Bascuas-Véntola, SM.; Hernando Hernando, MI.; Moraga Ballesteros, G.; Quiles Chuliá, MD. (2020). Structure and stability of edible oleogels prepared with different unsaturated oils and hydrocolloids. International Journal of Food Science & Technology. 55(4):1458-1467. https://doi.org/10.1111/ijfs.14469

Structure and stability of edible oleogels prepared with different unsaturated oils and hydrocolloids

Santiago Bascuas, Isabel Hernando* Gemma Moraga & Amparo Quiles

Departamento de Tecnología de Alimentos, Universitat Politècnica de València, Camí de vera s/n, Valencia 46021, Spain

Summary Edible oleogels, with three oil types (olive, sunflower and flaxseed), hydroxypropylmethylcellulose (HPMC) and xanthan gum (XG), as structuring agents, were developed using the emulsion-template approach, and subsequent drying of the emulsions using conventional or vacuum drying. Our results showed that for both drying methods, well-structured oleogels were obtained using olive and sunflower oils for the preparation. These oleogels showed oil losses <10% after 35 days of storage. However, unstructured non-homogeneous oleogels were obtained when using flaxseed oil and conventional drying, while it was not feasible to develop flaxseed oleogel with vacuum drying. Oleogels showed interesting rheological properties, including a high oleogel strength with an elastic modulus of the order 10^4–10^5 Pa, weak dependence on frequency, and good thermostability. Moreover, high oxidative stability was obtained for olive oil oleogels, using both conventional and vacuum drying, and for sunflower oleogels using vacuum drying. Still, the initial oxidation rates of sunflower oleogels using conventional drying should be improved in future studies.

Keywords Emulsion, hydroxypropylmethylcellulose, microstructure, oxidation, rheology, xanthan gum.

Introduction

Food products are regularly formulated with considerable amounts of solid fats that have a high content of saturated- and *trans*-fatty acids. Solid fats contribute to multiple functions in foods such as texture, flavour, firmness and functionality; desirable both for the consumer and the food industry (Co & Marangoni, 2012). However, there is a relationship between the consumption of solid fats and increased risk of cardiovascular disease, type 2 diabetes and ischaemic incidents (Estadella *et al*., 2013). In 2003, the World Health Organisation (WHO) and the United Nations Food and Agriculture Organization (FAO) recommended that saturated fat should not provide more than 10% of total caloric intake (Nishida *et al*., 2004). For this, industries give structure to vegetable (non-saturated) oils, using methods based in partial hydrogenation, producing solid fats. Conversely, the Food and Drug Administration (FDA) announced to remove the consideration of GRAS (generally recognised as safe) for partially hydrogenated oils (FDA, 2015), as they are the primary dietary source of artificial *trans*-fat in processed foods. Current trends of consumers who demand healthier diets without compromising quality have made the food industry concentrate their efforts on reducing the levels of saturated- and *trans*-fats. Thus, research strategies to replace saturated- and *trans*-fats have been conducted in which solid fats used in the industry are replaced with a variety of lipid sources (Kanjilal *et al*., 2016), carbohydrates (Onacik-Gür *et al*., 2016) and proteins (Paglarini *et al*., 2019). Still, the total or partial replacement of the solid fat negatively affects the sensory and mechanical properties of the food (Biguzzi *et al*., 2014). Therefore, the development of new solid fat substitutes with low saturated and high unsaturated fatty acids and *trans*-fat-free is the priority of many studies.

A promising alternative to replace saturated- and *trans*-fats is with the use of oleogels by structuring vegetable oils (Wassell *et al*., 2010). Edible oleogels are gelled systems where an oil continuous phase is immobilised in a three-dimensional network, with the assistance of an oleogelator or a combination of gelators. The process of formation for oleogels requires the use of gelling agents at low concentration, which have the ability to give structure to oils (>90%) (Abdolmaleki *et al*., 2019) and impart a solid-like material with the functionality (rheological, texturing, oil binding and

stabilising properties, etc.) of solid fats but an improved nutritional profile (Stortz *et al.*, 2012).

The hydrocolloid-based oleogelators are promising polymers used in food as methylcellulose (MC) (Patel *et al.*, 2014a, 2014b) and hydroxypropylmethylcellulose (HPMC) (Patel & Dewettinck, 2015; Meng *et al.*, 2018a). HPMC is an amphiphilic biopolymer derived from cellulose and is a stabilising additive (E464) in the food industry. Using HPMC as oleogelator is advantageous since it is inexpensive compared to more studied low molecular weight organogelators (Tavernier *et al.*, 2018; Scholten, 2019) generally recognised as safe (GRAS) and has beneficial effects on health (Maki *et al.*, 2009). However, there are limited studies considering the production of oleogels using HPMC, because of their hydrophilic nature. Hydrocolloids are unable to structure liquid oil because of their limited dispersibility in oil. Therefore, to disperse HPMC in oil, to achieve the required network formation for gelation, an indirect method is necessary, like the emulsion-template approach, which was first reported by Romoscanu & Mezzenga (2006). They used β-lactoglobulin proteins as the stabiliser for water continuous emulsions, which were then used as templates to achieve protein-in-oil gels using freeze-drying. Indirect physical gelation, using the emulsion-template method, is a multistep process; first hydrate the hydrocolloid, then prepare an oil-in-water emulsion (containing the hydrocolloid) followed by removal of the water, to obtain dried products driving the network formation. This results in the physical trapping of oil droplets in the polysaccharide matrix network (Patel *et al.*, 2014a). The dried product must be homogenised to obtain the oleogel. The addition of other hydrocolloids, like thickening agents, such as xanthan gum (XG), could increase the stability of HPMC oleogels by enhancing the bulk phase viscosity of the aqueous continuous phase and prevent oil droplet coalescence (Meng *et al.*, 2018a).

Oil type is a crucial factor when producing oleogels with high stability, rheological, textural and thermal properties like solid fats (Pehlivanoğlu *et al.*, 2017). The oleogel should be made with nutritious vegetable oils rich in mono and polyunsaturated fatty acids, and with zero *trans*-fatty acids (Co & Marangoni, 2012). Although some vegetable oils have been used to prepare HPMC oleogels, sunflower (Patel *et al.*, 2014a), soybean (Meng *et al.*, 2018a) and rapeseed (Oh *et al.*, 2019), no studies have been found comparing the effect of different types of oils (with different saturated/unsaturated fatty acid composition) on the structure and stability of oleogels with water-soluble polymers.

The aim of this study is to compare and analyse the impact of unsaturated oil type used in oleogel formulation, regarding the structural and stability properties, when HPMC and XG are used as gelling agents. The effect of vacuum drying is also studied as an alternative to conventional drying to improve the oxidative stability of the oleogels.

Materials and methods

Materials

Hydroxypropylmethylcellulose (HPMC; 4000 cP) was provided by Dow Chemical Company (Midland, MI, USA) and xanthan gum (XG; Satiaxine CX 931) by Cargill R & D (Vilvoorde, Belgium). Water (Bezoya, Segovia, Spain, with a calcium content 6.32 mg L^{-1}), oils; extra virgin olive oil (O) (Hacendado, Mercadona, Spain); refined sunflower oil (S) (Consum, Spain); and virgin flaxseed oil (F) (BIO CESTA, Spain) were purchased in supermarkets. The fatty acids compositions of oils (%, data provided by the supplier) were as follows: olive oil SFA: 14, MUFA: 78, PUFA: 8; sunflower oil SFA: 13, MUFA: 23, PUFA: 64; and flaxseed oil SFA: 11, MUFA: 18, PUFA: 71. Degree of oil unsaturation was measured using ISO 3961:2018 and the iodine values (g I_2 per 100 g oil) were 76.29 ± 2.01 for olive oil, 120.91 ± 6.08 for sunflower oil and 170.10 ± 7.98 for flaxseed oil.

Preparation of emulsions and oleogels

Based on the procedures described by Patel *et al.* (2014a) but with modifications we prepared emulsions and oleogels. HPMC (1 g) was dispersed in 38.4 g cold water using a stirrer (Heidolph RZR 1, Schwabach, Germany) at 31 ***g*** for 30 min, with the resulting aqueous solution stored at 8 °C overnight. Subsequently, 0.6 g of XG was added to the HPMC solution and stirred (Heidolph RZR 1) for 5 min, 60 g of oil was added and homogenised (Ultraturrax T18; IKA, Staufen, Germany) at 1230 ***g*** for 6 min. Three types of oil, O, S and F, were used in three emulsions formulations. The emulsions (EO, ES and EF) were dried, using two different drying conditions: conventional drying (C) in an oven (KB115; BINDER, Tuttlingen, Germany) at 80 °C for 10 h 30 min, and vacuum drying (V) using a vacuum drying oven (Vaciotem-T, J.P. SELECTA, Spain) at 60 °C/−0.85 bar for 14 h. These were the minimum time points needed to reach constant dry weight at the indicated conditions. The dried products were homogenised at 728 ***g*** (Ultraturrax T18; IKA) to produce the oleogels. Five oleogels (OC, OV, SC, SV and FC) were produced in triplicate. The flaxseed oleogel could not be obtained when vacuum drying was used to dry the emulsions in the conditions established in this study.

Microstructure of emulsions and oleogels

Analysis was conducted with a Cryo-scanning electron microscopy (Cryo-SEM). The samples were frozen by immersion in slush nitrogen and transferred to a cryogenic unit (CT 15000 C; Oxford Instrument, Oxford, UK) connected to a scanning electron microscope JEOLJSM 5410 (JEOL, Tokyo, Japan). After fracturing, etching and being coated with gold, the samples were observed at 15 kV at a working distance of 15 mm. The droplet size of the emulsions and oleogels was determined using the software Image J (National Institutes of Health, Bethesda, MD, USA).

Oil loss of oleogels

Determination was made by the percentage of oil migration over 35 days at 20 °C, using the method by Doan *et al.* (2016) with modifications. The weight of released oil was measured at time intervals 1, 2, 5, 7, 14, 21, 28 and 35 days. For this purpose, a funnel with a filter paper was positioned above an Erlenmeyer flask where the liquid oil from the oleogels dripped into. The weight of the funnel, the filter paper and the Erlenmeyer flask were measured (M1). Then, 10 g of oleogel was weighed (M3) and set into the funnel. Samples were removed at each time interval with a flat, small spatula. The weight of the funnel, the filter paper and the flask with the liquid oil released was measured again (M2). The results were expressed as g oil loss per 100 g oleogel, calculated using eqn 1 and were measured in triplicate for each sample.

$$\text{Oil loss} = \frac{\text{M2} - \text{M1}}{\text{M3}} \times 100\%. \quad (1)$$

Oil viscosity and polarity

Viscosity was determined using a viscometer (Haake ViscoTester VT6R Plus; Thermo Scientific, Walthan, MA, USA) equipped with spindle 1, at 60 r.p.m., at 25 °C. The total polar components percentage (% TPC) was evaluated, using a Testo® 270 (Testo Inc., Sparta, NJ, USA) at 45 °C, as this equipment is designed to operate over the range 40–200 °C.

Rheological measurements of emulsions and oleogels

Using a rotational rheometer (Kinexus Pro+, Malvern Panalytical, Malvern, UK), equipped with a Peltier plate cartridge a series of tests were performed at 20 °C with a parallel plate geometry (ϕ = 40 mm) and the geometry gap set at 1500 μm. For emulsion samples, amplitude sweeps (frequency = 1 Hz, stress = 1–500 Pa), frequency sweeps (stress = 10 Pa, frequency = 0.1–10 Hz) and flow measurements (shear rate 1 s^{-1} to 100 s^{-1}) were conducted. For oleogels samples, amplitude sweeps (frequency = 1 Hz, stress = 1–1000 Pa), frequency sweeps (stress = 100 Pa, frequency = 0.1–10 Hz) and temperature sweeps (frequency = 1 Hz, stress = 100 Pa, temperature = 5–120 °C) were conducted.

Oxidative stability of oleogels

Peroxide values (PV) and specific absorption in the visible ultraviolet (k_{232} and k_{270}) were used to study the oxidative stability of the oleogels during storage. The PV was analysed according to Cho & Lee (2015) and k_{232} and k_{270} were determined according to ISO 3656: 2011. All the samples were stored at 20 °C for 35 days and were evaluated every 7 days.

Statistical analysis

The results were statistically analysed using the analysis of variance (ANOVA) with the least significant differences (LSD) calculated at a level of significance $P < 0.05$; the statistical program Statgraphics Centurion XVI.II (StatPoint Technologies, Inc., Warrenton, VA, USA) was used.

Results and discussion

Microstructure of emulsions and oleogels

In the emulsions made with O and S (olive and sunflower oil, respectively) (Fig. 1a, b), the oil droplets with different sizes (ranging from 1 to 9 μm diameter) were distributed and trapped in a polymeric network with strong hydrocolloid-hydrocolloid interactions, probably stabilised by the addition of XG (xanthan gum), which increased the viscosity of the continuous phase and protected the oil droplets from coalescence (Patel *et al.*, 2014a; Meng *et al.*, 2018b). The interaction of XG with HPMC could also be increasing the thickness of the droplet surface layer (Meng *et al.*, 2018b). In the F emulsion (flaxseed oil) (Fig. 1c), the hydrocolloid network had limited visibility with greater connections between the oil droplets, not properly separated by the hydrocolloid network.

The oleogels produced by convection drying of O (Fig. 1d) and S (Fig. 1e) emulsions were observed as well-structured with individual oil droplets separated by the hydrocolloid network. However, the flaxseed oleogel (Fig. 1f) presented oil droplets of greater size (up to 52 μm diameter) and irregular form and define edges between oil droplets were lost in some areas. This indicates that during the conventional drying process, coalescence occurred between the flaxseed oil droplets. The polymeric network generated in flaxseed emulsions is evidently weaker, as the network has poor visibility in the emulsion; therefore, it is believed resists

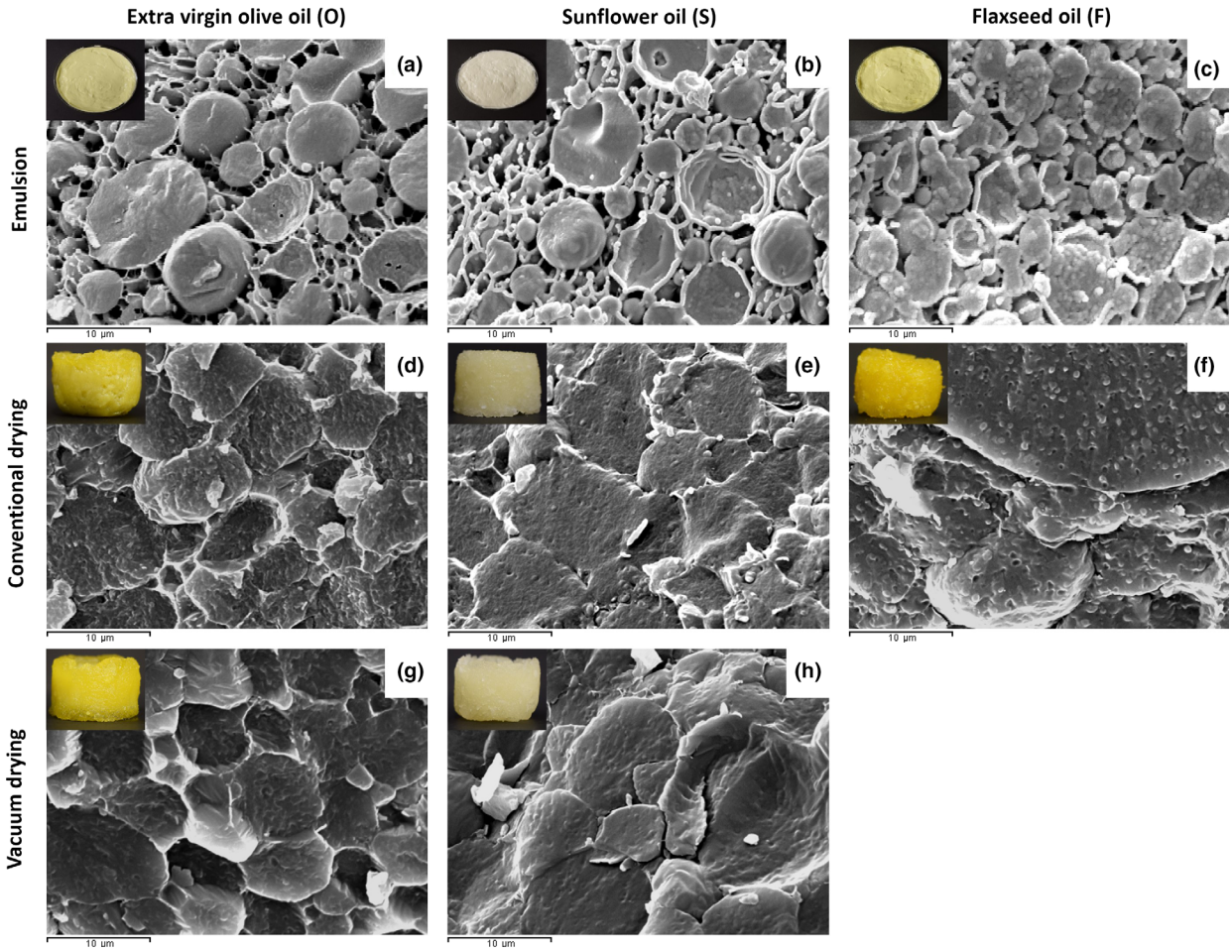

Figure 1 Cryo-scanning electron microscopy (Cryo-SEM) of emulsions (a–c), oleogels produced by conventional drying (d–f) and oleogels developed by vacuum drying (g, h). Images were taken at 3500×. Pictures of oleogels are provided to present the concept more clearly.

the drying process to a lesser extent, resulting in less homogeneous and unstructured oleogel (Fig. 1f). Oils with a low degree of unsaturation, such as olive and sunflower, form emulsions with strong polymeric networks stabilised by interactions between the structuring agents. This network resists the drying process resulting in oleogels with greater structural stability.

Vacuum drying produced oleogels from olive (Fig. 1g) and sunflower (Fig. 1h) oils, but not flaxseed. We believe that the expansion of the water vapour during vacuum drying led to a greater damage in the labile flaxseed network structure, where interactions between the polymer and the flaxseed oil occur, decreasing the interaction points between the hydrocolloids.

If the olive and sunflower oleogels obtained by both methods are compared, they all show a high degree of structuring. Thus, gel strength decreases when the interactions between polymer and oil are enhanced. Therefore, the nature of the oil and the gelling agent affects the formation process of physical polymer oleogels (Sawalha *et al.*, 2012).

Oil loss of oleogels

Fresh made oleogels had no oil loss; the greatest loss occurred during the first 24 h of storage (Table 1). This could be because of semi-crystallisation of the polymer network as suggested by Meng et al. (2018a, 2018b). These authors prepared oleogels with different types of HPMC and different gums as arabic, guar or xanthan gum and obtained similar results for oil loss values.

For the oleogels made with olive oil (OC and OV) and sunflower oil (SC and SV), significant losses of oil

Table 1 Oil loss (g oil loss per 100 g oleogel) during storage at 20 °C

	Conventional oven drying			Vacuum oven drying	
Storage (day)	OC	SC	FC	OV	SV
1	9.14^{aA} (0.50)	9.68^{aA} (0.13)	11.49^{aB} (0.08)	9.36^{aA} (0.17)	9.80^{aA} (0.20)
2	9.56^{abA} (0.47)	10.06^{bA} (0.10)	11.88^{bB} (0.04)	10.15^{bA} (0.12)	10.06^{bcA} (0.17)
5	9.79^{bcA} (0.43)	10.12^{bA} (0.18)	12.47^{cB} (0.23)	10.35^{bcA} (0.02)	10.16^{bcA} (0.17)
7	9.89^{bcA} (0.44)	10.19^{bA} (0.19)	13.00^{dB} (0.06)	10.45^{cA} (0.02)	10.26^{cA} (0.19)
14	9.92^{cA} (0.47)	10.22^{bA} (0.16)	13.33^{eB} (0.01)	10.50^{cA} (0.07)	10.32^{cA} (0.19)
21	9.96^{cA} (0.49)	10.26^{bA} (0.15)	13.92^{fB} (0.05)	10.50^{cA} (0.07)	10.35^{cA} (0.19)
28	9.96^{cA} (0.49)	10.26^{bA} (0.15)	14.23^{fB} (0.02)	10.55^{cA} (0.02)	10.35^{cA} (0.19)
35	10.02^{cA} (0.40)	10.26^{bA} (0.15)	14.31^{fB} (0.11)	10.55^{cA} (0.02)	10.35^{cA} (0.19)

Conventional (C) and vacuum (V) dried oleogels, prepared with extra virgin olive oil (OC and OV), sunflower oil (SC and SV) and flaxseed oil (FC). Values with different lowercase letters ($^{a,\ b,\ \cdots\ z}$) within the same column are significantly different ($P < 0.05$) according to the LSD multiple range test. Values with different capital letters ($^{A,\ B,\ \cdots\ Z}$) within the same row and the same drying treatment are significantly different ($P < 0.05$) according to the LSD multiple range test.

were detected up to day 2 of storage, after values remained stable. Oleogel FC showed significant losses of oil up to day 21 of storage with stabilised values afterwards. No significant differences were found between oleogels made with the same type of oil depending on the drying treatment.

When oleogels, prepared with different oil but with the same drying treatment, are compared, no significant differences over total storage time are observed between those made with olive and sunflower oils. Concerning conventional drying, flaxseed oleogels (FC) presented significantly higher oil loss values over total storage time. This would be related to the structure of the oleogels shown in Fig. 1, since the freshly prepared olive and sunflower oleogels presented a better structure than those prepared with flaxseed.

Oil viscosity and polarity

The apparent viscosity of the olive, sunflower and flaxseed oil used in this work were 95.67 ± 2.08 85, 76.33 ± 1.53 and 68.67 ± 3.51 mPa s, and their total polar components (%TPC) were 3%, 8% and 19%, respectively. Viscosity of the oils are inversely correlated with polarity (Kumar *et al*., 2013) and could be affecting the network formation and structure by modulating the network formation (Valoppi *et al*., 2017). Different correlations have been observed between the oil polarity and strength of the gel, depending on the gelling agent used. De Vries *et al*. (2017) reported that the gel strength of the network, formed by proteins aggregates, was affected by the polarity of the oil, resulting in weaker oleogels when using a more polar oil. However, Gravelle *et al*. (2012) attributed the increase in mechanical strength of the oleogel to an increase in the polarity of the oils using ethylcellulose as gelling agent. We believe, because of its polarity, the linolenic fatty acids of flaxseed oil could interact with the HPMC-XG network, increasing the hydrocolloid-oil interactions, consequently forming a weak non-homogeneous structure of flaxseed oleogel (Fig. 1).

Rheological measurements of emulsions and oleogels

The dynamic viscoelastic properties of all the emulsions, the elastic modulus (G'), viscous modulus (G'') and phase angle (δ) are shown in Fig. 2a. The limit of the linear viscoelastic region (LVR) in all the emulsions was ≈100 Pa (data not shown). In emulsions, G' values predominated G'', showing greater elastic behaviour. A low G' and G'' dependence on the frequency sweep and a phase angle of δ = 12°–15° suggested a system with a strong structure in all emulsions (Torres *et al*., 2007). Flaxseed emulsion (EF) presented a significantly higher G' value at 1 Hz ($G' = 1.41 \times 10^3 \pm 8.49 \times 10^1$ Pa) than EO ($G' = 1.15 \times 10^3 \pm 2.1 \times 10^2$ Pa) and ES ($G' = 1.06 \times 10^3 \pm 9.54 \times 10^1$ Pa, without significant differences between EO and ES. All the emulsions showed a strong shear thinning behaviour (Fig. 2b), with the apparent viscosity decreasing when the shear rate increased. The flaxseed emulsion presented a breakdown of the emulsion structure for the dynamic forces generated during shear, producing a marked decrease in the apparent viscosity. These results are in concordance with the microstructure of emulsions, where the oil droplets of the flaxseed emulsion were observed homogeneously distributed and packed, but the network was not as visible, as in the other emulsions. This resulted in a weak structure when a shear rate was applied.

The oleogels had stronger mechanical strength, showing higher G' values than in emulsions (Fig. 2c) and $G' \gg G''$ over the 0.1–10 Hz of frequency sweep

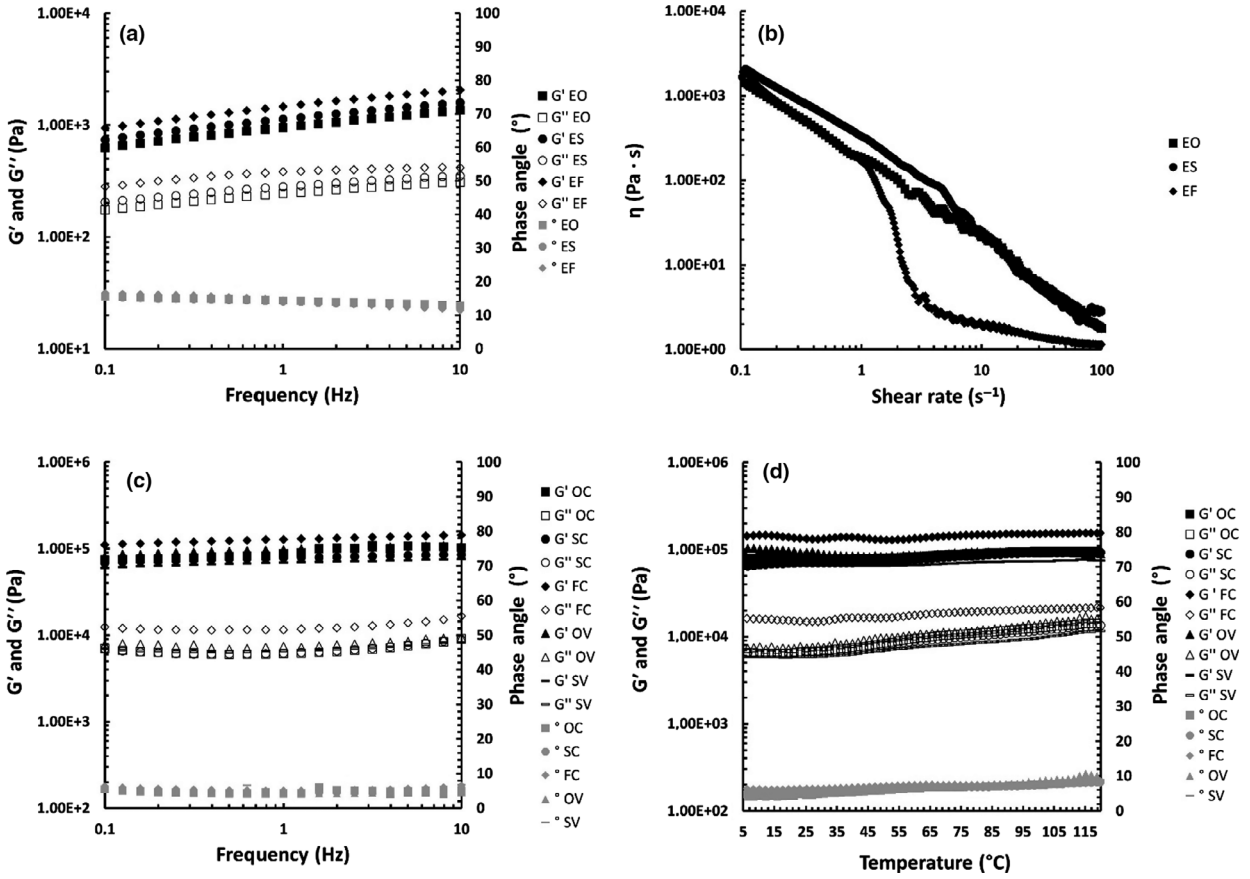

Figure 2 Frequency sweep (a) and flow measurement (b) for emulsions made with olive (EO), sunflower (ES) and flaxseed oil (EF). Frequency sweep (c) and temperature sweep (d) for oleogels developed with conventional (C) and vacuum (V) drying made with olive (OC and OV), sunflower (SC and SV) and flaxseed oil (FC).

Table 2 Peroxide value (meq kg^{-1}) during storage at 20 °C

	Conventional oven drying			Vacuum oven drying	
Storage (day)	**OC**	**SC**	**FC**	**OV**	**SV**
0	6.13^{aA}* (0.16)	16.22^{aB}* (0.68)	16.56^{aB} (0.48)	4.81^{aB} (0.12)	3.07^{aA} (0.15)
7	6.35^{aA}* (0.08)	18.27^{bB}* (0.42)	19.33^{bC} (0.59)	4.95^{abB} (0.07)	3.60^{aA} (0.33)
14	7.31^{bcA} (1.09)	21.68^{cB}* (0.62)	22.75^{cC} (0.26)	6.21^{bcA} (0.57)	5.28^{bA} (0.52)
21	8.10^{cA} (0.27)	30.60^{dB}* (0.96)	33.11^{dC} (0.39)	7.57^{cA} (1.40)	6.20^{bA} (1.16)
28	10.64^{dA} (0.89)	34.71^{eB}* (0.94)	35.14^{eB} (1.21)	10.99^{dA} (0.89)	10.71^{cA} (0.82)
35	12.27^{eA} (0.75)	44.22^{fB}* (1.27)	46.34^{fC} (0.51)	13.09^{eA} (0.72)	18.38^{dB} (0.91)

Conventional (C) and vacuum (V) dried oleogels, prepared with extra virgin olive oil (OC and OV), sunflower oil (SC and SV) and flaxseed oil (FC). Values with different lowercase letters ($^{a, b, \ldots z}$) within the same columns are significantly different ($P < 0.05$) according to the LSD multiple range test. Values with different capital letters ($^{A, B, \ldots Z}$) within the same row and the same drying treatment are significantly different ($P < 0.05$) according to the LSD multiple range test. *Means that there are differences ($P < 0.05$) between samples with the same oil type and different treatments.

applied, indicating a marked solid-like behaviour. The network formation, after the water removal, is responsible of the different rheological behaviour. The limit of the linear viscoelastic region (LVR) in all the oleogels was ≈300 Pa (data not shown). All oleogels showed a weak dependence of G' on the frequency with a low phase angle $\delta \approx 5°$ indicating strong gel strength. Regarding the oil type and drying conditions,

FC presented a significantly higher G' value at 1 Hz than OC ($G' = 8.86 \times 10^4 \pm 4.6 \times 10^3$ Pa), SC ($G' = 7.83 \times 10^4 \pm 4.95 \times 10^3$ Pa), OV ($G' = 9.78 \times 10^4 \pm 9.89 \times 10^3$ Pa) and SV ($G' = 6.88 \times 10^4 \pm 2.4 \times 10^3$ Pa) with no significant differences between OC, SC, OV and SV. Previously stated, during conventional drying, flaxseed oleogel presented a weak network structure (Fig. 1f) and a high oil loss (Table 1). The loss of the flaxseed oil during the rheological measurement could be the reason of a more compact network oleogel with higher G' value. Oleogels presented similar values to others prepared with 5–15% beeswax, propolis wax, a mixture of both (Fayaz *et al*., 2017), with a combination of 5% ethylcellulose (EC) and 5% surfactant (Gallego *et al*., 2013).

The elastic modulus (G') remained constant throughout the temperature sweep applied to the oleogels, up to temperatures of 120 °C (Fig. 2d). The absence of a cross-over point ($G' = G''$) indicates that all the oleogels did not show a gel-sol transformation. Though the hydrogel systems produced by HPMC and oleogels based on EC and waxes are thermo-reversible (Chang & Zhang, 2011; Davidovich-Pinhas *et al*., 2015; Martins *et al*., 2017), the oleogels made with HPMC and XG did not have the same behaviour showing thermostable behaviour. Abdolmaleki *et al*. (2019) compared the formulation of oleogels based on sodium caseinate, xanthan gum, guar gum and drying method (freeze and oven drier) with an industrial shortening. For the industrial shortening, the oil binding capacity (OBC) and the storage modulus (Pa) were 99.5%, and 276 545 Pa ($\approx 10^5$), respectively. Our oleogels showed an OBC and storage modulus of the order of 90% and 10^4–10^5 Pa, respectively.

Oxidative stability of oleogels

The peroxide value (PV) of fresh oils is <10 meq kg^{-1} (Codex Alimentarius, 2005). The acceptance limit in vegetable oils ranges between 15 and 20 meq kg^{-1}; actually rancidity can be perceptible at low PV. The PV of the olive (O), sunflower (S) and flaxseed oils (F) were 4.82 ± 0.14, 1.88 ± 0.12 and 5.08 ± 0.16 meq kg^{-1}, respectively.

Freshly made oleogels prepared by vacuum drying (OV and SV) had lower PV values than those prepared by conventional drying, with OV values like their correspondent oil. However, fresh OC, SC and FC presented higher PV values than those of their oils (Table 2). All the oleogels had PV values below the limit of acceptance (<20 meq kg^{-1}) after 35 days of storage, except conventionally dried flaxseed and sunflower oleogels (FC and SC). The oleogels prepared with olive oil, regardless of the treatment, showed significant increases in the PV values from

Table 3 Oxidation spectrophotometric parameters k_{232} and k_{270} during storage at 20 °C

	Conventional oven drying						Vacuum oven drying			
	OC		SC		FC		OV		SV	
Storage (day)	232 nm	270 nm	232 nm	270 nm	232 nm	270 nm	232 nm	270 nm	232 nm	270 nm
0	1.50^{abA*} (0.13)	0.88^{aB*} (0.10)	4.50^{aC*} (0.23)	5.33^{aC*} (0.15)	2.62^{aB} (0.19)	0.60^{aA} (0.07)	0.92^{aA} (0.04)	0.17^{aA} (0.07)	3.25^{aB} (0.03)	4.38^{aB} (0.09)
7	1.42^{aA*} (0.07)	1.11^{bB*} (0.13)	4.65^{abC*} (0.34)	5.52^{aC*} (0.34)	2.73^{aB} (0.23)	0.65^{aA} (0.07)	1.21^{bA} (0.11)	0.39^{bA} (0.10)	3.69^{bB} (0.23)	4.51^{aB} (0.13)
14	1.60^{abcA} (0.25)	1.03^{abB*} (0.07)	5.06^{bC*} (0.09)	5.50^{aC*} (0.19)	2.83^{aB} (0.12)	0.74^{aA} (0.10)	1.26^{bA} (0.13)	0.55^{bcA} (0.17)	4.27^{cB} (0.08)	4.76^{aB} (0.20)
21	1.75^{bcA*} (0.17)	1.04^{abA*} (0.15)	5.55^{cC*} (0.40)	5.62^{aB*} (0.19)	3.35^{bB} (0.26)	0.79^{abA} (0.19)	1.38^{bcA} (0.06)	0.66^{cdA} (0.01)	4.82^{dB} (0.07)	5.61^{bB} (0.24)
28	1.77^{bcA} (0.16)	1.14^{bA*} (0.11)	5.90^{cdC*} (0.15)	6.72^{bB*} (0.50)	3.46^{bB} (0.19)	0.96^{bcA} (0.12)	1.55^{cA} (0.25)	0.75^{dA} (0.05)	4.93^{dB} (0.03)	5.74^{bcB} (0.31)
35	1.91^{cA} (0.27)	1.39^{cA*} (0.06)	6.19^{dC*} (0.12)	7.16^{bB} (0.62)	3.61^{bB} (0.15)	1.08^{cA} (0.04)	1.61^{cA} (0.21)	0.78^{dA} (0.14)	5.25^{eB} (0.22)	6.12^{cB} (0.26)

Conventional (C) and vacuum (V) dried oleogels, prepared with extra virgin olive oil (OC and OV), sunflower oil (SC and SV) and flaxseed oil (FC). Values with different lowercase letters ($^{a, b \cdots z}$) within the same columns are significantly different ($P < 0.05$) according to the LSD multiple range test. Values with different capital letters ($^{A, B \cdots Z}$) within the same row and the same drying treatment are significantly different ($P < 0.05$) according to the LSD multiple range test. *Means that there are differences ($P < 0.05$) between samples with the same oil type and different treatments.

day 14 of storage. Sunflower and flaxseed oleogels, prepared using conventional drying, showed significant increases of the PV values gradually throughout the storage period. Drying under vacuum minimised the primary oxidation of SC during the first week with increases in PV values detected from day 14.

When comparing the oleogels made with olive oil by convention and vacuum drying, no significant differences were found from day 14 until the end of storage, indicating an adequate oxidative stability. The degree of oxidation of SC (regarding PV values) was significantly more severe than SV, indicating that vacuum drying decreases the oxidation of the oil because of the extraction of air bubbles formed inside the gel.

If oleogels subjected to conventional drying are compared, OC presented values of PV significantly lower than the oleogels SC and FC during the entire storage period. This could be explained by the composition of fatty acids, since the high content of polyunsaturated fatty acids present in sunflower and flaxseed oil are more susceptible to autoxidation than the monounsaturated fatty acids present in olive oil (Lee *et al*., 2007; Silalahi *et al*., 2017). Vacuum drying maintained similar PV values between the two types of oleogels (OV and SV) at days 14, 21 and 28, however, on day 35 of storage, the OV had significantly lower values than SV.

The measurement of absorbance in the ultraviolet range (k_{232} and k_{270}) provides indications about the quality of an oil and the state of oil preservation. The k_{232} and k_{270} are indicative, respectively, of conjugated trienes and the presence of carbonyl compounds (Malheiro *et al*., 2009). The k_{232} and k_{270} of the oils used in this study were 1.06 ± 0.05 and 0.05 ± 0.01 for olive oil, 3.40 ± 0.28 and 3.51 ± 0.14 for sunflower oil, and 2.4 ± 0.03 and 0.16 ± 0.01 for flaxseed oil, respectively. High initial values could be for the refined sunflower oil's containing oil refining products that also absorb at 232 and 270 nm (ISO 3656: 2011).

A gradual increase in k_{232} and k_{270} values throughout storage was detected for all the samples (Table 3) as previously observed by other authors. Bouaziz *et al*. (2008) and Borreani *et al*. (2017) observed a regular increase in k_{232} and k_{270} values as a function of storage for olive oils and for emulsions elaborated with HPMC and sunflower oil, respectively. Moreover, the values were significantly lower for vacuum dried oleogels than for conventionally dried, when comparing same type of oil. The use of vacuum drying allowed to reduce the drying temperature; thus, oxidation was reduced. On the other hand, the water removing process adopted during vacuum drying could be decreasing the oxidation of the oleogel as reported by Meng *et al*. (2018c)

The oleogels made with olive oil presented the lowest values of k_{232} when they were prepared using either conventional or vacuum drying (OC or OV). Regarding k_{270} values, they were also lower for OV, however, when using conventional drying, FC had significantly lower k_{270} values.

Conclusions

Olive oil and sunflower oil oleogels using HPMC and XG as structuring agents were successfully produced using conventional and vacuum drying techniques. However, flaxseed oil oleogels, using vacuum drying, could not be produced as part of this study. Oleogels developed with flaxseed oil and conventional drying had a poorly organised structure with coalesced fat globules, resulting in oil loss during storage. The olive oil oleogel produced by conventional drying and the olive oil and sunflower oil oleogels produced by vacuum drying had primary and secondary oxidative stability values within the accepted limits. The evaluation of antioxidant incorporation in the oleogels to minimise the deleterious effect of conventional drying temperature on sunflower oil quality, and the formulation of oleogels with oils with a high content in monounsaturated fatty acids would be interesting for future studies. This investigation provides a way to produce oleogels with potential applications in foods like bakery, meat and cream products.

Acknowledgments

The authors would like to thank Universitat Politècnica de València by FPI-UPV 2017 grant and the project RTI2018-099738-B-C22 from the 'Ministerio de Ciencia, Innovación y Universidades'. They would also like to thank Phillip John Bentley for assistance in correcting the English manuscript.

Conflict of interest

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

Ethical approval

Ethics approval was not required for this research.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

Abdolmaleki, K., Alizadeh, L., Nayebzadeh, K., Hosseini, S.M. & Shahin, R. (2019). Oleogel production based on binary and ternary

mixtures of sodium caseinate, xanthan gum, and guar gum: optimization of hydrocolloids concentration and drying method. *Journal of Texture Studies*, 1–10. https://doi.org/10.1111/jtxs.12469

Biguzzi, C., Schlich, P. & Lange, C. (2014). The impact of sugar and fat reduction on perception and liking of biscuits. *Food Quality and Preference*, **35**, 41–47.

Borreani, J., Espert, M., Salvador, A., Sanz, T., Quiles, A. & Hernando, I. (2017). Oil-in-water emulsions stabilised by cellulose ethers: Stability, structure and: *In vitro digestion*. *Food and Function*, **8**, 1547–1557.

Bouaziz, M., Fki, I., Jemai, H., Ayadi, M. & Sayadi, S. (2008). Effect of storage on refined and husk olive oils composition: stabilization by addition of natural antioxidants from Chemlali olive leaves. *Food Chemistry*, **108**, 253–262.

Chang, C. & Zhang, L. (2011). Cellulose-based hydrogels: Present status and application prospects. *Carbohydrate Polymers*, **84**, 40–53.

Cho, Y.J. & Lee, S. (2015). Extraction of rutin from Tartary buckwheat milling fractions and evaluation of its thermal stability in an instant fried noodle system. *Food Chemistry*, **176**, 40–44.

Co, E.D. & Marangoni, A.G. (2012). Organogels: an alternative edible oil-structuring method. *Journal of the American Oil Chemists' Society*, **89**, 749–780.

Codex Alimentarius Commission-Codex. (2005). *Codex Standards for Named Vegetable Oils: CODEX STAN 210 (revision 2005)*. Rome: FAO/WHO.

Davidovich-Pinhas, M., Barbut, S. & Marangoni, A.G. (2015). The gelation of oil using ethyl cellulose. *Carbohydrate Polymers*, **117**, 869–878.

De Vries, A., Gomez, Y.L., Van der Linden, E. & Scholten, E. (2017). The effect of oil type on network formation by protein aggregates into oleogels. *RSC Advances*, **7**, 11803–11812.

Doan, C.D., Patel, A.R., Tavernier, I. *et al*. (2016). The feasibility of wax-based oleogel as a potential co-structurant with palm oil in low-saturated fat confectionery fillings. *European Journal of Lipid Science and Technology*, **118**, 1903–1914.

Estadella, D., Nascimento, C.M., Oyama, L.M., Ribeiro, E.B., Dámaso, A.R. & Piano, A. (2013). Lipotoxicity: effects of dietary saturated and transfatty acids. *Mediators of Inflammation*, **2013**, 137579.

Fayaz, G., Goli, S.A.H., Kadivar, M. *et al*. (2017). Pomegranate seed oil organogels structured by propolis wax, beeswax, and their mixture. *European Journal of Lipid Science and Technology*, **119**, 1–11.

Food and Drug Administration [FDA] (2015). *Final determination regarding partially hydrogenated oils (removing trans-fat)*. Retrieved January 20, 2019, from https://www.fda.gov/food/ingredientspackaginglabeling/foodadditivesingredients/ucm449162.htm

Gallego, R., Arteaga, J.F., Valencia, C. & Franco, J.M. (2013). Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil. *Molecules*, **18**, 6532–6549.

Gravelle, A.J., Barbut, S. & Marangoni, A.G. (2012). Ethylcellulose oleogels: manufacturing considerations and effects of oil oxidation. *Food Research International*, **48**, 578–583.

ISO.(2011). Animal and vegetable fats and oils. Determination of ultraviolet absorbance expressed as specific UV extinction. International Organization for Standardization, Geneva (ISO 3656).

ISO.(2018). Animal and vegetable fats and oil.Determination of iodine value.Organization for Standardization, Geneva (ISO 3961).

Kanjilal, S., Shanker, K.S., Rao, B.V.S.K. *et al*. (2016). Application of low calorie hypocholesterolemic structured lipid as potential bakery fat. *International Food Research Journal*, **23**, 854–859.

Kumar, D., Singh, A. & Tarsikka, P.S. (2013). Interrelationship between viscosity and electrical properties for edible oils. *Journal of Food Science and Technology*, **50**, 549–554.

Lee, J., Lee, Y. & Choe, E. (2007). Temperature dependence of the autoxidation and antioxidants of soybean, sunflower, and olive oil. *European Food Research and Technology*, **226**, 239–246.

Maki, K.C., Reeves, M.S., Carson, M.L. *et al*. (2009). Dose-response characteristics of high-viscosity hydroxypropylmethylcellulose in subjects at risk for the development of type 2 diabetes mellitus. *Diabetes Technology & Therapeutics*, **11**, 119–125.

Malheiro, R., Oliveira, I., Vilas-Boas, M., Falcão, S., Bento, A. & Pereira, J.A. (2009). Effect of microwave heating with different exposure times on physical and chemical parameters of olive oil. *Food and Chemical Toxicology*, **47**, 92–97.

Martins, A.J., Cerqueira, M.A., Cunha, R.L. & Vicente, A.A. (2017). Fortified beeswax oleogels: effect of β-carotene on the gel structure and oxidative stability. *Food and Function*, **8**, 4241–4250.

Meng, Z., Qi, K., Guo, Y., Wang, Y. & Liu, Y. (2018a). Effects of thickening agents on the formation and properties of edible oleogels based on hydroxypropyl methyl cellulose. *Food Chemistry*, **246**, 137–149.

Meng, Z., Qi, K., Guo, Y., Wang, Y. & Liu, Y. (2018b). Macro-microstructure characterization and molecular properties of emulsion-templated polysaccharide oleogels. *Food Hydrocolloids*, **77**, 17–29.

Meng, Z., Qi, K., Guo, Y., Wang, Y. & Liu, Y. (2018c). Physical proterties, microstructure, intermolecular forces, and oxidation stability of soybean oil oleogels structured by different cellulose ethers. *Food Chemistry*, **246**, 137–149.

Nishida, C., Uauy, R., Kumanyika, S. & Shetty, P. (2004). The Joint WHO/FAO Expert Consultation on diet, nutrition, and the prevention of chronic diseases: process, product, and policy implications. *Public Health Nutrition*, **7**, 245–250.

Oh, I., Lee, J.H., Lee, H.G. & Lee, S. (2019). Feasibility of hydroxypropyl methylcellulose oleogel as an animal fat replacer for meat patties. *Food Research International*, **122**, 566–572.

Onacik-Gür, S., Zbikowska, A., Kapler, E. & Kowalska, H. (2016). Effect of barley β-glucan addition as a fat replacer on muffin quality. *Acta Scientiarum Polonorum, Technologia Alimentaria*, **15**, 247–256.

Paglarini, C.d.S., Martini, S. & Pollonio, M.A.R. (2019). Using emulsion gels made with sonicated soy protein isolate dispersions to replace fat in frankfurters. *LWT*, **99**, 453–459.

Patel, A.R. & Dewettinck, K. (2015). Comparative evaluation of structured oil systems: Shellac oleogel, HPMC oleogel, and HIPE gel. *European Journal of Lipid Science and Technology*, **117**, 1772–1781.

Patel, A.R., Cludts, N., Bin Sintang, M.D., Lewille, B., Lesaffer, A. & Dewettinck, K. (2014a). Polysaccharide-based oleogels prepared with an emulsion-templated approach. *ChemPhysChem*, **15**, 3435–3439.

Patel, A.R., Cludts, N., Sintang, M.D.B., Lesaffer, A. & Dewettinck, K. (2014b). Edible oleogels based on water soluble food polymers: Preparation, characterization, and potential application. *Food and Function*, **5**, 2833–2841.

Pehlivanoğlu, H., Demirci, M., Toker, O.S., Konar, N., Karasu, S. & Sagdic, O. (2017). Oleogels, a promising structured oil for decreasing saturated fatty acid concentrations: production and food-based applications. *Critical Reviews in Food Science and Nutrition*, **58**, 1330–1341.

Romoscanu, A.I. & Mezzenga, R. (2006). Emulsion-templated fully reversible protein-in-oil gels. *Langmuir*, **22**, 7812–7818.

Sawalha, H., Den Adel, R., Venema, P., Bot, A., Flöter, E. & Van Der Linden, E. (2012). Organogel-emulsions with mixtures of β-sitosterol and γ-oryzanol: influence of water activity and type of oil phase on gelling capability. *Journal of Agricultural and Food Chemistry*, **60**, 3462–3470.

Scholten, E. (2019). Edible oleogels: how suitable are proteins as a structurant? *Current Opinion in Food Science*, **27**, 36–42.

Silalahi, D.K.N., Yuliyanti, D., da Silva, M., Christianti, I., Mulyono, K. & Wassell, P. (2017). The stability of vitamin A in fortified palm olein during extended storage and thermal treatment. *International Journal of Food Science and Technology*, **52**, 1869–1877.

Stortz, T.A., Zetzl, A.K., Barbut, S., Cattaruzza, A. & Marangoni, A.G. (2012). Edible oleogels in food products to help maximize health benefits and improve nutritional profiles. *Lipid Technology*, **24**, 151–154.

Tavernier, I., Doan, C.D., Van der Meeren, P., Heyman, B. & Dewettinck, K. (2018). The potential of waxes to alter the microstructural properties of emulsion-templated oleogels. *European Journal of Lipid Science and Technology*, **120**, 1700393.

Torres, L.G., Iturbe, R., Snowden, M.J., Chowdhry, B.Z. & Leharne, S.A. (2007). Preparation of o/w emulsions stabilized by solid particles and their characterization by oscillatory rheology. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **302**, 439–448.

Valoppi, F., Calligaris, S., Barba, L., Šegatin, N., Poklar Ulrih, N. & Nicoli, M.C. (2017). Influence of oil type on formation, structure, thermal, and physical properties of monoglyceride-based organogel. *European Journal of Lipid Science and Technology*, **119**, 1500549.

Wassell, P., Bonwick, G., Smith, C.J., Almiron-Roig, E. & Young, N.W.G. (2010). Towards a multidisciplinary approach to structuring in reduced saturated fat-based systems-a review. *International Journal of Food Science and Technology*, **45**, 642–655.