

Curcumin loaded in Nanogel-reinforced Hydrogel for Improvement of Quality and Textural Properties of Barbari Dough and Bread

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Abstract

Increasing shelf-life and nutritional value of bakery products always are important. In this research, curcumin (cur) loaded in nanogel-reinforced hydrogel (isolated soy protein (ISP)/Sodium alginate (SA) nanogel- based cress seed gum (CSG) hydrogel) was used to improve rheological characteristics of dough and technological and organoleptic properties of Barbari bread (traditional Iranian bread). The effects of nanogel-reinforced hydrogel (at 0, 5.0, and 10.0% levels (flour basis) with and without cur on Barbari bread quality were investigated. The rheological properties of dough were evaluated by farinograph and extensograph analysis. The results showed that water absorption, consistency, energy and extensibility of dough increased with addition of composite hydrogels, while degree of softening 10 min after beginning reduced. Addition of hydrogel increased specific volume, porosity and hardness of the bread. The crumb lightness of cur-composite hydrogel increased (75.51 ± 0.06) in compared to control (69.19 ± 0.07). Presence of 10% hydrogel composite significantly increased (a^*) parameter of crust (9.96 ± 0.13) ($P < 0.05$). The enthalpy and endothermic peak temperature reduced due to incorporation of 10% (w/w) cur-composite in bread. The results showed the addition of 10% cur-composite improved the organoleptic properties of the bread and its shelf life.

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Keywords

Bread

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Introduction

In recent years, the awareness of consumers and producers regarding the healthy foods has increased. Therefore, the demand for natural ingredients has been increasing. Among the plants that have been considered due to the presence

of bioactive compounds, turmeric plant (Joung et al., 2016).

Curcumin (cur) as a natural polyphenolic compound is extracted from turmeric and has several antioxidants, anti-inflammatory, anti-cancer and other disease-healing properties. This bioactive compound is well tolerated in very high

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doses (12-8 g/day) (Rafiee, Nejatian, Daeihamed, & Jafari, 2019). Application of cur is limited due to low bioavailability after oral administration, poor solubility in water, low absorption, rapid metabolism and excretion from the gastrointestinal tract (Rafiee et al., 2019). Degradation of curcumin is occurred due to the thermal process and long-term storage (Coradini et al., 2014). Encapsulation of bioactive compounds increases their stability under harsh conditions (Huggett, Nowak, Markwick, Mutukumira, & Keener, 2018).

A suitable food source for enrichment with curcumin should be widely available. Bread is a staple food and one of the most important sources of nutrients (Azizi, Rajabzadeh, & Riahi, 2003; Nikooyeh et al., 2016). Therefore, bread can be a good candidate for curcumin fortification.

Hydrogel formation is a special method of curcumin entrapment through physical cross-links (electrostatic interactions) between ionic natural macromolecules (such as chitosan, gelatin, sodium alginate, etc.) (McClements, 2017). A way to achieve rapid response hydrogels is to make thinner and smaller hydrogels, such as microgels or nanogels (Farjami & Madadlou, 2017). An approach, to improve the thermal stability of curcumin in harsh thermal processing of baking, is the entrapment of nanoparticles within hydrogels and creating nanoparticle-reinforced hydrogel (Fei-Ping Chen, Bian-Sheng Li, & Chuan-He Tang, 2015). On the other hand, the loss of bread quality during storage is a big concern. Bread staling is a complex physicochemical process that results in crumb hardening and change of elasticity due to retrogradation, changes in starch and gluten (MANIA Salehifar, Seyedein Ardebili, & Azizi, 2009). In recent years, the use of additives, especially hydrocolloid compounds to delay the staleness of bakery products has been

growing (Khoshakhlagh, Mohebbi, & Koocheki, 2020).

Today, the use of native gums in the food industry to develop processed foods is growing and investigations on applying them have expanded (Behrouzian, Razavi, & Phillips, 2014; Zeynali, Naji-Tabasi, & Farahmandfar, 2019). One of the common native hydrocolloids is cress seed gum (CSG). The scientific name of this gum is *Lepidium Sativum* belongs to the family Crucifera. The main sugars of this gum are mannose (38.9%), arabinose (19.4%), galacturonic acid (8%), fructose (6.8%), glucuronic acid (6.7%), galactose (7.4%), rhamnose (1.9%) and glucose (0.1%) (Naji, Razavi, & Karazhiyan, 2013; Razmkhah, Razavi, & Mohammadifar, 2017; Shahbazizadeh, Naji-Tabasi, Shahidi-Noghabi, & Pourfarzad, 2021). The macromolecular component of CSG has a molecular weight of 540 kDa. CSG has a shear thinning behavior with high stability against thermal treatments (Naji & Razavi, 2014; Naji et al., 2013; Naji, Razavi, Karazhiyan, & Koocheki, 2012; Naji, Razavi, & Karazhiyan, 2012). In recent years, many studies have been done on CSG and its physicochemical properties are available (Behrouzian et al., 2014; Razavi & Karazhiyan, 2009). CSG can be used to design of hydrogel system (Shahbazizadeh, Naji-Tabasi et al. 2021).

Isolated soy protein (ISP) and sodium alginate (SA) were used for fabrication of nanogels. Nanogels are three-dimensional networks of cross-linked polymeric nanoparticles that are dispersed in a suitable solvent. ISP is a natural polymer that is widely used to create polymer networks for delivery of bioactive compounds (Fei-Ping Chen, Bian-Shen Li, & Chuan-He Tang, 2015). Sodium alginate, a linear anionic polysaccharide consisting of α -L-glucuronic acid and β -D-mannuronic acid with β -(1 and 4) junctions, as a biodegradable, and non-toxic polymer has several applications in

food delivery systems (Kwiecień & Kwiecień, 2018).

Therefore, the aims of this study were investigating the effects of curcumin-loaded/unloaded ISP/SA nanogel-based CSG hydrogel (0, 5, and 10% (flour basis)) on the dough rheological properties and physicochemical characteristics of Barbari bread during storage.

Materials and methods

Materials

Commercial AZAR GANDOM Barbari wheat flour (extraction degree 78%, ash 0.81%, protein 12.75% and gluten 31.5%) was obtained from a local market. Baker's yeast was obtained from Iran Melase Company (Tehran, Iran). Curcumin ($C_{21}H_{20}O_6$, 95% purity), $CaCl_2 \cdot 2H_2O$ Diphenyl-1-picrylhydrazyl were purchased from Sigma-Aldrich (USA). Cress seed gum (CSG) powder was obtained from Reyhan Gum Parsian Company. About 77% of CSG is carbohydrate and then ash is 11.5%. CSG also has low amounts of protein and fat. ISP was purchased from Shandong Yuxin Bio-Tech Co. (China). All chemical reagents were of analytical grade with the highest purity available.

ISP/AG nanogel based CSG hydrogel preparation

The NG based hydrogel composite preparation process consists of three steps:

Step I. Physically cross-linked CSG hydrogel was prepared based on Shahbazizadeh *et al.* (2020). Briefly, a solution of 1.5% (gr/100ml) of CSG was prepared by dispersing appropriate amounts of CSG in a solution of 0.2% (w/v) of calcium chloride and stored in the refrigerator overnight for complete dehydration. (Shahbazizadeh, Naji-Tabasi *et al.* 2021). A part of the $CaCl_2$ solution was kept to use in part III.

Step II. Cur-ISP/SA nanogel was prepared by the physical cross-linking

method (Neufeld and Bianco-Peled 2017, Shahbazizadeh, Naji-Tabasi *et al.* 2021). ISP/SA nanogel was prepared with concentration of ISP, SA, and $CaCl_2$ of 1.6% (w/v), 0.069% (w/v), and 0.008% (w/v), respectively. For producing nanogels, ethanol-soluble curcumin 0.04% (w/v) was added drop wise to heated ISP dispersion at concentrations of 1.0-4.0% (w/v), before sodium alginate was added. Then, the pH of ISP/SA dispersion was adjusted to 5.8 for creation of a soluble complex. After the heat treatment at 95 °C for 30 min, samples were immediately cooled in ice water. $CaCl_2$ solution was then added drop wise to the Cur-ISP/SA complex solution.

Step III. The composites were prepared by drop wisely addition of cur-ISP/SA nanogel suspension with particle size of (122-167) nm into CSG hydrogel before adding $CaCl_2$. 10:90 (v/v) ratio of NGs to hydrogel was prepared and named 10NG-bHydrogel. Then, the remained crosslinking protocol agent ($CaCl_2$) belonged to step I, was finally added to composite solutions and kept for 24 hrs.

Farinograph and extensograph assay

Different formulations of dough were prepared in the farinographic bowl (Brabender OHG-860704, Duisburg, Germany). Flour was mixed with the other ingredients and corresponding amounts of water to obtain the same final mass (877 g). The parameters acquired from farinogram included percentage of water to yield the consistency of 500 BU (water absorption: WA), time to reach the consistency of 500 BU (dough development time: DDT), time duration of the dough remained at a consistency of 500 BU (dough stability time: S), and the degree of softening (DS) of wheat flour dough contained cur-composite hydrogel (AACC 54-21.02).

An extensograph-E (Brabender, Duisburg, Germany) was utilized to examine the effects of different amounts of cur-loaded hydrogel composite on the

extensibility (E), the resistance to extension up to 50 mm (R_{50}), the maximum resistance (R_{Max}), and energy area or work input (A) of wheat flour dough based on AACCI method (AACCI 54-10.01).

Bread formulations and preparation

Baking Process: Bread was baked following the AACC method for straight-dough bread-making (AACC 146 International 10-10.03) (Tebben & Li, 2019). Basic Barbari bread formula based on 100 g flour consisting of compressed yeast 0.5%, salt 1% (flour basis), and water up to a consistency of 400 BU. According to the previous studies and our initial experiments, cur loaded or/unloaded -ISP/SA nanogel based CSG hydrogel composite was added to the flour at three concentration levels (w/w) of 0.0%, 5.0%, and 10.0% (flour basis). To prepare control 2, free curcumin powder was also added to flour. Acceptable daily intake of curcumin is 0-3 mgr per kilogram of body weight (Rafiee et al., 2019). The amount of curcumin powder was considered 18 mg per 300 gr dough, which was equal to bread contained 10% (w/w) cur- hydrogel composite. A straight dough process was carried out for preparing the bread. The ingredients were mixed. After mixing the components for 15 minutes at a constant speed (5 kg capacity, Ebtekar steel, IRAN, Tehran), dough was fermented (60 minutes at 30 °C and 75-85% relative humidity), divided into 300 gr pieces. After shaping and punching, the chins were secondary fermented for 20 minutes at 42 °C and 75-85% relative humidity, and then sheeted and baked in a rotating oven (Nane Salem Tabriz pokht, IRAN) at 260 °C for 13 minutes. Then, bread samples were cooled at room temperature and immediately packaged to prevent secondary contamination and subsequent tests were performed on them (Purfarzad, Karimi, Ghiyafe-Davoodi, Hematiyan-Sorki, & Razavi-Zadegan, 2009).

Moisture content

AACC-2000 standard No. 16-44 was used to perform this test.

Specific Volume

To measure the volume, the method of replacing the volume with millet grain in accordance with AACC standard, 2000 No. 10-72 was used. The specific volume (cm^3/g) was calculated as loaf volume/bread weight (Jalali, Sheikholeslami, Elhamirad, Haddad Khodaparast, & Karimi, 2020).

Crumb porosity

The image processing method was used to evaluate the porosity of bread crumb. For this purpose, a slice of bread crumb (4×4 cm) was prepared and their pictures were captured by a scanner (model: HP Scanjet G 3010) with a resolution of 300 pixels. The prepared image was analyzed by Image J software. The color image was converted to grayscale and after adjusting the threshold, the pore area fraction was investigated with ImageJ software (Naji-Tabasi & Mohebbi, 2015).

Color of crumb and crust

Bread crust and crumb color analysis were performed 2 hours after baking by determining the three indices (L^*), (a^*) and (b^*). The LAB parameters of captured images were determined by Image J software (Naji-Tabasi & Mohebbi, 2015).

Textural properties

The texture analysis was performed using a texture measuring device (TPA) TEXTURE ANALYSER model Brookfield –CT310k made in UK connected to a computer equipped with texture probe software. This device was equipped with a cylindrical probe with 25 mm diameter and 35 mm length (TA5). The target value was 4.0 mm for compression test (equal to 30% of thickness of Barbari bread), hold time

was 0 s, Trigger load was 7 g, and Test speed was 2.00 mm.s⁻¹. The maximum force required for the penetration of the probe was considered as hardness value (Milani, Pourazarang, & MORTAZAVI, 2009; M Salehifar, Shahbazizadeh, Khosravi-Darani, Behmadi, & Ferdowsi, 2013).

DSC studies

The thermal behavior of different formulation prepared breads after 0, 3 and 5 days of storage were investigated using a DSC (DSC-100 model, Spico Co., Iran) equipped with a liquid nitrogen cooling unit. 20 mg samples were placed in an aluminum pan and press-sealed with a perforated aluminum cover and heated from 20 to 350 °C under a nitrogen atmosphere with a flow rate of 10°C/min. An empty pan was used as a reference. According to DSC thermogram, onset (T_O), peak (T_P) temperatures and enthalpy changes (ΔH) were obtained (Naji-Tabasi, Razavi, & Mehditabar, 2017; Shahbazizadeh *et al.*, 2021).

Sensory evaluation

Sensory properties were determined by 25 trained panelists (age range of 24 to 40 years) in the format of a 5-point Hedonic Scale (5=like extremely and; 1=dislike extremely). The panelists were advised to drink some warm water between the two samples to eliminate the effect of each sample on the other. Sensory parameters were evaluated based on preference liking for color, texture, flavor, and overall acceptability (Milani *et al.*, 2009).

Statistical analysis

A completely randomized factorial design was used for statistical analysis. Means were compared by Duncan's multiple-range test (p< 0.05) with Minitab16. Each sample was prepared in three replications and the related tests were performed on them. Results were expressed by means of ± standard deviation.

Results and discussion

Farinograph properties of dough

The dough mechanical properties play a pivotal role to optimize gas retention and crumb structure formation (Shittu, Aminu, & Abulude, 2009). The dough developing time (DDT) is the time required in minutes from the beginning of adding water to the flour until the moment when the consistency of the dough begins to decrease (PEIGHAMBARDOUST, RAIESI, & EYVAZ, 2015). Dough development time (DDT) indicates the relative strength of flour gluten, and short development times indicate weak gluten protein (Koushki, Abras, & Azizi, 2011). The time required for the dough to develop or the time required for the dough to reach 500 BU is changed by adding hydrocolloids to the dough (Koushki *et al.*, 2011). The developing time (DT) of the dough indicates the strength of the flour, and higher values reflect stronger dough. Dough development time has a positive and significant relationship with stability. Flours with high development time should also have good stability (Koushki *et al.*, 2011).

According to the results of the Farinograph test (Table 1), the development time was in the range of (05:00) - (08:00) min. Free curcumin and low amounts of composite hydrogel were reduced DDT. It seems that few amounts of composite lead to rapid hydration and prevent lump formation during blending. This monotonous hydration will help to uniform distribution of moisture which probably reduced DDT (Asgari, Fadavi, & Seyedein, 2020). In this study, 10% (w/w) cur loaded/unloaded-composite hydrogel samples had good DT. The highest DDT was related to the treatment containing 10% (w/w) curcumin loaded and unloaded hydrogel. The structure of the composite and its strong bonding with the components of wheat flour which reinforced stability of dough network

(Ketilath, Azizi, & Fazeli, 2013). Dough development time and stability have a positive and significant relationship with each other. Flours with high development time should also have good stability (Koushki et al., 2011). Increase the amounts of CSG composite hydrogel leads to hydrogen bonds between composite and flour and consequently increased in DT and also formation of stable and stronger complexes between gluten and composite at high amounts (Asgari et al., 2020). The increase in

developing time by higher level of composite is attributed to the increase in the number of hydroxyl groups, increase in water absorption and formation of strong gel network (Asgari et al., 2020; Sadegh Nia, Azizi, Seyedin Ardebili, & Mohammadi, 2016). Also, increasing the composite resulted in the formation of a network similar to the gluten network and increased the strength and developing time of the dough (Sadegh Nia et al., 2016).

Table-1-pharinograph results of various formulation prepared dough.

| Parameter | Sample | | | | | |
|-----------------------------------|---------|----------|--------------------|---------------------|------------------------|-------------------------|
| | control | Free cur | 5% (w/w) composite | 10% (w/w) composite | 5% (w/w) cur-composite | 10% (w/w) cur-composite |
| Development time (DT) (mm) | 07:00 | 06:00 | 05:00 | 08:00 | 05:00 | 08:00 |
| Consistency | 511 | 485 | 514 | 505 | 514 | 505 |
| Water absorption (WA)% | 61.0 | 60.4 | 61.2 | 61.4 | 61.2 | 61.4 |
| Degree of Softening (DS) (10 min) | 10 | 8 | 9 | 3 | 9 | 3 |
| Degree of Softening (DS) (12 min) | 35 | 23 | 30 | 310 | 30 | 330 |
| Farinograph quality number (FQN) | 178 | - | 172 | - | 172 | - |

Water absorption is an important factor in bread production. Increasing the water absorption of the dough means increasing the shelf life of a product. As the amount of water absorbed increases, the time required for the formation, which in the farinograph is called the dough developing time, increases (Asgari et al., 2020).

As can be seen in Table 1, Water absorption (WA)% of the samples ranged from 60.8 to 61.4%, which negligibly had an upward trend by hydrogel addition. The optimum water for control and free curcumin dough was 61.0% and 60.4%, respectively. Free curcumin reduced the amount of water absorption and composite and cur-composite hydrogel increased it. As hydrocolloids were added as hydrogel structures in bread formulation, they did not have a noticeable increase the water absorption.

This is probably due to the hydrophobicity of soy protein in the composite structure, which reduces the water absorption capacity (Naghavi, Mogaddam, Peighambaroust, Ghaffari, & Azadmard-Damirchi, 2011).

Dough softness degree (DS) directly related to the weakness of the flour (Soleimanifard, Alami, & Najafian, 2015). Degree of softness after 10 min decreased in all treatments compared to control. Presence of free curcumin and the composite slightly decreased the degree of softness after 10 minutes. The reason of this case probably is thickening the gluten network due to CSG composite addition and finally strengthens of dough stability. The highest degree of softening after 10 min (indicating fast gluten network formation) (Sahari, Mohammadi, & Hamidi Esfehiani, 2014) was observed for control and 5.0% cur-loaded/unloaded

composite and the lowest was observed for 10% cur-loaded/unloaded composite. Cur-composite hydrogel did not affect this parameter. The highest and lowest softness degrees after 10 minutes were related to the control and 10% (w/w) unloaded composite, respectively. The reason for the decrease in the softness of the dough at different concentrations of the composite is probably due to the formation of a more stable and stronger complex with gluten (Soleimanifard *et al.*, 2015).

Softness degree after 12 minutes was also reduced in all samples except 10% (w/w) with/without cur-composite samples. The highest degree of softening at 12 min indicates good workability and strength of

dough (Sahari *et al.*, 2014). The dough containing 10.0% with/without cur-composite had the highest value, while the lowest was observed for free cur-bread. Therefore, it can be predicted that the presence of composite in bread will create a soft and desirable texture.

Failure to display a quantitative Farinograph number (FQN) indicates the strength of the resulting flour and all samples had the desired stability.

Extensograph properties of dough

The results of extensograph are directly related to the protein properties of gluten flour (Koushki *et al.*, 2011), which are shown in Table 2.

Table-2-Extensograph results of different formulation of Barbari dough.

| treatments | Water addition (%) | Fermentation time (min) | Energy (A) (cm ²) | R ₅₀ (BU) | E (mm) | R _{Max} (BU) |
|----------------------------------|--------------------|-------------------------|-------------------------------|----------------------|--------|-----------------------|
| control | 57.7 | 45 | 156 | 339 | 213 | 548 |
| | | 90 | 198 | 477 | 200 | 751 |
| | | 135 | 195 | 471 | 195 | 778 |
| Free cur | 58.8 | 45 | 154 | 330 | 214 | 526 |
| | | 90 | 199 | 444 | 210 | 724 |
| | | 135 | 191 | 456 | 206 | 706 |
| 5% (w/w) composite Hydrogel | 59.10 | 45 | 152 | 337 | 215 | 525 |
| | | 90 | 196 | 422 | 214 | 692 |
| | | 135 | 179 | 426 | 204 | 678 |
| 10% (w/w) composite Hydrogel | 59.30 | 45 | 162 | 325 | 332 | 496 |
| | | 90 | 179 | 404 | 211 | 646 |
| | | 135 | 178 | 414 | 203 | 680 |
| cur-5% (w/w) composite Hydrogel | 59.10 | 45 | 152 | 358 | 203 | 566 |
| | | 90 | 183 | 418 | 207 | 700 |
| | | 135 | 183 | 456 | 198 | 729 |
| cur-10% (w/w) composite Hydrogel | 59.30 | 45 | 170 | 358 | 218 | 578 |
| | | 90 | 197 | 501 | 194 | 772 |
| | | 135 | 200 | 494 | 196 | 798 |

The water addition increased from 57.7% in control to 58.8, 59.1 and 59.30% in free cur, 5 and 10% cur-loaded/unloaded composite hydrogels, respectively. The results confirmed water absorption and development time.

The viscoelastic behavior of the dough is the energy of the dough or the area under the curve (A). The energy required to stretch the dough until it breaks is a good

indicator of flour strength. The energy of free cur-dough was similar to control at all three fermentation times. Dough samples with 5% (w/w) cur-loaded/unloaded composite showed the lowest energy, at all three fermentation times (after 45, 90, and 135 min). The energy of samples containing composite (except 10% cur-composite) reduced. The results indicated that mixing wheat flour

with the composite at 5% level reduced the resistance to extension. Dough containing 10% (w/w) cur-composite showed the highest energy. The reason is the creation of a strong complex between flour starch and gluten network in the presence of 10% (w/w) cur-composite.

The resistance to extension up to 50 mm (R_{50}) predicts dough expansion properties and fermentation tolerance (Asgari et al., 2020). Dough with high R_{50} produce a better-quality during dough processing and baking. R_{50} increased in all treatments as the fermentation time increased. The presence of free curcumin and composite reduced the R_{50} . Cur-composite increased R_{50} (5% cur-composite sample at 45 minutes and the 10% cur-composite sample at 45, 90 and 135 mins). Extensograph results are directly related to the gluten properties. The change in dough resistance to extension can be explained by the interaction between the protein and the composite (Asgari et al., 2020). Increment of resistance to extension indicates gluten hardening. Since the glutenin component of the gluten plays a role in dough resistance to extension (Naghavi et al., 2011).

The extensibility (E) indicates the amount of extensibility of the dough against the force applied to the dough. The extensibility of all treatments decreased with increasing fermentation time. The extensibility of the dough in the free curcumin, 5% and 10% (w/w) cur-unloaded composite samples increased compared to control, at all fermentation

times. The change in the ratio of gliadin to glutenin influences on the dough elastic properties (Naghavi et al., 2011). The CSG composite reduced the maximum resistance (R_{max}) of the dough. 10% cur-composite samples at 45, 90 and 135 mins of fermentation time increased viscous behavior. In other words, 10% cur-composite increased R_{max} of the dough by creating a thicker wall in the dough.

Bread quality

Moisture content

The moisture content of bread samples ranged from 28.19 to 31.86 % (Table 3). Statistical analyses showed the effect of curcumin and different concentrations of loaded/unloaded composite hydrogels on moisture content were not significant ($p < 0.05$). Maleki et al. (2012) and Pourfarzad et al. (2014) reported moisture content of Barbari bread was 34.0% and 26.93%, respectively (Maleki, Milani, & Amiri, 2012; Pourfarzad, Khodaparast, Karimi, & Mortazavi, 2014). Similar results showed a decrease in moisture content in rice pastry due to the addition of high levels of CSG. In the mentioned study, the amount of moisture increased with the addition of CSG at 1% (w/w) and decreased at higher levels (Mollabashi, Nateghi, & Abdolmaleki, 2015). The reason for the decrease in moisture in high concentrations of CSG hydrogel composite can be probably considered as an increase in bonded water and a decrease in free water (Mollabashi et al., 2015).

Table 3 - Effect of curcumin, composite hydrogel, and curcumin-composite hydrogel on moisture, specific volume, hardness and crumb porosity of Barbari bread.

| treatments | Moisture (%) | Specific volume ($\text{cm}^3 \cdot \text{gr}^{-1}$) | Crumb porosity (%) | hardness (g) |
|-------------------|--------------|--|--------------------|---------------|
| control | 31.86±0.11a | 1.85±0.09b | 55.91±0.38b | 582.5±102.53b |
| Free cur - bread | 30.52±0.95a | 2.73±0.15b | 57.52±1.13b | 536.5±19.09b |
| 5% composite | 31.67±2.92a | 3.67±0.35a | 60.82±0.70a | 594.5±20.576b |
| 10% composite | 28.27±0.75a | 3.80±0.34a | 60.88±1.75a | 540.5±147.78b |
| 5% cur -composite | 29.03±0.77a | 3.76±0.62a | 64.53±1.30a | 662.5±27.57a |
| 10% cur-composite | 29.57±3.08a | 4.14±0.96a | 60.69±0.62a | 854.5±135.05a |

*Different letters indicate significant differences between breads at $p < 0.05$ by Duncan test.

Specific volume

The results of specific volumes are summarized in Table 3. By increasing unloaded composite hydrogel concentration to 10% (w/w), specific volume increased ($p < 0.05$). 10% (w/w) cur-composite hydrogel bread had the highest specific volume ($4.14 \pm 0.96 \text{ cm}^3 \cdot \text{g}^{-1}$) compared to control ($1.85 \pm 0.09 \text{ cm}^3 \cdot \text{g}^{-1}$) ($p < 0.05$). At a low level (5%) hydrogel and free curcumin did not have a significant effect on specific volume ($p > 0.05$).

The use of hydrocolloids reduces the size and increases the number of gas cells in the bread structure, which increases the specific volume and thus increases the volume. The increase in specific volume is usually due to the entrapment of gases in the cellular structure of proteins, especially gluten (Naji-Tabasi & Mohebbi, 2015). The results show that CSG composite increased gas retention and dough viscosity. The results were consistent with the observations of other researchers (SAHRAIYAN, Karimi, & SHEIKHOLESLAMI, 2018). Naji & Mohebbi (2015) reported by the addition of CSG, the specific volume was significantly increased. Hydrocolloids effect on the stability of gas cells by forming a thick layer around gas cells. Therefore, the gas output will be reduced and the bread specific volume will be improved (Naji-Tabasi & Mohebbi, 2015). The Mollabashi et al. (2015) reported similar results. They concluded that increasing the amount of CSG from 0.5 to 1% increased the specific volume of rice cookies (Mollabashi et al., 2015).

Crumb Porosity

Results of porosity evaluations showed that curcumin had no significant effect on the porosity of Barbari bread ($p > 0.05$) (Table. 3). Loaded and unloaded composite hydrogel significantly increased crumb porosity ($p < 0.05$). The porosity of bread contained 10% (w/w) composite hydrogel had lower porosity

compared to 5% (w/w) composite bread, but this difference was insignificant ($p > 0.05$). The highest and lowest porosity value was attributed to 10% (w/w) cur-composite bread ($64.53 \pm 1.30\%$) and the control sample ($55.91 \pm 0.18\%$), respectively. NGs-CSG hydrogel can improve water distribution and increases gas bubbles in Barbari bread dough, which increases the number of air bubbles (Mollabashi et al., 2015). Naji and Mohebbi (2015) had similar observations by the addition of CSG and xanthan gum at 1.0% (w/w). The glycoprotein complex of CSG (hydrophilic and hydrophobic groups) stimulates surface activity in the dough structure during rest and the structure of gel networks during the bread-making process. These complex structures strengthen the boundaries between the air cells formed in the dough and consequently increase gas retention during baking (Naji-Tabasi & Mohebbi, 2015). Mollaabsi et al. (2015) investigated the effect of CSG on the physicochemical and textural properties of rice pastries. They reported the number of air bubbles increased significantly with increasing CSG concentration compared to the control sample (Mollabashi et al., 2015).

Texture analysis

Hardness is the resistance of the bread against deformation, which influences on bread acceptance (Table. 3). The hardness of the bread containing free curcumin, 5 and 10 % (w/w) composite, had no significant difference with the control. The hardness of 5 and 10% (w/w) cur-hydrogel samples significantly increased compared to the control ($p \leq 0.05$). The sample treated with 10% (w/w) of the cur-hydrogel had the highest hardness value which is probably related to thicker layer of gas pores.

Color properties

Color properties play a pivotal role in the initial acceptance of bakery products by

consumers (Mollabashi et al., 2015). The results of evaluating the color of the crumb of Barbari breads are summarized in Table 4. Composite hydrogel addition significantly increased the lightness of crumb bread ($p < 0.05$). No significant difference was observed between 5 and 10% composite breads. In general, breads with added hydrocolloid evidence lighter crusts (Naji-Tabasi & Mohebbi, 2015). This could be attributable to the effect of hydrocolloids on water distribution, which impacts Maillard's reaction and caramelization. Mezaize et al., (2009) found a similar result for xanthan gum and guar gum gluten-free bread. Sciarini et al., (2010) reported that the lightness of breads containing gelatin and alginate was similar to control, but breads with xanthan gum and Carboxyl methyl cellulose showed a lighter crust and lower L^* value obtained by carrageenan addition. Cur-composite hydrogel significantly increased the lightness of the bread crumb ($p \leq 0.05$) (Table 4). The cur-composite also significantly increased the lightness of the bread crumb ($p < 0.05$). The highest L^* values were achieved by 5 and 10 % (w/w) cur-composite breads with (76.68 and 75.51, respectively), which showed the desirability of bread

color in these samples. Differences between L^* of cur-composite breads were not significant ($p < 0.05$). The treatments had no significant effect on a^* and b^* value of bread crumb ($p < 0.05$).

Color evaluation of various formulations of crust bread is summarized in Table 4. The L^* value of the treated bread crust had no significance in comparison to the control ($p < 0.05$). Mirzaei et al. (2009) studied the effect of guar gum and xanthan gum on the crust of gluten-free bread and observed no significant difference between their brightness control ($p > 0.05$).

The addition of hydrogel significantly increased a^* value of bread crust ($p \leq 0.05$). The a^* value of control bread was equal to 9.96, while by addition of 10% (w/w) cur-loaded/unloaded composite hydrogel a^* value reached to 14.17. It means that a^* of bread crust significantly increased by hydrogel addition ($p < 0.05$). The addition of curcumin significantly increased the amount of b^* of bread crust ($p < 0.05$). By adding curcumin into foods, their yellowness increases. Hydrogel and cur-hydrogel did not significantly effect on b^* value of bread crust ($p > 0.05$).

Table 4- Effect of curcumin, composite hydrogel, and curcumin-composite hydrogel on color properties of Barbari bread.

| Bread formulation | Crumb | | | Crust | | |
|-------------------|--------------|-------------|-------------|-------------|--------------|--------------|
| | L^* | a^* | b^* | L^* | a^* | b^* |
| Control | 69.19±0.07b | -3.68±0.02a | 16.34±0.13a | 56.21±0.41a | 9.96±0.13b | 22.46±3.67b |
| Free curcumin | 69.76±0.47b | -3.97±0.23a | 17.95±0.13a | 52.02±0.95a | 8.66±0.15b | 27.48±0.52a |
| 5% composite | 72.09±0.12ab | -3.52±0.03a | 14.99±0.69a | 52.31±0.69a | 11.51±0.01ab | 25.35±0.93b |
| 10% composite | 72.37±0.12ab | -2.94±1.5a | 15.43±0.86a | 49.16±3.41a | 13.58±2.17a | 22.97±0.61b |
| 5% cur-composite | 76.68±1.08a | -2.76±0.80a | 15.49±0.85a | 50.47±0.22a | 14.58±0.06ab | 26.65±1.03ab |
| 10% cur-composite | 75.51±0.06a | -2.81±0.84a | 16.44±0.59a | 51.34±0.39a | 14.17±0.65a | 27.03±0.83a |

*Different letters indicate significant differences between breads at $p < 0.05$ by Duncan test.

DSC studies

The effect of CSG composite addition on the thermal properties of Barbari-bread is shown in (Table 5). On the first day of storage, the peak temperature (T_p), and enthalpy (ΔH , J/g) were determined for

the endothermic peaks around 76-86 °C and 142-292 (J/g), respectively. The lowest enthalpy and endothermic peak temperature were observed in 10% (w/w) cur-loaded/unloaded composite bread. With increasing the cur-loaded/unloaded

composite from zero to 10% (w/w), the enthalpy and the endothermic peak temperature of treatments were decreased on the first day of storage.

Giovanni *et al.* (1997) reported that the enthalpy in the DSC test was equivalent to the amount of energy required to melt the starch crystals (Giovanelli, Peri, & Borri, 1997). This melting is an endothermic phenomenon and it increases during the storage of bread (B Nasehi, Mortazavi, & Razavi, 2005). On the third day of storage, the enthalpy as well as the endothermic peak temperature of control was higher than others. At the third day of storage, the enthalpy as well as the endothermic peak temperature of 5 and 10 % (w/w) cur-loaded/unloaded composite treatments was decreased compared to control. In a similar study, Tebban and Li evaluated the effect of xanthan gum on bread quality of whole wheat flour. The onset temperature (T_o), and peak temperature (T_p) were determined around 60 °C and 115-120 °C. These two peaks corresponded to the melting of retrograded amylopectin and the amylose-lipid complex, respectively. Samples were analyzed after 1 day and 5 days of storage. DSC revealed that xanthan gum decreased amylose-lipid complex and postponed the stalling of bread (Tebben & Li, 2019)

On the 5th day of storage, enthalpy and peak temperature of crystallization in 10% (w/w) cur-loaded composite were

lower than the control, which indicates less starch retro-gradation of the mentioned bread. With increasing the cur-loaded/unloaded composite from zero to 5 and 10% (w/w), the enthalpy and the endothermic peak temperature of treatments was decreased on the fifth day of storage.

During storage, 5 and 10% (w/w) cur-loaded/unloaded composite reduced the average enthalpy and endothermic peak temperature of treatments compared to control (Table 5). The bread containing 10% (w/w) cur-composite had less enthalpy than other formulations. In other words, the starch retro-gradation was less in mentioned bread. The average of melting peak temperature reduced as cur-loaded/unloaded composite level increased.

The physicochemical changes of bread during storage are mostly affected by starch, composed of two parts, amylose and amylopectin (MANIA Salehifar *et al.*, 2009). In this study, a great fraction of starch appears to interact with the composite especially in the highest level of the curcumin-loaded state. Therefore, less starch remains intact to recrystallize during storage. The main reason of bread staleness is the decrease in moisture and water migration from the crumb to the crust. With the addition of CSG hydrogel, the ability to water preservation increases (Mollabashi *et al.*, 2015).

Table 5 – Thermal properties of Barbari bread during five days storage period.

| bread | 3 th day | | 1 th day | | 5 th day | | Average of | |
|-------------------|-----------------------------------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|---|
| | Endothermic Peak Temperature (°C) | ΔH (J.gr ⁻¹) | Endothermic Peak temperature (°C) | ΔH (J.gr ⁻¹) | Endothermic Peak temperature (°C) | ΔH (J.gr ⁻¹) | Endothermic Peak temperature (°C) | Average of ΔH (J.gr ⁻¹) |
| control | 80.5 | 198.51 | 85.0 | 295.00 | 83.4 | 220.95 | 82.96 | 238.15 |
| Free cur | 83.2 | 292.89 | 83.7 | 228.88 | 83.1 | 256.51 | 83.33 | 259.42 |
| 5% composite | 86.2 | 279.48 | 79.5 | 174.38 | 75.3 | 163.26 | 80.33 | 205.70 |
| 10% composite | 76.2 | 142.99 | 76.8 | 119.81 | 76.2 | 197.52 | 76.4 | 153.44 |
| 5% cur-composite | 80.4 | 190.79 | 80.7 | 131.11 | 82.5 | 186.00 | 81.2 | 169.3 |
| 10% cur-composite | 79.9 | 148.43 | 80.1 | 133.83 | 73.8 | 97.38 | 77.93 | 126.54 |

Sensory properties

There was no significant difference between color, taste, and acceptance of treated bread and control ($p>0.05$) (Table 6). Addition of composite hydrogel significantly increased the texture score of treats compared to control ($p<0.05$). Despite the hardness of 10% (w/w) cur-composite bread on the first day of storage increased compared to other breads, its sensorial acceptability and texture score was higher than control. It seems that the sensory score of the texture is estimated based on the sum of the forces required to pull and slice the bread. But the texture analysis only includes the compression test. In 1988, Siho and his colleagues used Instron to evaluate the texture of chapati bread. In this study, they measured the forces required to cut, pierce, tear, and pull bread, and calculated sensory evaluation to determine the accuracy of the measurement. The results of this study showed that the force required to cut, pierce and pull the bread increases during storage, while the breaking force and the amount of elasticity decrease with increasing time. Statistical analysis of the results of sensory evaluation on the first day showed that 10% (w/w) cur-loaded/unloaded composite in terms of

taste and texture score received the highest score by sensory evaluators. 10% (w/w) cur-composite also had the highest value of overall acceptance.

On the second day of storage, a decrease in the sensory score of all treatments was observed (Table 6). Color scores of curcumin-containing breads significantly increased compared to control ($p<0.05$). Evaluation of the taste, texture and acceptance of treated breads on the second day insignificantly changed compared to control ($p<0.05$). The results of sensory evaluation verified more acceptability of 5 and 10% (w/w) cur-composite breads, which remained fresh during the storage period. Nasehi and Razavi (2019), studied the effect of okra gum and CMC on the quality characteristics and shelf life of Barbari bread. They showed that all samples prepared had good scores (Behzad Nasehi & Razavi, 2019). Sahari et al. 2014, found insignificant differences in sensory properties of breads made from different types of gum and stated that the samples containing gum had a higher quality than the control sample (Sahari et al., 2014). Based on the results, the addition of cur-composite did not change the sensory properties of the products, compared to control samples.

Table 6- The effect of curcumin, composite hydrogel and cur-composite hydrogel on the sensory properties of Barbari bread during storage.

| Storage time (day) | Bread formulation | Color | flavor | texture | Acceptance |
|--------------------|-------------------|-----------|-----------|------------|------------|
| 1 | Control | 4.8±0.44a | 4.2±0.83a | 4.4±0.54b | 4.4±0.54a |
| | Free curcumin | 4.4±0.89a | 4.0±0.71a | 4.0±0.71b | 3.8±0.84a |
| | 5% composite | 4.8±0.44a | 4.4±0.54a | 4.8±0.44ab | 4.6±0.54a |
| | 10% composite | 4.8±0.44a | 4.8±0.44a | 4.6±0.54a | 4.6±0.54a |
| | 5% cur-composite | 4.8±0.44a | 4.0±0.00a | 4.4±0.89ab | 4.6±0.54a |
| | 10% cur-composite | 4.4±0.54a | 4.8±0.44a | 5.0±0.00a | 4.8±0.44a |
| 2 | Control | 4.0±0.00a | 4.2±0.44a | 4.2±0.44a | 3.8±0.44b |
| | Free curcumin | 4.0±0.71a | 4.4±0.89a | 3.8±0.83a | 4.4±0.89b |
| | 5% composite | 4.2±0.84a | 4.0±0.71a | 4.0±0.83a | 3.6±0.54b |
| | 10% composite | 4.0±0.70a | 4.0±0.70a | 3.8±0.83a | 4.2±0.83b |
| | 5% cur-composite | 4.4±0.54a | 4.0±0.70a | 4.6±0.54a | 4.8±0.44a |
| | 10% cur-composite | 4.4±0.89a | 4.2±0.83a | 4.4±0.89a | 4.4±0.54ab |
| 3 | Control | 3.6±0.54b | 4.0±1.22a | 3.6±0.54b | 4.2±0.44a |
| | Free curcumin | 4.2±0.84a | 4.4±0.89a | 3.6±0.89b | 4.0±0.71a |
| | 5% composite | 3.6±0.44b | 4.0±0.54a | 3.8±0.44b | 4.2±0.54a |
| | 10% composite | 4.0±0.70b | 4.4±0.54a | 3.8±0.44b | 4.2±0.44a |

| | | | | |
|-------------------|-----------|-----------|-----------|-----------|
| 5% cur-composite | 4.4±0.44a | 4.4±0.70a | 4.4±0.54a | 4.4±0.54a |
| 10% cur-composite | 4.2±0.44a | 4.2±0.44a | 4.4±0.54a | 4.6±0.54a |

*Different letters indicate significant differences between breads at $p < 0.05$ by Duncan test.

Conclusion

Cur-CSG composite significantly increased the specific volume, and porosity of Barbari-bread. The hardness of samples increased as the cur-composite concentration increased. Hydrocolloids by forming thick layers influenced the stability of gas cells and caused more porosity in Barbari breads. NG-CSG composite hydrogel can interact with amylopectin and retard the starch staling, so it can increase bread shelf life. Therefore, the use of the cur-NG-hydrogel can be considered for the production of bread with high quality.

10% cur-ISP/SA nanogel-hydrogel produced bread with the most desirable sensory properties.

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Conflict Of Interest

The authors declare that they do not have any conflict of interest.

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کورکومین بارگذاری شده در هیدروژل تقویت شده با نانوذله برای بهبود کیفیت و خواص بافتی خمیر و نان بربری

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چکیده

ماندگاری فرآورده های نانویی و افزایش فواید فراسودمند آن حائز اهمیت است. در این تحقیق کورکومین بارگذاری شده در هیدروژل صمغ دانه شاهی تقویت شده با نانوذله پروتئین سویا/آلژینات (Cur-ISP/SA nanogel-CSG hydrogel) برای بهبود خواص فراسودمند و کیفی نان سنتی ایرانی (بربری) استفاده شد. اثرات هیدروژل کامپوزیت (در ۰، ۵ و ۱۰ درصد) با و بدون کورکومین بر کیفیت نان بربری ارزیابی شد. خواص رئولوژیکی خمیر با استفاده از فارینوگرافی و آنالیز اکستنسوگراف مورد ارزیابی قرار گرفت. نتایج نشان داد که جذب آب، قوام، انرژی و قابلیت انبساط خمیر با افزودن هیدروژل های کامپوزیت افزایش می یابد، در حالی که درجه نرم شدن خمیر ۱۰ دقیقه پس از شروع کاهش می یابد. با افزودن هیدروژل، حجم مخصوص، تخلخل و سختی نان به ترتیب ۵۵/۳۱، ۴/۷۸ و ۳۱/۸ درصد نسبت به شاهد افزایش یافت. فاکتور روشنی مغز نان در حضور هیدروژل کامپوزیت حاوی کورکومین از $۰/۰۷ \pm ۶۹/۱۹$ به $۰/۰۶ \pm ۷۵/۵۱$ افزایش یافت. وجود کامپوزیت هیدروژل ۱۰ درصد باعث افزایش معنی دار پارامتر (a^*) پوسته ($۹/۹۶ \pm ۰/۱۳$) شد ($p < ۰/۰۵$). کاهش آنتالپی و دمای پیک گرماگیر در نان حاوی ۱۰٪ (وزنی/وزنی) هیدروژل کامپوزیت مشاهده شد. نتایج نشان داد افزودن ۱۰ درصد هیدروژل کامپوزیت حاوی کورکومین باعث بهبود خواص ارگانولپتیک نان و ماندگاری آن می شود.

واژه های کلیدی: نان، هیدروژل کامپوزیت، خمیر، رئولوژی

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