J. Cosmet. Sci., 72, 399–417 (July/August 2021)

The Effect of Vegetable Oil Composition on the Structural Properties of Oleogels Based on Behenyl Alcohol/Behenic Acid Oleogelator System

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Accepted for publication May 27, 2021.

Synopsis

Recently, we described that the weight ratio (*R*) between behenyl alcohol (BO) and behenic acid (BA) in sunflower oil effects the textural and structural properties of the oleogel system. One *R* (7:3) was found as optimal since it led to an enhancement of the oleogel properties for both the hardness and the stability in terms of oil-binding capacity. However, what remains unknown is the effect of other vegetable oils. Therefore, in this study, we aim to test a range of different vegetable oils that are widely used in the cosmetic industry. All the oleogels were prepared by heating together at 85°C the oil and the fatty components under magnetic stirring. After heating, the samples were allowed to cool down quiescently to room temperature without any stirring. The oil properties tested included viscosity, density, and surface tension. The oleogel properties (hardness, oil loss, and gel stability) and their structure as a function of *R* were characterized at different length scales by coupling optical microscopy, differential scanning calorimetry (DSC), Small-Angle X-ray Scattering (SAXS), and Wide-Angle X-ray Scattering (WAXS) experiments. The same crystal structure evolution determined by SAXS and WAXS as a function of *R* was observed whatever the oil. In the DSC profiles and optical microscopy pictures, no oil effect was detected. However, our results highlighted two different optimal ratios, giving rise to the best oleogels in terms of stability (oil loss) and hardness as a function of the oil. For sunflower, apricot, and rapeseed oils, *R* = 7:3 was the optimal ratio, whereas *R* = 8:2 was the optimal ratio for olive and camelina oil. These observations were correlated with the fatty acid chain length composition of the oil. The results obtained have practical applications for the cosmetic industry since it establishes formulation rules for oleogel systems. Oleogels are based on BO and BA components, which are raw materials widely used for hair and skin applications. Different oils have different fatty acid chain lengths composition and as a result, the ratio between BO and BA needs to be adjusted in order to obtain the best oleogel in terms of texture and stability, which can then be used also to produce oil foams.

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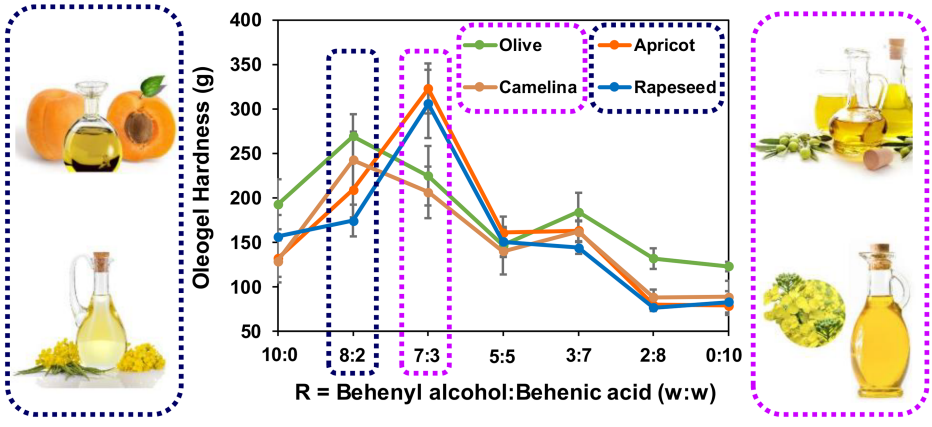
Graphical Abstract



INTRODUCTION

Oleogels are a class of soft materials that can entrap large volumes of liquid oils in self-assembled network (1). The presence of this network provides viscoelastic, or even gel-like properties. The formation of oleogels, which are systems containing mostly oil as the solvent, is a phenomena of interest for various applications ranging from food to cosmetics and pharmaceuticals to paints but also, more recently, for drug delivery and templating structures (2). The addition of specific polymers to the oil phase leads to oleogelation (3). For example, triblock copolymers of the Kraton type are used in cosmetic industry (4). Ethylcellulose is described in the literature for food application (5). Low molecular weight gelators can also be used to gel oils and are often able to gel oils at already very low concentrations of 0.1–1 wt.%. For this type of oleogels, immobilized oils keep the fluidity of the bulk liquid at the molecular level as shown by NMR self-diffusion experiments (6). One of the best known low molecular gelators in cosmetic industry is 12-hydroxystearic acid (7–11). Recently, studies have investigated new oleogelator systems for industrial applications including waxes, ceramides, ethyl cellulose, proteins, and so on (12–15). Moreover, combinations of known oleogelators such as fatty acids and fatty alcohols have also received a renewed interest (16). These two fatty components are both low molecular gelators and they can be used for food, pharmaceutical or cosmetic applications (17). Fifteen years ago, Gandolfo et al. were the first ones to show a synergistic effect for specific weight ratio (R) between fatty alcohol and fatty acid in oleogels (18). The authors showed a clear effect of *R* on the hardness of oleogels for the mixture of stearyl alcohol and stearic acid (18). Two optimums were found for oleogels based on sunflower oil: *R* = 7:3 and *R* = 3:7 (w/w). Recent studies demonstrated that the effect of *R* on textural properties of oleogel was because of the formation of small, platelet-shaped mixed crystals (19). An almost complete crystallization for these two *R* was observed. The parameters associated with a suitable spatial distribution of the crystals inside the oleogel led to an increase of hardness and stability of these oleogels (20). Therefore, the combination of stearyl alcohol and stearic acid is an easy way to obtain an oleogel more stable over time and temperature, and to improve as well as their mechanical properties. These two criteria are important for the commercial applications of these oleogels. For the system based on stearyl alcohol

and stearic acid and by comparing the results previously obtained in different oils, it is possible to see that the synergistic effect varies as a function of the oil (21). For example, only one optimum R = 8:2 was found in rapeseed oil, two optimum R = 3:7 and 7:3 in soybean oil, and two optimum R = 7:3 and 8:2 in canola oil (18). The variation of R as a function of the vegetable oil is still not explained in the literature. Recently, Shaink developed a model based on the Hildebrand equation to better understand these systems and to predict the phase diagram of stearyl alcohol and stearic acid in sunflower oil (22). However, the model does not account for the possible formation of mixed crystals that have been observed experimentally (22). Stearyl alcohol is the only fatty alcohol registered as self-affirmed and generally is recognized as a safe (GRAS) ingredient for oleogelation and therefore, can be used as an oleogelator for the food industry (23–25). For other applications, such as cosmetic or pharmaceutical products, longer alkyl chain fatty acids and fatty alcohols [e.g., behenyl alcohol (BO) and behenic acid (BA)] are more appropriate because of their better gelling properties (1,11,26). In the pioneering work about fatty alcohol/fatty acid oleogelator system, Gandolfo et al. studied the mixture of BO and BA in sunflower oil at 5 wt.% of total structurant (18). There was only a slight effect of the weight ratio for this system in comparison to the stearyl alcohol/stearic acid oleogelator system. Indeed, R seemed to reach a maximum in terms of oleogel hardness around 140 g for R = 7:3 and R = 8:2, but the oleogel hardness was already around 125 g for BO alone (R = 10:0) (18). In order to clarify the effect of R for BO and BA in sunflower oil, we investigated recently this system at higher structurant concentration (10 wt.%) (27). In this previous work, the same trend was obtained as for stearic acid and stearyl alcohol-based oleogels, with a clear enhancement of oleogel properties for specific R (27). One R (7:3) gave oleogels with both the highest hardness and stability in terms of oil-binding capacity. It was defined as optimal. R is a key parameter for oleogels based on BO and BA (27). In the literature, it is known for specific organogelators systems that a change in solvent type can alter the network formation and the resulting oleogel properties such as rheological properties (28–33). The interactions between the oleogelator and the solvent depend largely on the chemical composition and on the polarity of the solvent (28–32). The precise ratio of oleogelator-oleogelator interactions to oleogelator-solvent interactions is known to play a central role in the formation of an oleogel. However, the direct effects of solvent on the oleogel properties are still not well understood. For example, in ethylcellulose oleogels, the rheological properties depend on the polymer–solvent interactions, which are influenced by the molar volume of the solvent linked to the amount of unsaturation in oil (33). In oleogel based on the self-assembly of γ-oryzanol and β-sitosterol, the key parameter is the polarity of the oil (34). Not only the polarity affects oleogelator system, the viscosity of the oil phase which affects the gelation time and the final gel strength (35). In the same way, in oleogels based on monoglycerides, oils with different polarity and viscosity led to different gelation and crystallization behavior (36). One key parameter also is the polar minor components present inside the oils (37,38). For example, polyphenols in extra virgin olive oil decrease the oleogel hardness for ethylcellulose oleogels (38). The fatty acid chain length in the oil was also reported to modify the rheological behavior of oleogels (39). All these previous studies highlighted the complexity to make a clear link between oleogel properties and the nature of the oil used since there seem to be several factors contributing to the changes in gel formation and final gel properties (37). In the case of the BO and BA oleogelator system, the effect of the oil on the mixture and the resulting oleogel properties is not known. However, it is very important to determine this effect in terms of oleogels texture and stability, because

these oleogels have practical applications for the cosmetic industry since they are used to produce oil foams for skin and hair applications (11,40).

In this study, our objective is to fill this gap in knowledge by systematically investigating the effect of the nature of the oil on these systems. Four vegetable oils, which are widely used in cosmetic applications, were studied: olive, apricot, camelina, and rapeseed oil. The oils were not purified to study the real industrial products as they are used in cosmetic industry (11). The new results were compared with the previous results obtained for sunflower oils (27). First of all, the oleogel properties as a function of *R* in terms of structuring potential (hardness, oil loss and gel stability) were determined. Then, structural data was obtained using a multiscale approach. We correlated these observations with the fatty acid chain length composition of the oil.

MATERIALS AND METHODS

MATERIALS

All the ingredients used were of cosmetic grade, and classically incorporated in cosmetic products. BO (1-docosanol), 77.0% purity, impurities include 17.2% arachidyl alcohol (1-icosanol), 5% stearyl alcohol (1-octodecanol), and 0.6% lignoceryl alcohol (1-tetracosanol)), was purchased from BASF (Ludwigshafen, Germany). BA (docosanoic acid), 88.2% purity, impurities include 1% palmitic acid (hexadecanoic acid), 3.8% stearic acid (octadecanoic acid), 5% arachidic acid (eicosanoic acid), and 2% lignoceric acid (tetracosanoic acid), was purchased from KLK OLEO (Emmerich am Rhein, Germany). Rapeseed and olive oils were purchased from HUILERIES DE LAPALISSE (Lapalisse, France). Apricot kernel oil and Camelina oil were purchased from Naturex (Avignon, France). The fatty acid chain length of the vegetable oils was determined by the different suppliers using capillary gas chromatography analysis after alkaline treatment in accordance to the European Official Methods of Analysis (Table I). All the raw materials were used without further purification.

OIL PROPERTIES

The viscosity of the oils was determined using a rheometer (MCR502, Anton Paar GmbH, Graz, Austria) with a double gap geometry. After sample loading, the oils were equilibrated 30 min at 25°C before measurements. The shear rate was increased from 0.1 to $100 \cdot s^{-1}$. All the oils behaved as Newtonian liquids. The surface tension was measured using a Krüss K100 tensiometer under ambient conditions, with a typical temperature of 25°C ± 0.5°C. The surface tension was measured using a du Nouÿ ring method. The density of the vegetable oils was determined with a digital densitometer (DMA-4500, Anton Paar Graz, Austria). All the measurements were performed in triplicate.

SAMPLE PREPARATION

All concentrations are expressed as weight percentage, w/w. The oleogelator concentration was kept constant at 10 wt.% in 90 wt.% of oil. This concentration was chosen in order to form oleogels with sufficient crystals to produce then oil foams by whipping, otherwise not enough crystals were present to stabilize the air bubbles (40). The weight ratio (*R*)

Table I
Fatty Acid Chain Length Composition (%/w) and Degree of Unsaturation of each Carbon of the Oils.

Fatty Acid Chain Length Composition (%w/w)	Sunflower (%)	Olive (%)	Apricot (%)	Camelina (%)	Rapeseed (%)
Myristic acid (C14:0)	0.19	—	—	—	0.05
Total C14	0.19	—	—	—	0.05
Palmitic acid (C16:0)	7.33	11.30	5.34	5.70	4.56
Palmitoleic acid (C16:1)	—	1.00	0.86	—	0.21
Total C16	7.33	12.30	6.20	5.70	4.77
Margaric acid (C17:0)	—	—	—	—	0.07
Heptadecenoic acid (C17:1)	—	—	—	—	0.12
Total C17	—	—	—	—	0.19
Stearic acid (C18:0)	3.81	3.40	1.08	2.70	1.78
Oleic acid (C18:1)	27.23	75.10	60.02	18.80	62.71
Linoleic acid (C18:2)	58.71	7.30	29.10	20.80	18.21
Linolenic acid (C18:3)	0.79	0.70	0.80	30.20	8.60%
Total C18	90.54	86.50	91.00	72.50	91.30%
Arachidic acid (C20:0)	0.28	0.40	—	1.30	0.64%
Eicosenoic acid (C20:1)	0.23	0.30	—	13.00	1.35
Eicosanedienoic acid (C20:2)	—	—	—	—	0.57
Total C20	0.50	0.70	—	14.30	2.56
Behenic acid (C22:0)	—	0.10	—	—	0.38
Erucic acid (C22:1)	0.19	—	—	2.30	0.43
Total C22	0.19	0.10	—	2.30	0.81
Lignoceric acid (C24:0)	7.33	0.10	—	—	0.13
Nervonic acid (C24:1)	—	—	—	—	0.16
Total C24	7.33	0.10	—	—	0.29

was defined as: R = BO/BA. R between the BO and the BA varied from 0:10 to 10:0. In total, seven different formulations were prepared and studied for each oil: 10:0, 8:2, 7:3, 5:5, 3:7, 2:8, and 0:10. All the oleogels were prepared by following the same protocol. First, the oleogelator and the oil were heated together at 85°C in a water bath under magnetic stirring. When the oleogelator was completely dissolved and the samples was limpid and homogenous by naked eyes, the sample was maintained for 5 min at 85°C. All the formulations were liquid and homogeneous at 85°C. After heating, the samples were allowed to cool down quiescently to room temperature without any stirring, resulting in an estimated cooling rate of around 5°C/min. Upon cooling to room temperature, they all formed oleogels, which sustained their own weight when inverted. Each oleogel formula was prepared in triplicate. All the measurements were performed after 24 h of storage at

room temperature. The results of the oleogels based on sunflower oil previously published, have been added to this study in order to compare with the four new oils (27).

DIFFERENTIAL INTERFERENCE CONTRAST (DIC) MICROSCOPY

All the oleogels were analyzed by DIC Microscopy to study the shape and size of the crystals. An AxioImager M2 Microscope (ZEISS, Jena, Germany) connected to a Tri CCD APEX3200 3 × 3Mp Camera (JAI, Denmark) was used. A small amount of gel was placed on a glass microscope slide and covered with a coverslip. Samples were observed at room temperature, using a ×40 magnification and images were digitally captured and analyzed with Archimed software (v.11.3.1, Microvision).

TEXTURE PROFILE ANALYSIS METHOD

The hardness of the oleogels was determined by using the Texture Profile Analysis (TPA) method as described in the literature (18). A TA.XT Plus texture analyzer (Stable Micro Systems Ltd., Godalming, United Kingdom) was used. The measurements were analyzed with Exponent software (v.6.1.5.0, Stable Micro Systems Ltd. Godalming, United Kingdom). Immediately after preparation, molten gels were poured into a 30-mL (height: 40.00 mm, diameter: 53.00 mm) glass tub and cooled at room temperature and stored 24 h before measurements. The experiment was performed with a P/6 cylindrical stainless steel probe (height: 60.00 mm, diameter: 6.00 mm) with a 5 g trigger force. All the oleogels were penetrated once at 2 mm·s^{-1} for 10 mm with a pretest speed at 10 mm·s^{-1}. For each sample, the maximum force was recorded and the average force was calculated for each *R*. The hardness was defined as the maximum force.

OIL LOSS

A centrifuge equipped with temperature control unit (SIGMA 3–30K, Osterode am Harz, Germany) was used to evaluate the ability of the oleogel to hold oil at 25°C. Five gram of an oleogel were placed in a 30-mL centrifuge tube. Before the measurement, the tube was placed in a water bath at 85°C under magnetic stirring until complete melting of the oleogel occurred in order to remove the thermal history. The sample was then maintained for 5 min at 85°C. It was then weighed and stored for 24 h at room temperature to crystallize. All samples were centrifuged three successive times for 30 min at 14,000 rpm at 25°C. The excess liquid oil at the top was removed with a pipette just after each centrifugation step. The sample was weighed to measure the oil loss after three cycles of centrifugation. The percentage of oil loss was calculated by using the equation (1).

$$\%\,\text{oil loss} = 100 \times \frac{w_{\text{before centrifugation}} - w_{\text{after 3 cycles}}}{w_{\text{before centrifugation}}} \tag{3}$$

where, *w*: sample weight.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

To determine the melting properties of oleogels, thermal analysis was performed with a DSC 822^e (Mettler-Toledo, Viroflay, France). A 20-mL·min^{-1} flow of nitrogen was used

to keep an inert atmosphere in the oven of the DSC. The STARe software (v.15.00, Mettler-Toledo, Viroflay, France) was used to identify the onset, the maximum, the offset temperatures and the enthalpy of the peaks, for the melting and the crystallization curves. For all the measurements, 10 to 15 mg of sample were introduced in a 60-µL stainless steel DSC pan (Perkin Helmer) which was hermetically sealed. After loading the sample at 25°C, it was cooled down to 0°C at a speed of 25°C·min^{-1}. Then, after an isothermal period of 15 min to 0°C, each sample was heated and cooled twice from 0 to 80°C at the speed of 5°C·min^{-1}. The heating and cooling steps were separated by a 2-min isothermal step.

SMALL-ANGLE AND WIDE-ANGLE X-RAY SCATTERING

Small-Angle X-ray Scattering (SAXS) and Wide-Angle X-ray Scattering (WAXS) experiments were performed to determine the molecular packing inside the crystals. The measurements were performed with a SAXSpace (Anton Paar, Graz, AUustria. The X-ray source was a copper tube (CuKα1, λ = 1,54 Å) producing radiations with 40 kV and 50 mA. A line collimation with a parallel beam was used and the data were collected on a 2D image plate detector. SAXSDrive software (Anton Paar) was used to collect the data. OptiQuant software (Perkin-Helmer) was used to read the data. SAXStreat software (Anton Paar) was used for data reduction. The sample was introduced in a past cell hermetically sealed at 25°C (thickness: 1 mm, Anton Paar).

STATISTICAL ANALYSIS

Three oleogels were prepared and measured for each oil. All results were expressed as the mean ± standard deviation. The results were compared by one-way analysis of variance and Tukey's test to analyze statistical differences ($p < 0.05$). The analysis was done using PASW Statistics 18 (SPSS Inc., Chicago, IL.

RESULTS

MICROSTRUCTURE OF OLEOGELS AS A FUNCTION OF OILS

To obtain information on the microstructure of oleogels as a function of oils, we determined the size and shape of the crystalline particles contained in each oleogel by using DIC microscopy at 25°C. All the typical micrographs obtained for the seven oleogels from R = 10:0 (pure BO in oil) to R = 0:10 (pure BA in oil) are presented for all the oils in Figure 1. For the two extreme ratios (R = 10:0 and R = 0:10), platelet-shaped crystalline particles were observed whatever the oil used to produce the oleogel. The face of the platelets was oriented spontaneously parallel to the glass slide. The length and the width of the crystalline particles were on the order of magnitude of around 100–300 µm. When the concentration of BO was higher than the concentration of BA, in oleogels with R = 8:2 and 7:3, the appearance and size of the crystals drastically changed. For all the oils tested, the crystalline particles were very small (less than 50 µm in length) with needle-like structures. This change of shape was first described by Blake et al. for plant wax crystals (41). It was confirmed later also on oleogels based on stearyl alcohol/stearic acid system by Blach et al. (20). Same observations was done on oleogels made with pure fatty alcohols by Valoppi et al. (26). The authors have demonstrated, by cryogenic scanning electron microscopy, that the presence of needle-like structures comes from the

orientation of the platelets with their edges facing the glass surface of the microscopy slides (19,20). Thus, it is supposed that platelet-like structures were present for R = 8:2 and 7:3, whatever the oils. When the concentration of BA is increased, which corresponds to R = 5:5, 3:7 and 2:8, the size of the crystals increased (Figure 1). The crystalline

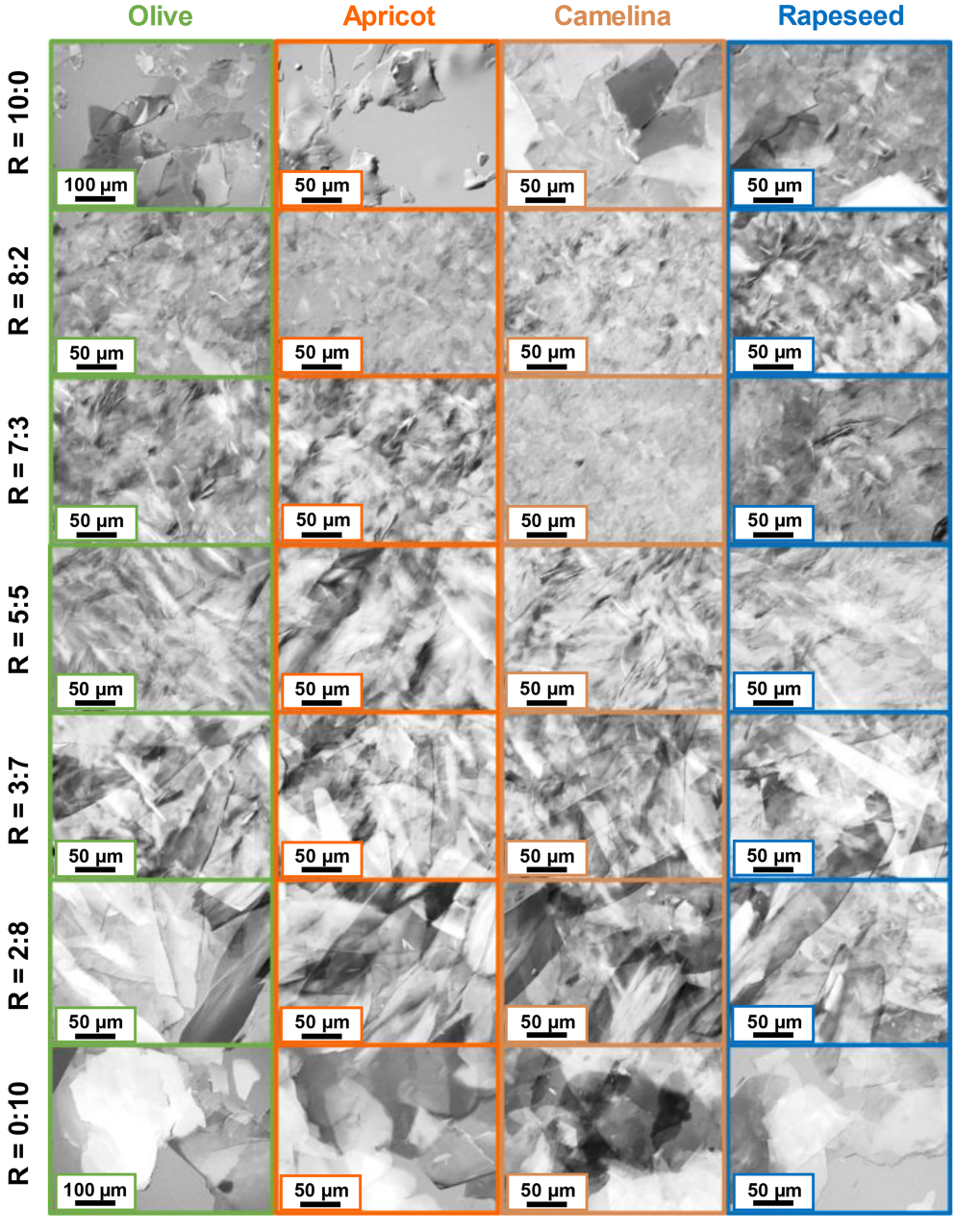


Figure 1. DIC images of oleogels as a function of R between behenyl alcohol: behenic acid (BO:BA) in the four vegetable oils. The scale is indicated on the images.

particles appeared to have a platelet shape. At the microscopic scale, the type of vegetable oil did not give any distinguishable features by DIC microscopy. All the oleogels studied here contained platelet-like crystals but their size varied depending on *R*. For all the vegetable oils tested (camelina, olive, apricot, and rapeseed), the same behavior was observed in terms of crystals size and shape evolution as a function of *R* (Figure 1). These results confirmed the microscopic results previously obtained for sunflower oil (27).

EFFECT OF THE OIL ON OLEOGEL PROPERTIES: HARDNESS AND STABILITY

The stability and mechanical properties of oleogels are important factors in industrial applications. To obtain quantitative information on these two factors, the hardness of all oleogels was evaluated by the TPA method and the so-called oil-binding capacity was determined by measuring the oil loss during centrifugation at high speed at 25°C (Figure 2). The significant different oleogels were determined by the Tukey's test.

In Figure 2A, the average hardness as a function of *R* for all the oils is shown. The lowest hardness was always obtained for *R* = 0:10 with values between 83 ± 12 g and 123 ± 5 g (Supporting Information Table SI.1). BA alone was not a good oleogelator to produce hard gels for any of the vegetable oils. For apricot and rapeseed oils, the highest hardness value was obtained for *R* = 7:3: 323 ± 28 g and 306 ± 38 g, respectively. For olive and camelina oils, the highest hardness value was for *R* = 8:2 (269 ± 25 g and 243 ± 32 g, respectively). The ratio *R* exhibiting the highest hardness varied as a function of the oil as demonstrated by the statistical analysis (Table SI.1)

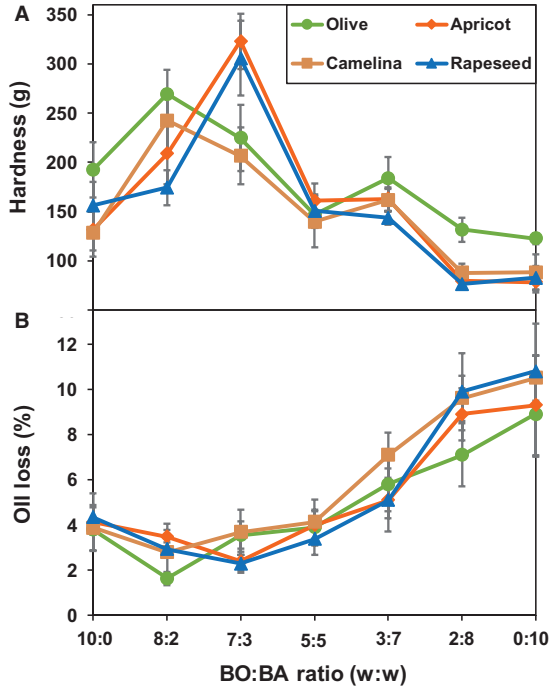


Figure 2. (A) Hardness and (B) oil loss of oleogels as a function of *R* between behenyl alcohol:behenic acid (BO:BA) in various oils: olive (green circle), apricot (red diamond), camelina (brown square), and rapeseed (blue triangle).

In Figure 2B, the oil loss of the oleogels as a function of *R* for the four oils is shown. All the values are presented in the Supporting Information Table SI.2. We observed the same global trend for all oils. The oil loss for pure BO (*R* = 10:0) was around 4%. By adding BA (*R* = 8:2 and *R* = 7:3), a decrease in the oil loss was observed for all the samples. The minimum values of oil loss were obtained for *R* = 8:2 and for *R* = 7:3 for apricot and rapeseed oils. Whereas the minimum values for the same parameter for olive and camelina oil were *R* = 8:2. Then, by increasing the amount of BA from *R* = 5:5 to *R* = 0:10, the oil loss increased for all the oleogel systems. The highest oil loss was reached for *R* = 0:10 corresponding to pure BA in oil.

By combining the results obtained for the hardness of the oleogels and their so-called oil-binding capacity and by applying statistical analysis, we observed two different behaviors (Table SI.1 and SI.2). Apricot and rapeseed oils exhibited an optimal *R* at 7:3 in terms of oleogels properties such as observed in our previous study for sunflower oil, whereas the optimal R appeared for the ratio 8:2 for olive and camelina oils (27). It is important to notice that the maximal values for the hardness and the minimum values for oil loss varied as a function of the oil (Table SI.1 and SI.2). This observation showed that for a given *R* the nature of the oil also had an impact on oleogel properties. We supposed that the polarity, viscosity, density, surface tension, presence of polar minor components in different amount as well as fatty acid chain length composition could explain this result (34–39).

EFFECT OF THE OIL ON THE THERMAL BEHAVIOR OF THE OLEOGELS

Another important parameter for industrial applications is the thermal behavior of the oleogels. In order to determine the effect of the oils on the thermal behavior of the oleogels as a function of *R*, DSC measurements were performed for all the oleogels.

For all the oils, the same melting and crystallization behaviors were observed as function of *R*. The typical DSC curves for camelina oil are presented in Figure SI.1. For all *R* and oils, one major peak was observed during both the crystallization and the melting, except for *R* = 3:7 and *R* = 2:8 showing an additional secondary peak on their profiles at lower temperatures than the main peak (Figure SI.1). We supposed that two different

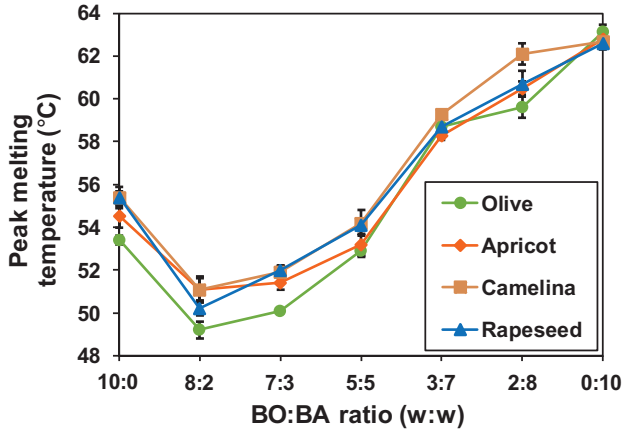


Figure 3. Main melting temperature of oleogels as a function of *R* between behenyl alcohol:behenic acid (BO:BA) in various oils: olive (green circle), apricot (red diamond), camelina (brown square), and rapeseed (blue triangle).

crystalline particles species were present for these ratios with different melting and crystallization temperatures (19,20). The same behavior was observed that has previously been seen for the sunflower oil (27). For all the oleogels, the evolution of the melting peak was plotted as a function of *R* (Figure 3). All the oils exhibited the same evolution as a function of *R* (Table SI.3). For *R* = 10:0, the melting temperature was around 55°C. The lowest melting temperature was reached for *R* = 8:2. By increasing *R*, an increase of the melting temperature was observed and reached a maximal value around 62°C for *R* = 0:10. For the total enthalpy of the endotherm, we observed the same trend for all oleogels: a decrease of the total enthalpy from *R* = 10:0 to *R* = 3:7 and then an increase until *R* = 0:10 (Table SI.3). When we compared these results with those obtained for stearyl alcohol/stearic acid based oleogels, we observed the same trend (42). This variation of enthalpy as a function of *R* was attributed to the formation of mixed crystals in the systems (16). For the thermal behavior of the oleogels, no oil effect was distinguished (Table SI.3). All the oleogels had the same behavior.

EFFECT OF THE OIL ON THE CRYSTAL STRUCTURE

To determine the crystals' nature (pure BO, pure BA, or mixed BO/BA) for each oleogel as a function of both *R* and the nature of the oil, Small and Wide-Angle X-ray scattering (SAXS and WAXS, respectively) measurements were performed at 25°C. From the SAXS regime, information about long spacing linked to chain length, chain tilt and number of chains per layer can be obtained. From the WAXS regime, information related to the short spacing can be obtained corresponding to the lateral packing of the chains. In Figure 4, all the spectra in the SAXS and WAXS regimes are shown. All the *d*-spacings are shown in Table II with the nature of crystalline structure.

In the SAXS regime, for *R* = 10:0 containing only BO, for all the oils, one main peak was detected corresponding to a *d*-spacing of around 57.1 Å and another additional peak with a *d*-spacing of around 48.3 Å (Figure 4A). Each of these peaks was followed by additional higher order reflections peak visible on the spectrum. The presence of these two long *d*-spacings indicated the coexistence of two different packing arrangements as already reported by Valoppi et al. for fatty alcohols in peanut oil (43). Based on the literature, it is supposed that some of BO molecules were crystallized in a double layer structure associated with *d* = 57.1 Å (43). The other BO molecules were organized into a triple layer structure with a *d*-spacing around 100 Å that can be deduced from the position of the second order reflection peak observed at *d* = 48.3 Å (19). In the WAXS region for all the oils, six peaks were detected, which were almost at the same position except a slight shift for the rapeseed oil (Figure 4B). We suppose that these peaks can be ascribed to two polymorphic forms, the β' and γ-form as described for fatty alcohols in peanut oil (43).

For all the oleogels containing only BA (*R* = 0:10), only one main peak followed by its higher order reflections was detected corresponding to a *d*-spacing of 48.3 Å. We suppose that BA molecules were crystallized in a double layer structure associated with *d* = 48.3 Å. Other additional peaks appeared on the SAXS curves coming from some polymorphic structures present inside the oleogels at low concentration. In the WAXS regime, five peaks were detected corresponding to the main crystalline structure present inside the oleogel (Table II). By comparing this result with the literature, we supposed that BA in the oleogels showed only one molecular packing arrangement and crystallized into the most stable C form with a monoclinic unit cell (44).

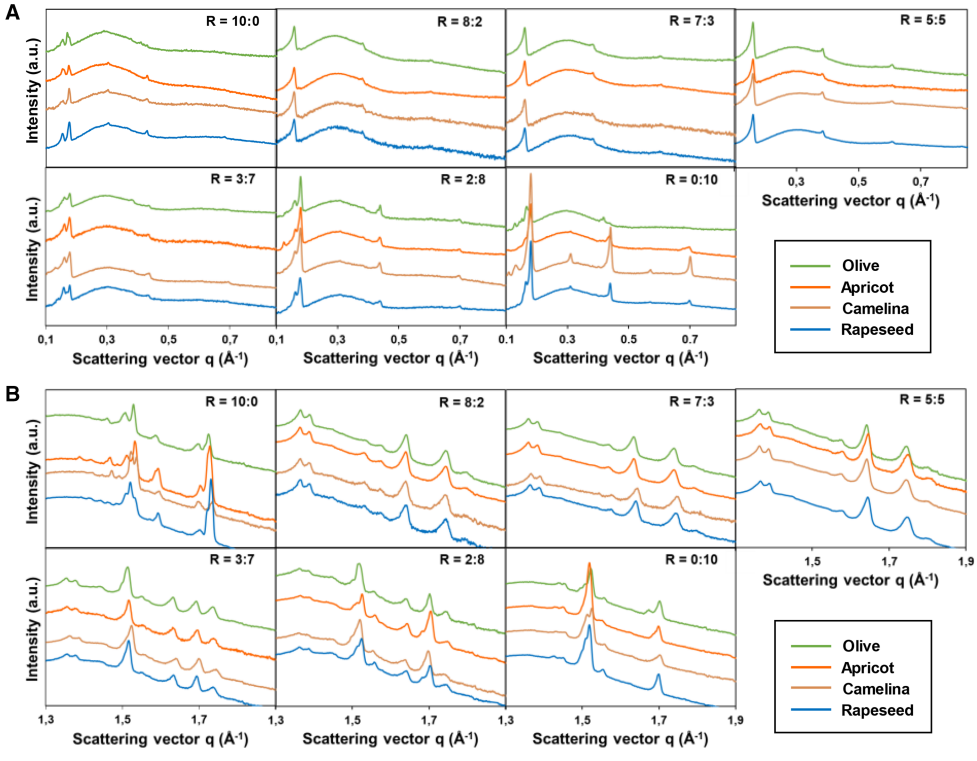


Figure 4. (A) SAXS and (B) WAXS spectra of oleogels with varying ratios of behenyl alcohol:behenic acid (BO:BA), with a total of 10 wt.% oleogelator in various oils: olive, apricot, camelina, and rapeseed. The measurements were carried out at 25°C. The spectra were shifted in intensity for clarity.

For *R* = 8:2, *R* = 7:3, and *R* = 5:5, all the oleogels exhibited the same SAXS and WAXS scattering profiles (Figure 4A and B). In the SAXS regime, only one main peak followed by its higher order reflections was detected. This peak gave a *d*-spacing of 57.1 Å. In the WAXS regime, six peaks were located at the same position whatever the oil used (4.6, 4.5, 4.0, 3.8, 3.6, and 3.5 Å). The *d*-spacing for the SAXS and WAXS regime could not be associated to the *d*-spacings measured for oleogels containing only BO (*R* = 10:0) or only BA (*R* = 0:10). This observation is in line with the results obtained by Blach et al. on oleogel based on stearic acid/stearyl alcohol (20). Therefore, only one type of crystal was present in those systems: mixed crystals of BO and BA. The two components co-crystallized to give only one crystalline structure as already observed in oleogels based on stearyl alcohol/stearic acid (19,20,22).

When the concentration of BA was higher than the concentration of BO (*R* = 3:7 and *R* = 2:8), the scattering spectra were similar for all oils. In the SAXS regime, for both *R* = 3:7 and *R* = 2:8, the peak corresponding to the *d*-spacing of 57.0 Å observed previously for *R* = 8:2, *R* = 7:3 and *R* = 5:5 remained. Mixed crystals were also present for these two ratios. Furthermore, another peak appeared on the spectra associated with a *d*-spacing of 48.3 Å corresponding to the *d*-spacing found for oleogels containing pure BA (*R* = 0:10). These two oleogels (*R* = 3:7 and *R* = 2:8) were then composed of mixed crystals of BO/BA and of pure BA crystals. The WAXS spectra confirmed this

result, since height peaks were identified in the WAXS regime. Five of these peaks corresponded to the ones determined previously for R = 8:2, 7:3, and 5:5 giving the same d-spacings (4.6, 4.5, 4.0, 3.8. and 3.6 Å). Three additional peaks were observed with d-spacings corresponding exactly to the ones obtained for the oleogels containing pure BA crystals (4.3, 4.15, and 3.7 Å). All the d-spacings are presented in Table II. The scattering intensity of the peak corresponding to the pure BA crystals increased from R = 3:7 to R = 2:8, whereas the scattering intensity of the peak corresponding to the mixed crystals decreased. The quantity of mixed crystals decreased in favor of pure BA crystals by increasing R.

The same effect of R was observed in terms of crystalline particles structure, regardless of the oil used to produce them. All the oleogels had the same crystalline structure as a function of R, which explained why all the oleogels exhibited the same thermal behavior by DSC. Mixed crystals between BO and BA were present for three ratios: R = 8:2, R = 7:3, and R = 5:5. The smallest crystalline particles were observed for R = 8:2 and R = 7:3, which correspond to molar ratios of around 2.4 and 4.2. The smallest crystals observed for R = 8:2 and R = 7:3 in the BO:BA system in comparison to the other ratios could come from a decrease in interfacial tension for these specific ratios (18). Indeed, in the literature, the same effect was observed by Gandolfo et al. for oleogels based on the mixed systems stearyl alcohol and stearic acid (18). Monolayers based on stearyl alcohol and stearic acid exhibited a minimum area per molecule leading to a decrease in interfacial tension for molar ratio equal to 3:1 (45). Therefore, Gandolfo et al. supposed that the nucleation rate linked to the interfacial energy increased for specific ratio in oleogels (18,46). This decrease of the interfacial energy could result into a decrease in the average crystal size (18,46). We suppose that in BO/BA system the same behavior could also occur for a molar ratio of 3:1 corresponding to an optimal weight ratio comprised between the weight ratio R = 8:2 and R = 7:3.

We proposed a schematic phase diagram to summarize our DSC and SAXS/WAXS results (Figure 5). For R =8:2, R = 7:3, and R = 5:5, mixed crystals of BO and BA were observed (one crystalline phase). For R = 3:7 and R = 2:8 the mixed crystals were present with pure BA crystals: two crystalline phases. As shown by DSC, the mixed crystals melt before the pure BA crystals for R = 3:7 and R = 2:8. This proposed phase diagram was in accordance with the phase diagram for the binary stearic acid/stearyl alcohol system in oil proposed by Bot and Flöter (16).

OIL PROPERTIES AND LINK WITH OLEOGEL PROPERTIES

From our multiscale approach, we did not observe an effect of the vegetable oil on the oleogel structural properties. The evolution of the microstructure observed by optical microscopy as function of R remained the same whatever the vegetable oils. In the same way, we determined by combining DSC and SAXS/WAXS experiments that the crystalline structure evolution as a function of R was the same for all the oils studied. We only observed an effect of oil on the oleogel physical properties, oleogels hardness, and oil loss. We compared the results described in this study with the previous ones obtained for the same BO/BA oleogelator system in the same conditions in sunflower oil, for which the optimal R was 7:3 (27). The oleogels were classified into two groups based on the optimal R obtained in terms of highest hardness and lowest oil loss during centrifugation process. The first group composed of sunflower, apricot, and rapeseed oils exhibited an optimal

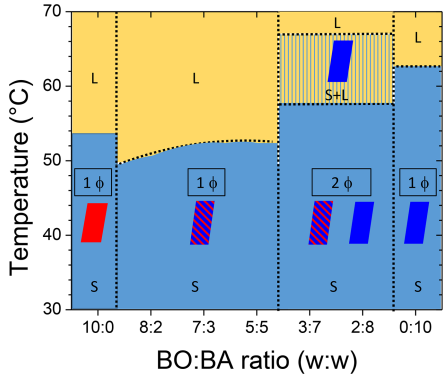


Figure 5. Schematic phase diagram for BO/BA oleogelator system in oil. One phase region is indicated by 1ϕ, and two phases region is indicated by 2ϕ. S corresponds to solid and L to liquid. Platelets crystals are drawn: pure BO in red, mixed BO/BA crystals in red and blue dashed, and pure BA in blue.

ratio at R = 7:3. The second group composed of olive and camelina oils exhibited an optimal ratio at 8:2.

To understand what is the link between the vegetable oils inside the two groups, we determined three oil properties at 25°C: surface tension, viscosity, and density (Table III). Sunflower, olive, apricot, and camelina oils had surface tension around 33 ± 0.7 $mN{\cdot}m^{-1}$. Only rapeseed oil exhibited a slightly higher surface tension around 35.4 $mN{\cdot}m^{-1}$ and was statistically different from the other vegetable oils (Table III). Therefore, in terms of the surface tension, a link was not found between the two groups found previously. For the viscosity, sunflower oil had the highest viscosity around 70.2 mPa.s. Camelina oil had the lowest one around 52.7 mPa.s. Olive and apricot oil had close values around 62.5 and 60.8 mPa.s, respectively. Rapeseed oil had a value around 56.1 mPa.s. Again, we found no link between the two groups obtained previously and the viscosity of the different oils. Moreover, all the vegetable oils had the same density from statistical analysis around 0.9 showing that the density was not the key parameter giving rise to the different oleogel properties as a function of the oil. In contrary to previous study on oleogels based on γ-oryzanol and β-sitosterol, which have shown that the viscosity of the oil phase affected the final gel strength of the oleogels, no link was observed in the case of the BO/BA system (35).

A key parameter described in the literature to affect the oleogel properties is the percentage of unsaturated fatty acids in oils (33). We compared the fatty acid chain unsaturation composition for all vegetable oils with oleogel properties (Table I). We observed that for the first group formed by the sunflower, apricot and rapeseed oils, there was no link between the oil compositions in terms of unsaturation of fatty acid. For example, sunflower oils contained 27.2% of oleic acid and 58,7% of linoleic acid, whereas apricot oil contained 60% of oleic acid and 29.1% of linoleic acid. In the same way, for sunflower oil with optimal R = 7:3, the total percentage of unsaturation in oils was around 86.9 wt.% and it was close to 86 wt.% for camelina oil with an optimal ratio for R = 8:2.

Another parameter already mentioned in the literature which could play a role on the oleogel properties was the fatty acid chain length composition of the vegetable oil (39). We compared the fatty acid chain length composition of vegetable oils with the oleogel properties (Table I). We observed that for the first group formed by the sunflower, apricot,

Table II

SAXS and WAXS Average Value for *d*-Spacings Measured for Oleogels in Olive, Apricot, Camelina, or Rapeseed Oils with Various Ratios of Behenyl Alcohol:Behenic Acid (BO:BA): (a) 10:0, (b) 8:2, (c) 7:3, (d) 5:5, (e) 3:7, (f) 2:8, (g) 0:10. The Nature of Crystals Deduced from SAXS/WAXS Results is Indicated: Pure BO, Pure BA, or Mixed Crystals BO/BA.

***R* = 10:0**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1, 48.3	4.3, 4.1, 4.1, 3.9, 3.7, 3.6	
Olive	57.1, 52.4	4.3, 4.2, 4.1, 3.9, 3.7, 3.6	
Apricot	57.1, 48.3	4.3, 4.2, 4.1, 3.9, 3.7, 3.6	Pure BO
Camelina	57.1, 48.3	4.3, 4.2, 4.1, 3.9, 3.7, 3.6	
Rapeseed	57.1, 49.1	4.3, 4.2, 4.1, 3.9, 3.7, 3.6	

***R* = 8:2**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Olive	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Apricot	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	Mixed BO/BA
Camelina	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Rapeseed	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	

***R* = 7:3**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Olive	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Apricot	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	Mixed BO/BA
Camelina	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Rapeseed	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	

***R* = 5:5**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Olive	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Apricot	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	Mixed BO/BA
Camelina	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	
Rapeseed	57.1	4.6, 4.5, 4.0, 3.8, 3.6, 3.5	

***R* = 3:7**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	
Olive	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	
Apricot	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	Mixed BO/BA
Camelina	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	+ pure BA
Rapeseed	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	

***R* = 2:8**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	
Olive	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	
Apricot	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	Mixed BO/BA
Camelina	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	+ pure BA
Rapeseed	57.1, 48.3	4.6, 4.5, 4.3, 4.1, 4.0, 3.8, 3.7, 3.6	

***R* = 0:10**

Oleogel	SAXS *d*-spacing (Å)	WAXS *d*-spacing (Å)	Type of crystals
Sunflower	48.3	4.4, 4.3, 4.1, 4.0, 3.7	
Olive	52.4, 48.3	4.4, 4.3, 4.1, 4.0, 3.7	
Apricot	48.3	4.4, 4.3, 4.1, 4.0, 3.7	
Camelina	69.8, 48.3	4.4, 4.3, 4.1, 4.0, 3.7	Pure BA
Rapeseed	52.4 , 48.3	4.4, 4.3, 4.1, 4.0, 3.7	

Table III
Surface Tension, Viscosity, and Density of the Vegetable Oils at 25°C. The Values Are the Average of Three Measurements. The Small Letters a to d Indicate Groups of Statistical Differences According to Tukey's test ($p < 0.1$)

	Sunflower	Olive	Apricot	Camelina	Rapeseed
Surface tension ($mN{\cdot}m^{-1}$)	32.5 ± 0.7[a]	33.7 ± 0.3[a]	33.5 ± 0.5[a]	33.1 ± 0.6[a]	35.4 ± 0.2[b]
Viscosity at 25°C (mPa.s)	70.2 ± 0.2[a]	62.5 ± 0.7[b]	60.8 ± 0.8[b]	52.7 ± 0.5[c]	56.1 ± 0.3[d]
Density 25°C ($g.cm^3$)	0.92 ± 0.01[a]	0.91 ± 0.01[a]	0.91± 0.01[a]	0.92± 0.01[a]	0.90 ± 0.01[a]

and rapeseed oils, they all had a percentage of fatty acid with 18 carbons (C18) equal or higher than 90%. For the second group formed by the olive and camelina oil, they both had a percentage of fatty acid with C18 lower than 90%: 86.5% for olive oil and 72.5% for camelina oil. The key parameter leading to two different optimal *R* in terms of oleogel properties seems to be directly linked to the percentage of fatty acid chain with a length of 18 carbons. Our findings are in agreement with previous results showing that the fatty acid chain length in the oil can modify the rheological behavior of oleogels (39). It is important to emphasize that in our study we used commercial cosmetic grade oils without further purification steps, since our goal was to study cosmetic industrial oleogel systems, which can be used directly to produce oil foams from hair and skin treatments (40). However, based on the recent literature on the role of minor polar compounds in different oleogel systems, it appears that to confirm our results on the effect of fatty acid chain length on the oleogel properties it would be necessary in a future study to remove these polar compounds for each oil (34). By removing these polar compounds, it would be possible to understand their effect on the BO/BA oleogelator system. For example, in the oleogelator system based on γ-oryzanol and β-sitosterol, Scharfe et al. demonstrated a strong impact of polar minor compounds on the self-assembled structures and on the resulting oleogel properties (34). In the same way, polyphenols, which are minor polar compounds of extra virgin olive oil, decreased the oleogel hardness for ethylcellulose oleogels (38). Moreover, to better understand the links between the nature of the oils and the effect of *R*, it would be necessary to study a wider range of oils in terms of polarity, viscosity, density, fatty acid chain length, and so on.

CONCLUSIONS

In this study, we showed that *R* influenced the oleogel properties (i.e., hardness and oil-binding capacity) for all the vegetable oils tested. The optimum *R* was different depending on the type of oil: *R* =7:3 or *R* = 8:2. However, these two *R* were around the specific 3:1 molar ratio, for which a minimum area per molecule could occur leading to a decrease of the interfacial energy and into a decrease in the average crystal size. Therefore, at the optimum *R*, small crystals were formed as a co-crystal form of BO and BA. The small crystals might contribute to the enhancement of the oleogel hardness and oil-binding capacity.

We classified the oils into two groups. The first one composed of sunflower, apricot, and rapeseed oils, which exhibited an optimal weight ratio at *R* = 7:3. The second one composed of olive and camelina oils, which exhibited an optimal weight ratio at 8:2. We highlighted that the key parameter leading to two different optimal *R* in terms of oleogel

properties was the fatty acid chain length composition of the oil, more precisely the percentage of fatty acid chain with a length of 18 carbons. Above 90% of fatty acid chain with a length of 18 carbons in the oil, the optimal ratio was 7:3, below 90% the optimal ratio was 8:2. In the literature, the fatty acid chain length in the oil is described as possible parameter modifying the orientation of the platelet crystals inside the liquid oil giving rise to different rheological properties (39). The different orientation of the platelet crystals formed by the oleogelator system could lead to a modification of the distribution of the crystalline material inside the oil, resulting in different rheological properties as a function of the oil. To verify this hypothesis, complementary measurements would be necessary in order to use the model developed by Miyazaki and Marangoni based on the cellular solid approach of Gibson and Ashby (47,48). This model was successfully applied to different oleogels to explain the relationship between the mechanical properties of oleogels and their microstructure (20,48).

As perspective also to continue this work, it would be interesting to study the effect of minor polar compounds of each oil by removing them as described recently by Scharfe et al. (37). By removing these polar compounds, it would be possible to understand their effect on the BO/BA oleogelator system in terms of oleogel structures and properties (38).

Our results obtained with cosmetic grade raw materials have practical applications for the cosmetic industry since it shows how to obtain the best oleogels in terms of texture and stability, and then to use them to produce oil foams (11,40). As a function of the fatty acid chain length composition of the oil, the ratio between BO and BA can be adjusted in order to tune the oleogel properties.

ACKNOWLEDGMENTS

This research was supported by L'OREAL R&I.

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