

## Comparison of different indirect approaches to design edible oleogels based on cellulose ethers

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### ABSTRACT

Growing public concern about the adverse health effects of overconsumption of saturated fat has contributed to the rising research interest in the field of using healthy oils to construct edible structured oils (oleogels) as fat-based alternatives. In this study two indirect methodologies (the emulsion template approach and the foam template approach) were investigated to prepare oleogels with hydroxypropyl methylcellulose and methylcellulose as gelling agent at three different oil concentrations. Microstructure, texture, rheology, and oil retention capacity were measured to evaluate the structural and physicochemical properties of oleogels. Results showed that the emulsion-based oleogel effectively inhibited the aggregation of droplets. The dry emulsion showed independent droplets and an oil retention capacity of 100%. In foam-type oleogels the oil retention rate was negatively correlated with the oil content. The oleogels prepared by both methods have excellent mechanical properties and gel strength, with a predominance of the elastic versus the viscous behavior. Hydroxypropyl methylcellulose and methylcellulose had different degrees of influence on the structure and mechanical properties of the two oleogels. The results of this paper provide guidance for the development and application of cellulose-based oleogels as healthy alternatives to saturated fat.

### 1. Introduction

Solid fat such as shortenings, butter, palm fat, cocoa butter etc., are widely used in bakery products, chocolate, spread sauces, quick-frozen food, snacks, and other industrial foods due to their ability to endow technological and organoleptic properties (flavor, taste, texture, etc.) (Feichtinger & Scholten, 2020; Gómez-Estaca et al., 2019; Naeli, Milani, Farmani, & Zargaraan, 2022). Solid fat functional properties depend to a large extent on the crystal network structure of the high melting point components in the fat used. Without saturated fatty acid (SFA), these fats would not be able to provide the required structure and texture. However, excessive intake of saturated fat has potential risks for cardiovascular disease (Adili, Roufegarinejad, Tabibiazar, Hamishehkar, & Alizadeh, 2020), diabetes (Oh, Lee, Lee, & Lee, 2019), or metabolic syndrome (Bascuas et al., 2021), which seriously endangers human health.

An alternative to conventional solid fat is oleogelation. Oleogelation confers solid properties to a liquid oil and requires the use of gelators or structurants to form a three-dimensional network polymeric structure to trap the liquid oil (Davidovich-Pinhas, Barbut, & Marangoni, 2015; Li

et al., 2021). In recent year, the development of edible oleogels based on polymers has been flourishing. Initially, researchers focused on small fat-soluble molecules e.g., waxes (Yılmaz & Ögütçü, 2015), mono-glycerides, diglycerides, long-chain fatty acids (Martins, Vicente, Cunha, & Cerqueira, 2018) or long-chain fatty alcohols (Lupi et al., 2013). Later, the interests gradually shifted from small polymers to edible natural polymers being developed due to their more plentiful and economical availability (Matalanis & McClements, 2013), such as proteins (de Vries, Gomez, van der Linden, & Scholten, 2017; de Vries, Jansen, van der Linden, & Scholten, 2018; Mohanan, Tang, Nickerson, & Ghosh, 2020), polysaccharides (Patel et al., 2014), hydroxypropyl methylcellulose (HPMC), and methylcellulose (MC) (Patel & Dewettinck, 2015; Zetzl et al., 2014).

The methodologies to prepared oleogels with polysaccharides as structure agents required indirect approaches, as the oil cannot directly interact with the polysaccharide. In the direct methods, the gelling agent is directly mix with oil to form a gel at the appropriate temperature (Shi et al., 2021). The emulsion template approach and the foam template approach are two of the indirect methodologies available. The emulsion template approach involves forming an emulsion and, subsequently

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water removal to form the oleogel. In the foam template approach (Patel, Schatteman, Lesaffer, & Dewettinck, 2013) the hydrocolloid is hydrated in water to develop its structure, lyophilized, and finally the oil is incorporated in the dry foam to obtain the oleogel.

Abdollahi, Goli, and Soltanizadeh (2020) prepared oleogels by foam template method using gelatin and xanthan gum biopolymers with high gel strength, good thixotropy, and thermal stability. In contrast, Pan et al. (2021) required the addition of proanthocyanidins to stabilize the emulsion and prepare highly stable oleogels. Patel et al. (2015) compared wax crystals, hydrophilic cellulose derivative and gelled water droplets as structurants to prepare oleogels, exploring the impact of different structurants and preparation methods on the structural properties, functions, and limitations of oleogels. In other studies, different surfactants were also added to gelators to improve the gel strength of oleogels. However, in food development, the amount and type of gelling agents should be as little as possible to avoid health concerns from consumers. Hence, selecting appropriate gelling agents and a simple methodology to prepare oleogels is the most required.

In our previous work, oleogels with favorable mechanical properties and stable structure using MC or HPMC without additional thickeners by an emulsion template method have been successfully prepared and applied as conventional fat replacers in chocolate and baked pasta products (Espert, Hernández, Sanz, & Salvador, 2021; Espert, Salvador, & Sanz, 2020; Espert, Sanz, & Salvador, 2021). The current work aims to compare the differences in properties (microstructure, rheological properties, texture and oil binding capacity) between the emulsion template and foam template approaches for the preparation of oleogels with the purpose of providing a basic guide for further expansion of emulsion-based and foam-based oleogels for applications in the food industry. Methylcellulose and hydroxypropyl methylcellulose ethers were used as gelators and the effect of three different oil concentration in the oleogel structure and properties were also studied.

## 2. Materials and methods

Methylcellulose (A4M) (30% methoxyl content) and hydroxypropyl methylcellulose (F4M) (29% methoxyl, 6.8% hydroxypropyl) were kindly supplied by The Dow Chemical Company (Bomlitz, Germany). Sunflower oil was purchased from Deoleo S.A. (Córdoba, Spain).

### 2.1. Oleogel preparation

- 1) Emulsion template approach.** The oleogel obtained by the emulsion template was prepared as previously described (Espert et al., 2020). Three emulsions with different oil content (18%, 33% and 47% w/w), each with a cellulose concentration of 1.5% (w/w), were prepared. Briefly, the cellulose was added in oil and dispersed via a Heidolph stirrer (RZR 1) (Heidolph Instruments, Germany) for 2 min with low speed (200 rpm). Then water at 10 °C was added and homogenized by a high-speed disperser (Ultraturrax T-18, IKA, Germany) for 1 min at 16,500 rpm. After homogenization the color of the mixture turned into milky white, that means the emulsion was prepared successfully. The emulsion was collected and placed in an aluminum mold (245 × 140 mm) and heat into a forced-convection oven (Binder GmbH, Germany) at 60 °C for 48 h to remove moisture, until the final humidity was below 0.5% (w/w). Finally, the dried samples with a final oil concentration of 92%, 96%, and 97% (w/w) were sheared with a high-speed dispersing machine (Moulinex, Groupe SEB, France) to form the oleogel.
- 2) Foam template approach.** The method referred by Oh and Lee (2018) with slight modifications was employed. 6 g cellulose was dissolved in 94 g hot water (85 °C), and then 200 g cool water (below 10 °C) were added and the mixture was dispersed with a stirrer (RZR 1, Heidolph Instruments, Germany) at 400 rpm for 10 min. The resulting solution was homogenized using a high-speed disperser (Ultraturrax T-18, IKA, Germany) at 16,500 rpm for 2 min, and

finally the sample was lyophilized using a laboratory freeze dryer (Lyobeta 6 PL, Telstar, Spain). The freeze-dried sample was minced with a grinding machine. Finally, the required oil to achieve 92%, 96%, and 97% oil concentration in the final oleogels was added slowly to the freeze-dried samples and stirred until a uniform oleogel is formed.

### 2.2. Visual appearance

Photos of the different oleogels were taken by a digital camera with at 1x objective to compare their appearance and morphological characteristics.

### 2.3. Microstructure

The microstructure of the samples with the highest oil concentration (96%) was studied by light microscopy (LM) using a Nikon Eclipse 80i light microscope (Nikon Co., Ltd., Tokyo, Japan) with a built-in camera (Exwave HAD, model No. DXC-190, Sony Electronics Inc., Park Ridge, New Jersey, USA. UU.). The samples were cut with a stainless-steel cutter to obtain thick sections that were placed on a glass slide for microstructure observation. The images were captured with x4 magnification and stored at 1280 × 1024 pixels using the microscope software (NIS-Elements M, Version 4.0, Nikon, Tokyo, Japan).

For the scanning electron microscopy (SEM), both the foam and the emulsions oleogels were gold coated using POLARON E6100 Equipment (10<sup>-4</sup> mbar, 20 mA, 80 s) and observed in a Jeol JSM 6300 Scanning Electron Microscope at 15 kV and at a working distance of 15 mm with x50 magnification.

### 2.4. Determination of oil binding capacity

10 g oleogel were placed on a filter paper. The total mass of the sample and filter paper was recorded after 24 h. The oil-binding capacity (OBC) of oleogel after 24 h was calculated from the following formula:

$$OBC(\%) = 100\% - \frac{W_t - W_0}{F_{oleogel}} (\%)$$

Where,  $W_t$  stands for the mass of filter and sample after 24 h,  $W_0$  stands for the initial weight of the filter, and  $F_{oleogel}$  stands for the weight of oil in oleogel.

### 2.5. Rheological measurements

The rheological measurements of the oleogels were determined on a control stress rheometer model AR-G2 (TA Instruments, Montreal, QC, Canada) equipped with a 40 mm hatch parallel plate geometry and a Peltier temperature control system. Stress and frequency tests were carried out at 20 °C. Oscillatory stress sweeps from 0.1 to 1000 Pa were performed at a constant frequency of 1 Hz to determine the linear viscoelastic region. Frequency sweeps (from 0.1 to 100 Hz) and temperature sweeps (from 20 to 90 °C, 1 Hz) were conducted in the linear viscoelastic region. Rheological data were recorded with TRIOS Software (TA Instruments, Montreal, QC, Canada). Each assay was carried out twice.

### 2.6. Texture analysis

Texture analysis of oleogels were evaluated with a texture analyzer (TA. XT. Plus texture analyzer, Stable Micro Systems Ltd. Surrey, UK). Oleogel samples were placed into 2\*2\*2 cm cube mold and a cylindrical probe with a diameter of 1 cm was selected to penetrate the sample 6 mm at a speed of 1 mm/s. Hardness was analyzed by Exponent software (version 6.1.4.0, Stable Micro Systems Ltd.) and calculated as the maximum force obtained at 6 mm penetration.

## 2.7. Statistical analysis

Each experiment was repeated three times, and all results were analyzed by One-way ANOVA in SPSS 8.5 (OriginLab Corporation, Northampton, MA, USA). Tukey test was used to determine The effect of the increase of temperature among values ( $p < 0.05$ ) and data were represented as mean  $\pm$  deviation (SD).

## 3. Results and discussion

### 3.1. Appearance

Fig. 1 shows the appearance of emulsion-based and foam-based oleogels obtained with the two types of cellulose and three different oil contents. The appearance of the emulsion-based oleogels was not very much influenced by the type of cellulose and the oil contents, all the oleogels appearing as white granular crystalline solids (Fig. 1A and B). The A4M sample showed some adhesion of the oleogel particles at the higher oil concentration (Fig. 1B). In the foam-based oleogels differences were found depending on the oil concentration and type of cellulose. At 92% oil content (Fig. 1C and D) oleogels showed white aggregated clusters, and fragments of cellulose could still be observed on the surface after fragmentation, implying that these points are not fully saturated with oil. When the oil content increased to 96%, the A4M foam based oleogels appear as a yellowish semi-solid gel, while the surface of the F4M oleogel was smoother and more elastic and the oil was strongly absorbed in the gel network, reflecting a more suitable spatial conformation formed by the broken cellulose fragments after oil adsorption. At 97% of oil content, F4M oleogel showed obvious oil leakage (Fig. 1D), indicating that the maximum oil adsorption capacity of F4M oleogel was about 95%, which was slightly weaker than that of A4M sample.

### 3.2. Microstructure

A different microstructure was found among the A4M and F4M in the dry product obtained by the emulsion template and foam template approach with the optical microscopy and SEM. In Fig. 2A, it can be seen that in the A4M dry product (with 96% oil content) droplets showed

aggregation and increase in droplet size (up to 50–200  $\mu\text{m}$  in diameter), but exhibit relatively intact spherical droplet morphology and an un-flattened network spherical surface. In contrast, the structure of the F4M sample showed large-scale aggregation and flocculation (Fig. 2B) during the drying process, as well as the inability to observe a normal droplet structure. This may be related to F4M containing a considerable portion of the hydrophilic group itself, where the lipophilic segments of F4M chains were adsorbed on the surface of oil droplets during the formation of emulsions, while the hydrophilic segments stretched into the aqueous phase and formed trailing tails or loops, which makes the F4M emulsion droplet structure more vulnerable to losing stability in drying processes compared to the lipophilic A4M (Li, Al-Assaf, Fang, & Phillips, 2013; Wollenweber, Makieviski, Miller, & Daniels, 2000). However, F4M with rigid backbone structure was not easily bent and did not easily occupy enough interfacial area, resulting in only a few F4M chain segments being adsorbed on the surface of oil droplets (Meng, Qi, Guo, Wang, & Liu, 2018), so the emulsion droplet structure formed was easier to aggregation during the thermal drying process. Fig. 2C and D shows the microstructure of the two cellulose dry foam samples, which are completely different from the emulsions, and a porous fibrous polymer network structure with inhomogeneity can be clearly observed in both samples. The difference is that the network structure of A4M is densified (Fig. 2C) and partially stacks are connected in a lamellar pattern, while the network structure of F4M foam is relatively sparse with larger pores and thicker mesh fibers.

SEM was employed to further analyze the effect of preparation method and cellulose type on the microstructure of the oleogels. Fig. 3A showed the microstructure of A4M dry product, with different sized oil droplets distributed and captured in the polymer network. The irregular droplet structure was also observed for the F4M sample at high magnification (Fig. 3B), but some of the defined edge regions between the oil droplets were lost, indicating that coalescence occurred between the oil droplets during drying, suggesting that F4M is less resistant to thermal drying, causing a poorly homogeneous and unstructured oleogel (Bascuas, Hernando, Moraga, & Quiles, 2020). The SEM of the two foam-based samples were completely different, A4M formed a complete paper-like fragment instead of a gridded structure containing porosity (Fig. 3C), in accordance with Patel et al. (2013). They assumed that it

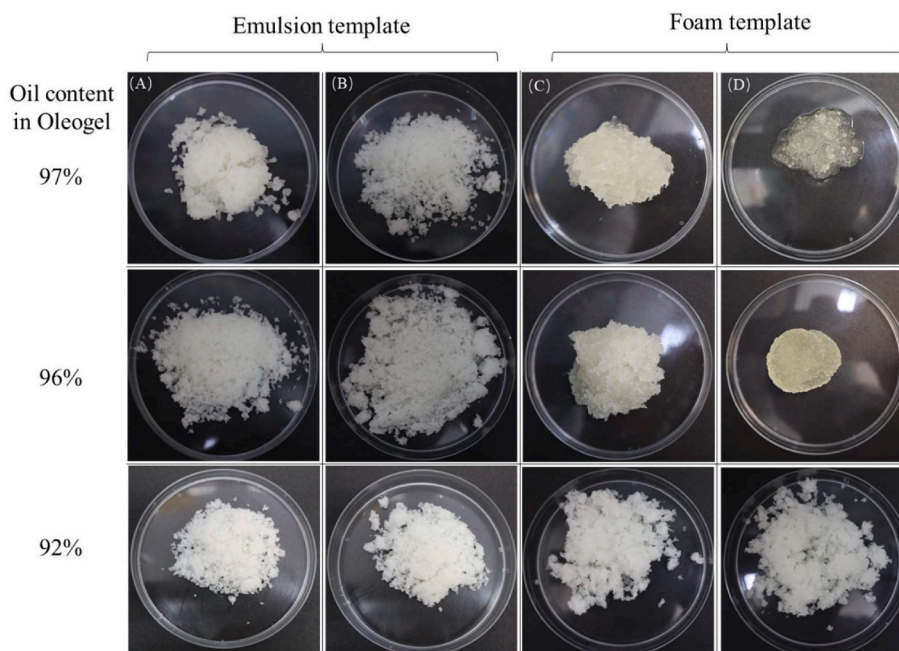


Fig. 1. Appearance of cellulose-based oleogel obtained by the emulsion and foam template approaches. (A) A4M cellulose; (B) F4M cellulose; (C) A4M cellulose; (D) F4M cellulose.



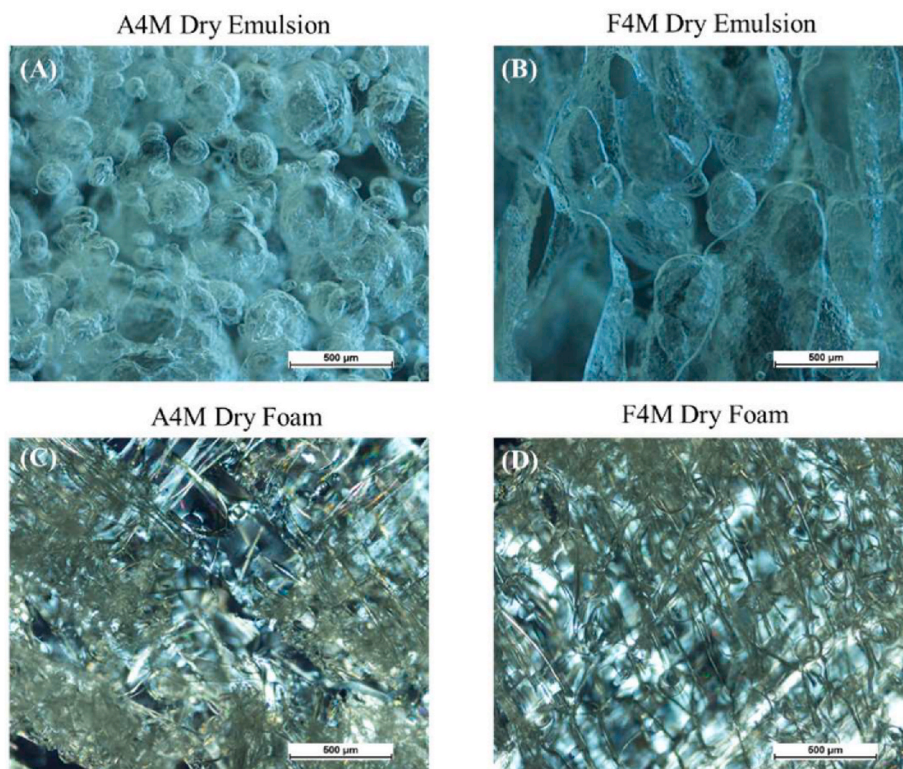


Fig. 2. Light microscopy images of the different cellulose -based oleogel at 97% oil content.

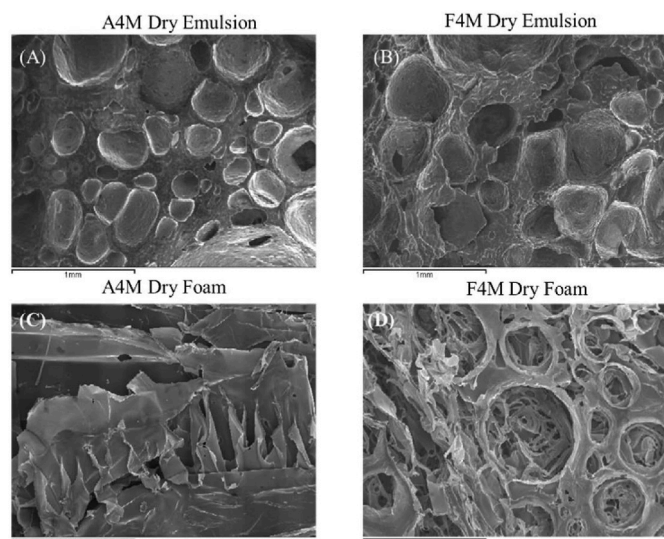


Fig. 3. SEM images of the different cellulose-based oleogel at 97% oil content.

was the emergence of Ostwald maturation and coalescence destabilization of A4M during the lyophilization process leading to inhomogeneous poredistribution and size, and the formation of needle-like structure. It is remarkable that the foam prepared with F4M with porous sponge structure is clearly visible in each layer of the network structure and stacked into a three-dimensional structure with relatively uniform size and distribution of pores (Fig. 3D). A similar structure was observed by Tanti, Barbut, and Marangoni (2016b) exploring the effect of different drying methods on HPMC and MC oleogels as stabilizers in peanut butters. During the preparation of the oleogels the dry foam was broken, but the network of small lamellar polymers remained and adsorbed liquid oils in a physical means thus forming a new gel network,

meanwhile the sophisticated three-dimensional structure provides a large surface area for the polymer/oil combination.

### 3.3. Oil binding capacity

Oil binding capacity (OBC) reflects the ability of the oleogel to trap liquid oil, therefore is an essential parameter for assessing the physical stability of the oleogel network. Table 1 shows the OBC of the foam template oleogels after 24 h. The increase in oil content was negatively correlated with OBC. The OBC of the A4M oleogels decreased from 99.9% to 91% when the oil content increased from 92% to 97%. In F4M oleogels the OBC decreased from 100% to 84%. The OBC results indicate that 92% oil content is the maximum oil percentage which can be retained in the foam oleogel structure. For higher oil concentrations (96% and 97%) the adsorption capacity of the foam oleogel is fulfilled and the excess oil released. Thus the maximum oil adsorption is reached at 92% oil. This phenomenon can also be observed in the appearance of the foam oleogels (Fig. 1) where a yellow color is observed at the higher oil concentrations (96% and 97%), while a white snowflake shape without the yellow color is observed at the optimum 92% oil concentration. Overall, the oil adsorption capacity of A4M foam-based oleogels is significantly higher than that of F4M, which indicates a more compact

Table 1

Effect of cellulose type and oil content in the oil binding capacity (OBC) of foam template oleogels.

Cellulose type	Oil content (%)	Oil binding capacity (%)
F4M	92	100 ± 0.10 <sup>a</sup>
	96	96 ± 1.39 <sup>b</sup>
	97	84 ± 1.35 <sup>d</sup>
A4M	92	99.9 ± 0.10 <sup>a</sup>
	96	97 ± 0.68 <sup>b</sup>
	97	91 ± 1.30 <sup>c</sup>

<sup>a-d</sup> Means with different letters for each column indicate significant differences between oleogels ( $p < 0.05$ ).



network structure in A4M oleogels with a stronger restraining force to prevent oil leakage in comparison to F4M. Jiang, Du, Li, Liu, and Meng (2021) suggested that oil adsorption capacity of HPMC foam-based oleogels is mainly determined by the capillary forces that make up the functional network structure, and the correlation between capillary force strength and pore size clearly affects spontaneous absorption because the strength is inversely proportional to pore size (Mosquera, Rivas, Prieto, & Silva, 2000).

The OBC of all the emulsion template oleogels was 100% (data not shown in Table 1). The differences in the OBC between emulsion and foam template method is in agreement with their appearance in Fig. 1. In the emulsion template oleogels a white powder is obtained at all oil concentrations, although for 92% the white color is more intense. Bascuas, Salvador, Hernando, and Quiles (2020) obtained oil loss percentages of 10% in emulsion template oleogels using hydroxypropyl methylcellulose (HPMC) and xanthan gum (XG) as structuring agents. The higher OBC of emulsion template oleogels of the present work can be related to the different methodology employ to obtain the initial emulsion. Meng et al. (2018) employed different cellulose to prepare emulsion-based oleogels with oil loss even up to 19%.

### 3.4. Rheological measurement

#### 3.4.1. Stress sweep

The stress sweeps corresponding to the different oleogels are shown in Fig. 4. In all the oleogels,  $G'$  values were over 10 times higher than  $G''$  values, indicating the predominant solid-like behavior of the oleogels. The linear viscoelastic region (LVR) was negatively correlated with the oil content, which indicates that the structural resistant to the applied stress of the oleogels with 92% (w/w) oil content is higher than 96% and 97%, indicating a more stabilized structure with higher resistance to the applied stress at the lowest oil content. Also, in all the oleogels  $G'$  and  $G''$  values gradually decreases with the increase of oil concentration. The increase weakness of oleogel structure with the increase in oil content might be associated to the decrease of the relative concentration of the cellulose ether, leading to a weaker network structure (Oh & Lee, 2018). F4M oleogel showed higher structural resistant in comparison to A4M, which could be explained due to the superior interfacial properties of HPMC (F4M oleogel) which will result in more homogenous droplets and a stronger gel network structure.

In comparison to the emulsion template oleogels, the LVR of the foam template oleogels was slightly greater indicating the highest strength of the foam-based oleogels. The lowest values of the viscoelastic

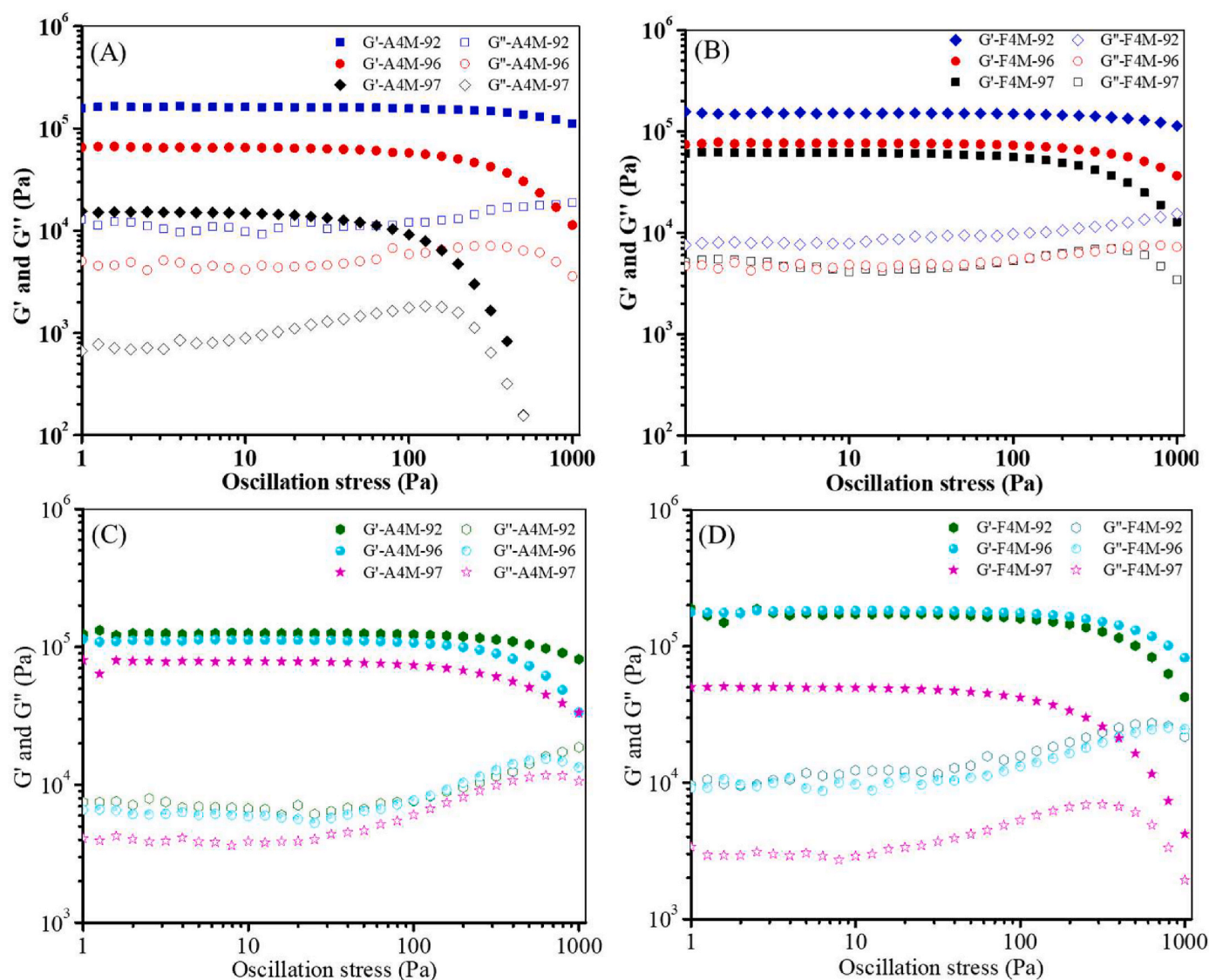


Fig. 4. Effect of cellulose type and oil content in the stress sweeps. (A) and (B) are the emulsion template oleogels corresponding to A4M and F4M cellulose, respectively; (C) and (D) are the foam template oleogels corresponding to A4M and F4M cellulose oleogels, respectively.

functions and the lowest LVR were found in the A4M emulsion oleogel with the highest oil content (96%). For oil concentrations lower than 96%, the difference of  $G'$  value between AFM and F4M samples was not significant. However, when the oil content increased to 96%, the  $G'$  value of A4M was much higher ( $8 \times 10^4$  Pa) than that of F4M ( $5 \times 10^4$  Pa), which is associated to the higher oil retention rate of A4M. The highest strength and oil binding capacity of the oleogels obtained with the A4M could be associated to its higher hydrophobic properties in comparison to F4M. This is attributed to the fact that MC forms a separate polymer network after lyophilization treatment, which can be verified in Fig. 3. The polymer networks further formed the independent polymer flake networks after absorbing oils (Tanti et al., 2016b), resulting in a more complex three-dimensional network and having a higher gel stability than physically crushed emulsion-based oleogels. Surprisingly, the weakening effect produced by high oil content on gel strength was more noticeable in F4M foam-based oleogels, although at lower oil concentrations it showed high gel strength (Fig. 4D). When the oil content increased to 97%,  $G'$  values of A4M foam-based oleogel was much higher than that of F4M, which is associated to its higher hydrophobic properties.

### 3.4.2. Frequency sweep

The frequency dependence of  $G'$  and  $G''$  of the different oleogels are shown in Fig. 5.  $G'$  was higher than  $G''$  in all the frequency sweep studied. The slope of the trend line of  $G'$  versus frequency was close to 0 in all the systems, indicating a low frequency dependence associated to high gel strength. Similar results were obtained by Tanti, Barbut, and Marangoni (2016a) using hydroxypropyl methylcellulose and methylcellulose to prepare oleogels to replace shortening in sandwich cream via foam template method, where HPMC oleogels showed higher gel strength than MC oleogels. Similarly to the results found in the stress sweep tests, the overall gel strength of foam-based oleogels was generally higher than that of emulsion-based, especially at the highest oil concentration.

The dynamic moduli of all samples at 1 Hz were statistically compared (Table 2). In general foam-based oleogels showed significantly higher values of  $G'$  and  $G''$  than emulsion-template oleogels at the same oil content. Foam-template oleogels, F4M at 92% oil had the highest  $G'$  value ( $2.3 \times 10^5$  Pa). Increasing the oil content resulted in a significant decrease in both  $G'$  and  $G''$ . This result is more noticeable in emulsion-based oleogels, especially in A4M with 97% oil.  $\tan \delta$  informs about viscoelasticity and is related to the strength of the internal structure of the gel. Higher value of  $\tan \delta$  (closer to 1) indicate a weaker

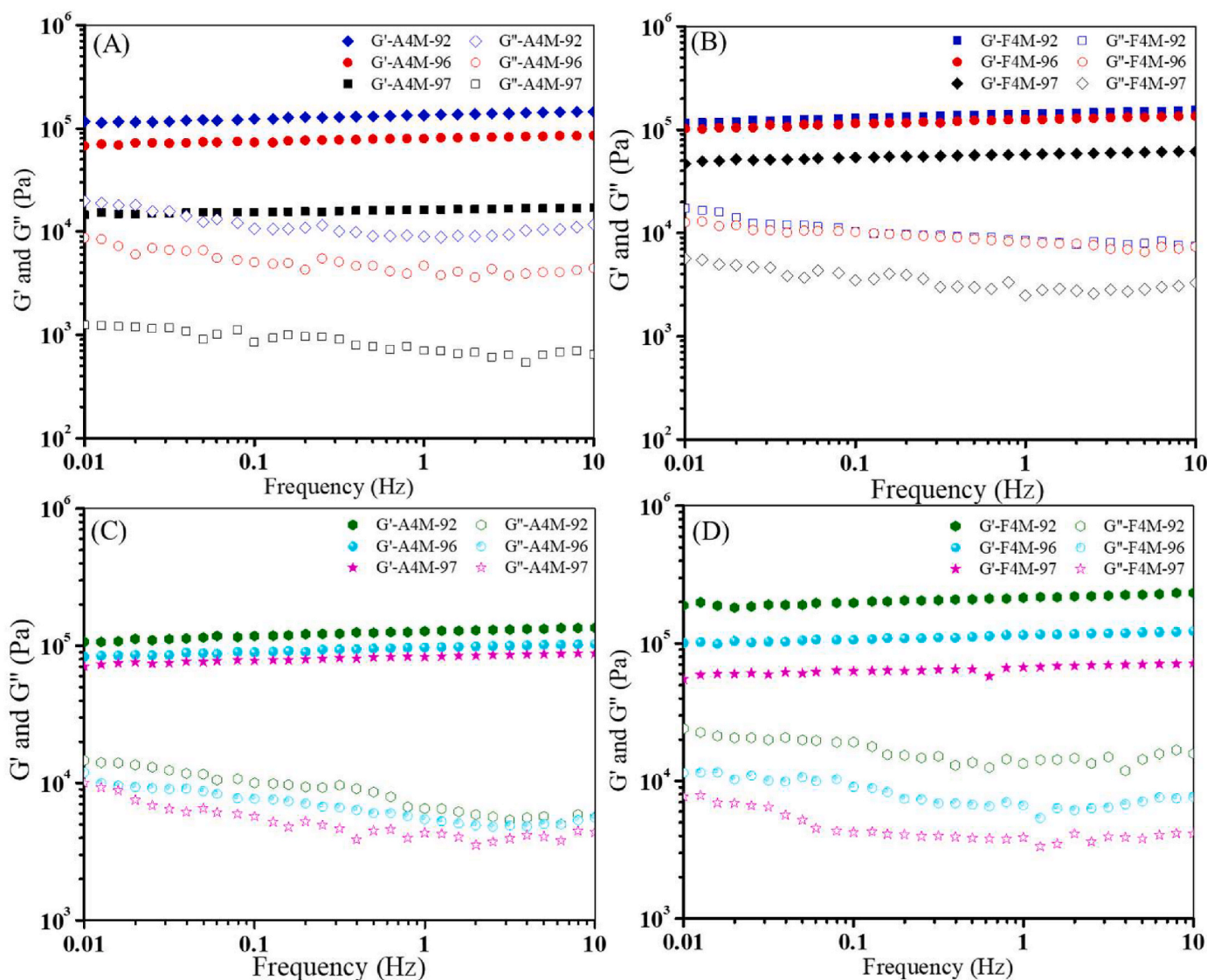


Fig. 5. Effect of cellulose type and oil content in the frequency sweeps. (A) and (B) are the emulsion template oleogels corresponding to A4M and F4M cellulose, respectively; (C) and (D) are the foam template oleogels corresponding to A4M and F4M cellulose oleogels, respectively.

**Table 2**

Viscoelastic rheological parameters (at 1 Hz) of the different oleogels.

Sample	Emulsion template						Foam template					
	A4M			F4M			A4M			F4M		
	92%	96%	97%	92%	96%	97%	92%	96%	97%	92%	96%	97%
$G'$ (Pa)	123571 ± 11499 <sup>b</sup>	71891 ± 8782 <sup>d</sup>	14869 ± 1606 <sup>f</sup>	133794 ± 9081 <sup>b</sup>	124526 ± 691 <sup>b</sup>	59777 ± 1868 <sup>e</sup>	149882 ± 3246 <sup>b</sup>	112254 ± 14656 <sup>c</sup>	83165 ± 3453 <sup>d</sup>	230177 ± 16415 <sup>a</sup>	123572 ± 7428 <sup>b</sup>	73936 ± 6593 <sup>d</sup>
$G''$ (Pa)	8133 ± 484 <sup>b</sup>	3576 ± 210 <sup>e</sup>	758 ± 60 <sup>g</sup>	8543 ± 458 <sup>b</sup>	7760 ± 38 <sup>b</sup>	3566 ± 102 <sup>f</sup>	8964 ± 192 <sup>b</sup>	5476 ± 414 <sup>c</sup>	4297 ± 42 <sup>d</sup>	11547 ± 517 <sup>a</sup>	5981 ± 106 <sup>c</sup>	3631 ± 181 <sup>e</sup>
Tan $\delta$	0.07 ± 0.02 <sup>a</sup>	0.05 ± 0.01 <sup>a</sup>	0.05 ± 0.02 <sup>a</sup>	0.07 ± 0.03 <sup>a</sup>	0.06 ± 0.02 <sup>a</sup>	0.06 ± 0.02 <sup>a</sup>	0.06 ± 0.03 <sup>a</sup>	0.05 ± 0.03 <sup>c</sup>	0.05 ± 0.01 <sup>a</sup>	0.05 ± 0.03 <sup>a</sup>	0.05 ± 0.01 <sup>a</sup>	0.05 ± 0.03 <sup>a</sup>

<sup>a-g</sup> Means with the different letter for each raw indicate significantly difference between oleogels ( $p < 0.05$ ).

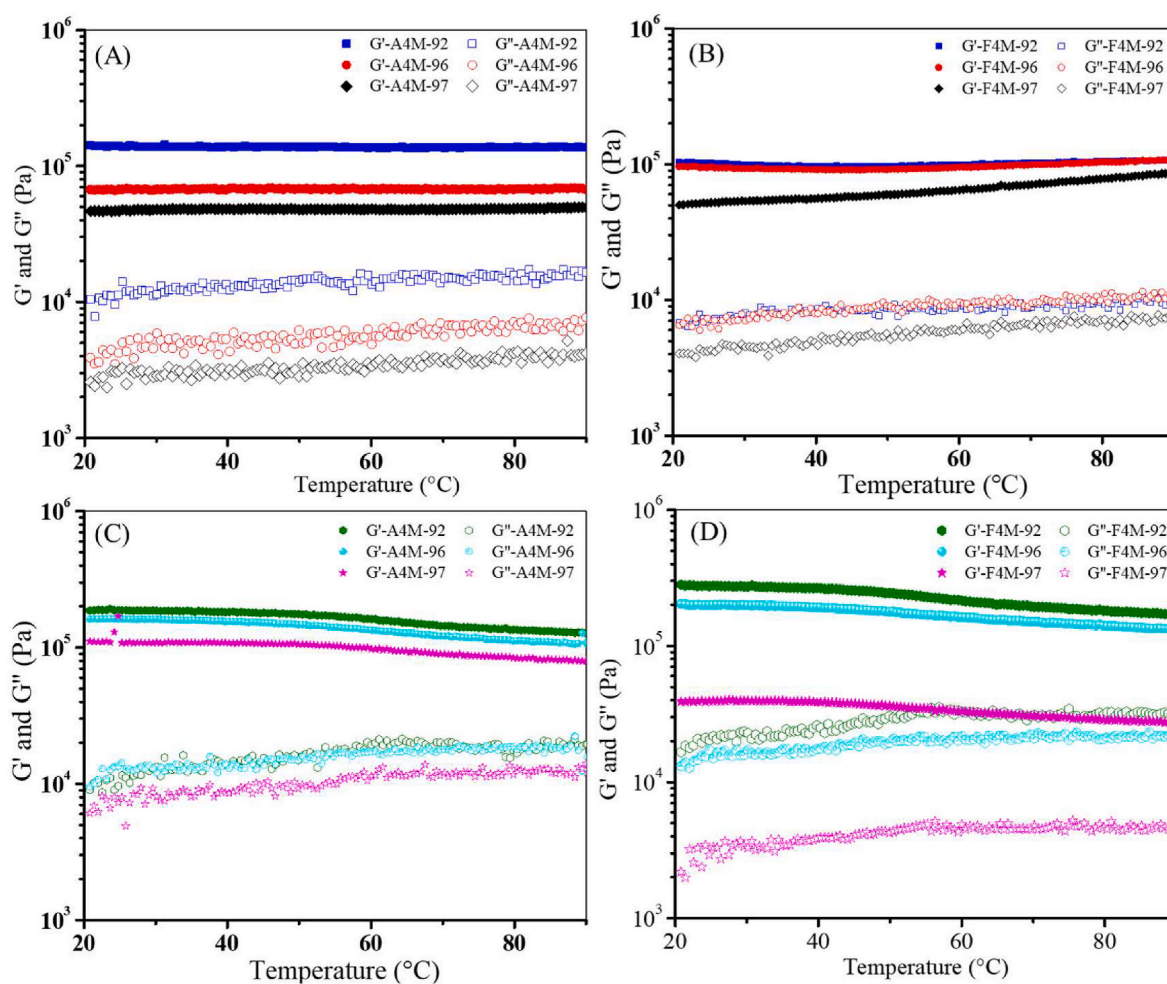
internal solution structure (Bascuas et al., 2021). All the oleogels showed tan  $\delta$  values lower than 0.1, with no significant differences among them. These lower values of tan  $\delta$  indicate a great predominancy of the elastic properties versus the viscous properties reflecting the predominant solid like structure of the oleogels.

### 3.4.3. Temperature sweep

The effect of the increase on temperature from 20 to 90 °C on the oleogel viscoelastic properties was investigated to determine the temperature sensitivity of the oleogel structure (Fig. 6). In the emulsion-based oleogels, values of  $G'$  and  $G''$  showed only a very slight decrease with the increase in temperature indicating a high thermal stability. The foam template oleogels also showed very good thermal stability,

although slightly lower than the emulsion template oleogels. In the foam template oleogels at temperature higher than 50 °C, the  $G'$  values showed a slight decrease, which was a result of the gel network structure melting and collapsing upon heating, leading to a decrease in gel strength.

The excellent thermal stability of cellulose oleogels prepared both by the emulsion and the foam template approaches is a positive advantage in terms of their future application as fat replacers in food application. Previous studies in other oleogels types revealed a lack of thermal stability. For example, oleogels prepared using beeswax as gelling agent showed significant gel structure damage (sharp decrease in  $G'$  value) at 50 °C, which was caused by the melting of the gelling agent crystals (Gómez-Estaca et al., 2019). Also, oleogels prepared using ethylcellulose



**Fig. 6.** Effect of cellulose type and oil content in the temperature sweeps. (A) and (B) are the emulsion template oleogels corresponding to A4M and F4M cellulose, respectively; (C) and (D) are the foam template oleogels corresponding to A4M and F4M cellulose oleogels, respectively.



or waxes were thermally reversible (Gómez-Estaca et al., 2019; Rodríguez-Hernández, Pérez-Martínez, Gallegos-Infante, Toro-Vázquez, & Ornelas-Paz, 2021; Tavernier, Doan, Van derMeeren, Heyman, & Dewettinck, 2018). The thermal results obtained revealed that the cellulose ether oleogels obtained by both the foam and the emulsion template approaches would be a promising option when thermal stability is a requirement.

### 3.5. Texture measurement

The force/time curves during the penetration test of the different oleogels are shown in Fig. 7. Penetration force curves showed an upward trend, indicating that the oleogel had a compact and stable structure. The maximum force value of the emulsion-based oleogels decreased significantly with increasing oil content (Table 3), which was due to the cellulose content of the emulsion is relatively reduced with the increase in the oil content, which weakened the gel network leading to a decrease

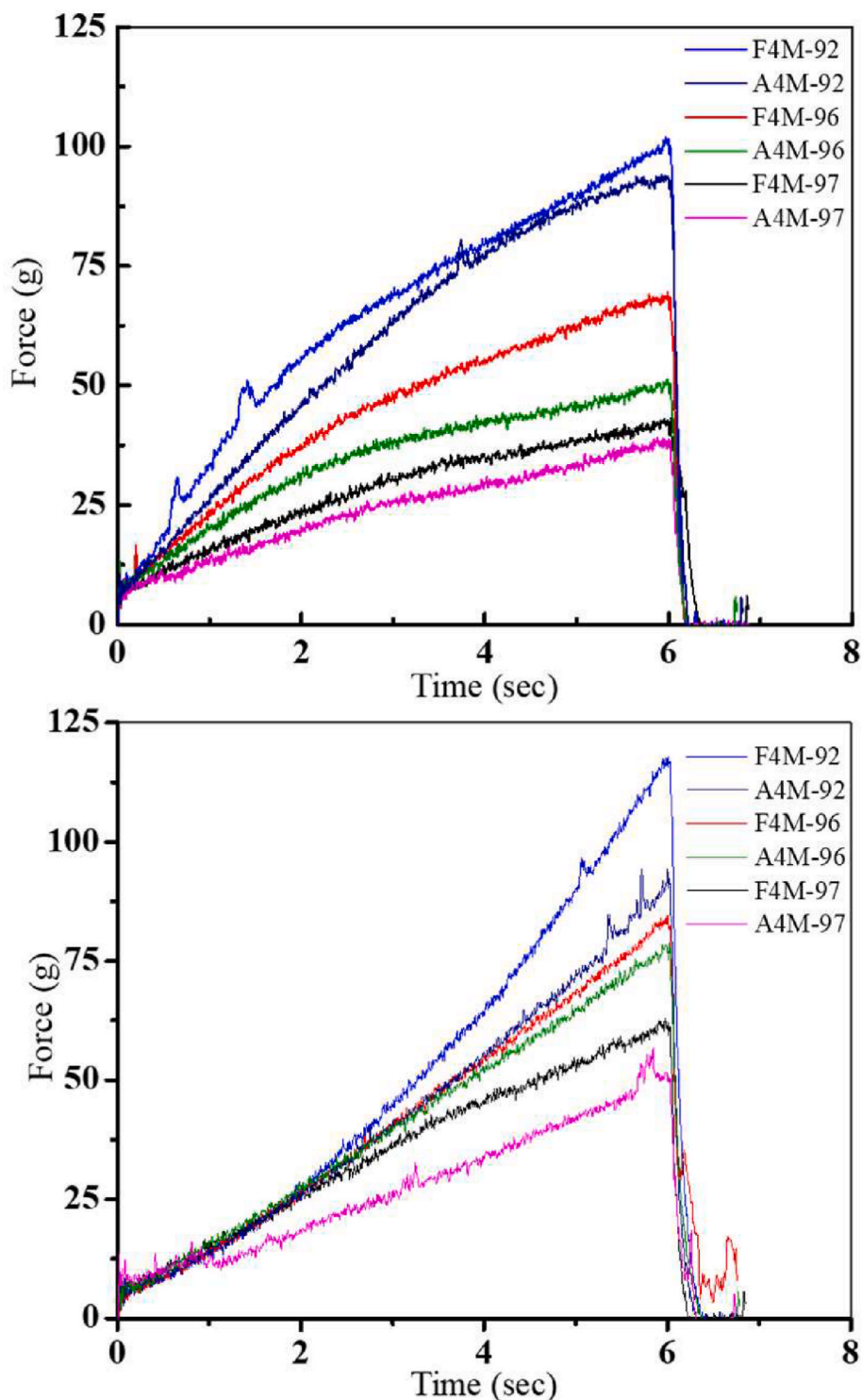


Fig. 7. Penetration curves of emulsion template (A) and foam template (B) oleogels.

**Table 3**  
Hardness of oleogels obtained by emulsion and foam template approaches.

Cellulose type	Oil content (%)	Max. Force (g)	
		Emulsion template	Foam template
F4M	92	101.90 ± 1.80 <sup>B</sup>	117.80 ± 2.07 <sup>aA</sup>
	96	69.57 ± 1.15 <sup>cB</sup>	84.46 ± 1.46 <sup>cA</sup>
	97	42.76 ± 0.94 <sup>eB</sup>	62.33 ± 1.22 <sup>eA</sup>
A4M	92	94.11 ± 1.43 <sup>bA</sup>	91.84 ± 1.19 <sup>bA</sup>
	96	51.34 ± 1.08 <sup>dB</sup>	78.43 ± 1.94 <sup>dA</sup>
	97	38.86 ± 1.26 <sup>fB</sup>	51.77 ± 1.04 <sup>fA</sup>

<sup>a-f</sup> Means with different letters for each column indicate significant differences between oleogels ( $p < 0.05$ ).

<sup>A-B</sup> Means with different letters for each row indicate significant differences between oleogels ( $p < 0.05$ ).

in the hardness of the gel (lower values of maximum force). This is in agreement with the rheological results. Similarly, other authors also found a positive correlation among the oleogels elastic values and hardness (Li et al., 2021; Tanti et al., 2016a). The maximum force of F4M emulsion oleogels was higher than that of A4M for the same oil content, the reason being that the F4M showed a large aggregation of emulsion droplets into chunks and formation of larger oil droplets in the dried oleogel (Fig. 2) and a stronger granularity of the gel fragments after shearing, resulting in a higher hardness. Similar phenomenon was also observed in the foam-based oleogels (Fig. 7B). Hardness of the foam-based oleogels was higher than that of the emulsion-based oleogel samples when compared at the same oil level (except for 92%). The reason for the pattern may be related to the formation mechanism of the oleogels. In foam-based oleogel a solid gel with good viscoelasticity (Fig. 2) formed by adsorbing liquid oils and fats through a three-dimensional cellulose network structure (A4M) or a cellulose stack structure (F4M) filled with pores, which has a strong resistance to deformation, while the emulsion-based oleogel shows a solid granular texture after shearing and a relatively loose structure in the unit volume, leading to a slight difference in hardness.

#### 4. Conclusion

The structure and physical properties of cellulose oleogels with different oil contents prepared by the emulsion template and the foam template approaches were evaluated. Oleogel obtaining method and oil content had more effect on the oleogel structure than the type of cellulose. The methodology to obtain the oleogels affected the structural properties of the final oleogels. The emulsion template oleogels were solid-like, non-fluid, and had 100% oil retention capacity. In contrast, the foam template oleogels were semi-solid, and their oil retention capacity decreased with increasing oil content. The gels prepared by both methods have an excellent gel strength and low dependence on frequency and temperature. The variation of the methodology, oil content and type of cellulose allow the obtention of oleogels with different properties and functions, so a wide range of semi-solid or solid-like fat products with a healthy lipid profile suitable for food applications could be obtained.

#### Author statement

Each contributing author (Qi Wang, Maria Espert, Virginia Larrea, Amparo Quiles, Ana Salvador and Teresa Sanz), hereby consent and authorize the publication of the article entitled "Comparison of different indirect approaches to design edible oleogels based on cellulose ethers".

#### Declaration of competing interest

The authors of the article titled "Comparison of different indirect approaches to design edible oleogels based on cellulose ethers"

declare that there is no conflict of interest.

#### Data availability

The authors are unable or have chosen not to specify which data has been used.

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