Cellulose ether oleogels obtained by emulsion-templated approach without additional thickeners

Esper, M*, Salvador, A. and Sanz. T.

¹Instituto de Agroquímica y Tecnología de Alimentos (CSIC),

Avda. Agustín Escardino 7,

46980 Paterna, Valencia, Spain

***Corresponding author: mespert@iata.csic.es**

Tel: +34963900022

ABSTRACT

In this research, the suitability of methyl cellulose (MC) and hydroxypropyl methylcellulose (HPMC) as unique oleogelators (without additional thickeners) to obtain sunflower-based oleogels by emulsion template approach was investigated. For this purpose, different oleogels were designed taking into account the following variables: 1) the type of cellulose ether: MC or HPMC; 2) cellulose ether concentration (0.5, 1 and 2%); and 3) the oil concentration in the initial emulsion (47 and 60%). The texture, rheology, oil retention properties and microstructure of the obtained oleogels were compared and discussed. Results highlighted that stable structured oil systems can be obtained by using cellulose ethers. The most determining factor in the physical properties of the oleogels was the initial oil concentration and the hydrocolloid concentration, regardless of the type of hydrocolloid used (MC or HPMC). The increase in cellulose ether concentration provided harder oleogels with high mechanical strength, which was linked to more stable systems with enhanced oil binding capacity, reaching values up to 95%. On the other hand, the increase in oil in the initial emulsion decreased the quality of the systems, providing a softer structure with lower ability to retain the oil. The possibility to provide solid structure to sunflower oil by using MC and HPMC would be a promising approach to solid fat substitution in *trans* free and low saturated fat foodstuffs.

Keywords: oil structuring, emulsion, physical properties, methylcellulose, hydroxypropyl methylcellulose

1. Introduction

The excess of saturated fats in the diet is related to health problems, such as the increase of cardiovascular diseases, type II diabetes, metabolic syndrome and obesity, among others. However, saturated fats are responsible for many high-quality attributes in the food we consume, mainly in relation to texture, aroma, taste and stability (Rogers, 2009). This positive and fundamental contribution of saturated fatty acids to sensory properties and to the technological manufacture of food is the main reason why, today, the replacement of certain fats (e.g. palm fat), or the reduction of saturated fats, is so complex (Peng & Yao, 2017; Drewnowski, 1992).

One recent alternative for saturated fatty acid reduction that could provide systems with high plasticity is oleogelation (Singh, Auzanneau, & Rogers, 2017; Martins, Vicente, Cunha, & Cerqueira, 2018). Oleogels are defined as gel systems where a continuous liquid oil phase is immobilised in a network of self-assembled molecules of an oleogelator or a combination of gelators (Luo et al., 2019). For the formation of an oleogel, the use of gelling or structuring agents in the oil is essential, which form a three-dimensional network capable of retaining large quantities of oil and conferring structure to the liquid oil.

Substances mostly used as gelling agents in the production of oleogels are hydrophobic in nature. They are classified as low molecular weight gelators (LMWGs) and polymeric gelators. Low molecular weight gelling agents are the most extensive gelators and include fatty acids, fatty alcohols, mono-, di- and tri-acyl glycerides, ceramides, waxes, phytosterols, alpha-oryzanol and sorbitan derivatives (Abdolmaleki, Alizadeh, Nayeibzadeh, Hosseini, & Shahin, 2019). Contrary, the group of polymeric gelators is very limited, given the low oil solubility of polymers. However, in this group is ethylcellulose (EC) which is an extremely effective oleogelator, but has the limitation of requiring high heating temperatures, above their glass transition temperature (approximately 140 °C) (Dey, Kim & Marangoni, 2011; Laredo, Barbut, & Marangoni, 2011; Zetzl, Marangoni, & Barbut, 2012). Another example of a biopolymer with gelling capacity is chitin, which can be used as nanocrystals (Nikiforidis & Scholten, 2015) or modified as hydrophobic whiskers (Huang, He, Lu, Zhou, Stoyanov, Pelan, & Zhang, 2015).

The main limitation in the field of oleogelation within food technology, is finding oleogelators that are effective at low concentrations, cheap, readily available and, most

importantly, have the required regulatory approval for use in edible products (Patel & Dewettinck, 2016). In this regard research about the potential of hydrocolloids as oil gelling agents has gained increased interest.

Hydrocolloids have a long history of use in food manufacturing, and can be obtained from renewable and environmentally friendly sources. The limitation of hydrocolloids is that they cannot be used directly in the production of oleogels, since they lack the necessary solubility in hydrophobic solvents. For this reason, they required indirect methods to be able to act as oleogelators, such as the emulsion template approach (Romoscanu & Mezzenga, 2006).

In the emulsion template approach the oleogel is obtained after evaporation of the aqueous phase of an emulsion, resulting in the formation of a structure that could trap oil. The drying of the concentrated emulsions generally produces the coalescence of oil droplets, a phenomenon that can be prevented if the interface is reinforced so that it resists the dehydration produced by the evaporation of water. The capacity for oil retention is explained due to the formation of a microstructure where oil droplets are tightly packed together in a polymer matrix. Achieving this microstructure is attributed to the presence of a very well-structured interface around the oil droplets in the emulsion.

Stable oleogels have been obtained through the emulsion template approach using MC or HPMC in combination with additional thickeners, mainly xanthan gum (XG) (Patel, Cludts, Sintang, Lewille, Lesaffer, & Dewettinck, 2014). The properties of oleogels prepared with different types of HPMC or MC and XG, and the effect of HPMC concentration was studied by Meng, Qi, Guo, Wang, & Liu (2018a) and Meng, Qi, Guo, Wang, & Liu (2018b), respectively. Also, other polysaccharides such as carboxymethyl cellulose, sodium alginate, arabic gum, guar gum, flaxseed gum or locust bean gum, as well as XG has been investigated as additional thickening agents in HPMC oleogels (Meng et al., 2018b).

Although the existing research always formulates MC and HPMC in combination with additional thickeners, stable highly concentrated (50%) oil in water emulsions can be obtained only with MC or HPMC, without the need of additional thickeners (Tarancón, Salvador, & Sanz, 2013). These MC and HPMC emulsions based on sunflower oil have been successfully applied as semi-solid fat replacer in biscuits and cocoa creams (Espert, Bresciani, Sanz, & Salvador, 2019; Tarancón, Salvador, & Sanz, 2013). The difference

among these emulsions and the ones requiring additional thickeners is the methodology employed to disperse and further hydrate the cellulose ethers. To obtain the MC or HPMC emulsions without the need of an additional thickener, the cellulose powder has to be first dispersed in the oil phase and the emulsion is obtained in a second step through addition of the water phase at low temperature. With this methodology, the functionality as emulsifier and thickener of the cellulose ethers is fully developed and a thick and stable emulsion is obtained (Sanz, Salvador, Fiszman, & Laguna, 2014).

The chemical substitution (methyl or hydroxypropylmethyl), the degree of substitution and the molecular weight of the cellulose ether affect the emulsification ability, and the emulsion microstructure, rheological and thermal gelation properties (Espert et al., 2017). So, it is expected that the type of cellulose ether may also have an influence in the emulsion stability during the dehydration process and in the final oleogel structure, properties and stability. In this work the suitability of MC and HPMC, as unique oleogelators, to obtain oleogels by the emulsion template approach is investigated. The different variables investigated were: 1) the type of cellulose ether: MC or HPMC; 2) cellulose ether concentration (0.5, 1 and 2%); and 3) the oil concentration in the initial emulsion (47 and 60%). The texture, rheological behaviour, oil retention properties and microstructure of the obtained oleogels were compared and discussed.

2. Materials and methods

2.1 Materials

Methylcellulose (A4M) (30% methoxyl content) and hydroxypropyl methylcellulose (F4M) (29% methoxyl, 6.8% hydroxypropyl), both with viscosity of 4000 mPa s at 2% aqueous solution at 20 °C, measured by The Dow Chemical Company following reference methods ASTM D1347 and ASTM D2363, were donated by The Dow Chemical Company (Bomlitz, Germany). Sunflower oil “Koipesol” was purchased from Deoleo S.A. (Córdoba, Spain).

2.2 Preparation of samples

- Emulsions

The design of oleogels was started from the formulation of oil in water emulsions. Twelve emulsions were prepared: emulsions with A4M and emulsions with F4M,

formulated with different fat content (47% and 60% (w/w)) and with different hydrocolloid proportion (0.5, 1 and 2% (w/w)).

The emulsions were prepared by first dispersing the cellulose ether in the oil using a Heidolph stirrer (RZR 1) (Heidolph Instruments, Germany) at 280 min^{-1} for five minutes. Then, water at $10\text{ }^{\circ}\text{C}$ was gradually added to hydrate the mixture under continuous stirring for 30 s. At last, the mixture was homogenized using a high-energy dispersing unit (Ultraturrax T-18, IKA, Germany) at 6500 rpm for 15 s and at 17500 for 60 s.

- *Dried product*

The dried product was obtained after emulsion drying. This step was performed using a conventional drying oven (JP Selecta S.A., Barcelona, Spain) at $60\text{ }^{\circ}\text{C}$. Each emulsion was placed in an aluminum tray (245x140 mm) and dehydrated for a range of 24 to 72 hours to a final humidity of $0\pm 1\%$, obtaining a sheet of about 10 mm. Drying percentage was verified by weight difference between the emulsion and the dry product. The total elimination of water from the emulsion results in the formation of solid samples with a high proportion of oil (98-99.5%) retained in the structure formed by the hydrocolloid.

- *Oleogel*

To obtain oleogel samples, the dried product was sheared using an A320R1 mincer (Moulinex, Groupe SEB (France)). The dried product sheet was subjected to 6 cycles of 4 seconds each one. Then, the mixture obtained was finally molded and stored at refrigeration temperature ($4 \pm 1\text{ }^{\circ}\text{C}$) to get a homogeneous paste.

2.3 Rheological measurements

Viscoelasticity of the oleogels was tested using a controlled stress rheometer (AR-G2, TA Instruments (Crawley, England)) equipped with a Peltier heating system. A 20 mm diameter plate–plate sensor geometry with a serrated surface was employed, setting a gap of $1500\text{ }\mu\text{m}$. Small amplitude oscillation sweeps (SAOS) were performed in order to analyse the viscoelastic properties of the oleogels. To determine the extent of the linear viscoelastic region (LVR) stress sweeps were carried out at 1 Hz, setting a stress range of 0,1-2000 Pa. Then, frequency sweeps were performed from 10 to 0.01 Hz within the LVR (200 Pa). Each assay was carried out 3 times with oleogels of different batches, always at a temperature of 20°C .

2.4 Instrumental analysis of texture

Texture measurements were performed with a TA–XT plus texture analyser (Stable Micro Systems, Godalming, UK) with a 25 kg load cell. Penetration test was carried out using a SMS P/10 cylindrical probe (10mm diameter). Oleogel sample was placed in plastic buckets (20 x 30 mm) and stored at refrigeration temperature for 2 hours. Then, samples were tempered to 20°C and were measured to a depth of 6 mm at a rate of 1 mm/s, with a 5 g trigger force. Force-time profiles were recorded as well as the maximum force and area under the curve (AUC). Each oleogel formulation was prepared three times (different batches) and two replicates were measured from each batch.

2.5 Oil-binding capacity

Oil-binding capacity (OBC) was measured by using a previously described method (Blake, Co, & Marangoni, 2014; Huang, Hallinan, & Maleky, 2018) with some modifications. A small disc of sample (approximately 10 g) was placed on a piece of filter paper (125 mm diameter) at room temperature. Oil loss after 24 hours was calculated as the following formula:

$$OL = \frac{(W_t - W_0)}{F_{oleogel}} \quad (1)$$

Where, OL stands for oil loss, W_t stands for weight of filter at time t (24h), W_0 stands for weight of filter at time 0 and $F_{oleogel}$ stands for the fat content of the oleogel.

The OBC was calculated by means of the following formula:

$$\% \text{ OBC} = 100 - \% \text{ OL} \quad (2)$$

Two replicates of each formulation (two batches) were measured.

2.6 Microstructure

To study the structure of the oleogels a high performance full-HD digital microscope (EVO Cam II, Vision Engineering Ltd., England) was employed. 10x and 40x magnifications were used, with and without white lighting.

2.7 Statistical analysis

Multifactor analysis of variance (ANOVA) was performed on the textural parameters to evaluate differences among samples. Three factors were considered: a) the type of cellulose ether (MC or HPMC); b) the cellulose ether concentration (0.5, 1 and 2%); and c) the oil concentration in the initial emulsion (47 and 60%). The means were compared using Tukey test and the statistical significance was determined at $p < 0.05$. Statistical analysis was performed using XLSTAT statistical software (version 2010. Addinsoft, Barcelona, Spain).

3. Results and discussion

3.1 Visual appearance

Oleogels composed of either methylcellulose (A4M) or hydroxypropyl methylcellulose (F4M) as unique ologelators at 0.5, 1 and 2% were obtained by an emulsion-template approach technique, at two levels of oil concentration in the initial emulsion (47 and 60%).

Figure 1 shows the appearance of the initial emulsion, the dried product and the final oleogel, corresponding to the emulsion with 47% oil and 1% A4M, as a representative example. The initial emulsion (Figure 1A) showed a semi-solid, not plastic consistency, which easily flows. After emulsion dehydration, a sheet of dried product is obtained (Figure 1B), which is an aerated structure where the spaces previously occupied by the water are now empty; the oil (>98% (w/w)), although not visually appreciable, should be strongly trapped in the network formed by the cellulose ether. In Figure 1C the final oleogel after refrigeration storage at 4°C is shown. The oleogels showed a solid-like appearance and a more yellowish colour compared to the emulsion and the dried product. In the oleogel, the oil is expected to be less trapped in the cellulose network than in the dried product due to the mechanical process applied during chopping the dried product, which could be a reason of the change in colour, although destabilization or appreciable oil release it is not visualized. Discussion about the oil retention capacity of the oleogels is shown in a following section of the manuscript.

3.2 Texture measurements

The effects of cellulose type, cellulose concentration, and initial oil concentration on the mechanical properties of the oleogels were determined using a penetration test. The texture profiles curves of the oleogels obtained from 47% and 60% oil emulsions are shown in Figure 2. The force/time profiles correspond to a compact gel structure; the

force increases linearly as a function of time and there is neither an indicative peak of the structure breaking nor the subsequent drop in force. Values of maximum force (hardness) and area under the curve (AUC) were determined from the curve profiles to compare objectively the behavior of the different oleogels (Table 1). Three factors were considered for statistical analysis (cellulose type, cellulose concentration and oil concentration). Significant differences were found with respect to the concentration of cellulose ($p < 0.001$) and the concentration of oil ($p < 0.001$). The increase in cellulose concentration increases significantly both maximum force and AUC values indicating an increase in gel consistency, regardless of the type of cellulose ether used (A4M and F4M). The increase in the force and AUC values with cellulose concentration reveals a more compact network structure, which is expected to be more efficient to retain the oil. Meng et al. (2018b) found a similar effect in the texture of xanthan gum and HPMC based oleogels by increasing HPMC concentration.

Oleogels obtained from the emulsions with 60% oil showed in general lower values of maximum force and AUC (Table 1), which reflects their lower consistency in comparison to the ones obtained from emulsions with 47% oil. Therefore, the initial amount of oil in the emulsions has a significant impact on the characteristics of the gel, since the highest oil concentration, the weakest systems are obtained, revealing that the oil/water ratio in the initial emulsion affects the stability of the emulsion during the drying step, and it is a very important aspect in the formation of an effective polymer network able to trap the oil. Nevertheless, oleogels formulated with 0.5% F4M showed higher AUC and maximum force values at 60% initial oil concentration than for the same oleogel with 47% initial oil. For cellulose A4M, the increase in concentration also increase significantly the force and AUC values, while in cellulose F4M the effect of concentration was only significant for the highest concentration (2%), being no significant the differences found among 0.5 and 1% concentrations. Like oleogels obtained from emulsions with 47% oil, there was an increase in consistency as the cellulose concentration increased, but in this case, the type of cellulose was relevant as for F4M oleogels there were no significant differences among 0.5 and 1%.

3.3 Rheological properties

The extension of the linear viscoelastic region of the different oleogels at 1 Hz is shown in Figure 3, where values of the elastic moduli (G') and the viscous moduli (G'') versus the shear stress wave amplitude are plotted.

All the oleogels showed a great resistance to the applied stress, reflecting their high stiffness. The highest extension of linear viscoelastic response was found at the cellulose concentration of 2% for both A4M and F4M oleogels at the two initial oil concentrations studied, with values of G' which remain independent of the applied stress for values up to 1000 Pa, reflecting their highest stiffness. For lower concentrations, differences between F4M and A4M can be observed, with a slightly lower extension of the viscoelastic region for F4M. In both celluloses and for the two initial oil concentrations, the lowest G' values and the highest sensitivity to the applied stress was found for the concentration of 0.5%. The frequency sweep or mechanical spectra of the oleogels obtained from 47% and 60% oil emulsions is shown in Figure 4 and 5, respectively. In all the oleogels, the plateau area of the mechanical spectra was observed with values of G' always higher than values of G'' and a low frequency dependence, reflecting a solid-like rheological behavior. No effect of the type of cellulose neither of the initial oil concentration was observed. On the other hand, for the same initial oil concentration and cellulose type the increase in cellulose concentration always increase the values of the moduli and the viscoelasticity (values of $\tan \delta$ closer to 0). The highest viscoelasticity was found for the oleogels obtained from the 47% oil emulsion with 2% (A4M $\tan \delta = 0.07$ and $G' = 570630$ Pa; F4M $\tan \delta = 0.07$ and $G' = 536599$ Pa (at 1 Hz)). For 0.5% a significantly higher values of $\tan \delta$ was obtained (0.11 for A4M and F4M oleogels) and also a decrease in G' values (A4M = 314773 Pa and F4M = 305244 Pa), reflecting the decrease in viscoelasticity with the decrease in cellulose concentration. By increasing the initial oil content (60%), similar values were obtained for higher concentrations of cellulose (2% A4M $\tan \delta = 0.08$ and $G' = 547260$ Pa; 2% F4M $\tan \delta = 0.08$ and $G' = 518219$ Pa). No significant differences were found from 1 to 2% of cellulose, while the lowest viscoelasticity was found for the 0.5% oleogels, with no significant differences among both types of cellulose (A4M $\tan \delta = 0.11$ and $G' = 268710$ Pa; F4M $\tan \delta = 0.11$ and $G' = 237034$ Pa).

The important contribution of the polymer concentration in the viscoelastic functions was also found by other authors, who concluded that higher concentration of polymer resulted in oleogels with higher mechanical strength and better oil binding capacity (Meng et al., 2018b; Huang, Hallinan, & Maleky, 2018).

It is interesting to note that all the oleogel samples showed higher values of the viscoelastic functions and higher resistance to the applied stress than other previous

oleogels composed of cellulose ethers plus additional thickeners. Oleogels based on HPMC and xanthan gum showed G' values below 10000 Pa and a linear viscoelastic response below 1 Pa (Meng et al., 2018a, 2018b; Patel, Cludts, Sintang, Lesaffer, & Dewettinck, 2014), in comparison to the G' values above 100000 Pa and the linear viscoelastic response above 100 Pa of the oleogels obtained in the present study. These values were even higher than those obtained in oleogels formulated with other oleogelators agents such as protein-polysaccharide complexes, ethylcellulose or waxes (Blake, Co, & Marangoni, 2014; Luo et al., 2019; Tavernier, Patel, Van der Meeren, & Dewettinck, 2017; Whitby & Onnink, 2014).

3.3 Oil loss and oil-binding capacity

Oil loss informs about the oil-binding capacity (OBC) of the oleogels. Lower oil released (higher OBC) is a desirable property in oleogels, which implies a high capability to retain the oil in their structure and a suitable physical stability.

The oil loss from the different oleogels after 24 h is shown in Figure 6. In the oleogels obtained from the emulsions with 47% oil, no significant effect of the type of cellulose was observed ($p>0.05$). However, cellulose concentration did have a significant influence. A significant increase in oil loss was found for both F4M and A4M oleogels with the decrease in concentration from 1% to 0.5%. Oil loss also increased from 2% to 1% but the differences observed were no significant. The highest oil loss occurred in the oleogels with the lowest cellulose concentration (0.5%). OBC increased from values of 79% (HPMC F4M) and 77% (MC A4M) at 0.5% to values of up to 95% at 2% cellulose concentration, for both F4M and A4M oleogels. The positive effect of cellulose concentration in OBC may be attributed to the formation of a stronger physical network with higher capacity to retain the oil droplets, also increasing the mechanical strength. These findings are consistent with those reported by Meng et al. (2018b) who concluded that the increase of HPMC concentration in the oleogel resulted in a higher mechanical strength and better oil-binding capacity. The highest oil loss was found in the oleogel obtained from the emulsion with 60% oil and 0.5% HPMC F4M (66.2% OBC) (Figure 7B). At 60% initial oil, a significant effect of the type of cellulose was found for 0.5%, with a significantly lower oil loss in MC A4M (85.4% OBC). For both initial oil concentrations (47% and 60%), the critical polymer concentration would be 1%, since a significant increase in oil loss is found at 0.5%.

With the exception of this oleogel (A4M, 0.5%), the highest OBC was found in the oleogels with lower initial oil concentration (47%). In summary, a minimum cellulose concentration of 1% is required, being the emulsion with the lower initial oil concentration (47%) the most appropriate to develop a suitable structure during emulsion dehydration to trap the oil.

It should be noted that the results of OBC showed an adequate retention of oil in the period considered as “long-term oil-binding” (Blake, Co, & Marangoni, 2014). These results confirm the high capability of oleogels to retain the oil in their structure, which results in a suitable physical stability.

3.4 Digital imaging

To get further information, microstructure of the different systems was investigated using high definition digital imaging. Figure 7 shows the macrophotographs of the oleogels obtained from the 47% oil emulsions. The oleogels with MC at 0.5% and 1% were dry and not very compact. More transparent areas where the oil is dispersed in the structure can be observed. Nevertheless, the oleogels with MC at 2% are more compact and no free oil is appreciated, denoting that the oil is totally trapped in the network formed by the cellulose. In samples with HPMC, a similar behavior can be observed, although in this case, the system with 0.5% HPMC shows a smoother and more homogeneous appearance, which agree with their lower values of maximum force and AUC. Oleogels with HPMC at 1 and 2% were more heterogeneous than those with MC.

The macrophotographs of oleogels with 60% initial oil (Figure 8) show a much more “wet” appearance, compared to 47% initial oil oleogels. Higher oil concentration in the initial emulsion, may have decreased the functionality of the cellulose network decreasing the oil binding capacity in the final oleogel. At 0.5% cellulose concentration, both the MC and HPMC oleogels with 60% initial oil showed a more transparent structure (allows a greater proportion of light), brighter and not very compact. This result is in good agreement with the prominent oil loss in these systems. With increasing cellulose concentration, the oleogel becomes denser and more compact.

The macrographs results also confirm that an initial oil concentration of 47% is the most suitable, and that for both 47% and 60% initial oil, the concentration of cellulose ether is the determining factor in the final oleogel structure rather than the type of cellulose ether.

4. Conclusions

Stable oleogels can be obtained by an emulsion template approach with the employ of MC or HPMC as unique oleogelator, without need of additional thickeners. The most important factors affecting the new oleogels characteristics were cellulose ether concentration and oil concentration in the initial emulsion, while cellulose type was not a determinant factor. A positive relationship was found among hardness and oil-binding capacity. The increase in cellulose concentration increase the hardness and the viscoelasticity of the oleogels and increases significantly oil-binding capacity. On the other hand, the increase of oil in the initial emulsion decrease the quality of the oleogels, with the development of a softer structure with lower ability to retain the oil. This study demonstrates the ability of the cellulose ethers MC and HPMC to stabilize oil globules during emulsion dehydration, forming a compact and solid dehydrated structure able to retain 95% oil. These MC or HPMC oleogels are a new alternative to provide solid structure to liquid oils and to replace conventional solid fat rich in saturated fatty acids.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Acknowledgments

This work was funded by grant RTI-2018-099738-B-C21 from the Spanish Ministry of Economy, Industry and Competitiveness.

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.
- Blake, A. I., Co, E. D., & Marangoni, A. G. (2014). Structure and physical properties of plant wax crystal networks and their relationship to oil binding capacity. *Journal of the American Oil Chemists' Society*, 91(6), 885-903.
- Dey, T., Kim, D. A., & Marangoni, A. G. (2011). Ethylcellulose oleogels. In *Edible oleogels* (pp. 295-311). AOCS Press.
- Drewnowski, A., (1992). Sensory properties of fats and fat replacements. *Nutrition Reviews*, 50, 17-20.

- Espert, M., Borreani, J., Hernando, I., Quiles, A., Salvador, A., & Sanz, T. (2017). Relationship between cellulose chemical substitution, structure and fat digestion in o/w emulsions. *Food Hydrocolloids*, 69, 76-85.
- Espert, M., Bresciani, A., Sanz, T., & Salvador, A. (2019). Functionality of low digestibility emulsions in cocoa creams. Structural changes during in vitro digestion and sensory perception. *Journal of functional foods*, 54, 146-153.
- Huang, H., Hallinan, R., & Maleky, F. (2018). Comparison of different oleogels in processed cheese products formulation. *International journal of food science & technology*, 53(11), 2525-2534.
- Huang, Y., He, M., Lu, A., Zhou, W., Stoyanov, S. D., Pelan, E. G., & Zhang, L. (2015). Hydrophobic modification of chitin whisker and its potential application in structuring oil. *Langmuir*, 31(5), 1641-1648.
- Laredo, T., Barbut, S., & Marangoni, A. G. (2011). Molecular interactions of polymer oleogelation. *Soft Matter*, 7(6), 2734-2743.
- Luo, S. Z., Hu, X. F., Jia, Y. J., Pan, L. H., Zheng, Z., Zhao, Y. Y., ... & Jiang, S. T. (2019). Camellia oil-based oleogels structuring with tea polyphenol-palmitate particles and citrus pectin by emulsion-templated method: preparation, characterization and potential application. *Food Hydrocolloids*, 95, 76-87.
- Martins, A. J., Vicente, A. A., Cunha, R. L., & Cerqueira, M. A. (2018). Edible oleogels: an opportunity for fat replacement in foods. *Food & function*, 9(2), 758-773.
- Meng, Z., Qi, K., Guo, Y., Wang, Y., & Liu, Y. (2018a). Physical properties, microstructure, intermolecular forces, and oxidation stability of soybean oil oleogels structured by different cellulose ethers. *European Journal of Lipid Science and Technology*, 120(6), 1700287.
- Meng, Z., Qi, K., Guo, Y., Wang, Y., & Liu, Y. (2018b). Macro-micro structure characterization and molecular properties of emulsion-templated polysaccharide oleogels. *Food Hydrocolloids*, 77, 17-29.
- Nikiforidis, C. V., & Scholten, E. (2015). Polymer organogelation with chitin and chitin nanocrystals. *RSC Advances*, 5(47), 37789-37799.
- Patel, A. R., & Dewettinck, K. (2016). Edible oil structuring: an overview and recent updates. *Food & function*, 7(1), 20-29.
- Patel, A. R., Cludts, N., Sintang, M. D. B., Lewille, B., Lesaffer, A., & Dewettinck, K. (2014). Polysaccharide-based oleogels prepared with an emulsion-templated approach. *ChemPhysChem*, 15(16), 3435-3439.

- Patel, A. R., Cludts, N., Sintang, M. D. B., Lesaffer, A., & Dewettinck, K. (2014). Edible oleogels based on water soluble food polymers: preparation, characterization and potential application. *Food & function*, 5(11), 2833-2841.
- Peng, X., & Yao, Y. (2017). Carbohydrates as fat replacers. *Annual review of food science and technology*, 8, 331-351.
- Rogers, M. A. (2009). Novel structuring strategies for unsaturated fats—Meeting the zero-trans, zero-saturated fat challenge: A review. *Food Research International*, 42(7), 747-753.
- Romoscanu, A. I., & Mezzenga, R. (2006). Emulsion-templated fully reversible protein-in-oil gels. *Langmuir*, 22(18), 7812-7818.
- Sanz, T., Salvador, A., Fiszman, S.M. & Laguna, L. (2014). Fabricación y aplicación de emulsión sustituta de grasa. *Patente Española ES 2 408 690*.
- Singh, A., Auzanneau, F. I., & Rogers, M. A. (2017). Advances in edible oleogel technologies—A decade in review. *Food research international*, 97, 307-317.
- Tarancón, P., Salvador, A., & Sanz, T. (2013). Sunflower oil–water–cellulose ether emulsions as trans-fatty acid-free fat replacers in biscuits: texture and acceptability study. *Food and bioprocess technology*, 6(9), 2389-2398.
- Tavernier, I., Patel, A. R., Van der Meeren, P., & Dewettinck, K. (2017). Emulsion-templated liquid oil structuring with soy protein and soy protein: κ -carrageenan complexes. *Food Hydrocolloids*, 65, 107-120
- Whitby, C. P., & Onnink, A. J. (2014). Rheological properties and structural correlations in particle-in-oil gels. *Advanced Powder Technology*, 25(4), 1185-1189.
- Zetzl, A. K., Marangoni, A. G., & Barbut, S. (2012). Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters. *Food & function*, 3(3), 327-337.

TABLES

Table 1. Textural parameters obtained from penetration curves of the different oleogels prepared from emulsions with 47% and 60% initial oil content (n=6).

		MAX. FORCE (N)		AUC (N s)	
Oleogel sample		47% oil	60% oil	47% oil	60% oil
A4M	0.50%	1.25 ^{CD} (0.08)	0.73 ^D (0.02)	4.58 ^{FG} (0.54)	2.69 ^G (0.03)
	1%	2.18 ^{BCD} (0.17)	2.08 ^{BCD} (0.36)	8.21 ^{DE} (0.80)	6.51 ^{DEF} (0.42)
	2%	6.61 ^A (1.69)	3.40 ^B (0.49)	20.23 ^B (1.62)	12.93 ^C (1.60)
F4M	0.50%	0.83 ^D (0.14)	1.71 ^{BCD} (0.03)	2.67 ^G (0.41)	5.79 ^{EF} (0.06)
	1%	2.52 ^{BC} (0.07)	1.62 ^{BCD} (0.20)	8.87 ^D (0.14)	5.43 ^{FG} (0.30)
	2%	6.99 ^A (0.73)	3.45 ^B (0.02)	23.47 ^A (0.82)	12.45 ^C (0.34)

AUC: Area under the curve.

Values in parentheses are standard deviations.

^{ABCDEFGH} Values with the same letter for each parameter are not statistically different ($p < 0.05$) according to Tukey's test.

Figure 1. Visual appearance of emulsion (A), dry product (B) and oleogel (C).

Figure 2. Force-time profiles of the different oleogels with 47% (A) and 60% (B) initial oil content.

Figure 3. Stress sweep of the different oleogels formulated with 47% (A) and 60% (B) initial oil contents.

Figure 4. Evolution of G' and G'' values as a function of frequency of the different oleogels formulated with 47% initial oil content and A4M (A) or F4M (B). G' : filled symbols; G'' : empty symbols.

Figure 5. Evolution of G' and G'' values as a function of frequency of the different oleogels formulated with 60% initial oil content and A4M (A) or F4M (B). G' : filled symbols; G'' : empty symbols.

Figure 6. Oil loss (%) of the different oleogels formulated with 47% (A) and 60% (B) initial oil contents. Values with the same letter are not statistically different ($p < 0.05$) according to Tukey's test.

Oil content	MC	10x	10x (light)	40x
47%	0.5%
	1%
	2%

Oil content	HPMC	10x	10x (light)	40x
47%	0.5%
	1%
	2%

Figure 7. Macrophotographs of the different oleogels formulated with 47% initial oil content and different cellulose ether at different concentrations.

Oil content	MC	10x	10x (light)	40x
60%	0.5%
	1%
	2%

Oil content	HPMC	10x	10x (light)	40x
60%	0.5%
	1%
	2%

Figure 8. Macrophotographs of the different oleogels formulated with 60% initial oil content and different cellulose ether at different concentrations.