The Exploitation of Xanthan Cryogels as Pattern for Edible Oleogel Preparation

Ghasemi, Parisa; Noshad, Mohammad*+; Mehrnia, Mohammad Amin; Jooyandeh, Hossein

Department of Food Science & Technology, Agricultural Sciences and Natural Resources University of Khuzestan, Mollasani, I.R. IRAN

ABSTRACT: *In this study, xanthan gum was used to produce cryogel and conversion of cryogel to oleo-gels, and the structural and chemical characteristics of the produced oleo-gels were investigated. Results showed, the produced oleo-gels (COS) contained about 66% oil content and they have able to holding oil at about 60%. The pseudo-second-order model can predict the oil absorption kinetics of cryogels. There was no difference between the number of fatty acids of sunflower oil and COS. ^{1}H NMR and ^{13}C NMR signals, the hydroperoxide (initial oxidation product), and aldehydes (secondary product oxidation) were not revealed in COS. Also, it was observed no exothermic process in the curve in Differential Thermal Analysis (DTA)curve up to 350 °C. AFM is the formation of a uniform, homogeneous, and stable gel network that matched the results of the mechanical properties of the COS.*

KEYWORDS: *Cryogel; Oleogel; Xanthan; chemical properties.*

INTRODUCTION

Organo-gels or oleo-gels are semisolid systems derived from liquid oil trapping in a three-dimensional network, without changing the chemical properties of the oil. In fact, they are semi-solid systems that are created based on the gelling of organic solvents with low molecular weight compounds or macromolecules soluble in the oily phase[1-3]. The use of oleo-gels has been studied for the production and replacement of fat in food products in the last decade and, they were used in various fields according to their high potential [4-7].

Biopolymer gelators are mainly hydrophilic in nature, so, they are suitable as a porous structural agent for oil sorption. Gels made of polymers are usually more common, in which their most abundant is: the protein gels of milk, alginate, gelatin, carrageenan, and starch, which are widely known and studied. Several ways are used to construct oleo-gels based on the nature of gelatours [1,2,8,9].

One of these ways is the use of cryogels. Cryogels are porous gels that are formed as a result of cryogenic treatment (freezing, storage in freezing at a specific time, and thawing) from low and high molecular weight materials, colloid systems are also able to form gels. The structure of cryogels usually has large pores (or very large pores). Undoubtedly, solutions of any size are able to disperse in them, causing mass transfer with nanoscale and even micro-scale [10,11]. According to literature, freezing-thawing cycles of a system is the most factor that affects the size, shape, and macroporous distribution

** To whom correspondence should be addressed.*
+ E-mail: Noshad@asnrukh.ac.ir
1021-9986/2021/4/1229-1237 9/$/5.09

of oleogels. Also, in studies on the effect of freezing temperature on porosity, it has been shown that lower temperatures caused small pore sizes in the samples, while by increasing the freezing time and the number of freezing cycles, cavities with larger sizes are created in the sample [12].

Xanthan gum is an anionic polysaccharide that is commercially produced from the fermentation of glucose, sucrose, and lactose by *Xantomonas campestris* [13]. This polysaccharide consists of D-mannose, D-glucose, and D- glucuronic acid. Xanthan gum is a hydrocolloid solution that is completely soluble in cold and hot water, and its solutions have gel properties and the ability to keep suspended particles[14]. Xanthan gum can be converted to cryogel in a convenient process (by directly freeze-thaw treatment) than other polysaccharides such as hyaluronan and carboxymethylated curdlan which require acidic conditions to form the cryogel. Also, the results of the research have shown that freezing and thawing cause a strong gel and flexibility by Xanthan gum [15].

Therefore, the potential of using cryogels in the production of oleo-gels has been investigated for the first time. For this purpose, xanthan gum was used to produce cryogel and it was investigated the effect of the number of freezing cycle in the preparation of cryogel, conversion of cryogel to oleo-gels, and the structural and chemical characteristics of the produced oleo-gels.

EXPERIMENTAL SECTION

Xanthan gum was prepared by the chemical company (Sigma-Aldrich) and Ladan sunflower oil was purchased from the local market in Mollasani, Iran.

Preparation of oleo-gels oil of sunflower

First, xanthan gum with 1.5% wt (A primary experiment was carried out to obtain the optimum xanthan concentration needed to produce gel) was mixed with distilled water at ambient temperature, and then put on the magnetic stirrer for 2 h (for homogeneity), and then solutions was stored in the refrigerator for 24 h (to hydration) and then stored in a freezer at -20 °C for 24 h (F1T1), then transferred to a freeze drier and allowed to dry completely (samples of cryo-gels put on the Freeze drier for 72 h to dry completely). For investigating the freezing cycle, the second cycle (F2T2) (storage period was 24 h in a refrigerator, 24 h freezing at -20, 24 h at ambient temperature, 24 in the freezer at -20 and 72 h freeze-drying) and the third cycle (F3T3) (second cycle storage period was repeated again) was done, and then the cryogel samples (F1T1, F2T2, F3T3) were immersed in sunflower oil for 2 h at two temperatures of 25 °C and 40 °C.

Oil Holding Capacity (OHC)

1(g) of oleo-gels **was** put between filter paper and then samples were centrifuged for 30 minutes at 9000 (g). The oil holding capacity was calculated from the ratio of oil held in the oleo-gel after centrifuge and the total weight of oil in the samples [2].

Oil content

The oil content was determined using the Hexane extraction method. For this purpose, the oleo-gel was cut into small pieces (1×1×1cm) and weighed, then the solvent was separated by soxhlet for 75 min [16]. This extraction method was repeated twice with hexane. The oil percentage (content) of the samples was calculated as follows:

$$\text{Oil content} = \frac{W_0 - W_1}{W_0} \quad (1)$$

W_0= Initial weight of oleogel; W_1= Weight of oleogel after soxhlet.

Kinetics of oil absorption

Different kinetic models have been proposed for absorption analysis. Pseudo-first-order and Pseudo-second-order models are commonly used for oil absorption. In this work, both models are used for empirical absorption kinetics data. A quasi-first-order model can be used in many cases of absorption, such as systems that are close to equilibrium, systems with a solvent independent of time, or linear equilibrium of absorbing isotherms, while the quasi-second-order model is used to describe the process of chemical absorption [17]. The quasi-first-order equation can be obtained

$$\ln \frac{Q_m}{Q_m - Q_t} = k_1 t \quad (2)$$

Where $Q_m(g/g)$ is the maximum absorption of oil, Q_t is the absorption of oil at time *t*, and k_1 is the obtained absorption constant from the slope of $ln\left[Q_{m/}(Q_m - Q_t)\right]$

versus *t*. The quasi-second-order equation becomes linear (Eq.3):

$$\frac{t}{Q_t} = \frac{1}{Q} t + \frac{1}{k_2 Q_m^2} \quad (3)$$

By matching t/Q_t versus t, the absorption rate of k_2 constant can be determined.

Texture analyzer (TPA)

The oleo-gel texture characteristics (hardness, gumminess, and cohesiveness) were investigated by a texture analyzer (TA.XT. PLUS). For this purpose, a cylindrical probe with a diameter of 6 mm and a speed of 1 (m/s) up to 40% of the sample compression was used [18].

Thermal analysis

The Simultaneous Thermal Analyzer (STA) (STA 504, Bahr, Germany) was used to carry out.

Thermogravimetry/Differential Thermal Analyzer (TG-DTA) of oleo-gel. Approximately 15 mg of the sample was placed inside an alumina crucible for analysis at a temperature range of 50 to 300 °C, with a heated rate of 10 ℃/min at argon gas [19].

NMR spectroscopy

NMR is an acceptable analytical method for heated oil at relatively high temperatures. 10mg of oleo-gel for ^{1}H NMR and 45 mg of oleo-gel for ^{13}C NMR was dissolved in $CDCL_3$ (about 600 µL) and transferred to the NMR tube. ^{1}H NMR was used to determine the oleo-gel oxidation and ^{13}C NMR was used to determine the structure of triacylglycerols. The Bruker NMR spectrometer (Avanca 400 MHZ) and the 5 mm tube, were used. Change of the chemical shift is expressed by the unit δ (ppm) [20, 21].

Fatty acid profile

Fatty acid profiles of sunflower oil and sunflower oil oleo-gels were done by gas chromatography. One microliter of each sample was injected into the device. Its temperature was increased from 140 °C to 240 °C with the rate of 4 °C/min and then kept for 25 min. The detector temperature and injection sites were 300 ℃ and 280 ℃, respectively, and nitrogen gas was used as carrier gas [22].

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 [23].

Statistical analysis

Experiments were evaluated based on a completely randomized design. To evaluate the effect of freezing cycles and immersion oil temperature on the properties of oleogels, analysis of variance (ANOVA) was used. To compare the means and investigating the impacts of treatments, the Duncan Multiple Range test was utilized. During all stages of statistical analysis, SPSS 19 was used for analyzing the data. At least three repetitions were performed for each experiment.

RESULTS AND DISCUSSION

Oil Holding Capacity (OHC) and oil content

Based on the results of this study, the produced oleo-gels contained about (66±1.1 to 64±0.8%) oil content and they have able to holding oil at about (60±1.9 to 64.87± 1.8%), which can be used as a high potential carrier for functional compounds and lipid-soluble drugs. Also, based on the results, reduced freezing temperature and the number of freezing cycles have not been significantly affected ($P<0.05$) on the oil content and oil holding capacity of oleo-gel. This means that the number of cycles did not affect the oil absorbent hydrophobic groups in the cryogel structure (Table 1).

Hardness

The hardness expresses the gel network strength. The number of molecules in the binding regions plays an important role in determining the properties of the gel, so the gel becomes harder with more points [24]. Based on the obtained results (Table 2), the oleo-gels that prepared from cryogels (with two freezing cycles) were more rigid than other samples, which probably due to the effect of the freezing cycle and exit freezing process on the gel structure and creation of the number of connection points is more in the gel building. Also, increasing the temperature during immersion of cryogels in oil reduced the hardness of the oleo-gel were attributed to weakening of the structure due to an increase in temperature.

Table 1: Effect of the number of freezing cycles and immersion oil temperature on oil content and OHC.

Source	DF	Oil content (%)	OHC (%)
Intercept	1	42.023 **	39.611 **
Number of freezing cycles(A)	2	38.510^{ns}	11.570^{ns}
Immersion oil temperature (B)	1	2.421^{ns}	1.159^{ns}
A × B	2	1.255^{ns}	2.396^{ns}
Error	6	4.734	4.391

ns: not significant at (P<0.05)

Table 2: Effect of number of freezing cycles and immersion oil temperature on Hardness, Gumminess and Cohesiveness.

Source	Hardness (N)		Gumminess (N×mm)		Cohesiveness	
	DF	Mean square	DF	Mean square	DF	Mean square
Corrected Model	5	19.17*	5	2.3*	5	5.35*
Intercept	1	1416.5*	1	173.21*	1	5233.4*
Number of freezing cycles(A)	2	10.77*	2	0.43^{ns}	2	0.003*
Immersion oil temperature (B)	1	72.89*	1	10.66*	1	0.001^{ns}
A × B	2	0.71^{ns}	2	0.004^{ns}	2	0.001^{ns}
Error	6	1.59	6	0.118	6	0.001

*ns: not significant at (P<0.05); *: significant at (P<0.05).*

Gumminess

Gumminess is seen in the form of adhesion to the production and adhesion to the fingers and mouths, which is a negative factor in the latter case for products such as bakery products, pudding, and salad dressing[25]. Based on the obtained results (Table 2), the oleo-gels that were prepared from cryogels with two freezing cycles had the highest adhesion to other samples. Due to the Gumminess theory and mechanism, intermolecular forces such as hydrogen bond and van der Waals force is a factor to make the adhesion in the material[26, 27]. Therefore, more free hydroxyl groups are available for hydrogen bonding for the oleo-gels prepared from cryogels with two freezing cycles, which has increased adhesion in the samples. Also, increase the temperature during immersion of cryogels in oil caused a decrease in the Gumminess of the oleo-gel (Table 2).

Cohesiveness

The cohesiveness is the required work to achieve the transformation that indicates the internal power of the bonds in the sample[28]. Based on the obtained results (Table 2), increasing the number of cycles in the preparation of cryogels caused a significant decrease ($P < 0.05$) in the amount of oleo-gel cohesiveness were attributed to the weakening of the structure due to freezing. Also, the temperature increasing during oil absorption reduced the cohesiveness of the samples.

Based on preliminary tests and the results of oil holding capacity, oil content, and texture analysis, cryogels which were produced by a Freezing-Thawing Cycle (F1T1) and were immersed in oil at 25 °C, were selected as an optimum cryogel (COS). Then its structural and thermal properties were evaluated (Fig. 1).

Kinetic Analysis of Oil Absorption

The kinetics of oil absorption by COS was studied and the results have been shown in Table 3. The results show that produced cryogel has a high potential for oil absorption, which is probably due to the porous structure of the sample. Also, the results showed that the speed of oil absorption was very rapid, so that in the first 1 min the amount of oil absorption reached the equilibrium state. Temperature also increases the rate of oil diffusion in the cryogel structure, due to its effect on the viscosity of the oil. Based on the results, for both temperatures,

Table 3: The kinetics of oil absorption by COS.

Temperature (°C)		25 (ºC)	40 (ºC)
Maximum absorption capacity,	Q_m (g/g)	63.8 ± 2.2	66.1 ± 1.4
Pseudo-first order	R^2	0.957	0.987
	K_1	0.175	0.211
Psedudo-second order	R^2	0.972	0.99
	K_2	0.043	0.051
Temperature (°C)		25 (ºC)	40 (ºC)
Maximum absorption capacity,	Q_m (g/g)	63.8 ± 2.2	66.1 ± 1.4
Pseudo-first order	R^2	0.957	0.987
	K_1	0.175	0.211
Psedudo-second order	R^2	0.972	0.99
	K_2	0.043	0.051

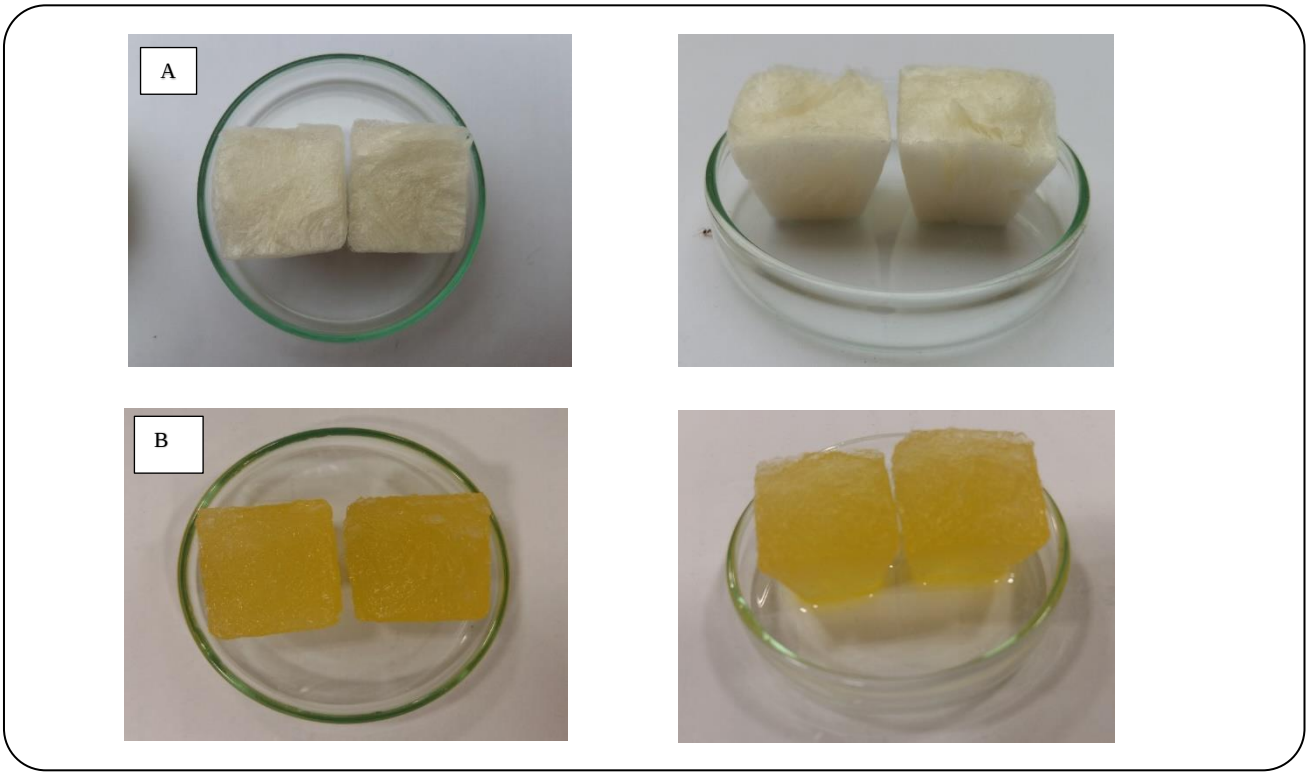

Fig. 1: Cryogels were produced by a freezing-thawing cycle (F1T1) (A) and were immersed in oil at 25 °C (COS) (B).

the coefficient factor (R^2) of the pseudo-second-order equation was greater than the quasi-first-order equation. Therefore, the pseudo-second equation can predict the absorption of oil by cryogels. The adsorption rate constant (K_1, K_2) increased by increasing temperature, indicating a higher rate of oil absorption in the samples.

Fatty acid analysis

Linoleic acid, oleic acid, and palmitic acid are the major fatty acids of sunflower oil. According to Table 4 (fatty acid profile of sunflower oil and COS), these fatty acids are the major fatty acids of COS, yet, and has not been observed the difference between the number of fatty acids

Table 4: Fatty acid profile of sunflower oil and oleogels.

Fatty acid	Sunflower oil	COS
C14	0.44 ± 0.08 (%)	0.46 ± 0.1 (%)
C16	6.68 ± 0.9 (%)	7.76 ± 1.1 (%)
C16:1	0.12 ± 0.2 (%)	0.17 ± 0.07 (%)
C18	3.23 ± 0.2 (%)	3.1 ± 0.1 (%)
C18:1	35.2 ± 1.4 (%)	34.5 ± 1.1 (%)
C18:2	53.48 ± 1.9 (%)	52.84 ± 2.1 (%)
C18:3	0.46 ± 0.1 (%)	0.51 ± 0.17 (%)

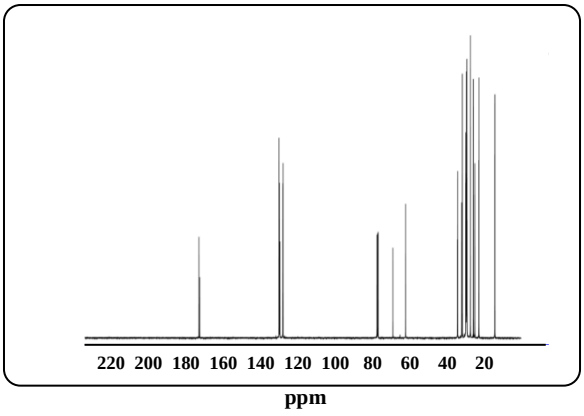

Fig. 2: ^{13}C NMR spectra of COS.

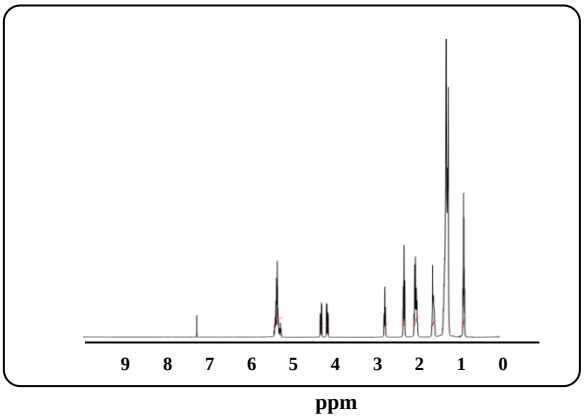

Fig. 3: ^{1}H NMR spectra of COS.

of sunflower oil and COS, which indicates the stability in the amount of sunflower oil fatty acids in COS.

^{13}C NMR spectra

^{13}C NMR is an effective spectrometer for analyzing and determining the structure of the triacylglycerol. Fig. 2 shows the obtained spectrum of the COS. Resonances can be grouped into different parts. Carbonyl carbons appeared between 172.1 and 173.13 ppm, and unsaturated carbon appeared from 127.09 to 119.6 ppm and glycerol carbon appeared at 68.88 and 64.05 ppm, that at this part the carbon atoms have overlap with the Hydroxyl group in the sterol and fatty alcohols. In addition, the parts from 27.17 to 14.34 ppm are aliphatic carbons[29,30].

^{1}H NMR Spectra:

^{1}H NMR was used to investigate the stability of edible oils at room temperature. The position of the resonance signal in the spectrum is called the chemical shift and, represents the symbol δ. The chemical shift gives useful information about the type of H nucleus in the sample [31, 32]. Sunflower oil is easily identifiable due to the high content of linoleic acid compared to edible oils [33]. The intensity of the signal is 627.2 ppm. The linoleic acid protons are 8.55 ppm for terminal methylene and 106.2 ppm for alcohol proton, respectively. Linoleic acid contains two internal groups of methylene alkyl. Glycerol and unsaturated protons appear between 4.10 ppm and 5.40 ppm, while saturated proton signals appear between 0.8 ppm and 2.80 ppm. The presence of proton hydroperoxide in the range of 8.09-8.19 ppm and 9.30-9.90 ppm for aldehyde represents the oxidation of edible (fig 3) oils. In the ^{1}H NMR signals, the hydroperoxide (initial oxidation product) and aldehydes (secondary product oxidation) were not revealed in COS, which indicates that no oxidation has occurred [33, 34].

Thermal Analysis

The TG-DTA test was performed to examine the thermal behavior of sunflower oil oleo-gel. Figure 4 shows

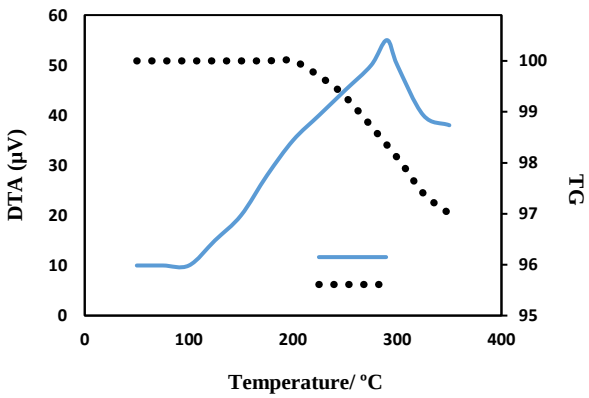

Fig. 4: Thermal Analyzer of COS.

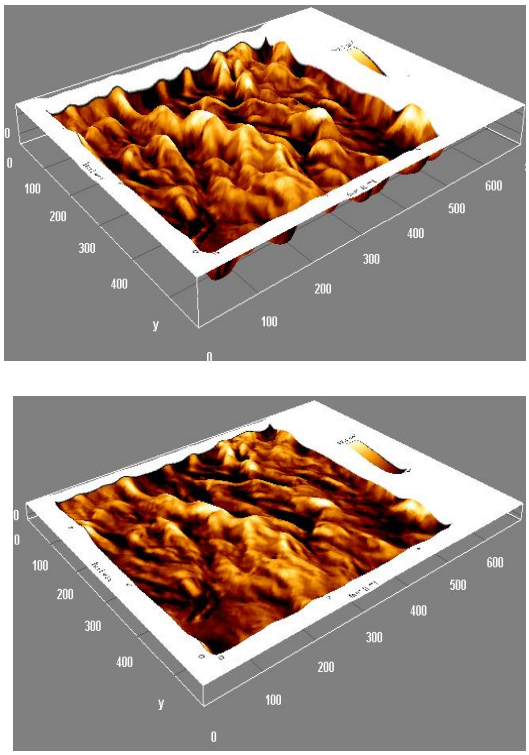

Fig. 5: AFM of COS.

the TGA thermogram of the COS. According to Fig. 4, it can be seen that by increasing temperature from ambient temperature to 100 °C (evaporation temperature) was not observed weight loss in the samples, which indicates very little water in the samples. This can be due to the that the gels were dried before being immersed in oil using a freeze dryer. With increasing temperature, the weight loss of the sample began at a temperature of 220 °C and only about 3% of weight loss was observed in the samples until 350 °C, which indicates the high resistance of the sample to thermal decomposition. Also, due to the fact that it was observed no exothermic process the curve in the differential thermal analysis curve (DTA) up to 350 °C, it can be concluded that no oxidative degradation has occurred in the samples.

AFM

The atomic force microscope (AFM) can be used to evaluate the real nature of the sample and provide three-dimensional information from three sample surfaces. In the phase images of the AFM, is clearly visible the formation of the xanthan cryogel network in the COS (Fig 5). Liquid oil is surrounded in the penetration with different diameters by the coral-like network that is made of polymer filament, which showing polymer-polymer interactions and the formation of hydrogen bonds between polymer threads. According to that this method only evaluates the oleo-gel level, it is believed that such a network exists in the gel. The apparent investigation of the oleo-gel status indicates the formation of a uniform, homogeneous, and stable gel network that matched the results of the mechanical properties of the COS.

CONCLUSIONS

Cryogela can be easily converted to oleogels. The number of freezing cycles in cryogel production had no significance ($P<0.05$) on the oil content and OHC of COS. Based on cryogels which were produced by a freezing-thawing cycle (F1T1) and were immersed in oil at 25 °C, were selected as an optimum COS. The conversion of F1T1 to COS did not affect the fatty acid profile, and also the ^{1}H NMR and ^{13}C NMR showed the main peak of xanthan gum and sunflower oil in COS. The uniform, homogeneous, and stable gel network of COS were confirmed by AFM. Our novel oleogel by trapping oil inside a cryogel matrix with appropriate mechanical characterizes could be suitable for extending novel materials, e.g., in pharmaceutical, nutraceutical, and food applications.

Acknowledgments

The authors would like to express their sincere thanks to the Research Deputy of Agricultural Sciences and the Natural Resources University of Khuzestan for the financial support.

Received : Oct. 14, 2019 ; Accepted : Feb. 17, 2020

REFERENCES

[1] De Vries A., Hendriks J., Van Der Linden E., Scholten E., Protein Oleogels from Protein Hydrogels *via* a Stepwise Solvent Exchange Route, *Langmuir*., **31(51)**: 13850-13859 (2015).

[2] Manzocco L., Valoppi F., Calligaris S., Spilimbergo S., Nicoli M.C., Exploitation of κ-Carrageenan Aerogels as Template for Edible Oleogel Preparation, *Food Hydrocolloids*., **71**: 68-75 (2017).

[3] Martins A.J., Silva P., Pastrana L.M., Cunha R.L., Cerqueira M.A., Vicente A.A., Hybrid Gels: Influence of Oleogel/Hydrogel Ratio on Rheological and Textural Properties, *Food Res. Int.*, **116**: 1298-1305 (2019).

[4] Oh I., Lee J., Lee H.G., Lee S., Feasibility of Hydroxypropyl Methylcellulose Oleogel as an Animal Fat Replacer for Meat Patties, *Food Res. Int.*, (2019).

[5] Qiu C., Huang Y., Li A., Ma D., Wang Y., Fabrication and Characterization of Oleogel Stabilized by Gelatin-Polyphenol-Polysaccharides Nanocomplexes, *J. Agric. Food Chem*., **66(50):** 13243-13252 (2018).

[6] Demirkesen I., Mert B., Utilization of Beeswax Oleogel- Shortening Mixtures in Gluten- Free Bakery Products, *J. Am. Oil Chem. Soc*., (2019).

[7] Da Silva T.L., Chaves K.F., Fernandes G.D., Rodrigues J.B., Bolini H.M., Arellano D.B., Sensory and Technological Evaluation of Margarines with Reduced Saturated Fatty Acid Contents Using Oleogel Technology, *J. Am. Oil Chem. Soc*., **95(6)**: 673-685 (2018).

[8] Singh A., Auzanneau F.-I., Rogers M., Advances in Edible Oleogel Technologies–A Decade in Review, *Food Res. Int*., **97**: 307-317 (2017).

[9] Saberian H., Hamidi Esfahani Z., Banakar A., Ohmic Heating of Aloe Vera Gel: Electrical Conductivity and Energy Efficiency, *Iran. J. Chem. Chem. Eng.(IJCCE)*, **37(5)**: 157-165 (2018).

[10] Plieva F.M., Karlsson M., Aguilar M.-R., Gomez D., Mikhalovsky S., Galaev I.Y., Pore Structure in Supermacroporous Polyacrylamide Based Cryogels, *Soft Matter*., **1(4)**: 303-309 (2005).

[11] Humpolíček P., Radaszkiewicz K.A., Capáková Z., Pacherník J., Bober P., Kašpárková V., Rejmontová P., Lehocký M., Ponížil P., Stejskal J., Polyaniline Cryogels: Biocompatibility of Novel Conducting Macroporous Material, *Scientific Reports*, **8(1)**: 135 (2018).

[12] Phimolsiripol Y., Siripatrawan U., Henry C.J.K., Pasting Behaviour, Textural Properties and Freeze–Thaw Stability of Wheat Flour–Crude Malva Nut (Scaphium Scaphigerum) Gum System, *J. Food Eng.*, **105(3)**: 557-562 (2011).

[13] Zakeri A., Pazouki M., Vossoughi M., Use of Response Surface Methodology Analysis for Xanthan Biopolymer Production by Xanthomonas Campestris: Focus on Agitation Rate, Carbon Source, and Temperature, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36(1)**: 173-183 (2017).

[14] Kumar A., Rao K.M., Han S.S., Application of Xanthan Gum as Polysaccharide in Tissue Engineering: A Review, *Carbohydrate Polymers.*, **180**: 128-144(2018).

[15] Giannouli P., Morris E., Cryogelation of Xanthan, Food Hydrocolloids, **17(4)**: 495-501 (2003).

[16] Gómez-Estaca J., Herrero A.M., Herranz B., Álvarez M.D., Jiménez-Colmenero F., Cofrades S., Characterization of Ethyl Cellulose and Beeswax Oleogels and their Suitability as Fat Replacers in Healthier Lipid Pâtés Development, *Food Hydrocolloids.*, **87**: 960-969 (2019).

[17] Feng J., Nguyen S.T., Fan Z., Duong H.M., Advanced fabrication and Oil Absorption Properties of Super-Hydrophobic Recycled Cellulose Aerogels, *Chemical Engineering Journal*, 270: 168-175(2015).

[18] Da Silva S.L., Amaral J. Ribeiro T.M., Sebastião E.E., Vargas C., De Lima Franzen F., Schneider G., Lorenzo J.M., Fries L.L.M., Cichoski A.J., Fat Replacement by Oleogel Rich in Oleic Acid and Its Impact on the Technological, Nutritional, Oxidative, and Sensory Properties of Bologna-Type Sausages, *Meat Science*, **149**: 141-148(2019).

[19] Rehman K., Amin M.C.I.M., Zulfakar M.H., Development and Physical Characterization of Polymer-Fish Oil Bigel (Hydrogel/Oleogel) System as a Transdermal Drug Delivery Vehicle, *JOS*, ess14101 (2014).

[20] Pedro A.C., Bach F., Stafussa A.P., Menezes L.R.A., Barison A., Maciel G.M., Haminiuk C.W.I., 1H NMR And Raman Spectroscopy of Oils and Extracts Obtained From Organic and Conventional Goji Berries: Yield, Fatty Acids, Carotenoids and Biological Activities, *Int. J. Food Sci. Technol.*, **54(1)**: 282-290 (2019).

[21] Ribeiro M.D.M., Ming C.C., Lopes T.I., Grimaldi R., Marsaioli A.J., Gonçalves L.A.G., Enzymatic Synthesis of Structured Lipids from Liquid and Fully Hydrogenated High Oleic Sunflower Oil, *Int. J. Food Prop*., **21(1)**: 702-716(2018).

[22] Moghtadaei M., Soltanizadeh N., Goli S.A.H., Production of Sesame Oil Oleogels Based on Beeswax and Application as Partial Substitutes of Animal Fat in Beef Burger, *Food Res. Int*., **108**: 368-377 (2018).

[23] Zetzl A.K., Gravelle A.J., Kurylowicz M., Dutcher J., Barbut S., Marangoni A.G., Microstructure of Ethylcellulose Oleogels and its Relationship to Mechanical Properties, *Food Structure*, **2(1-2)**: 27-40 (2014).

[24] Bonczar G., Wszołek M., Siuta A., The Effects of Certain Factors on the Properties of Yoghurt Made From Ewe's Milk, *Food Chemistry*, **79(1)**: 85-91 (2002).

[25] Domagala J., Sady M., Grega T., Bonczar G., The Influence of Storage Time on Rheological Properties and Texture of Yoghurts with the Addition of Oat-Maltodextrin as the Fat Substitute, *Int. J. Food Prop.*, **8(2)**: 395-404 (2005).

[26] Panagiotopoulou E., Moschakis T., Katsanidis E., Sunflower oil Organogels And Organogel-in-Water Emulsions (Part II): Implementation in Frankfurter Sausages, *LWT*, **73**: 351-356 (2016).

[27] Banerjee S., Bhattacharya S., Food Gels: Gelling Process and New Applications, *Crit. Rev. Food Sci. Nutr.*, **52(4)**: 334-346 (2012).

[28] Rahman M.S., Al-Farsi S.A., Instrumental Texture Profile Analysis (TPA) of Date Flesh as a Function of Moisture Content, *J. Food Eng.*, **66(4)**: 505-511 (2005).

[29] Li J., Vosegaard T., Guo Z., Applications of Nuclear Magnetic Resonance in Lipid Analyses: An Emerging Powerful Tool for Lipidomics Studies, *Progress in Lipid Research*, **68**: 37-56 (2017).

[30] Kim B.-S., Takemasa M., Nishinari K., Synergistic Interaction of Xyloglucan and Xanthan Investigated by Rheology Differential Scanning Calorimetry, and NMR, *Biomacromolecules*, **7(4)**: 1223-1230 (2006).

[31] Knothe G., Kena J.A. r, Determination of the Fatty Acid Profile by 1H-NMR Spectroscopy, *Euro Fed Lipid*, **106(2)**: 88-96 (2004).

[32] Alonso-Salces R.M., Holland M.V., Guillou C., 1H-NMR Fingerprinting to Evaluate the Stability of Olive Oil, *Food Control*, **22(12)**: 2041-2046 (2011).

[33] Guillén M.D., Goicoechea E., Detection of Primary and Secondary Oxidation Products by Fourier Transform Infrared Spectroscopy (FTIR) and 1H Nuclear Magnetic Resonance (NMR) in Sunflower Oil During Storage, *J. Agric. Food Chem*., **55(26)**: 10729-10736 (2007).

[34] Guillén M.D., Ruiz A., Monitoring the Oxidation of Unsaturated Oils and Formation of Oxygenated Aldehydes by Proton NMR, *Euro. Fed. Lipid*, **107(1)**: 36-47 (2005).