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ORIGINAL ARTICLE

Edible Utilization of Xanthan- guar Oleogels as a Shortening Replacement in Sponge Cake: Physicochemical Properties

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KEYWORDS	ABSTRACT: The present study aims at using xanthan and guar gums in producing and application of oleogels (Ole-
Guar gum;	XG) as an alternative to shortenings on quality properties of sponge cake (Oleo-cake). The influence of xanthan and
Oleogels;	guar gums on rheological, thermal and structure properties and fatty acid compositions of the oleogels was evaluated.
Physicochemical	Results showed that application of xanthan and guar gums oleogels has no effect on the amount and type of fatty
properties; Sponge cake;	acids. The use of guar gum in xanthan solution with short spacing peaks can show higher intensity than with long
Xanthan gum	spacing peaks. They enhanced both elastic modulus and viscous moduli and the strain-thinning behaviour for storage
	modulus in high strain amplitudes. As substitution of shortening with oleogels is increased to 75%, firmness,
	cohesiveness and chewiness of cake samples were decreased. Results showed that substituting the shortening with
	oleogels increased L* and a* colour values. Sensory analysis showed that substituting the shortening with oleogels up
	to 75% increased overall acceptability of cakes.

INTRODUCTION

One of the most important properties of fat is its physical structure which can be suitable for determining its application type in food productions [1, 2]. Hydrogenation is one of the important and common techniques for improving the functional properties of vegetable oils. However, studies have shown that during the hydrogenation process, the probability of trans isomer production in fat is 10-40%. Consumption of trans isomers increases the LDL and decreases HDL in the body and hence leads to most cardiovascular diseases, diabetes and increased rate of cancer among the human beings [2, 3]. Therefore, researchers are seeking to find a solution for producing the fat without any change in fatty acid structure and isomer production. Within recent years, using the oleogels for transforming

the edible oils with high nutritional value into the solid structure without hydrogenation process has been highly noticed by the researchers [4-6]. Oleogels are semisolid systems in need of the oil as the continuous phase and the structure agent as the dispersed phase[7, 8]. Oleogels can be produced via preparing the emulsion containing more than 60% oil via hydrocolloids (methyl cellulose, gelatine and pectin) and then the freeze-drying method [5, 8 and 9]. Stabilization is an important feature of hydrocolloids. It increases the viscosity and constant phase consistency and prevents instability of emulsion [10].

The two hydrocolloids are used together to create the new rheological properties or improve such properties in food products and reduces the production costs [11]. Galactomannans similar to guar gum is able to depict synergistic interaction, including high viscosity or gel formation with several polysaccharides such as xanthan, agar and carrageenan gums. Galactomannans potential in synergistic interaction with other polymers usually increases by their galactose decrease and the distribution pattern of galactose on the main chain. This synergistic behaviour is commercially precious among the polysaccharides because these behaviours create new textures (e.g two-phase gel structures) [12-15].

Xanthan gum is an extracellular polysaccharide secreted by *Xanthomonas campestris* microorganism. Xanthan is a biomaterial easily solved in cold water, and its viscosity is highly stable in a wide range of temperature and pH [12, 16, and 17].

Guar is a gum obtained from the underground gland of *Synopsis tetragonolobus* plant. Its viscosity is not affected by pH, as the guar gum is structurally neutral [13].

Due to the fact that there has been a limit study on the use of the xanthan and guar gums in oleogels production, the current study aimed to employ the xanthan and guar gums with oleogels as an option for shortening the quality properties of cake.

MATERIALS AND METHODS

Wheat flour for confectionary was prepared with 11.7% moisture, 0.6% ash, 10.3% protein and 17.7% wet gluten. Sunflower oil, sugar, shortening, baking powder, skim milk and vanilla were provided from the local shop (Mollasani, Iran). Xanthan gum (CAS Number: 11138-66-2) and guar gum (CAS Number: 9000-30-0) were provided from Sigma Aldrich Inc.

Preparing the emulsion and oleogels

The stock solution of xanthan and guar gum was prepared by dispersing xanthan and guar powder in deionized water and stirred for 60 min then the solution stored in room temperature for 24 h to ensure the materials were completely dissolved. A primary experiment was carried out to obtain the optimum xanthan and guar concentration necessary for product emulsion. The emulsion was prepared with sunflower oil addition (60%wt) to xanthan solution (1wt%, as the continuous phase of emulsion) via the high-speed mixer at 13000 (rpm), then the guar gum solution (1%wt with ratio 1:1 to xanthan solution) was immediately added in the stirring solution. In the initial experiments, adding guar gum to xanthan gum caused emulsion and more stable oleogels than when xanthan gum was added to guar gum. Produced emulsions were dried via freezedryer at (-80 °C) for 48h. To devise a united texture in dried oleogels, we mixed the samples for the 30 (s) at 11000 rpm by Ultra-turrax (Ultra Turrax T25, IKA, Werke GmbH & Co. KG, Staufen, Germany).

Determining the rheological properties

These tests were conducted using rheometer (Anton paar, MCR 302 Series, Austria) equipped with a 20 mm parallel plate geometry, and the gap between the two plates was adjusted to 1 mm to measure the viscoelastic characteristics (loss modulus, storage modulus). First, the amplitude sweep test (0.01-100%) at fixed frequency (1 Hz) and temperature (25°C) was performed to evaluate the linear viscoelastic region (LVE) of samples. Then a strain on 0.05% (within the LVE) was a choice to run a frequency sweep from 0.1 to 10 Hz at 25°C [18].

X-Ray Diffraction (XRD)

To determine the structural properties of produced oleogels, XRD (GNR explorer X-ray diffractometer, Italy) with copper lamp at room temperature over the range of 2Θ angles from 5° to 40° with the scanning speed of 2°/min was used [19, 20].

Differential Scanning Calorimetry (DSC)

The thermal behaviour was investigated by using the Differential Scanning Calorimeter (Metter Toledo DSC 822, Switzerland) equipped with liquid nitrogen cooling system. Aluminium pan was used as the reference [19]. 5 mg of the samples were transferred to the aluminium pan and were treated as explained below:

Heating speed was set on 5°C per minute and the evaluation temperature range was chosen between $20^{\circ}C - 100^{\circ}C$.

(Atomic Force Microscope) AFM

An atomic force microscope (AFM) was used to study the structure of the oleo-gels. The gels were coated on a piece of mica substrate and the samples were immersed in a container containing isobutanol for extra oil after 24 h, at room temperature. After leaving the solvent from the sample, an atomic force microscope (Nano wizard II JPK, Germany) equipped with the DME-SPM software was examined [21].

Cake formulation

The basic formulation of sponge cake included flour (100g), egg (70g), sugar powder (70g), shortening (52g), whey powder (4%), skim milk powder (2%), baking powder (2%), vanilla (0.5g) and water (30g). Sugar and shortening were initially mixed for 4 min. After adding egg, 15 ml water was added. Then, all powdery materials together with remaining water were added. Stirring continued till a uniform paste was obtained [22]. Then, cake shortening was substituted by the oleogels (contain sunflower oil 98% (w/w) and water 2%(w/w)) produced in 5 levels of 0, 25, 50, 75 and 100% (Control, Ole-25%cake, Ole-50% cake, Ole-75%-cake and Ole-100% cake). Then, the samples were put in the oven for 20 min in 195^oC. Cooked cakes were finally kept in polypropylene packages insulated from the humidity and oxygen until the tests are implemented.

Fatty acids composition

The fatty acids methyl ester was prepared in accordance with method No. AOCS Ce 2-66 as well as by analysing through chromatography gas device (Thermo Finnigan-Rodano, Italy) equipped with flame ionization detector and capillary column CP Sil 88 flexible fused with length, diameter and internal thickness of 100 m, 0.25 mm and 0.2 μ m, respectively, based on the method No. 1e- AOCS 91. An injection was made with ration (1:1) and helium was used as the carrier gas. The column temperature was programmed at 140 °C as an initial temperature and raised to 240 °C at 3.2 °C min⁻¹. [23].

Texture

Texture analyser (TA.TXplus Texture Analyser, Stable Micro Systems, U.K) was used for examining the texture profile analysis of samples. In this test, a piece $(20\times20\times20 \text{ mm})$ of the cake was prepared. Flat-faced cylindrical probe with the external diameter (35mm) was used for compressing each sample to 50% of its initial height (10 mm) with speed of (30 mm min⁻¹). The parameters measured were hardness, cohesiveness and chewiness [24, 25].

Color

Cakes' colours were evaluated by using the chromatography device of Konica Minolta (Model CR-400, Japan). Values of L^* (brightness index), a^* (redness index) and b^* (yellowish index) are determined in this test [26, 27].

Sensory analysis

Sensory evaluation of the cake slices was performed by a ten member trained panel. Panelists were aged 22–28 (60% females and 40% males) with experience in sensory evaluation of foods. Measurements were performed in individual booths with controlled illumination and temperature. Panelists were asked to indicate how much they liked or disliked each sample on a 5-point hedonic scale (5 = like extremely; 1 = dislike extremely) according to texture, color, taste and overall preference. The entire experiment was repeated three times (all judges scored all samples on each session for a total of three sessions) and the sensory scores were presented as the overall mean [28].

Statistical analysis

The data reported in this study are the mean, of a minimum of three replicates. All data were subjected to analysis of variance (ANOVA) and later to the Duncan's multiple range test to evaluate significant differences among treatments at p=0.05. Statistical analyses were performed using SPSS 23.0 (SPSS Science, Chicago, IL, USA).

RESULTS

AFM

The results of AFM showed the formation of a uniform, homogeneous, and stable gel network that indicating polymer-polymer interactions and the formation of hydrogen bonds between polymer threads and surrounding oil in the penetration with different diameter by coral-like network that made of polymer filament (Figure 1). Results showed the oleogel produced had $98\pm1.1\%$ (wt.) sunflower oil and $2\pm0.47\%$ (wt.) moisture content.

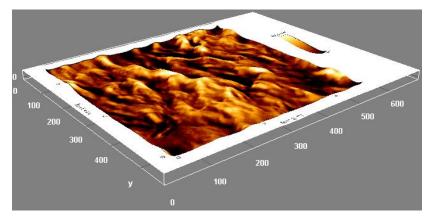
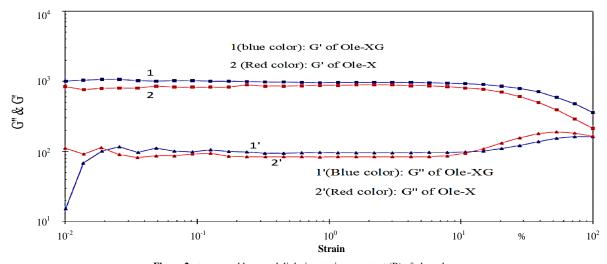
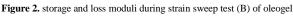


Figure 1. AFM of oleogel

Rheology behaviour

In view of the results (Figure 2), adding guar gum to xanthan solution expands the linear region in samples indicating the strong gel formation. Results given in Figure 1B show that the viscoelastic behaviour of produced gels is of weak gel type.





DSC

DSC curve shows that the oleogels produced only by xanthan gum no endothermic and exothermic peaks were observed. While by adding guar gum, a peak was revealed on the DSC curve of oleogels (Fig 3). No melting peak was also seen for oleogels produced only by xanthan gum (Ole-X). When xanthan and guar gums are used, enthalpy change was 87.1 mJ. Maximum peak temperature was 92°C. Peaks range between 65 0 C and 100°C. While as xanthan was used, no peak was observed in Figure 3.

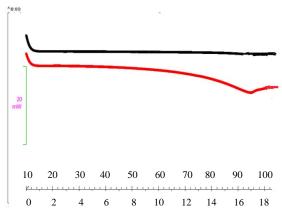


Figure 3. DSC curve of Ole-X and ole-XG

XRD

Figure 4 shows that when xanthan gum is only used, peaks with long spacing indicate higher intensity than the peaks with short spacing. While as the guar gum is added, peaks with short spacing indicate higher intensity than the peaks with long spacing.

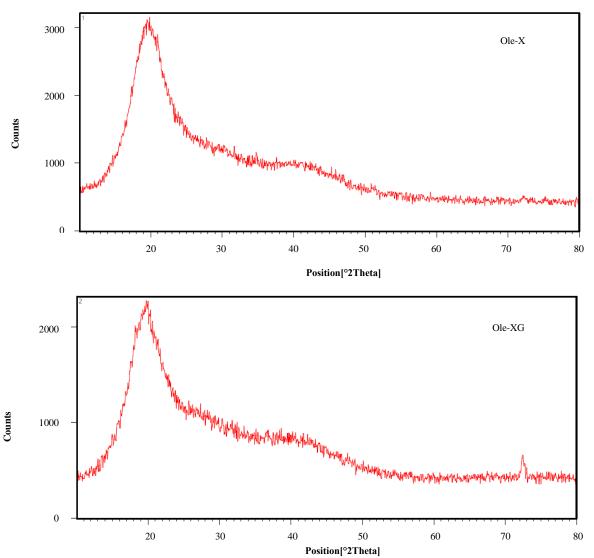


Figure 4. XRD plots for Ole-X and Ole-XG

Fatty acids compositions

Results obtained from analysis of fatty acids compositions are shown for different samples in Table 1

As it is seen, oleic acid and linoleic acid are predominant fatty acids of sunflower oil.

Fatty Acids	Sunflower Oil	Ole –XG	Control cake	Ole-75% cake
C4	-	-	49.5 ± 0.87	21.6 ± 0.34
C6	-	-	13.45 ± 0.24	0.68 ± 0.11
C8	-	-	7.87 ± 0.53	-
C16	6.64 ± 0.87	6.57 ± 0.24	3.57 ± 0.41	7.9 ± 0.25
C18	3.29 ± 0.24	3.32 ± 0.11	-	2.8 ± 0.14
C18:1	26.76 ± 0.37	27.05 ± 0.1	5.3 ± 0.34	24.3 ± 0.27
C18:2	61.88 ± 0.17	61.54 ± 0.22	6.03 ± 0.51	24.1 ± 0.16

Table 1. Fatty acids compositions of sunflower oil, Ole-GX, control cake and Ole-75% cake.

Texture

On the basis of results shown in Table 2, substituting the shortening by oleogels in cake formulation reduces the amount of samples' hardness.

As substitution of shortening with oleogels is increased to 75%, cohesiveness of samples is decreased indicating the increased amount of brittleness of samples' textures which is likely due to the interactions between the hydrophilic compounds and hydrophobic in the cake matrix. Adding the oleogels up to 75% improved the chewiness of cake indicating the role of oleogels used in cake formulation in minimizing the gluten network connections.

Color

Results (Table 2) showed that substituting the shortening with oleogels increased significantly (p<0.05) of the

brightness index (L^{*} value) among the samples. Results (Table 2) obtained from evaluation of colour index (a^{*}) indicate that as the level of oleogels in initial formulation of cake is increased, the value of such index is also increased [29].

Sensory analysis

Results obtained from the sensory analysis show that substituting the shortening with oleogels up to 75% enhanced the acceptability of cakes' organoleptic properties in such a way that cake containing 75% oleogels has the most overall acceptance among the sensory evaluators (Figure 5).

Treatment	Firmness (N)	Cohesiveness	Chewiness (N)	L* value	* value
Control	3.32 ± 0.17^{AB}	0.58 ± 0.1^{AB}	$1.95\pm0.14~^{AB}$	66.03 ± 1.5 ^D	-2.79 ± 0.14 ^C
Ole-25%	$2.38\pm0.1~^{\rm AB}$	$0.51\pm0.14~^{B}$	$1.22\pm0.1~^{BC}$	66.66 ± 1.8 ^C	-2.75 \pm 0.1 ^C
Ole-50%	$2.33\pm0.14~^{AB}$	$0.49\pm0.12\ ^{\rm B}$	$1.11\pm0.1~^{\rm BC}$	68.44 ± 1.2 ^B	$\text{-}2.53\pm0.1~^{\text{BC}}$
Ole-75%	$1.95\pm0.19\ ^{B}$	$0.47\pm0.1~^{\rm B}$	$0.97\pm0.2~^{\rm C}$	$68.9 \pm 1.3 \ ^{\rm B}$	$\textbf{-2.16} \pm 0.15 \ ^B$
Ole-100%	$3.65\pm0.12\ ^{\rm A}$	$0.68\pm0.15\ ^{\rm A}$	$2.57\pm0.14~^{\rm A}$	$71.27\pm0.9\ ^{A}$	-0.77 \pm 0.1 $^{\rm A}$

Table 2. Effect of substitution of shortening with Ole-XG on colour and texture properties of cake

The same letters in columns means no statistical differences between samples (P < 0.05).

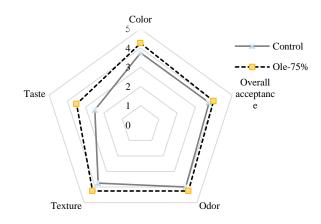


Figure 5. Sensory analysis of control and Ole-75% cakes.

DISCUSSION

Most food products including gels and polysaccharide concentrated solutions can be classified as the viscoelastic materials. Therefore, rheological tests are very important for describing the natural building and properties of food products [9, 30]. Strain determination equivalent to the end of the linear viscoelastic region is a criterion from building resistance or the ability to keep the form against the mechanical stresses imposed on the product during the transportation. In the critical strain, network building begins to collapse, hence, the critical strain, as a symbol, expresses the capability to change the system form (or transition from semisolid to semiliquid behaviour). In addition to using these curves for determining the linear region, they can be used for discriminating the mechanical resistance of samples, e.g. for strong and weak gels. In variable strain test, more strong gels remain in the linear region than the weak gels [31, 32]. According to results, adding guar gum leads to linear modulus' changes in produced gel within a higher strain range. Furthermore, as guar gum is added, values of both elastic modulus and viscous moduli ,as well as the space between two moduli, are increased indicating an increase in gel strength and firmness of network [31]. Weak gels have higher G' than G" and moduli of both are changes in parallel to each other. Meanwhile, in the

studied frequency amplitude (Data not shown), moduli G' and G'' do not cross each other and value of elastic modulus is higher than the viscous modulus showing low-frequency dependency [33]. Concerning the results, increased loss modulus and decreased storage modulus with an increase in frequency can be interpreted as below: when low frequencies are applied to the material, it has sufficient time for rearrangement the broken bonds in frequency cycle, but as the high frequencies are applied, the material does not have opportunity to rearrangement the broken bonds and as the bonds are broken, the viscous part is increased and shows the viscoelastic behaviour [31, 33]. Adding the guar gum decreases the strain-thinning behaviour for storage modulus in high strain amplitudes among the samples which this is likely due to the formation of hydrogen bond between two or more xanthan molecules with side chains of guar gum.

Results of this study show that any increase in melting temperature and thermal stability of oleogels depends on the concentration and existence of guar gum in the production of oleogels. In oleogels produced by xanthan and guar gums with initial and final maximum temperatures, DSC peaks are within 60-90 ⁰C and it can be argued that the produced oleogels have gel and solid network.

Higher intensity of peaks with long spacing for oleogels produced by xanthan gum shows self-rearrangement and rearrangement of the most gelator molecules. Therefore, the higher intensity of peaks with short spacing indicates high picking in molecule' layers. So, any change in intensities of peaks with short and long spacing indicates the rearrangement in oleogels molecules depending on gelator type and its concentration [20, 34].

On the basis of results, converting the sunflower oil to oleogels by use of xanthan and guar gums has no effect on the amount and type of fatty acid, so that in produced oleogels, oleic acid and linoleic acid were the predominant fatty acids in the sample. Based on the results (table 2), substituting the shortening by oleogels in producing the cake increases the amount of fatty acids with high nutritional value (ϖ_6 and ϖ_9) among the samples. Therefore, cake nutritional value can be improved by substituting the shortening by oleogels in producing the cake [6, 20].

Decreasing hardness of cake due to the capabilities of xanthan and guar gums in holding water or interactions among the hydrophilic compounds existing in gum with gluten protein [35]. Due to exposed to high values of fats' β ' crystals, shortenings increase the hardness and substituting the shortening by oleogels decreases the amount of fats' β ' crystals and increases the nonsaturation in cake which it likely can be a reason for decreasing the samples' hardness [31]. 100% substitution of shortening with oleogels leads to increased hardness of samples, which is likely due to the hydrophobic bonds between oil and hydrophobic sections of amino acids. In addition, the amount of saturation and liquidity of oil are increased while using the oleogels, this can lead to better distribution flour and sugar crystals between the oil particles. While as the shortening is used in making the cake, due to post-crystallization and agglomeration of fat crystals during the baking process, intermolecular connections are reduced in cake matrix which itself leads to the increased cohesiveness in sample texture [9].

In general, one of the oil functions in bakery products' formulations is to create the brilliance on the sample's crust surface, while as the shortening is substituted by the oleogels, since the amount of accessible liquid oil in samples is increased, probably this leads to an increase in brightness and brilliance index among the samples. The existence of hydrocolloid in oleogels' structures likely increases the moisture content in samples and as a result, a smooth surface is made on the crust by which the light reflected from the product increases and the value of colour index (L*) enhanced [36].

By substituting the shortening with oleogels, the amount of accessible liquid oil in the sample is increased. An increase in free oil is able to encompass the protein existing in the formulation and by this, Maillard reaction, known as an effective reaction in creating the colour in bakery products, can be prevented and accordingly it is known as a preventing factor in creating the red colour in samples [36].

Any increase in acceptance of organoleptic properties of cakes containing the oleogels is likely due to effect the oleogels on the amount and composition of fatty acid and samples' textures.

CONCLUSIONS

This study investigated the production of oleogels with xanthan and guar gums. Based on results, oleic acid and linoleic acid were the predominant fatty acids in oleogels. In oleogels produced by xanthan and guar gums with initial and final maximum temperatures, DSC peaks are within 60-90 °C and it can be argued that the produced oleogels have gel and solid network whereas, no melting peak was seen for oleogels produced only by xanthan gum when xanthan gum is only used, peaks of XRD with long spacing indicate higher intensity than the peaks with short spacing. Also, substituting the shortening by oleogels in producing the cake increases the amount of fatty acids with high nutritional value (ω_6 and ω_9) and acceptance of organoleptic properties among the samples. The results of this study showed that the addition of guar and xanthan gum can be used as a suitable and novel method for the construction of sunflower oil and use the produced oleogels as an alternative to shortening for improving nutrition and quality properties of cake.

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Conflict of interest

No conflict of interest is declared.

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