Characterization of ethyl cellulose and beeswax oleogels and their suitability as fat replacers in healthier lipid pâtés development

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ABSTRACT

Ethyl cellulose (EC-OG) and beeswax (W-OG) oleogels were prepared using a lipid mixture of olive, linseed, and fish oils with an optimal fatty acid composition from a health standpoint, and designed to have solid-lipid functionality for use as animal fat replacers for pork liver pâtés. W-OG exhibited a more rigid, ordered, brittle structure that melted at temperatures of ≈ 55 °C, whereas EC-OG was softer and more deformable, with a high degree of conformational flexibility and high thermal stability. Pork liver pâtés were successfully formulated by total or partial substitution of backfat by EC-OG or W-OG, and the products obtained possessed an optimal fatty acid profile from a health standpoint (high PUFA/SFA ratio and low n-6/n-3 ratio). Neither technological behavior (emulsion stability) nor physicochemical properties (color and texture) were significantly affected by reformulation, as compared to a control sample in which pork backfat was used. Reformulation significantly increased lipid oxidation, which was especially evident for EC-OG at the highest substitution level during refrigerated storage. Beeswax oleogel had no significant effect on any of the sensory parameters evaluated, whereas ethyl cellulose oleogel had a negative effect that was

25 directly related to substitution level. However, all samples were rated near the scale
26 “neutral.” The ingredients developed are good candidates for development of healthier
27 pork liver pâtés, based on their composition and technological and sensory properties.
28 Health claims may be made according to EU regulations because they are a *source of α -*
29 *linolenic acid* and a *source of omega-3 fatty acids*.

30 **Keywords**

31 Healthier oil combination; functional foods; polyunsaturated fatty acids; meat product;
32 organogel

33

1. INTRODUCTION

Pâtés are traditional cooked products that are commonly consumed in many countries. They are generally prepared from meat, including pork backfat as a fat source, and many of them also include liver, among other additives and spices. These products may present some negative health concerns related not only to their high fat content, which may be up to 40%, but also to their fatty acid composition, which is typical of animal fat. This means that they present a low PUFA/SFA ratio (≈ 0.28) and a high n-6/n-3 ratio ($\approx 7-12$) (Delgado-Pando, Cofrades, Rodríguez Salas, & Jiménez Colmenero, 2011; Martin, Ruiz, Kivikari, & Puolanne, 2008). Health recommendations suggest that the PUFA/SFA ratio should be above 0.4 (Wood et al., 2004), whereas the n-6/n-3 ratio should be no higher than 5 (Deng, Padilla-Zakour, Zhao, & Tao, 2015).

Increasing consumer concern about the diet-health relationship has prompted the development of healthier meat products based on their lipid composition, with reformulation standing out as the most important strategy to accomplish this objective (Jimenez-Colmenero et al., 2015; Muguerza, Gimeno, Ansorena, & Astiasarán, 2004). In order to reduce fat or cholesterol contents or improve the fatty acid profile, reformulation generally entails replacement of the animal fat present in traditional products with another lipid more in line with health recommendations. In this connection, vegetable or marine oils have been employed as the fat source for the development of meat products such as patties, sausages, frankfurters, or pâtés (Barbut, Wood, & Marangoni, 2016a; Delgado-Pando, Celada, Sánchez-Muniz, Jiménez-Colmenero, & Olmedilla-Alonso, 2014; Domínguez, Pateiro, Sichert Munekata, Bastianello Campagnol, & Lorenzo, 2017; Salcedo-Sandoval, Cofrades, Ruiz-Capillas, Carballo, & Jiménez-Colmenero, 2015). Delgado-Pando, Cofrades, Ruiz Capillas, Solas, and Jiménez-Colmenero (2010) studied the fatty acid composition of three

different oil sources (olive, linseed, fish) with potential for use as fat replacers. They found that olive oil contained 15% SFA, 45% MUFA (with almost 72% of oleic acid) and 9% PUFA, whereas linseed oil contained low levels of SFA (10%) and high levels of PUFA (68%), n-3 fatty acids being the most representative ones. Fish oil, which is a well known source of n-3 PUFA, contained 35% PUFA, the most abundant being EPA (18.7%) and DHA (12%). According to this work, the mixture of these oils in the proportion 44.39% olive–37.87% linseed–17.74% fish stands out as a lipid source for development of healthier meat products because it provides a better approximation to an optimal lipid profile from a health standpoint than the use of individual lipids. Frankfurters and pâtés formulated with this oil mixture have proven their effectiveness in reducing LDL-cholesterol and oxidized LDL levels when consumed by volunteers at increased cardiovascular risk (Delgado-Pando et al., 2014).

Replacing solid animal fat with vegetable or marine liquid lipids is a considerable technical challenge, as the functionality and texture of the lipid phase present in meat products has a major effect on several product properties. It is well documented that meat products formulated with alternative lipid materials have different physicochemical characteristics from those of their traditional counterparts, resulting in a negative effect on the desired quality attributes of the reformulated products (Grasso, Brunton, Lyng, Lalor, & Monahan, 2014; Muguerza et al., 2004). Specifically, pâtés with an improved fatty acid profile have been developed by the addition of vegetable or marine oils, although they generally presented lower consistency and emulsion stability (Domínguez et al., 2017; Martin et al., 2008). A possible way to overcome this problem is to structure the liquid lipids into soft matter structures with solid-lipid functionality in line with that of animal fats (Jimenez-Colmenero et al., 2015; Patel & Dewettinck, 2016). The literature regarding the application of lipid structured materials in meat

product development is scarce; however, the amount of research has grown considerably in recent years. Products such as various kind of sausages, frankfurters, patties, and pâtés have been developed (Barbut et al., 2016a; Barbut, Wood, & Marangoni, 2016b; Jimenez-Colmenero et al., 2015; Kouzounis, Lazaridou, & Katsanidis, 2017; Salcedo-Sandoval et al., 2015).

Among organogelation systems for meat product development, ethyl cellulose gels stand out because of the possibility of textural modifications to resemble the properties of traditional products (Barbut et al., 2016a; Zetzl, Marangoni, & Barbut, 2012). The properties of oleogels are strongly dependent on processing and compositional parameters such as processing time and temperature; heating/cooling rates; ethyl cellulose molecular weight and concentration; the presence, type, and concentration of plasticizer; and the degree of oil unsaturation (Davidovich-Pinhas, Barbut, & Marangoni, 2015; Gravelle, Barbut, & Marangoni, 2012; Gravelle, Barbut, Quinton, & Marangoni, 2014). From this it is deduced that studies must be performed for each lipid type to be structured. With regard to meat product development, Barbut et al. (2016a) formulated frankfurters in which beef fat was replaced with ethyl cellulose oleogels made from canola oil, obtaining similar hardness values in both samples. However, there are no reports on the formulation of pâtés using ethyl cellulose oleogels as animal fat substitutes.

Another way to develop oleogels with potential applications in food product development is the use of waxes, including carnauba wax, candelilla wax, rice bran wax, and beeswax, among others (Martins, Cerqueira, Fasolin, Cunha, & Vicente, 2016; Mert & Demirkesen, 2016; Ögütçü & Yilmaz, 2014; Patel, Babaahmadi, Lesaffer, & Dewettinck, 2015; Yilmaz & Ögütçü, 2014). In this regard, good results have been

achieved in the development of low-saturated-fat hazelnut fillings, margarine-like products, chocolate paste, cakes and cookies (Doan et al., 2016; Hwang, Singh, & Lee, 2016; Mert & Demirkesen, 2016; Patel et al., 2014; Yilmaz & Ölütcü, 2015). An interesting paper has recently been published as a preliminary approach for the application of wax oleogels in meat product development (Moghtadaei, Soltanizadeh, & Goli, 2018). In that work, oleogels were prepared from sesame oil and beeswax and employed as partial animal fat replacers in the formulation of beef burgers. The authors found a reduction in cooking loss and fat absorption, although cooking shrinkage and lipid oxidation increased significantly. This proves the potential of wax oleogels as fat substitutes for meat product development and emphasizes the need to continue research on this topic to improve product quality.

The objectives of the present work were to develop and characterize animal fat replacers by structuring a healthier lipid mixture (olive, linseed, fish) with two different organogelators (ethyl cellulose and beeswax), and to study their suitability to be employed as functional ingredients for pork liver pâtés, taking into consideration their physicochemical, sensory, and nutritional attributes.

2. MATERIALS AND METHODS

2.1 Materials and reagents

Lipid sources were: olive oil (Carbonell Virgen Extra, SOS Cuétara SA, Madrid, Spain), linseed oil (Natursoy SL, Alimentos Ecológicos, Castellterçol, Spain), and fish oil (Omevital 18/12 TG Gold) from Cognis GmbH, Illertissen, Germany. Ethyl cellulose with a viscosity of 10 cP (EC-N10AqualonTM) was kindly donated by Ashland (Netherlands). Beeswax was acquired from Manuel Riesgo SA (Madrid, Spain). Sorbitan monostearate was from Sigma-Aldrich (Madrid, Spain). Pork liver, meat, and

backfat were acquired at local markets. Spices added to pâtés were from Frutarom savory solutions (Germany). All other reagents were of analytical grade and acquired from Sigma-Aldrich (Madrid, Spain).

2.2 Oleogel development

Ethyl cellulose oleogel was prepared according to the method described by Barbut et al. (2016a) with slight modifications. An olive oil–linseed oil–fish oil mixture (44.39%–37.87%–17.74%) was prepared and placed in Pyrex beakers together with ethyl cellulose (11 g/100 g oleogel) and sorbitan monostearate (3.67 g/100 g oleogel), and subsequently heated in a thermostatic bath set at 170 °C under constant stirring using an overhead mechanical stirrer (model AGV-8, Bunsen, Madrid, Spain). The mixture temperature was controlled with a Daq pro 5300 model thermocouple (Omega, Madrid, Spain), and it was left to stand for 10 min once a temperature of 160 °C had been reached. The sample was then sonicated using a Qsonica ultrasound probe at 100 Hz amplitude for 2 consecutive cycles of 1 min each at 30 s intervals. The resulting solution was immediately poured into plastic containers (35 mm wide by 65 mm high), kept for 60 minutes at room temperature in darkness, and then stored at 3 ± 1 °C overnight until analysis. This oleogel is referred to as EC-OG throughout this text.

For the beeswax oleogel preparation, the oil mixture (same composition as described above) and beeswax (11 g/100 g oleogel) were heated under constant stirring in a Thermomix® food processor (TM-31 Vorwerk, Wuppertal, Germany) at 65 °C, speed 3, until complete melting and mixing. The resulting solution was then immediately poured into plastic containers (35 mm wide by 65 mm high) and stored at 3 ± 1 °C after standing for 30 min at room temperature in darkness. Analyses were performed after overnight storage. This sample is referred to as W-OG throughout this text.

2.3 Oleogel characterization

2.3.1 Small amplitude oscillatory strain (SAOS) measurements

SAOS testing was performed using a Kinexus pro rheometer (Malvern Instruments Ltd., Worcestershire, UK). Measurements were taken using parallel-plate geometry (20 mm diameter and 1 mm gap). Samples were allowed to stand for 5 min before analysis to ensure both thermal and mechanical equilibrium at the time of measurement. Temperature was controlled to within 0.1 °C by Peltier elements in the lower plates kept at 25 °C, except when temperature sweeps were carried out. To determine the linear viscoelastic (LVE) region, strain amplitude sweeps were run at 1 Hz by varying the shear strain (γ) of the input signal from 0.01 and 0.001 up to 10% for EC-OG and W-OG, respectively. Frequency sweeps were run subjecting the samples to stress that varied harmonically with time at variable frequencies from 0.01 to 10 Hz and $\gamma = 0.01\%$ for EC-OG and 0.001% for W-OG, respectively. Temperature sweeps were performed from 25 to 80 °C at a linear heating rate (5 °C/min) with the oscillation frequency set at 1 Hz. For both frequency and temperature sweeps, the strain amplitude was set at 0.1 and 0.01%, within the LVE range for EC-OG and W-OG, respectively.

2.3.2 Instrumental color

It was determined with a 3500d spectrophotometer (Konica Minolta Business Technologies, Tokyo, Japan) set to D₆₅ illuminant/10° observer, based on the CIELAB color system. Results were expressed using the polar coordinates L*C*h°, where L* is lightness, C* is the chromaticity, and h° is the hue angle. Simple transformations were used to convert a* and b* coordinates to C* and h° chromatic parameters (Gómez-Estaca, Calvo, Sánchez-Faure, Montero, & Gómez-Guillén, 2015). Ten readings were taken per sample.

2.3.3 Lipid oxidation

TBARS were determined according to the method of Maqsood and Benjakul (2010) with modifications. One gram of finely comminuted oleogel was dispersed with 3 mL of 0.26% butylhydroxytoluene (BHT) by sonication (Qsonica sonicator equipped with a microtip) at 75 Hz for 5 s; the test tube containing the sample was immersed in an ice bath to avoid heating. Afterwards, 8 mL of TBARS reagent (15% trichloroacetic acid, 0.375% thiobarbituric acid, 0.25% hydrochloric acid) was added, and the mixture was vortexed and sonicated again (75 Hz, 5 s). Test tubes were placed in a water bath set at 100 °C for 15 min and then immediately placed in an ice-water bath to cool down. Afterwards, 4 mL of 4M ammonium sulfate and 4 mL of hexane were added sequentially and vigorously vortexed for 30 s. The lower phase was collected after centrifugation in a Heraeus Multifuge 3L centrifuge (DJB Labcare Ltd., Buckinghamshire, England) set at 5000 rpm/10 °C/30 min, and the absorbance at 532 nm was measured in a Shimadzu UV-1800 spectrophotometer (Shimadzu Inc., Kyoto, Japan). Results were expressed as mg malonaldehyde (MDA)/Kg oil.

2.3.4 Attenuated Total Reflectance (ATR)-FTIR spectroscopy

Measurements of oleogel samples were taken at room temperature using a PerkinElmer Spectrum™ 400 spectrometer (PerkinElmer Inc., Madrid) in mid-IR mode, equipped with an ATR (attenuated total reflectance) sampling device containing a diamond/ZnSe crystal. Spectra were acquired with Spectrum software version 6.3.2. Approximately 25 mg of sample was placed directly on the surface of the ATR crystal and lightly pressed with a flat-tip plunger. Spectra were scanned in the 4000–650 cm⁻¹ wave number range with a scan speed of 0.20 cm/s and 8 accumulations at a resolution of 4 cm⁻¹. Nine measurements of each sample were taken. Three sum spectra were then analyzed for

each type of oleogel. A background spectrum was scanned under the same instrumental conditions before each series of measurements. The frequency (cm^{-1}) and half-bandwidth of the $\nu_{\text{as}}\text{CH}_2$ ($\sim 2923 \text{ cm}^{-1}$) and $\nu_{\text{s}}\text{CH}_2$ ($\sim 2854 \text{ cm}^{-1}$) bands were measured (Grams/AI version 9.1, Thermo Electron Corporation, Waltham, MA).

2.4 Pâté development

Five pâtés with a reduced fat content of 15% were formulated (Table S1). Samples were a control batch with pork backfat as the principal fat source (C); WPR and WTR, in which pork backfat was partially or totally substituted by beeswax oleogel; and EPR and ETR, in which pork backfat was partially or totally substituted by ethyl cellulose oleogel. The ingredients were sequentially milled and mixed in a Thermomix® food processor (TM-31 Vorwerk, Wuppertal, Germany) at velocity position 4, in the following order: milled meat (4 min), liver (2 min), backfat or oleogel (4 min), and additives previously dissolved in water (1 min). Finally, the mixture was homogenized at velocity 7 until a uniform batter was obtained. The total processing time was ≈ 12 min. The batters were poured in ≈ 40 g aliquots onto plastic containers 35 mm in diameter and 50 mm in height, and then immersed in a thermostatic bath set at 85°C for ≈ 25 min (5 min at 80°C in the thermal center), the product temperature being controlled with a thermocouple (Daq Pro 5300, Fourier Systems). Samples were cooled in ice and stored in the refrigerator ($3 \pm 1^\circ\text{C}$) until analysis.

2.5 Pâté characterization

Emulsion stability, proximate composition, pH, color, texture, fatty acid analysis, and sensory analysis were determined within the first 2 days after preparation, whereas lipid oxidation was monitored after 7, 30, and 60 days of chilled storage ($3 \pm 1^\circ\text{C}$).

Emulsion stability was determined (in quadruplicate) as the fluid losses during cooking (Delgado-Pando et al., 2011). The containers containing the sample were opened after the heat treatment and left to stand upside down for 30 min to release the exudate onto a plate that had previously been weighed. Water and fat losses were determined after heating the total fluid release for 16 h at 105 °C. Total fluid release (TFR), water loss (WL), and fat loss (FL) were determined gravimetrically and expressed as % of initial sample weight. Proximate composition (protein, fat, moisture, and ash content) was determined according to official methods (AOAC, 2005). Instrumental color was determined as described for the oleogels (section 2.3.2). The pH was determined on an 827 Metrohm pH-meter (Metrohm AG, Switzerland) at room temperature on homogenates of pâtés in water in a ratio of 1:10 (w/v). Four determinations were performed for each sample.

For texture analysis, six replications of a penetration test were performed in a TA-XTplus Texture Analyzer (Stable Micro Systems Ltd., Godalming, UK) equipped with a 50 N load cell. A 12 mm diameter flat probe was used, which penetrated 10 mm into the sample placed in the cylindrical-shaped container (35 mm in diameter and 30 mm high) at a speed of 0.8 mm/s. Tests were performed on the samples at room temperature immediately after refrigeration at 3 °C. The parameters obtained from the corresponding force–distance curves were penetration force (N) at 10 mm and gel strength (N mm), defined as the area below the force–distance curve (Delgado-Pando, Cofrades, Ruiz-Capillas, Triki, & Jiménez-Colmenero, 2012b).

Fatty acid profile was determined according to the method of Lee, Tweed, Kim, and Scollan (2012). Ten mg of freeze-dried sample was derivatized into fatty acid methyl esters (FAMES) in triplicate, using 0.5 M sodium methoxide in anhydrous methanol and

251 acetyl chloride in anhydrous methanol. FAMES were extracted with 4 mL of hexane and
252 used for GC analysis (1 μ L). The fatty acid profile was determined in an Agilent 7820A
253 gas chromatograph with FID detector. Separation was performed in an Agilent HP-23
254 column (60 m, 0.25 mm i.d., 0.25 μ m film thickness, ref. 19091H-136) with split
255 injection (40:1) and helium at a constant flow of 1.2 mL/min. Detector temperature was
256 set at 260 °C and injector temperature at 250 °C. Identification was done by comparing
257 retention times with a standard of 37 fatty acids (SupelcoTM 37 FAME Mix 47885-U,
258 USA). The internal standard C13:0 was used for quantification, which was added to the
259 sample in the non-methylated state before methylation. Results were expressed as mg
260 fatty acid/g oil.

261 Lipid oxidation was determined by TBARS according to the method of Delgado-Pando,
262 Cofrades, Ruiz-Capillas, Triki, and Jiménez-Colmenero (2012a). For this purpose, 4 g
263 aliquots of each sample were placed in centrifuge tubes, and 1 mL of distilled water and
264 10 mL of 10% trichloroacetic acid were added, after which the mixture was
265 homogenized with a vortex stirrer for 30 s. Then 5 mL of 20 mM 2-thiobarbituric acid
266 was added and the mixture was stirred again for 30 s. Each tube was centrifuged for 5
267 min at 2600 g (Heraeus Multifuge 3 L-R, DJB Labcare Ltd., Buckinghamshire, UK),
268 and the supernatant was collected and kept in darkness for 20 h at 20 ± 2 °C. The
269 absorbance at 532 nm was measured in a Shimadzu UV/VIS 1203 spectrophotometer,
270 and results were expressed as mg malonaldehyde (MDA)/Kg, based on a standard curve
271 prepared from 1,1,3,3-tetraethoxypropane in advance.

272 A hedonic sensory analysis was performed by an untrained panel (29 women, 11 men)
273 selected from ICTAN-CSIC staff with the sole requirement of being consumers of pâté,
274 in two independent sessions. An amount of ≈ 5 g of each pâté was spread on rusks and

presented to the panelists, who were instructed to rinse their mouth with bread and water between samples. Odor, color, texture, and overall acceptability were evaluated on a 10-point scale, 0 being considered as “dislike strongly” and 10 as “like strongly.” Means and standard deviations of the ratings for each attribute were calculated.

2.6 Statistical analysis

Statistical tests were performed using the SPSS® computer program (SPSS Statistical Software, Inc., Chicago, IL, USA). One-way and two-way analyses of variance (ANOVA) were conducted. Differences between pairs of means were assessed on the basis of confidence intervals using the Tukey-b test. The level of significance was $p \leq 0.05$.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization of oleogels

General appearance, dynamic viscoelastic properties, and color

Irrespective of the method of organogelation, smooth, yellowish, self-standing, homogeneous gels were obtained, indicating that this form of oil structuring gave rise to plastic fat which retained solid-like properties, an essential aspect for use as a substitute for animal fat. Small amplitude oscillatory strain (SAOS) measurements showed that both oleogels behaved as solid-like materials, as elastic stresses were greater than viscous stresses throughout the LVE range (Table 1). However, the two oleogel systems presented different characteristics, as beeswax gels showed significantly higher and lower values ($p < 0.05$) of complex modulus (G^*) and $\gamma_{\max}$, respectively, than those of ethyl cellulose (Table 1). This indicates that beeswax produced denser but less deformable gels than those produced with ethyl cellulose. On the other hand, both gels

showed values of $\tan \delta < 1$ but > 0.1 (Table 1), reflecting a weak gel character. Moreover, $\tan \delta$ was significantly lower in W-OG than in EC-OG, so the ratio of energy dissipated to energy stored was higher in EC-OG than in W-OG. These results indicate that the beeswax molecule seems to reinforce the oleogel matrix, increasing the crosslink density in the oil system and making more rigid, stronger but less deformable oleogels as compared with ethyl cellulose. This is due to the different chemical composition of the two gelators, leading to different gelation mechanisms and, consequently, different conformational structures. It is already well known that the structure of EC is a polymer network held together by physical bonds, mainly hydrogen bonds (Gravelle & Marangoni, 2018), while in the case of beeswax the fatty acids and triglycerides assemble into a crystal by van der Waals interactions, making a particle network (Martins et al., 2016). Gelation requires the creation of a continuous network, often achieved by crystal cross-linking or entanglement, trapping the mobile phase (Cerqueira et al., 2017). A less bulky conformation, as in the case of beeswax, allows the approach of molecules that can interact more closely with their neighbors through short-range interactions, leading to stronger, elastic structures (Cerqueira et al., 2017; Toro-Vazquez et al., 2007). Therefore the chemical nature of beeswax produces a structure with greater crosslink density, enabling a larger volume of the mobile oil phase to become trapped as compared to ethyl cellulose.

The mechanical oleogel spectra obtained from the frequency sweeps are shown in Figure 2. In both cases, storage moduli (G') were larger than viscous moduli (G'') irrespective of frequency, indicating again that both organogels behaved as solid-like materials. While G' moduli proved to be practically frequency-independent, G'' increased slightly at low frequencies (0.01–0.1 Hz), mainly in the W-OG samples, again reflecting the weak gel character seen in the strain amplitude sweep (Lopes da Silva &

Rao, 2007). Moreover, the differences between the two viscoelastic moduli were less than one order of magnitude in both organogels, although in the case of W-OG both moduli were greater than those of EC-OG, which means that more deformation energy can be stored, and at the same time more energy can be lost during shear. These two effects are compatible, indicating that the network formed in the W-OG samples is rigid and at the same time more sensitive to shear (Herranz, Tovar, Borderias, & Moreno, 2013). This result could also indicate that, to some extent, this type of network could be easily damaged.

To shed light on the stability of the oleogels in response to thermal treatment, the thermomechanical profiles of the two oleogels were studied in the LVE range (Figure 3). Changes in G' (indicator of gel formation) and $\tan \delta$ (indicator of network stability) with increasing temperature (from 25 to 80 °C) were monitored (Chen & Huang, 2008). In the case of EC-OG there was a continuous slight decrease in G' as temperature rose (Figure 3A), reflecting partial disruption of the network by heating, mainly due to the rupture of physical interactions, mostly hydrogen bonds (Davidovich-Pinhas et al., 2015). Those authors also found a certain degree of gel weakening, with G' decreasing as temperature increased. This behavior was corroborated by the changes in $\tan \delta$, which increased slightly up to 50 °C and then remained constant up to 80 °C (Figure 4B). In any case, the values of $\tan \delta$ were always between 1 and 0.1 indicating the solid-like character and good stability of the bonds that formed the networks. Therefore, EC-OG withstands high temperatures quite well. In contrast, the G' (Figure 3C) and $\tan \delta$ (Figure 4D) profiles of W-OG were very different. G' decreased slightly up to 52 °C and immediately afterwards decreased sharply until 60 °C, showing an important rupture of the network (G' values around 0 kPa). These results are in agreement with the

melting temperature (54.2 ± 0.1 °C) obtained by DSC measurement (data not shown), and with the observations found by Martins et al. (2016), who reported a pronounced decrease in G' and G'' moduli in the range between 45 and 55 °C in beeswax organogels. They associated this marked decrease with complete melting of the gelator network in the organogel. This complete loss of structure after 52 °C reflects the “brittle” nature of this network, which can break up easily because of the chemical composition of beeswax, as reported in the stress and frequency sweep sections. Therefore, W-OG produced rigid but brittle networks, making them less temperature stable.

With regard to optical properties, the objective measure of color showed that the hue angle (h°) was between the first and second quadrants, that is, between yellow and green, with no significant differences between the two oleogels (Table 1). Hence, the differences between the two samples must be attributed mainly to luminosity (L^*) and chromaticity (C^*), the W-OG sample being more luminous and featuring a more intense yellow color than EC-OG ($p \leq 0.05$).

Lipid oxidation

As ethyl cellulose and wax oleogel manufacturing processes involve the application of thermal treatments, the evaluation of lipid oxidation is very interesting, especially in view of the use of highly unsaturated oils, as in the present work. The initial oxidation level of the oil mixture was 0.177 ± 0.023 mg MDA/Kg oil. After overnight storage (3 ± 1 °C), both oleogel systems showed significantly ($p \leq 0.05$) higher TBARS values (0.524 ± 0.007 mg MDA/Kg oil and 0.340 ± 0.042 mg MDA/Kg oil for EC-OG and W-OG, respectively) than the oil mixture, indicating oxidation of lipids, mainly as a consequence of the oleogel manufacturing process. This is especially true for EC-OG,

which attained higher TBARS values, and should be attributed to the high processing temperatures needed to unfold ethyl cellulose for gel formation (Gravelle et al., 2012), in contrast to W-OG, which is produced at 65 °C, a temperature high enough to ensure effective wax melting and mixing with the oil. Furthermore, the constant stirring during oleogel preparation may have also contributed to the lipid oxidation observed in the two samples, resulting from the incorporation of greater amounts of air.

In spite of the importance of lipid oxidation for the quality of oleogels, especially for ethyl cellulose ones because of the high processing temperatures applied, there is very little literature on this topic. Gravelle et al. (2012) reported the progressive accumulation of lipid oxidation products (hydroperoxides and TBARS) when canola oil was heated to 140 °C during a 120 min experiment. They found that holding heating times beyond 20 min resulted in an accumulation of ≈ 10 meq hydroperoxides/Kg oil, which, according to the authors, is the upper limit for oil to be considered “fresh.” On the basis of those results the authors stated that a processing time of 15–20 min would be optimum for ethyl cellulose unfolding and mixing with the oil while limiting lipid oxidation.

Attenuated Total Reflectance (ATR)-FTIR spectroscopy

ATR-FTIR spectra of EC-OG and W-OG in the 2960–2830 cm^{-1} region at 0 days are shown in Figure 4. This infrared region is dominated by two strong bands, resulting from the asymmetric ($\nu_{\text{as}}\text{CH}_2$) and symmetric ($\nu_{\text{s}}\text{CH}_2$) stretching vibrations of the acyl CH_2 groups, respectively (Casal & Mantsch, 1984; Herrero, Carmona, Pintado, Jiménez-Colmenero, & Ruíz-Capillas, 2011). The increase in frequency and/or the broadening (increase of half-bandwidth) of these bands are mainly attributable to a decrease in the conformational order of the lipid acyl chains and to an increase in their

dynamics. Although non-significant changes were observed in the half-bandwidth of these bands, a significantly lower frequency was detected in W-OG, which can be attributed to a greater ordering, probably due to closer packing of the lipid acyl chains (Casal & Mantsch, 1984). The frequency of about 2920 cm^{-1} in the case of W-OG seems to be more characteristic of conformationally highly ordered acyl chains, as found in solid-like hydrocarbons, whereas the frequency values of EC-OG (approx. 2924 cm^{-1}) could be more characteristic of conformationally disordered acyl chains (Casal & Mantsch, 1984). A weak band at around 3473 cm^{-1} could also be observed in the EC-OG spectra, which was not significantly noticeable in the W-OG spectra (Figure 4B). This band has been attributed to OH stretching vibrations, which are related to intramolecular or intermolecular hydrogen bonding between polysaccharides (Fayaz et al., 2017; Yilmaz & Ögütçü, 2014). The absence of a well-resolved band in this spectral region ($3450\text{--}3550\text{ cm}^{-1}$) has also been described by other authors in other beeswax oleogels, mainly related to physical interaction between the components (Fayaz et al., 2017; Yilmaz & Ögütçü, 2014). With regard to these spectroscopic results, EC-OG appeared to exhibit more disordered acyl chains related to intra- or intermolecular hydrogen bonding within the polymer chains, while W-OG showed more packing of lipid acyl chains related to physical interactions between oleogel components. These structural characteristics could be related to the rheological properties found for these oleogels because in EC-OG there was a partial disruption caused by heating of the network, mainly due to the rupture of weak interactions (non-covalent crosslinks), such as hydrogen bonds. However, W-OG showed rigid and denser but brittle networks.

3.2 Suitability of oleogels as fat substitutes for healthier pork liver pâtés

Proximate composition, pH, and fatty acid profile

The proximate composition of the various samples is consistent with the formulation and target composition. Generally, no differences ($p>0.05$) in moisture, protein, fat, and ash contents were found among the pâtés (Table 2). Only animal fat was present in the control sample (C), whereas in the other samples, where pork backfat was partially replaced (WPR and EPR) or totally replaced (WTR and ETR) by oleogel, the lipid fraction also contained vegetable and fish oils (with a constant lower amount of fat of meat and liver origin). The pH values of the pâtés ranged between 6.5 and 6.7 (Table 2), similar to those found for similar meat products (Delgado-Pando et al., 2011). Although the replacement of animal fat by oleogels increased ($p\leq 0.05$) pH, these variations are of limited importance.

The main differences in fatty acid content among the pâtés was due to the levels of substitution of pork backfat by oleogels. As no differences ($p>0.05$) were found for the same pork backfat substitution level (partial or total) irrespective of the organogelator (EC and W), the fatty acid composition results (Table 4) are presented as the mean of WPR and EPR (for partial substitution) and of WTR and ETR (for total substitution). This is consistent with the fact that in each case the samples were formulated with the same amount and type of lipid material (Table S1) and the final products had similar ($p>0.05$) fat contents (Table 2).

In the control sample, MUFA had the highest content (6.61 mg/g) of fatty acid, followed by SFA and PUFA (5.81 and 1.48 mg/g, respectively), oleic acid being the most abundant fatty acid (Table 3). These results are consistent with the composition of the pork fat present in the sample. Replacing the pork backfat with oleogel produced significant changes in the fatty acid profile (Table 3). These changes were consistent with the proportion of fat replacement established and the composition of the oils

present in the oleogels. In this regard, as the proportion of animal fat replacement by oleogel increased, the SFA content decreased ($p \leq 0.05$) and PUFA increased ($p \leq 0.05$), while MUFA experienced fewer quantity variations. Generally, these changes are consistent with the strategy of product reformulation for healthier lipid development using a similar combination of oils (Delgado-Pando et al., 2011).

An interesting aspect is the presence of n-3 PUFA. In comparison with the control pâté (C), the samples formulated with oleogels contained higher ($p \leq 0.05$) proportions of α -linolenic (C18:3n-3), EPA (C20:5n3), and DHA (C22:5n3) fatty acids, with total n-3 PUFA levels almost 30 times higher than in the all-pork-fat sample. The long-chain n-3 PUFA contents (EPA+DHA) of the reformulated pâtés were 370 and 610 mg/100 g for partial and total pork backfat substitution pâtés, respectively (Table 3), which means similar amounts to those reported in other n-3 enriched pâtés with a similar combination of oils (Delgado-Pando et al., 2011). The consumption of n-3 PUFA has been linked to reduced risk of cardiovascular disease, which in the case of long-chain n-3 PUFA may also imply a reduced risk of certain types of cancer, diabetes mellitus, inflammatory disease, multiple sclerosis, and clinical depression (Garg, Wood, Singh, & Moughan, 2006; McAfee et al., 2010). In proportion to the level of replacement of pork fat by a healthier lipid combination (present in oleogels) an increase ($p \leq 0.05$) in the PUFA/SFA ratio was observed, while the opposite effect ($p \leq 0.05$) was produced in the case of the n-6/n-3 ratio (Table 3). These values are lower than those reported in various types of reformulated liver pâté (Delgado-Pando et al., 2011) and much lower than those normally found in this type of product (D'Arrigo et al., 2004; Echarte, Conchillo, Ansorena, & Astiasarán, 2004; Estévez, Ventanas, Cava, & Puolanne, 2005). The reduction of these ratios has various health implications because it has been linked to a reduced risk of various pathologies, including diabetes, cancer, CVD, etc. Additionally,

according to European regulations (Regulation 432/2012), health claims may be made on pâté with added oleogels, as they are a *source of α -linolenic acid* and a *source of omega-3 fatty acids*. No oleogels have been formulated that contain a healthy fatty acid composition, so this study presents a high degree of innovation from this viewpoint because of its impact on the product.

Emulsion stability, color, and texture

Cooking losses in the various products ranged between 2.6 and 5.7%, mainly caused by water loss (>85%), with little or no effect due to the presence of oleogels (Table 2). This has two main aspects. On the one hand, the excellent water- and fat-binding properties of these meat matrixes irrespective of the formulation, and on the other the good behavior of the two types of oleogel when used in strategies of (partial or total) substitution of animal fat. This is consistent with the fact that the reformulated products (healthier lipid composition) had a similar composition (Table 2) and that the different nature of the lipid materials present in the control sample and in the reformulated samples had a very limited effect on emulsion stability. Although it has been pointed out that the level of unsaturation of lipid materials may condition emulsion stability, in general, little or no effect was observed on meat emulsion stability owing to the presence of different oils (Delgado-Pando et al., 2011). Other authors (Barbut et al., 2016a, 2016b; Moghtadaei et al., 2018) reported that the presence of oleogels decreased cooking losses in meat products; this behavior has been attributed to the larger fat globules in the meat batter associated with the presence of organogel, which probably helps to reduce liquid loss from this system (Barbut et al., 2016a).

Generally, the color parameters were scarcely affected by the pâté formulation (Table 2), as a decrease ($p \leq 0.05$) in L^* only occurred in the case of total replacement of pork

backfat by the oleogel formulated with ethyl cellulose (EC-OG). Although the two types of oleogel had different color characteristics (Table 1), their dilution within the meat matrix made these characteristics unimportant with regard to the product. Reports concerning the consequences of these reformulation processes on the L^* parameter vary. Whereas L^* decreased in minced products such as pork breakfast sausage and beef burger as a result of the presence of EC or beeswax oleogels (Barbut et al., 2016b; Moghtadaei et al., 2018), in comminuted meat products such as frankfurter it was not influenced (Barbut et al., 2016a) or even increased (Kouzounis et al., 2017). Frankfurter made with sunflower oleogels had higher lightness values than the all-animal-fat control (Panagiotopoulou, Moschakis, & Katsanidis, 2016a).

Comparing the control sample (C) with the reformulated products, it can be seen that the partial or total replacement of pork backfat by the two types of oleogels did not affect ($p>0.05$) the penetration force; on the other hand, although there were some significant variations in gel strength resulting from the effect of the formulation, they were of little quantitative importance (Table 2). This means that, in spite of the differences in the rheological properties of the two oleogels (Table 1, discussed earlier), these differences did not appear when the oleogels were incorporated into the meat matrix and underwent the (mechanical and thermal) processes required for preparation of the product. There are very few studies on the effect of the presence of oleogels on the texture of meat products, and the results reported differ. In various meat products it has been seen that softer structures are formed when animal fat (from beef or pork) is replaced by oleogels. This was the case with frankfurters (Barbut et al., 2016a) and pork breakfast sausages (Barbut et al., 2016b), using various proportions (8, 12, or 14%) of ethyl cellulose organogels, or frankfurters prepared with sunflower oil oleogel structured with monoglycerides and phytosterols (Kouzounis et al., 2017). On the other

hand, it has also been reported that replacement of animal fats with a beeswax oleogel (sesame oil) led to a reduction in the hardness of raw burgers, although this behavior was less evident in cooked burgers (Moghtadaei et al., 2018). It has also been found that a canola oil EC oleogel produced a frankfurter with similar textural characteristics to those of a beef fat control product (Zetzl et al., 2012). The results found in our study show the suitability, with regard to texture, of these new healthier lipid materials to be used to replace animal fat.

Lipid oxidation

TBARS values were affected ($p \leq 0.05$) by formulation and storage (Table 4). Initially all the samples presented relatively low values, and the product that had the highest oxidation values was the one that contained the highest proportion of the oleogel formulated with ethyl cellulose (ETR pâté). With the exception of the ETR sample, lipid oxidation was low throughout storage, well below the reported minimum needed to detect objectionable flavors in processed meat products (Delgado-Pando et al., 2012a). Generally, TBARS values increased significantly ($p \leq 0.05$) during storage, although in some cases (partial substitution of pork backfat by the two oleogels, WPR and EPR samples) there was a slight decrease after 30 days of storage. The existence of this behavior – a peak followed by a decline in the TBARS value – in various meat products, including healthier lipid pâté, and the factors to which it is attributable have been reported previously (Delgado-Pando et al., 2012a). The ETR product, reformulated with total substitution of pork backfat by the ethyl cellulose oleogel (EC-OG), presented a different behavior: not only did it have the highest initial levels of oxidation but also the levels increased progressively and markedly during storage (Table 4). This behavior is consistent with the high level of oxidation of this oleogel, associated with the

preparation conditions, as discussed earlier. These results suggest that, although its presence in the meat product favors oxidation, the extent to which this happens varies with the level of incorporation: it is relatively not very marked when the oleogel is used in smaller proportions (partial substitution), whereas the susceptibility of the system to lipid oxidation increases extraordinarily when there is total substitution of pork backfat by this oleogel. The various factors (prooxidant and antioxidant activities) that may influence lipid oxidation behavior in these products have been described by Delgado-Pando et al. (2012a). An increase in lipid oxidation owing to the presence of beeswax oleogels in beef burger (Moghtadaei et al., 2018) has been reported. However, it has also been found that replacement of pork fat by sunflower oil in the form of an oleogel, structured with γ -oryzanol and phytosterols (Panagiotopoulou et al., 2016a) or monoglycerides and phytosterols (Kouzounis et al., 2017), did not have an adverse effect on lipid oxidation in frankfurters. To the best of our knowledge, there is no previous report on the effect of animal fat substitution by EC oleogels in pork liver pâtés.

Sensory analysis

Sensory evaluation of the pâtés was affected ($p \leq 0.05$) by the formulation (Table 5), although the effect was associated more with the type of oleogel (EC-OG or W-OG) employed than with the level of substitution of pork backfat. With respect to the control sample (C), the reformulation based on the use of W-OG did not affect ($p > 0.05$) any of the sensory parameters evaluated. However, the use of ethyl cellulose oleogels caused decreases in the color, taste, and overall acceptability values of the pâtés, the magnitude and significance of which varied with the quantity present in the pâté. Significant decreases only took place in color and overall acceptability in the case of total

substitution of pork backfat by this oleogel (ETR sample), and in taste irrespective of the level of substitution. The results of the sensory color evaluation of the pâté are consistent with those found for the determination of lightness (Table 2). With regard to texture, no significant differences in acceptability as an effect of the formulation were found ($p>0.05$), and these results coincide with the instrumental measurement of texture. It is interesting to note that for all the reformulated products the attributes evaluated scored above-average values on the scale (above the “neutral” point on the scale). Therefore, similarly to what was reported by other authors (Kouzounis et al., 2017; Panagiotopoulou, Moschakis, & Katsanidis, 2016b) in the case of frankfurters, the pâtés formulated seemed to have no objectionable attributes, as judged by the panelists. Sensory panelists could not detect any difference in texture and color of burgers formulated with sesame oil oleogel (Moghtadaei et al., 2018). Barbut et al. (2016a) reported differences in sensory attributes (such as hardness and juiciness) of frankfurter owing to the presence of EC oleogels, but they also indicated that oleogels can be formulated to tailor the textural and sensory characteristics of emulsion-type meat products.

4. CONCLUSION

An oil mixture with an optimal fatty acid composition from a nutritional standpoint was successfully structured into solid-like structures using ethyl cellulose or beeswax as oleogelators. Ethyl cellulose produced more deformable and cohesive gels with greater temperature stability than their beeswax counterparts, which resulted in rigid and brittle gels. These specific rheological properties could be related to the particular lipid structure, which caused the oleogels containing ethyl cellulose to exhibit more intra-/intermolecular hydrogen bonding while those with beeswax exhibited more packing of

the oleogel lipid acyl chains associated with physical interactions between their components. The oil-structuring manufacturing process induced lipid oxidation, especially in ethyl cellulose oleogel. Pork liver pâtés were successfully formulated by total or partial substitution of backfat by the ingredients developed, and the products obtained possessed an optimal fatty acid profile from a health standpoint (high PUFA/SFA ratio and low n-6/n-3 ratio). The technological behavior of the reformulated products was not significantly affected as compared to the control sample, and the same was also true for product characteristics such as color and texture. Lipid oxidation increased significantly as a result of fat substitution, but oxidation values were low except for the highest fat substitution by ethyl cellulose oleogel, especially during refrigerated storage. From the sensory acceptability tests it can be concluded that fat substitution by beeswax oleogel had no significant effects on any of the parameters evaluated, whereas substitution by ethyl cellulose had a negative effect that was directly related to the substitution level. However, all the samples were rated near “neutral” on the scale.

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Supplementary Material

Table S1. Formulation of the various pâtés (g /100 g). C: control sample formulated with pork backfat; WPR: partial substitution of pork backfat by beeswax oleogel; WTR: total substitution of pork backfat by beeswax oleogel; EPR: partial substitution of pork

613 backfat by ethyl cellulose oleogel; ETR: total substitution of pork backfat by ethyl
614 cellulose oleogel.

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HIGHLIGHTS

- Oleogel (OG) manufacturing process induced lipid oxidation
- Pâtés formulated with partial or total substitution of pork backfat by OGs
- Emulsion stability, texture, and color of pâtés not affected by fat replacement
- Reformulation increased lipid oxidation but it was low, except for ethyl cellulose
- Beeswax oleogel-added pâtés had sensory attributes similar to control one

Figure 1. Strain sweeps of ethyl cellulose (EC-OG) and beeswax (W-OG) oleogels. Open symbols G'' , closed symbols G' . $T = 25\text{ }^{\circ}\text{C}$.

Figure 2. Mechanical spectrum data of ethyl cellulose (EC-OG) and beeswax (W-OG) oleogels. Open symbols G'' , closed symbols G' . $T = 25\text{ }^{\circ}\text{C}$.

Figure 3. Thermal profiles from 15 to 80 °C of wax (W-OG; a, b) and ethyl cellulose (EC-OG; c, d) oleogels.

Figure 4. ATR-FTIR spectra in the 2960–2830 cm^{-1} (A) and 3650–3300 cm^{-1} (B) regions of ethyl cellulose (EC-OG) and beeswax (W-OG) oleogels.

Table 1. Optical and viscoelastic properties of ethyl cellulose (EC-OG) and beeswax (W-OG) oleogels.

		EC-OG	W-OG
Optical properties	Lightness (L*)	25.9 ± 0.1a	36.7 ± 0.3b
	Hue angle (h°)	92.6 ± 2.0a	94.0 ± 0.0a
	Chromaticity (C*)	2.7 ± 0.1a	21.0 ± 0.1b
Viscoelastic properties (limit values of LVE range)	$\sigma_{\max}$ (Pa)	149 ± 4a	217 ± 15b
	$\gamma_{\max}$ (%)	0.398 ± 0.0002b	0.031 ± 0.0003a
	G* (kPa)	37.4 ± 1.3a	694 ± 15.2b
	tan δ	0.228 ± 0.0003b	0.199 ± 0.015a

Different letters in the same row (a, b) indicate differences as a function of organogelation system ($p \leq 0.05$).

Table 2. Some physicochemical and technological properties of the pork liver pâtés developed: proximate composition (fat, moisture, protein, ash), pH, emulsion stability (total fluid loss, TFL; water loss, WL; lipid loss, LS), optical properties (lightness, L*; hue, h°; chromaticity, C*), and texture (penetration force, gel strength). Batch denominations as in Table 1.

		C	WPR	WTR	EPR	ETR
Proximate composition	Fat (%)	14.4 ± 0.3a	15.4 ± 1.2a	16.2 ± 0.1a	15.9 ± 0.2a	15.7 ± 0.0a
	Moisture (%)	66.1 ± 0.1a	65.3 ± 0.2b	65.2 ± 0.1b	65.1 ± 0.3b	65.4 ± 0.1b
	Protein (%)	15.0 ± 2.3a	13.4 ± 0.4a	13.1 ± 0.1a	13.4 ± 0.1a	13.7 ± 0.3a
	Ash (%)	3.3 ± 0.0a	3.3 ± 0.0a	3.3 ± 0.0a	3.2 ± 0.1a	3.3 ± 0.0a
pH		6.49 ± 0.01a	6.55 ± 0.02b	6.58 ± 0.01b	6.66 ± 0.02c	6.72 ± 0.04d
Emulsion stability	TFL (%)	3.19 ± 0.86a	4.78 ± 0.30ab	2.56 ± 0.81a	5.72 ± 1.67b	2.66 ± 1.03a
	WL (%)	2.76 ± 0.87a	4.26 ± 0.27ab	2.28 ± 0.73a	5.01 ± 1.46b	2.34 ± 0.94a
	FL (%)	0.42 ± 0.08a	0.52 ± 0.04ab	0.29 ± 0.08a	0.71 ± 0.20b	0.32 ± 0.1a
Optical properties	L*	61.5 ± 1.4b	61.7 ± 0.7b	61.6 ± 0.9b	62.0 ± 0.9b	58.3 ± 1.1a
	h°	70.1 ± 1.9a	71.1 ± 2.1a	73.9 ± 3.4a	70.3 ± 2.8a	70.6 ± 2.7a
	C*	14.9 ± 0.5a	15.0 ± 0.5a	15.4 ± 0.4a	15.1 ± 0.5a	14.8 ± 0.4a
Texture	Penetration force (N)	0.94 ± 0.1a	0.99 ± 0.05a	0.91 ± 0.20a	1.22 ± 0.23a	1.28 ± 0.12a
	Gel strength (N mm)	7.18 ± 0.7ab	7.32 ± 0.99ab	6.14 ± 0.69a	8.71 ± 1.56b	8.76 ± 1.06b

Different letters in the same row (a, b, c, d) indicate significant differences (p≤0.05) as a function of formulation.

Table 3. Fatty acid composition (mg fatty acid/g pâté) of the pork liver pâtés developed.

	C	Partial substitution	Total substitution
C16:0	3.46 ± 0.05a	2.44 ± 0.02b	1.63 ± 0.03c
C18:0	2.02 ± 0.03a	1.42 ± 0.07b	0.95 ± 0.08c
ΣSFA	5.81 ± 0.08a	4.20 ± 0.06b	2.92 ± 0.03c
C18:1n9c	5.78 ± 0.08a	5.83 ± 0.07a	5.65 ± 0.23a
ΣMUFA	6.61 ± 0.09b	6.51 ± 0.08b	6.19 ± 0.25a
C18:2n6c	1.14 ± 0.03a	1.32 ± 0.02b	1.32 ± 0.04b
C18:3n3	0.07 ± 0.00a	1.40 ± 0.04b	2.31 ± 0.09c
C20:5n3	0.01 ± 0.00a	0.22 ± 0.01b	0.36 ± 0.01c
C22:6n3	0.01 ± 0.00a	0.15 ± 0.00b	0.25 ± 0.01c
ΣPUFA	1.48 ± 0.04a	3.35 ± 0.06b	4.43 ± 0.15c
ΣPUFA/ΣSFA	0.25 ± 0.01a	0.80 ± 0.03b	1.52 ± 0.05c
ΣPUFAn-3	0.10 ± 0.00a	1.68 ± 0.05b	2.75 ± 0.11c
ΣPUFAn-6	0.23 ± 0.01a	0.30 ± 0.01b	0.28 ± 0.01b
ΣPUFAn-6/ΣPUFAn-3	2.37 ± 0.07c	0.18 ± 0.00b	0.10 ± 0.00a

As no significant differences ($p>0.05$) were found as a function of organogelator (ethyl cellulose or beeswax), results are expressed as the mean ± standard deviation of WPR and EPR (partial substitution) and WTR and ETR (total substitution).

Table 4. TBARS (mg MDA/Kg) of the pork liver pâtés developed, during refrigerated storage (3 ± 1 °C). Batch denominations as in Table 1.

	Day 7	Day 30	Day 60
C	$0.108 \pm 0.001a/x$	$0.156 \pm 0.003a/y$	$0.184 \pm 0.006a/z$
WPR	$0.129 \pm 0.020ab/x$	$0.326 \pm 0.063b/y$	$0.215 \pm 0.019a/x$
WTR	$0.149 \pm 0.003b/x$	$0.304 \pm 0.062b/y$	$0.420 \pm 0.034a/z$
EPR	$0.109 \pm 0.009a/x$	$0.388 \pm 0.125b/y$	$0.240 \pm 0.048a/z$
ETR	$0.198 \pm 0.005c/x$	$1.473 \pm 0.181c/y$	$2.512 \pm 0.226b/z$

Different letters in the same column (a, b, c) indicate significant differences ($p \leq 0.05$) as a function of formulation. Different letters in the same row (x, y, z) indicate significant differences as a function of storage time.

Table 5. Sensory analysis of the pork liver pâtés developed. Batch denominations as in Table 1.

	Color	Taste	Texture	Overall acceptability
C	$7.8 \pm 1.9b$	$7.4 \pm 2.1b$	$7.0 \pm 2.5a$	$7.5 \pm 2.2b$
WPR	$7.15 \pm 1.6ab$	$6.4 \pm 1.8ab$	$6.4 \pm 2.3a$	$6.4 \pm 2.0ab$
WTR	$7.2 \pm 1.8ab$	$6.0 \pm 2.2ab$	$6.8 \pm 1.9a$	$6.3 \pm 2.2ab$
EPR	$7.2 \pm 1.6ab$	$5.7 \pm 2.2a$	$6.5 \pm 2.2a$	$6.0 \pm 2.3ab$
ETR	$6.3 \pm 2.2a$	$5.5 \pm 2.4a$	$6.0 \pm 2.2a$	$5.3 \pm 2.4a$

Table S1. Formulation of the various pâtés (g /100 g). C: control sample formulated with pork backfat; WPR: partial substitution of pork backfat by beeswax oleogel; WTR: total substitution of pork backfat by beeswax oleogel; EPR: partial substitution of pork backfat by ethyl cellulose oleogel; ETR: total substitution of pork backfat by ethyl cellulose oleogel.

	Meat	Liver	Pork backfat	Oleogel	Water	Other*
C	19.2	33	14.6	0	27.4	5.8
WPR	19.2	33	6	9	27	5.8
WTR	19.2	33	0	15	27	5.8
EPR	19.2	33	6	9	27	5.8
ETR	19.2	33	0	15	27	5.8

*Other ingredients were: 2% milk powder, 2% NaCl, 1% sodium caseinate, 0.5% sodium tripolyphosphate, 0.3% seasoning.