştirilebileceğini desteklemiştir.
Anahtar kelimeler: Gıda hidrokolloidleri, keçiboynuzu meyvesi, kakao tozu, tekstür, duyusal analiz

INTRODUCTION

Carob tree (*Ceratonia siliqua* L.) is grown mainly in Mediterranean countries, including Turkey and belongs to the legume family (Zhu *et al.*, 2019). Carob fruit generally includes two main parts as 80–90% pulp and 10–20% seeds by weight, having approximately 50–65% sugars, 1–5% proteins, ~11% dietary fibers, 1–6% minerals and 0.2–0.8% lipids (Tounsi *et al.*, 2017). Carob pulp is rich in natural sugar content (mainly sucrose, glucose and fructose), cellulose, fibers, minerals and phenolic compounds giving healthy benefits such as anti-oxidant, anti-cancer, anti-diabetic and anti-reflux effects and it gives functional property and sensory quality to food products (Zhu *et al.*, 2019). Meanwhile, the seeds are used to produce Locust Bean Gum (LBG) which is very important food additive acting as thickener, stabilizer, gelling agent in food industry such as ice cream, ketchup, mayonnaise, candies, bakery products. LBG is partially soluble at room temperature and the main chain of LBG consists of (1-4) linked beta-D mannose residues. LBG dissolves in water at room temperature to a limited extent, but the solubility of LBG increases as the temperature increases. While LBG (E410) does not show significant gelling properties when used alone, it is generally used together with guar, agar, ϰ-carrageenan or xanthan, as it has good gelling properties. When the hot solution is cooled together with xanthan and carob bean gums, which do not show gelling properties on their own, they undergo gelation due to the formation of junction areas between the two polymers.

Xanthan gum (XN) is a water-soluble exo-polysaccharide consisting of (1-4) linked beta-D glucose units produced by fermentation using *Xanthomonas campestris* as bacteria. Xanthan gum (E 415), which is widely used in the food industry, acts as an emulsifier and stabilizer in products such as chocolate, soft drinks and bakery products. Since it shows pseudoplastic properties, the gummy structure felt in the mouth is lighter and thus improves the texture of the product. For example, it increases the water holding capacity in bakery products, improves the structure, or acts as a stabilizer in ready-made foods or dairy products, preventing syneresis and providing solution stabilization (Palaniraj and Jayaraman, 2011). When XN is used together with galactomannans such as LBG, they show a synergistic effect and display different rheological properties in the product (Higiro *et al.*, 2006).

Carob molasses (pekmez) or carob syrup as another form which is produced by cold press technique can be consumed as energy and nutrient source for consumers, especially children who need urgent energy requirement. Carob flour (powder) is another sweet byproduct obtained from carob pulp which is grinded into powder as a source of dietary fiber. It is a good alternative to replace cocoa powder due to similar bitter taste and flavor, healthy feature, caffeine and theobromine free composition (Nasar-Abbas *et al.*, 2016). Due to these positive effects and low-cost value, nowadays it has been started to replace cocoa powder up to a point (around 40-50%) without affecting the taste and other properties (Akdeniz *et al.*, 2021). When their compositions are compared, it is seen that carob reduces the addition of processed sugar when used as a cocoa replacement because of its high sugar content. Carob powder has lower fat content (around 0.6%) and higher dietary fiber (up to 40%) as compared to cocoa powder containing 23% fat and between 5 and 33% fiber thereby showing nutritional advantages over cocoa powder (Nasar-Abbas *et al.*, 2016). About 50% of the carob dietary fiber (by weight) is associated with polyphenols which are condensed tannins (proanthocyanidins), gallic acid, catechins, quercetin glycosides, epicatechin gallate and epigallocatechin gallate differentiating from other fiber sources (Nasar-Abbas *et al.*, 2016). Similarly, cocoa powder is antioxidant rich source including polyphenols mainly flavonoids, however compositions of cocoa powder and carob flour could change according to several factors as origin, process conditions (Benković *et al.*, 2018).

Sesame paste, also called as tahini is another natural energy source, lipid and protein rich food (Tounsi *et al.*, 2019). Becoming one of the popular foods in Turkey and other East Asian and Middle Eastern countries, tahini is made from sesame seeds with the help of grinding, dehulling and roasting processes (Alpaslan and Hayta, 2002). Sesame paste/carob molasses blend is widely consumed due to its enriched content. Until last years, this blend had been made by consumers at home but now blend products as spreadable cream could be seen in the markets. Since this blend is a simple oil in water type emulsion, stability and prevention of phase separation becomes important for product quality besides mouthfeel of the product (Alpaslan and Hayta, 2002).

Carob products have been used in so many food applications such as wafer cream with carob pod, rice-based extruded snacks (Arribas *et al.*, 2019), muffin with carob flour (Červenka *et al.*, 2019), high-protein bread with carob flour (Hoehnel *et al.*, 2019), sponge cakes enriched with carob syrup and carob flour (Fidan *et al.*, 2020), carob spread with hazelnut puree as a nutritious snack for children (Aydın and Özdemir, 2017), pasta enriched with carob flour (Biernacka *et al.*, 2017), carob fruit enriched meat (Macho-González *et al.*, 2020). Rheological, sensory, and other quality properties of individual carob molasses or their blend with sesame paste were also analyzed in several past studies (Alpaslan and Hayta, 2002; Sengül *et al.*, 2007; Benkovic *et al.*, 2019). However, they were spreadable products rather than bar type products. Carob based and snack-like bar formulations has not been encountered to understand the addition of different type of gums on final product stability and properties.

Nowadays, "functional or healthy food" has become a crucial criteria for so many consumers since they demand to have a healthy eating habits and to take high nutritional value from food products (Ibrahim *et al.*, 2021). Achieving both excellent organoleptic characteristics and nutritious composition in a single product could be challenging. Dates and honey are among the widely used alternative natural substitutes used in snack bar production (Ibrahim *et al.*, 2021). Here, carob-based bar formulations were investigated to see the effect of different kind of gum addition on final product properties. For this purpose, carob syrup and carob flour were combined with tahini and enhanced with another carob byproduct which was LBG (locust bean gum) or its replacement with XN (xanthan gum) to obtain an energy bar like product which was alternative to chocolate due to similar taste and appearance. The effects of amount and gum type were assessed by evaluating the sensory, viscosity, moisture, color and texture properties.

MATERIALS AND METHODS

Materials

Carob syrup and carob flour (0.5% fat) were purchased from local carob manufacturer (Kebal, Mersin, Turkey) and LBG was supplied from Meysut Food Co. Inc. (Mersin, Turkey). XN was obtained from Sigma-Aldrich (St. Louis, MO) to be used as thickening and stabilizing agent. Tahini (Koska, Turkey) with 11.5% fiber, 22% protein, 48.8% fat content and cocoa powder (Altınmarka, Turkey) with 10-12% fat were bought from local markets.

Preparation of Carob Bars

In this study, main ingredient was chosen as carob syrup instead of carob molasses. Since carob syrup is produced by cold press technique, it has a high potential of nutrient value and less HMF formation. For the preparation of samples; cocoa powder and carob flour were used separately or mixed at equal ratios at total 28.8 % (w/w) concentration. Similarly, LBG and XN were added either individually or as a mixture at equal ratio keeping their concentration at 2%. These concentrations were determined according to sensory analyses as mentioned in sensory part. Fig. 1 summarized decision stages for final compositions. Basically, cocoa/carob flour, carob syrup, tahini and given gums were weighed in accordance with the formulations specified in Table 1.

Firstly, water and non-gum substances were mixed in a beaker. In a separate beaker, gum was dissolved in water using a homogenizer (Daihan

HG-15D, Germany) at 700 rpm for 60 seconds to obtain a homogeneous solution. Then, all ingredients were combined and mixed together. Finally, the prepared samples were shaped by using aluminum foil with dimensions of 10 x 2 x 2 cm and then packed with nylon locked bags to be stored until analyses.

Table 1 Prepared bar compositions for Sensory I and II tests

Sample Code	Cocoa%	Carob flour %	Carob syrup %	Tahini %	Water %	LBG %	XN
a. Trials for optimal replacement concentration of cocoa powder with carob flour							
841	14.55	14.55	23.30	23.30	23.30	1	-
621	-	29.10	23.30	23.30	23.30	1	-
507	29.10	-	23.30	23.30	23.30	1	-
962	23.30	-	23.30	23.30	29.10	1	-
b. Trials for determining optimal gum concentrations in bar formulations							
205	14.40	14.40	23.10	23.10	23.10	2	-
389	14.55	14.55	23.30	23.30	23.30	0.5	0.5
162	14.40	14.40	23.10	23.10	23.10	1	1
471	14.55	14.55	23.30	23.30	23.30	1	-

LBG: Locust bean gum, XN: Xanthan gum Note: Sample codes were given randomly

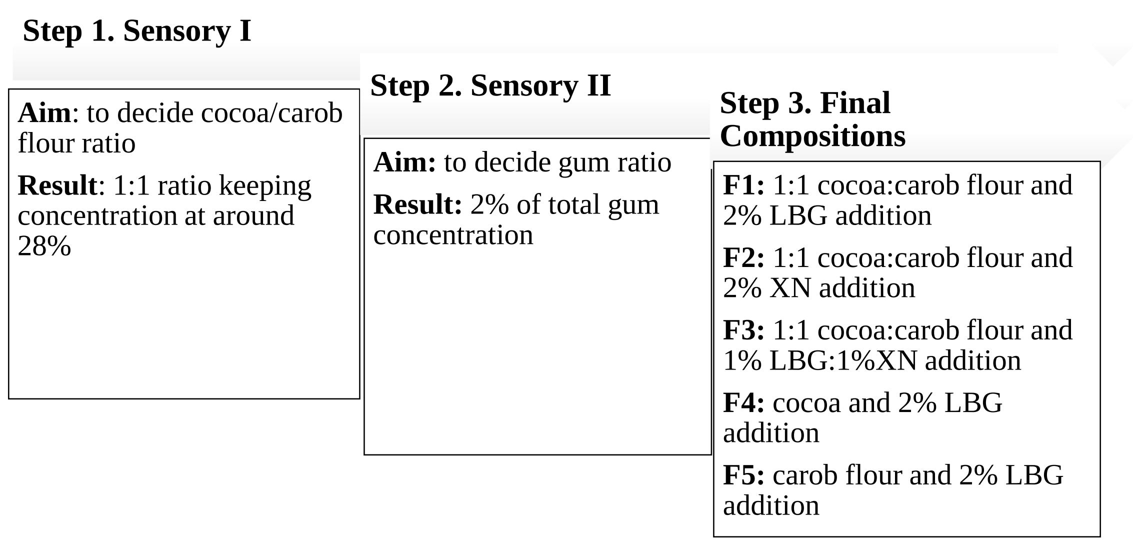

Fig. 1 Decision stages for final bar compositions

Bar samples were produced based on the following designs: the first set as sensory analysis was implemented as Table 1a to choose carob flour / cocoa powder combination and then second set was implemented as given in Table 1b to decide gum concentration in the final formulation conducting another sensory analysis (they were explained in further sections). The reason for division of sensory evaluation into two parts was to keep number of sensory samples as low as possible. Otherwise, it would be too hard for panelists to compare the samples. Due to the same reason, trial combinations in each analysis were kept at low level and not increased. Finally,

Table 2 was used in all bar preparations to see the effect of each gum type and ratio on final product quality. Five selected combinations for further analyses were named from F1 to F5 as: F1 (cocoa/carob powder blend with 2% LBG), F2 (cocoa/carob powder blend with 2% XN), F3 (cocoa/carob powder blend with 1:1 LBG:XN blend), F4 (cocoa powder with 2% LBG), F5 (carob flour with 2% LBG).

Table 2 Compositions of final carob bar formulations

Formulation	Cocoa powder%	Carob flour %	Carob syrup %	Tahini %	Water %	LBG %	XN %
F1	14.40	14.40	23.05	23.05	23.10	2	-
F2	14.40	14.40	23.05	23.05	23.10	-	2
F3	14.40	14.40	23.05	23.05	23.10	1	1
F4	28.80	-	23.05	23.05	23.10	2	-
F5	-	28.80	23.05	23.05	23.10	2	-

LBG: Locust bean gum, XN: Xanthan gum

Sensory Evaluation

In this study, sensory analysis was conducted in two steps to decide acceptable combinations of different ingredients in the formulation. In the light of previous studies, half portion replacement was chosen for cocoa/carob flour mixture (Brassesco *et al.*, 2021).

All the samples were composed of same basic ingredients: cocoa powder, carob flour, carob syrup, tahini and gum (with/out LBG and XN) with varying proportions. To determine cocoa powder/carob flour addition and gum concentration in the study, sensory tests were evaluated in two steps. First aim was to determine consumer acceptance of cocoa replacement with carob flour. Herein, four different combinations were applied as the first set to find out the most acceptable combination (Table 1a). For this purpose, sensory scores were held on among the following samples: half portion replacement of cocoa powder (sample code of 841), single addition of carob flour (621), single addition of cocoa powder (507), single but less amount of cocoa powder addition (962). The second step was to determine the most acceptable gum concentration and type. Since gums are generally used in the range of 1 and 2% in food recipes (Renou *et al.*, 2013), 1 and 2% of LBG and its half replacement with XN were selected to conduct sensory tests due to their potential synergistic behavior.

Sensory analysis was carried out according to the study of (Özdemir and Gökmen, 2017) with slight modifications. Sensory evaluation was performed by 40 semi-trained panelists (20 women and 20 men) asking them to fill down a questionnaire giving guidelines about how to score them (Supp. Mat 1). Instructions were given to panelists before the test. They were asked to evaluate appearance, color, taste, aroma, texture, after taste and general acceptability using 7-point hedonic scale ranging from “dislike extremely” to “like extremely”. Scores of 4 and above were considered as acceptable for the selection criteria. The samples were prepared at the same day and coded with 3-digit random numbers. As explained before, they were presented in Table 1.

Storage Studies

To see the effect of storage temperature and time on physical and textural properties of bars, they were packed in nylon locked bags and stored at 30 °C and 40 °C for one week duration. At the beginning, the literature was checked for shelf-life assessment of bar including acceleration method, as well. Thus, these temperatures were also chosen according to the literature (Corrigan *et al.*, 2012; Çınar and Aydın, 2020; Singh *et al.*, 2020; Ekafitri *et al.*, 2021). Moisture content measurement was periodically done at predetermined time intervals (day 0, 1, 2, 3, 4 and 7) for five different formulations. Color and textural measurements were then carried out at the beginning (day 0) and at the end of storage time (day 7) duration.

Physical Analyses

Firstly, viscosities of the gum solutions at 1% and 2% concentrations were measured with Sinewave Vibro Viscometer SV-10/SV-100 (A&D Company Limited, Japan) at room temperature. The samples were subjected to vibration by oscillating gold covered two sensor plates at frequency of 30 Hz and an amplitude of less than 1 mm.

Moisture content of the samples were determined by using oven method in triplicate (AOAC, 2016). It was measured at the beginning and after the end of 7 days of storage period at 30 and 40 °C.

Color measurements were conducted using DataColor 110™ Benchtop Spectrophotometer (New Jersey, USA) to obtain L, a, b and total color change (ΔE) values. L, a and b represent lightness, green to red and blue to yellow variation, respectively (Saberi *et al.*, 2016). Then, ΔE could be calculated by using the Eqn. (1) below:

$$\Delta E = \sqrt{(L^* - L) + (a^* - a)^2 + (b^* - b)^2} \quad (1)$$

where L, a and b represent the values belonging to the sample, L*, a*, and b* are the values of reference material (white paper was used as the reference).

Textural Properties

Hardness could be defined as the force required to achieve a given deformation of a product (Rosa *et al.*, 2015). Adhesiveness refers to capability of product to become sticky including combination of cohesive and adhesive forces and indicative for viscosity and viscoelasticity of the sample (Goksel *et al.*, 2013). Hardness and adhesiveness measurements of carob bars were done by using Texture Analyser (Brookfield Engineering Laboratories INC., USA) with TA10 cylindrical probe (12.7 mm D, 35 mm L). The method of Benkovic et. al. (2019) was modified with pre-experiments in order to compare textural properties of different bar formulations (Benkovic *et al.*, 2019). Each sample (uniform square of 2 x 2 cm) was subjected to 25% compression TPA test with 0.05 N trigger load, test-speed of 0.5 mm/s and return speed of 0.5 mm/s.

Statistical Analysis

The analyses of variance (ANOVA) were conducted to establish the effect of each variable and Tukey's HSD test was performed for comparison at the 5% significance level ($p < 0.05$). One-way, two-way and generalized linear models were used depending on the number of dependent variables. The analyses were performed in triplicate and standard deviations were calculated.

RESULTS AND DISCUSSION

Sensory Evaluation

Sensory test is one of the substantial studies in foods to understand acceptability of new products.

As given in Fig. 2, the first sensorial analysis was performed to optimize the ratios of carob flour, cocoa powder, carob syrup, tahini and water by using only LBG obtained from carob seeds. In that part, LBG concentration was kept constant and at the lowest level. For this purpose, the formulations with the given percentages in Table 1a were used. Appearance, color, taste, aroma, structural feature, after taste, and general acceptance were evaluated among all panelists. Female panelists gave the highest score to cocoa/carob flour added samples in all criteria except for appearance and color (they were also very close). Male panelists also evaluated samples giving high scores to both to cocoa/carob flour (1:1 ratio) added (sample code: 841) and only carob flour added formulations (sample code: 621). Interestingly, the samples including only cocoa gave the lowest scores. This could be due to the unattractive taste combination between cocoa and carob syrup. Considering overall average results, the use of cocoa/carob flour blend (1:1) was decided for further formulations as the most acceptable ratio regarding to appearance, texture, color and taste. Additionally, there was not a significant difference between individual use of carob flour and its blend use with cocoa powder ($p \leq 0.05$) on consumer preferences. Hence, final compositions for further analyses were decided including both of them to see their effects on final product properties, as well. Generally, carob flour added bars had similar sensory scores giving higher results above average but the highest scores were obtained in 2% LBG addition especially in general acceptability

Note: Check Table 1 for sample coding details

Fig. 2 Sensory analysis of carob bar formulations for first step (top) and second step (bottom)

After performing the first sensorial analysis and examining the data, the most suitable formulation (sample code: 841) with cocoa/carob flour blend was tested with varying concentrations of LBG and XN in accordance with the formulations specified in Table 1b. For this purpose, 2% gum blend (1% LBG and 1% XN) was used in formulation of sample 162, 1% gum blend (0.5% LBG and 0.5% XN) was used in the formulation of sample 389, 1% LBG was used in the formulation 471, and 2% LBG was used in the formulation of sample 205. In order to determine final product formulations to be analyzed for further measurements, sensorial analysis was finally performed on these products. Similarly, 20 male and 20 female panelists evaluated them according to independent variables of appearance, color, taste, aroma, structural feature, after taste, and general acceptance. Preferences were changed depending on gender ($p \leq 0.05$). General acceptability scores for sample codes 205, 389, 162 and 471 were found as 5.32, 4.84, 4.95 and 4.58 for female panelists, while for male panelists were found as 4.47, 4.26, 3.87, 4.25, respectively. Thus, 2% concentration of LBG (w/w) and its half replacement with XN was chosen for overall formulations to understand their impacts on quality of products prepared with/out carob flour and cocoa powder. As a result, final experimental design was shaped as given in Table 2 for the rest of the study.

Storage Studies

Moisture analysis

Table 3 shows moisture content of each fresh and stored samples at 30 and 40 °C. As expected, moisture percentage decreased as storage time increased due to water loss. At the beginning during 30 °C storage, sample F2 made by carob/cocoa blend with 2% XN gave significant difference than sample F3 (cocoa/carob flour blend with 2% LBG-XN) ($p \leq 0.05$). The results implied that the use of mixture of two gums could create difference in moisture content of fresh cocoa/carob flour mixed samples giving the highest value. This could support the ability of gum blends to retain water in their structure. Ghebremedhin et al. (2020) states that XN undergoes a conformational change from a rigid ordered helix structure to disordered shape at higher temperatures. Previous studies show intermolecular bonding between the xanthan in its coil conformation and galactomannans such as LBG so LBG could be trapped in helix structure of XN for gelling process forming junction zones (Ghebremedhin *et al.*, 2020). This gel network might have entrapped higher free water leading higher moisture content in fresh F3 samples. However, this difference was lost during storage at 40 °C. Keeping gum type and concentration as constant, fresh samples with cocoa (F4) gave the higher result than samples with only carob flour or cocoa/carob flour blend. However, it didn't achieve to hold it and the sample lost the highest amount moisture among the samples at 30 °C. As samples were stored at 40 °C, the lowest moisture loss was observed in F5 samples at the end of 7 days. This indicated that the presence of carob flour preserved moisture loss on the contrary to cocoa powder.

Carob flour, as a promising ingredient, could improve water holding capacity and water absorption ability of end product due to its dietary fiber content (Nasar-Abbas *et al.*, 2016). Samples with carob flour (F5) seem to retard moisture loss when compared to cocoa powder (F4) at the end of two storage conditions. These results were in agreement with the explanations given by study (Nasar-Abbas *et al.*, 2016) that carob flour could extend shelf-life acting as humectant. Products with high carob flour in other words with high fiber content have a potential to maintain water due to hydrophilic characteristics (Rosa *et al.*, 2015).

Color analysis

Color results of all samples were displayed in Table 4. Lightness (L) and total color change values (ΔE) of fresh samples did not show significant difference ($p \leq 0.05$). On the other hand, the highest redness (a) was given in sample F5. b values of fresh samples F2 and F5 also differed than others.

Table 3 Moisture analyses of carob bar formulations

a.						
30 °C	Day					
	0	1	2	3	4	7
F1	$29.61^{b} \pm 0.28$	$29.29^{b} \pm 0.95$	$29.19^{b} \pm 0.55$	$29.23^{a} \pm 0.08$	$28.02^{a} \pm 0.13$	$27.46^{ab} \pm 1.33$
F2	$29.43^{b} \pm 0.32$	$29.90^{ab} \pm 0.85$	$29.54^{ab} \pm 0.69$	$29.41^{a} \pm 0.13$	$29.64^{a} \pm 0.09$	$27.80^{ab} \pm 0.80$
F3	$30.42^{a} \pm 0.38$	$30.27^{ab} \pm 0.71$	$30.09^{ab} \pm 0.30$	$31.01^{a} \pm 0.69$	$28.84^{a} \pm 0.61$	$28.91^{a} \pm 0.26$
F4	$30.15^{ab} \pm 0.03$	$31.23^{a} \pm 0.81$	$31.59^{a} \pm 1.63$	$30.78^{a} \pm 1.66$	$29.26^{a} \pm 0.93$	$25.49^{b} \pm 1.02$
F5	$29.52^{b} \pm 0.07$	$29.64^{ab} \pm 0.28$	$29.35^{ab} \pm 0.44$	$29.11^{a} \pm 0.19$	$29.48^{a} \pm 0.37$	$28.72^{a} \pm 0.79$
Lettering should be considered for each day, separately.						
b.						
40 °C	Day					
	0	1	2	3	4	7
F1	$29.61^{b} \pm 0.28$	$29.58^{a} \pm 0.25$	$27.91^{a} \pm 1.07$	$26.53^{a} \pm 2.86$	$24.26^{ab} \pm 0.94$	$20.18^{ab} \pm 0.05$
F2	$29.43^{b} \pm 0.32$	$29.29^{a} \pm 0.42$	$28.38^{a} \pm 0.26$	$27.60^{a} \pm 0.47$	$25.31^{a} \pm 0.42^{a}$	$21.90^{ab} \pm 0.25$
F3	$30.42^{a} \pm 0.38$	$30.10^{a} \pm 0.64$	$28.01^{a} \pm 0.83$	$26.62^{a} \pm 0.56$	$21.69^{c} \pm 0.55^{c}$	$16.71^{b} \pm 3.15$
F4	$30.15^{ab} \pm 0.03$	$29.79^{a} \pm 1.22$	$29.52^{a} \pm 1.04$	$26.26^{a} \pm 0.61$	$22.63^{bc} \pm 0.85$	$20.16^{ab} \pm 2.32$
F5	$29.52^{b} \pm 0.07$	$28.76^{a} \pm 0.33$	$28.69^{a} \pm 0.58$	$27.82^{a} \pm 0.90$	$24.67^{a} \pm 0.43$	$22.67^{a} \pm 0.56$
Lettering should be considered for each day, separately.						

F1 (cocoa/carob powder blend with 2% LBG), F2 (cocoa/carob powder blend with 2% XN), F3 (cocoa/carob powder blend with 1:1 LBG:XN blend), F4 (cocoa powder with 2% LBG), F5 (carob flour with 2% LBG). Lettering was done based on 5 % significant level conducting ANOVA. Lettering should be considered for each storage temperature and each day, separately.

High b values characterize products as strong yellow/gold staining (Rosa *et al.*, 2015). Among fresh samples, the sample with the highest a and b data was the F5 sample prepared using only carob as given in Table 4. In other words, a and b values showed a significant change only for F5 sample (formulated by only carob flour) ($p \leq 0.05$). As a result of storage at 40 °C the L, a and b values of the F5 sample were found to be the highest ($p \leq 0.05$). When storage temperature was analyzed, it was found as a crucial factor on color values of the samples. Color values among the samples were changeable with temperature. Moreover, color values especially L and ΔE differed between samples F4 and F5 at 30 °C. This refers the potential effect of cocoa powder or carob flour on product lightness at definite temperatures. Cocoa powder gave slightly darker color than carob powder used in this study. Opposite to our results, in the study of (Rosa *et al.*, 2015), use of carob flour instead of cocoa powder made the samples darker. It has also been observed that the use of carob flour instead of cocoa darkened the color in this study. According to their results; L value of the sample using 100% cocoa powder was measured as 47.06, while the L value of the sample using 50% cocoa powder and 50% carob flour was measured as 44.29 and the L value of the sample using 100% carob flour was measured as 38.58. However, it also depends on origin, type and alkalization degree of used cocoa or carob powder. Since original color of added cocoa powder was darker than carob flour in this research, the results were good agreement with the expectations. In overall, all the samples could be classified as dark bars due to L values less than 50.

Texture properties

Hardness and adhesiveness values of final formulations were obtained for both fresh and stored samples. They were presented in Fig. 3. In fresh samples, it ranged between 9 and 79 N but the values were not significantly different except for F5 sample. As seen in Fig. 3, the hardest structure as 79.72 N was obtained in sample F5 prepared with carob flour and 2% LBG ($p \leq 0.05$). In general, according to statistical analyses, 30 °C of storage had soft textures whereas fresh samples displayed very high adhesive structures among fresh and stored samples at 30 and 40 °C. Depending on five freshly prepared samples, F5 was differentiated from others in hardness with greatest value. This indicated high impact of single selection of cocoa powder or carob flour individually in the formulations. Additionally, this revealed that hardness was influenced by type of gum giving higher results in the presence of LBG. However, it did not keep its effect during storage and all of the samples started to give similar values at the end of 7 days of storage. This was not the case for adhesiveness. F2 bar prepared by single XN differed with the greatest adhesiveness value among fresh samples and this behavior proceeded after 7 days of storage time at different temperatures, as well.

The results of (Benkovic *et al.*, 2019) supported higher hardness values which was not favorable property, with the increase of the amount of carob flour. Furthermore, they did not obtain a trend in firmness with the change of temperature. The results could be explained by weakening structure as a result of cocoa interference with other ingredients and disturb the matrix by softening the texture (Biernacka *et al.*, 2017). At this point, other examples could be found for cocoa and carob flour relation in other food products. For instance, in the study of (Rosa *et al.*, 2015), effect of cocoa replacement with carob flour was examined on gluten free cake formulation. They showed a possibility to prepare cakes from soy and banana flours, using carob flour as a cocoa powder replacer. They developed the softest cakes by cocoa powder addition whereas softness decreased with increasing replacement of cocoa with carob flour (up to 75% replacement). Similarly, our results did not promote individual use of carob flour due to very high firmness instead suggested its replacement with cocoa powder. Lastly, another chocolate study presented increasing hardness of the chocolates by adding higher concentrations of carob flour (Akdeniz *et al.*, 2021).

Table 4 Color analysis results of bar formulations

Fresh				
Formulation	L	a	b	ΔE
F1	$22.19^{a} \pm 0.13$	$0.94^{b} \pm 0.20$	$0.34^{c} \pm 0.08$	$71.45^{a} \pm 0.12$
F2	$21.71^{a} \pm 0.45$	$1.28^{b} \pm 0.13$	$0.60^{a} \pm 0.45$	$71.94^{a} \pm 0.45$
F3	$21.95^{a} \pm 0.47$	$1.12^{b} \pm 0.18$	$0.64^{c} \pm 0.17$	$71.70^{a} \pm 0.48$
F4	$22.37^{a} \pm 0.29$	$0.98^{b} \pm 0.21$	$0.49^{c} \pm 0.14$	$71.27^{a} \pm 0.29$
F5	$22.42^{a} \pm 0.49$	$2.05^{a} \pm 0.11$	$1.33^{b} \pm 0.22$	$71.25^{a} \pm 0.49$

Lettering should be considered for each column, separately.

30 °C Storage				
Formulation	L	a	b	ΔE
F1	$21.76^{a} \pm 0.41$	$0.92^{b} \pm 0.05$	$0.47^{b} \pm 0.25$	$71.89^{b} \pm 0.40$
F2	$21.87^{a} \pm 0.10$	$0.92^{b} \pm 0.08$	$0.57^{b} \pm 0.22$	$71.77^{b} \pm 0.11$
F3	$21.02^{ab} \pm 0.37$	$1.03^{b} \pm 0.02$	$0.40^{b} \pm 0.04$	$72.62^{ab} \pm 0.37$
F4	$19.28^{b} \pm 0.45$	$0.70^{b} \pm 0.10$	$-0.01^{b} \pm 0.25$	$74.36^{a} \pm 0.46$
F5	$21.19^{a} \pm 1.13$	$1.91^{a} \pm 0.42$	$1.26^{a} \pm 0.22$	$72.47^{b} \pm 1.14$

Lettering should be considered for each column, separately.

40 °C Storage				
Formulation	L	a	b	ΔE
F1	$19.04^{b} \pm 0.35$	$1.13^{a} \pm 0.03$	$0.35^{a} \pm 0.06$	$74.62^{a} \pm 0.35$
F2	$20.68^{ab} \pm 1.17$	$0.91^{a} \pm 0.05$	$0.26^{a} \pm 0.16$	$72.97^{ab} \pm 1.17$
F3	$20.29^{ab} \pm 0.28$	$1.15^{a} \pm 0.11$	$0.40^{a} \pm 0.22$	$73.36^{ab} \pm 0.27$
F4	$19.56^{ab} \pm 0.95$	$0.77^{a} \pm 0.11$	$0.32^{a} \pm 0.09$	$74.08^{ab} \pm 0.94$
F5	$21.75^{a} \pm 0.55$	$1.26^{a} \pm 0.27$	$0.80^{a} \pm 045$	$71.89^{b} \pm 0.55$

Lettering should be considered for each column, separately. Storage day was chosen as the last day (at the end of 7 days of storage). Lettering was conducted based on 5 % significant level by ANOVA. Lettering should be considered for each storage temperature and each color parameter, separately.

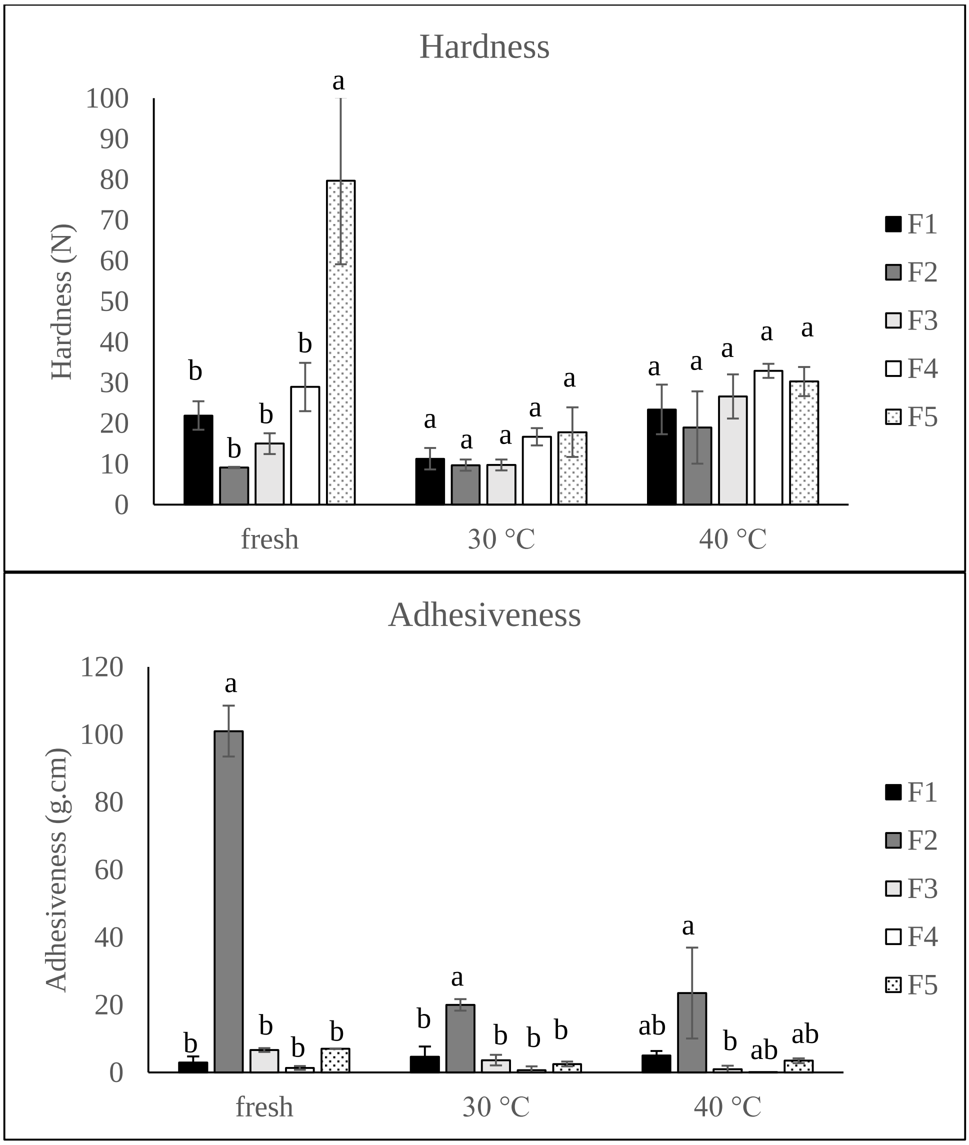

Fig. 3 Texture results of fresh and stored carob bar formulations. F1 (cocoa/carob powder blend with 2% LBG), F2 (cocoa/carob powder blend with 2% XN), F3 (cocoa/carob powder blend with 1:1 LBG:XN blend), F4 (cocoa powder with 2% LBG), F5 (carob flour with 2% LBG). Lettering was conducted based on 5 % significant level. Lettering shows statistically difference of the samples within each storage conditions, separately.

Adhesiveness data showed an increase with the increase of carob flour portion while it gave the lowest results in samples (F4) prepared with single cocoa powder and 2% LBG addition. The use of 2% XN instead of LBG created a crucial increase in adhesiveness emphasizing the importance of gum types. In the study of (Benkovic *et al.*, 2019), it was observed that the consistency and hardness values increased in higher amount of carob flour added the samples. The reason for this is that the sugar content of carob flour is high and the gelatinization effect increases accordingly.

Gums could act as stabilizers and emulsifiers besides their ability for water absorption, gelatinization and adhesive properties (Rosa *et al.*, 2015). These properties could vary regarding to gum type, concentrations, sample preparation conditions, etc. LBG as a polysachharide is mainly composed of galactomannan consisting a linear chain of (1→4)-linked β-D-mannopyranosyl units with (1→6)-linked α-D-galactopyranosyl residues as side chains. The galactomannan molecule displays extended ribbon-like structure at the solid state and a semi flexible coil-like conformation in solution. The galactose to mannose ratio of locust bean gum is approximately 1:3.1–1:3.9 (Barak and Mudgil, 2014). LBG is partially soluble in cold water and it could form a gel in the presence of large amount of sucrose. It also shows a beneficial synergistic increase in gel strength in the presence of other gums such as xanthan gum, kappa-carrageenan etc. up to a point. Thus, gum addition could increase viscosity and could act as thickening agent in food products such as bakery and ice cream products. It also resists to phase separation and increase end product quality (Barak and Mudgil, 2014). Since LBG is a neutral and semi-flexible polymer with low mobility (Ghebremedhin *et al.*, 2020), high hardness values in LBG samples were expected. On the other hand, negative side chains in XN could trigger electrostatic repulsions and showed less resistance to applied force in texture measurements. However, this phenomenon did not still create significant difference between the same group samples.

According to our results, LBG caused less adhesive property as compared to XN. Hence, half replacement of XN with LBG resulted in less adhesive structure as compared to single use of XN. XN made softer texture than LBG addition and their blend again gave intermediate firmness in the same formulation. This referred to add XN gum into formulation if it was aimed to decrease the hardness value. Since xanthan has a double-strand helix conformation in its native state and has a cellulose backbone and trisaccharide side chains with glucuronic acids and a pyruvate group, it influences final softness transforming rigid helix-coil structure into flexible coils (Higiro *et al.*, 2006).

Vibroviscometer results showed that XN exhibited higher viscosity values at 1% concentration when compared to LBG whereas this difference was not observed at 2% concentration (Table 5). However, their blend at total 2% concentration showed a high increase in viscosity indicating their synergistic behavior.

Table 5 Viscosity values of gum solutions in distilled water

Sample	Viscosity (mPa.s) at 25 °C
1% XN	$184^{d} \pm 2$
1% LBG	$89.5^{e} \pm 0.7$
1% XN:LBG blend	$221^{c} \pm 8.5$
2% XN	$231.3^{bc} \pm 7.1$
2% LBG	$261.3^{b} \pm 27.2$
2% XN:LBG blend	$433.6^{a} \pm 12.1$

In particular, when XN and LBG are mixed together, they give a network whose strength vary according to the temperature and weight ratio between the two polymers. For instance, double helix ordered structure is seen at low temperatures while random coil conformation is observed at higher temperatures (> 45 °C) (Sandolo *et al.*, 2010). Gelling, thickening property and synergism could also be affected by other factors such as side chains of polymers, branching degree of galactomannans (higher number of galactose units suppress gelation), molecular weight, etc. In cold conditions, they exhibit synergy due to interaction with each other and higher binding density but this is not the case for high temperatures. In other words, their interaction at high temperatures might not give a significant rheological improvement (Renou *et al.*, 2013). Moreover, their response could be time dependent instead of instantaneously occurrence. Whereas elastic modulus could show an increase with time, viscous modulus could be stable (Renou *et al.*, 2013). Owing to cross-linked polymers in these blends, in the presence of LBG, greater force is required with increasing deformation. The polymer chains are stretched by pulling them apart and firmer network is obtained. It is seen that XN-LBG blends show maximum modulus range referring to maximum synergistic effect around 1:1 blend ratio (Ghebremedhin *et al.*, 2020) and so this was chosen as LBG replacement ratio. Viscoelastic properties of LBG, XN and 1:1 blend support texture results. LBG is stated as viscous, on the other hand XN is reported as more elastic polymer in the literature (Higiro *et al.*, 2006). In other words, LBG has poor viscoelastic properties than XN and this might have led to higher firm and less adhesive structure in F1 sample than others.

CONCLUSION

The findings demonstrated that it was possible to develop new-generation snack food with carob flour replacing half portion with cocoa powder and enhancing structure with food hydrocolloids to increase acceptability and high quality in final product. Sensory analyses showed that addition of gum with high concentration (2%) was acceptable regarding to taste, flavor, aroma, texture and general preference. Texture analyses emerged the importance of gum type and combination of cocoa/carob powder in the formulation. The presence of XN created softness and very high adhesiveness in products, whereas LBG led firm but less adhesive texture. Regarding to cocoa and carob powder, they also caused differences in product properties due to their unique compositions. Due to its nature color, starch and fiber content, bars formulated with carob flour were associated with similar color when compared to cocoa powder but total color change differed during warm temperature storage most probably due to browning reactions. Intermediate texture values were obtained in the combination of cocoa powder and carob flour and also in XN:LBG blend. Thus, it could be recommended that carob and tahini based snack bar formulations could be developed combining gums and cocoa/carob flour.

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Supp. Mat. 1 Sensory evaluation score procedure

Basic Sensory Properties	Score	Definition of graded property
Appearance	7	Smooth, glossy surface, homogeneous, perfect color distribution
	1	Completely rough, matte surface, homogeneous and smooth non color
Color	7	Ideal brightness and homogeneous color distribution
	1	Unwanted, dull color
Taste	7	Unique flavor and sweetness
	1	Unacceptably annoying stranger flavor, spoiled taste
Aroma	7	Unique, aromatic (cocoa, hazelnut, milk, etc.); strong aroma
	1	Foreign odor; sour; bad
Texture	7	Soft structure that melts homogeneously in the mouth; spreadable
	1	Very sandy; stickiness
After taste	7	Distinctive positive taste and sweetness in the mouth afterwards
	1	Unacceptably, irritating foreign taste in the mouth, spoiled taste
General acceptability	7	Very good
	6	Medium good
	5	Less well
	4	Middle
	3	Little bad
	2	Middle bad
	1	Very bad