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Article

Microstructure, Physical Properties and Oxidative Stability of Olive Oil Oleogels Composed of Sunflower Wax and Monoglycerides

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Abstract: The utilization of natural waxes to form oleogels has emerged as a new and efficient technique for structuring liquid edible oil into solid-like structures for diverse food applications. The objective of this study was to investigate the interaction between sunflower wax (SW) and monoglycerides (MGs) in olive oil oleogels and to assess their physical characteristics and storage stability. To achieve this, pure SW and a combination of SW with MGs in a 1:1 ratio were examined within a total concentration range of 6-12% w/w. The formed oleogels were characterized based on their microstructure, melting and crystallization properties, textural characteristics, and oxidative stability during storage. All the oleogels were shelf-stable, and as the concentration increased, the hardness of the oleogels also increased. The crystals of SW oleogels were long needle-like, while the combination of SW and MGs led to the formation of crystal aggregates and rosette-like crystals. The differential scanning calorimetry and FTIR showed that the addition of MGs led to different crystal structures. The oxidation results revealed that oleogels had low peroxide and TBARS values throughout the 28-day storage. These results provide useful insights about the utilization of SW and MGs oleogels for potential applications in the food industry.

Keywords: oleogels; sunflower wax; lipid structuring; crystallization; FTIR; storage

1. Introduction

Solid fats are essential components of food products, as they significantly contribute to their technological and organoleptic characteristics, aligning with consumers' preferences for food structure, aroma, and taste [1,2]. Nevertheless, their use in food products should be limited in accordance with the recommendations of the World Health Organization [3] and the Food and Agriculture Organization of the United Nations (FAO) [4], which advocate for reducing the intake of saturated fatty acids due to their association with an increased risk of various diseases [1,5]. An alternative approach that has garnered attention in recent years involves the use of oleogels as a substitute for traditional fats and for the delivery of bioactive compounds [6–8]. Oleogels are formed by entrapping liquid vegetable oils within a three-dimensional network using small amounts of one or more gelators, resulting in structures that mimic the properties of solid fats [9–12]. Specifically, a vegetable oil, often with high nutritional value, and structuring agents undergo heating to a temperature exceeding the melting point of the gelators. As the mixture subsequently cools, a crystal network forms, establishing a self-assembling system that traps the liquid phase through the creation of weak interactions, such as hydrogen bonds, van der Waals forces, and electrostatic interactions [13,14]. Various substances have been successfully employed as gelators to form oleogels, including mono- and diglycerides, fatty acids, fatty alcohols, phytosterols, waxes etc. [15–17].

Monoglycerides (MGs) are extensively studied for their satisfactory gelling ability, and their physicochemical and structural properties which render them appropriate for numerous food applications [6,18,19]. The characteristics of the produced MGs oleogels are impacted by factors including their concentration, the oil type, and the processing conditions [1]. Nevertheless, a

concentration exceeding 10% w/w is deemed appropriate for establishing a crystalline network that traps the oil [19]. Therefore, in order to both decrease the MGs concentration and enhance the stability and physicochemical properties of oleogels, MGs can be combined with other structurants, such as phytosterols [8,20,21], waxes [22–25] etc. Waxes are another type of structurants that can be effective at forming crystalline structures at low concentrations [26]. Several natural waxes have been studied in the literature, including carnauba [27,28], rice bran [26,29], candelilla wax [30,31], sunflower wax [25,32], and beeswax [33,34]. Typically, waxes consist of a variety of chemical constituents, such as long-chain fatty alcohols, long-chain fatty acids, straight-chain alkanes, and wax esters [35]. The individual components in waxes differ both in concentration and in ingredients according to their type. Waxes which are rich in wax esters and fatty alcohols create oleogels with higher hardness [25,36]. Even though wax-based oleogels result in desirable physical properties and oxidative stability compared to MGs oleogel [37], they lead to unpleasant waxy mouthfeel, limiting their use [38].

A combination of gelators, e.g., waxes and MGs, can form oleogels with desirable physicochemical characteristics, while reducing the unpleasant waxy sensation in the mouth and at the same time minimizing the total concentration of structurants. Barroso *et al.* [23] concluded that a 1:1 ratio of MGs and sunflower wax (SW) in flaxseed oil resulted in improved properties of oleogels. Pakseresht *et al.* [36] studied a combination of MGs with carnauba wax in various ratios and demonstrated that an 85:15 ratio had higher structural properties and oxidative stability properties. Additionally, in our previous research [25], we observed that blending SW and MGs in a 1:1 ratio at a total structurant concentration level of 15% w/w yielded oleogels that were both stable and significantly harder than those produced from any other tested mixtures of various waxes and MGs; however, the samples were brittle and friable. Hence, the aim of this study was to develop oleogels with SW and MGs, employing low concentrations of structuring agents, while, at the same time, maintaining their physical and structural attributes. Different total concentrations of either SW or SW combined with MGs were examined to find the optimal combination for the first time. To investigate this goal, concentrations of structurants ranging from 6 to 12 % w/w were examined by assessing the textural properties, the melting and freezing behavior and the oxidation stability over time.

2. Results and Discussion

2.1. Oleogel Appearance

The visual appearance of olive oil oleogels containing increasing quantities of SW and SW in combination with MGs in a 1:1 ratio is depicted in Figure 1. In all cases, self-stable oleogels were formed, effectively capturing the liquid oil within a solid state.

The color of the oleogels is directly affected by the liquid oil, as well as the type and the concentration of the structural agents used, as demonstrated in the literature [24,25]. Oleogels formed with SW and MGs exhibited high L^* values, ranging from 72 to 80, which increased with the increase of structurants concentration (Table 1). The SW samples consistently appeared brighter than those formed by SW and MGs at the same total concentration. Generally, MGs oleogels had lower L^* values compared to oleogels based on waxes [25], and therefore the combination of SW with MGs lead to darker color.

In all oleogels, the parameter a^* had negative values (Table 1), indicating a green hue, as there were no significant differences noted between the samples. Concerning the parameter b^* , all oleogels exhibited positive values, suggesting a yellow hue. In most cases, the b^* value was higher when using the combination of SW and MGs compared to solely SW at the same concentration. Overall, the samples displayed hues of greenish-yellow tones, which is directly affected by the olive oil used to form the oleogels [24].

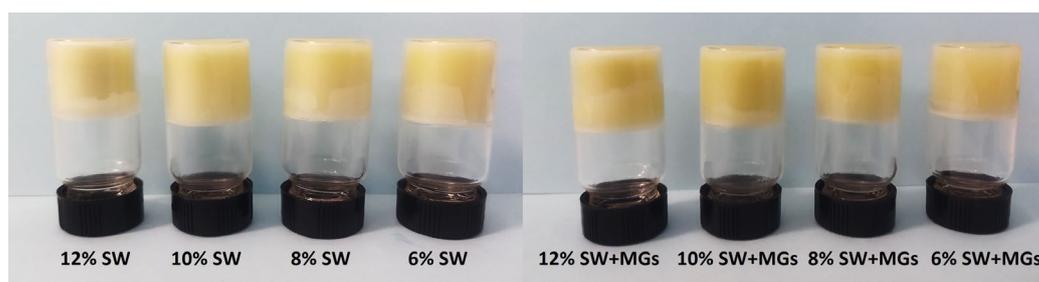


Figure 1. Visual appearance of oleogels creating using sunflower wax (SW) and monoglycerides (MGs) in olive oil.

Table 1. Impact of structural agent on physicochemical and color parameters of oleogels.

Sample	Physicochemical parameters		Color parameters		
	Hardness	Cohesiveness	L^*	a^*	b^*
6% SW	7.36 ± 0.42 e,f	0.168 ± 0.013 a,b	76.1 ± 1.1 d	-8.9 ± 0.1 a	30.9 ± 0.6 a
6% [SW + MGs]	3.51 ± 0.24 f	0.182 ± 0.025 a	72.2 ± 1.2 e	-7.8 ± 0.2 a	28.2 ± 0.7 c
8% SW	13.27 ± 0.65 c,d,e	0.091 ± 0.003 b,c	76.4 ± 1.4 d	-8.5 ± 0.2 a	27.6 ± 0.8 c,d
8% [SW + MGs]	10.20 ± 1.69 d,e,f	0.095 ± 0.026 b,c	75.8 ± 1.0 c,d	-8.3 ± 1.7 a	30.0 ± 0.5 a,b
10% SW	15.32 ± 0.77 c,d	0.081 ± 0.010 c	80.0 ± 0.9 a,b	-8.4 ± 0.1 a	26.8 ± 0.5 d,e
10% [SW + MGs]	19.98 ± 2.5 c	0.043 ± 0.012 c	77.2 ± 2.2 c,d	-8.6 ± 0.2 a	27.1 ± 0.8 d,e
12% SW	27.32 ± 1.45 b	0.070 ± 0.012 c	81.0 ± 0.9 a	-8.3 ± 0.1 a	26.6 ± 0.3 e
12% [SW + MGs]	35.74 ± 0.09 a	0.024 ± 0.001 c	78.7 ± 1.4 b,c	-9.1 ± 0.2 a	29.5 ± 0.9 b

* Data are presented as the means \pm standard errors. Means with different superscript letters at the same parameter are significantly different ($P < 0.05$).

2.2. Microstructural Assessment

The crystal structure of oleogels produced with varying concentrations of SW and SW combined with MGs was investigated through polarized light microscopy after 24 hours of oleogel formation (Figure 2). In the oleogel micrographs, areas with a darker appearance indicate the presence of olive oil, being optically isotropic, whereas the bright areas indicate the presence of crystalline structures.

Figure 2 depicts SW crystals featuring a long needle-like form, creating highly structured crystal networks capable of trapping considerable oil volumes. The efficiency of wax oil-gelling properties is affected by the particular components they contain, specifically, wax esters (96–97%) and free fatty acids (3%) [35,39]. Fayaz *et al.* [19] pointed out that the presence of the predominant wax ester is associated with the formation of long needle-like crystals. The crystals of SW exhibit a needle-like shape and as the concentration increased in the system, the crystal network became denser and the crystal size decreased. A very similar crystal morphology, long needle-like crystals of SW, was also observed by Doan *et al.* [40] at concentration level of 5% using olive oil, and by Ögütçü and Yılmaz [41] in soybean oil at concentration range of 3-10%.

Oleogels based in MGs exhibit needle-like crystals, characteristic of MG crystallization, as extensively studied in the literature [20,42]. Several researchers reported that this crystallization type is related with the presence of β -crystals of MGs oleogels [43,44]. The size and the type of crystals can be influenced by a variety of factors, including the concentration of the gelling agent, the type of edible oil used in gel formation, the cooling rate, and the combination with other ingredients [19,45]. However, it is important to note that the addition of SW in combination with MGs as structurants resulted in changes in the crystals morphology (Figure 2). As illustrated in Figure 2, the crystals of SW combined with MGs create aggregates, which increase in number and decrease in size with increasing total concentration of structurants. These results confirm the findings of our previous

research [25] which reported that, in the case of combined structurants, the length of the crystals was notably smaller compared to those created by each structuring agent individually, i.e. SW and MGs. Moreover, these results are in agreement with Barroso *et al.* [23], who observed spherulite crystals very closely packed with the presence of some bigger crystals in the oleogels formed with 6% w/w SW and MGs at the same concentration in flaxseed oil and stored at 5 °C. The formation of these crystals probably resulted from the interaction between the polar moieties or aliphatic chains of MGs and SW [22,23,36].

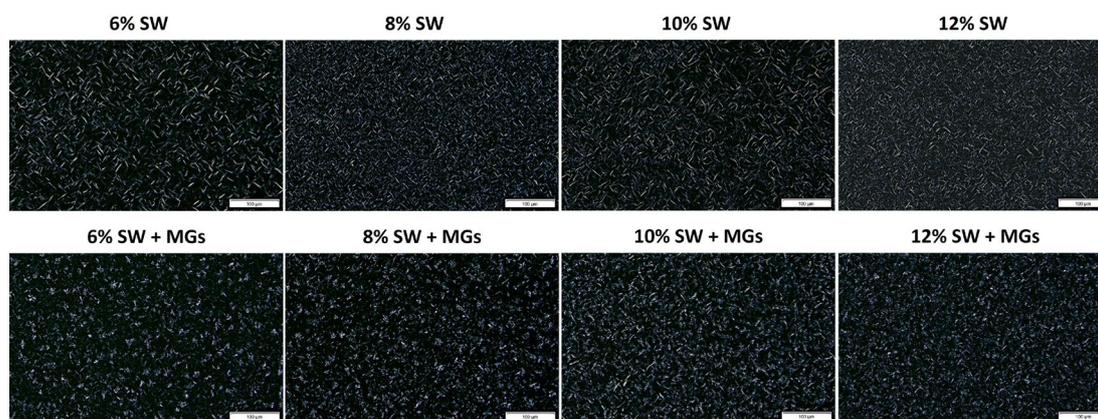


Figure 2. Polarized light micrographs of olive oil oleogels prepared with different concentrations of sunflower wax (SW) and sunflower wax with monoglycerides (SW+MGs) in a 1:1 ratio (scale 100 μm).

The crystal morphology of the 6% and 10% oleogels with either SW or both SW and MGs was investigated using polarized light microscopy after 1, 7, and 14 days (Figure 3) of incubation at 5 °C. During the two-week storage, the oleogels with solely SW did not exhibit any change in crystal type for both concentrations studied. These findings align with Doan *et al* [40] who did not observe any change in crystal type for up to 2 weeks. However, these authors reported that aggregates of spherulite crystals appeared in SW oleogels after three weeks of storage. On the other hand, in the case of SW and MGs oleogels, besides the crystal aggregates, rosette-like crystals were formed, increasing in size and number during the storage period. The alteration in the crystal morphology of SW plus MGs oleogels is reflected in the changes observed in the FTIR spectra, as discussed in Section 2.5. The mixed crystals observed in SW and MGs oleogels are more prominent at low gelling agent concentration.

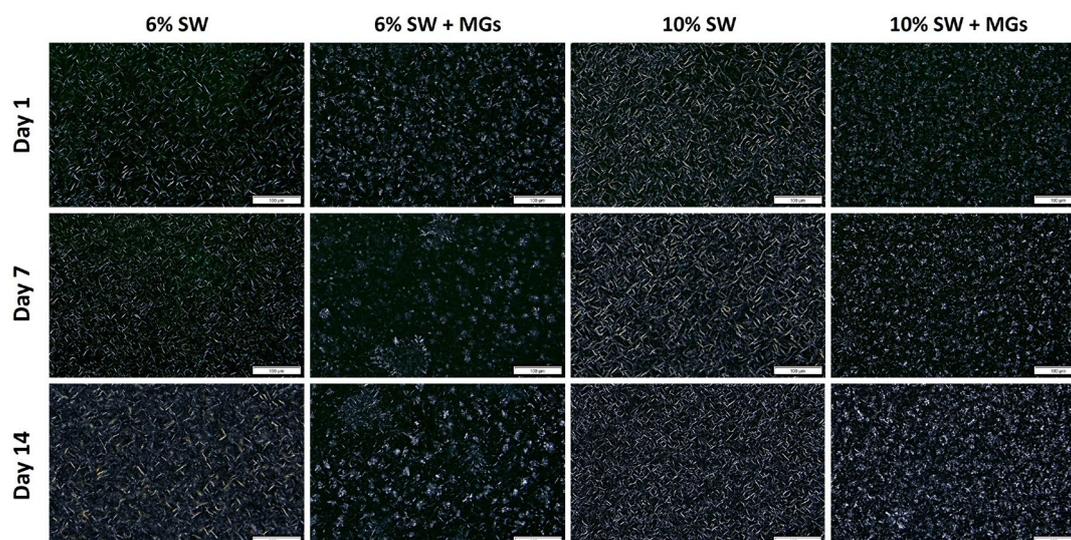


Figure 3. Polarized light micrographs of olive oil oleogels prepared with 6 and 10% (w/w) of sunflower wax (SW) and sunflower wax with monoglycerides (SW+MGs) in a 1:1 ratio stored at 5 °C for 1, 7 and 14 days (scale 100 μm).

2.3. Thermal analysis

The characterization of the melting and crystallization behavior of olive oil oleogels, formed with varying concentrations of either SW or combinations of SW and MGs, are depicted in Figure 4 and Figure 5. The oleogels composed solely of SW exhibited a single endothermic peak in the heating process (Figure 4a and 4c), which shifted to a higher temperature with an increase in the wax concentration. Specifically, the DSC analysis showed that the melting point of 6% SW was 60.2 °C, while for 12% SW was 64.1 °C. Similar trends regarding the effect of wax concentration on melting point values were reported by Martini *et al.* [46] who studied SW, paraffin wax and beeswax at different concentrations, i.e. 1-10%, using several types of oils. In general, SW is mainly composed of a significant quantity of long-chain wax esters (96–97%, mainly C22–24), a small fraction of free fatty acids (3%, C16–22), and trace amounts of free fatty alcohols and hydrocarbons [35,39]. Therefore, the high melting temperature of SW oleogels is a result of the significant amount of long-chain wax esters. As depicted in Figure 4a, a minor shoulder was observed subsequent to the main endothermic peak, associated with wax esters, indicating the melting of additional molecular components, likely the free fatty acids [40]. This shoulder vanished during crystallization (Figure 4b) and second heating run (Figure 4c), creating a broader crystallization/melting peak, which indicates an overlapping melting point with the dominant wax ester fraction. This shoulder was detected solely at a 6% SW concentration, likely attributed to the low wax concentration in the oleogel, coupled with the high precision of the μ DSC instrument and the low heating rate (1 °C/min).

The μ DSC analysis demonstrated that the combination of SW with MGs in a 1:1 ratio led to two endothermic peaks during the initial heating phase, three exothermic peaks in the cooling run, and five endothermic peaks during the second heating cycle. Generally, as the quantity of added wax and monoglycerides increased, the melting/crystallization temperatures and enthalpies also increased [10,36,47]. Regarding the first heating run, the endothermic peak was observed for 6% and 10% SW+MGs oleogels at 52.8 and 57.6 °C, respectively. In the case of 6% SW+MGs, a small shoulder was detected at 58.4 °C which is likely associated with the melting of monoglycerides. However, this shoulder is not distinct in the case of 10% SW+MGs, resulting in a broader peak from both SW and MGs, as described above. The resulting melting points observed in this study are in agreement with those documented in the existing literature. Specifically, Öğütçü and Yılmaz [41] stated that the melting point of oleogel formed with 3% SW was 58.4 °C, while Hwang *et al.* [47] reported that the melting point of oleogels formed with 0.5–10% SW in soybean oil ranged for 47 to 65 °C.

The crystallization profile of oleogels showed a broad exothermic peak at 58.3 and 60.5 °C for 6% and 10% SW, while in the case of 6% and 10% SW+MGs oleogels the first exothermic peak was noted at 55.6 and 58.3 °C, respectively. As evident from the results, the concentrations of 6% SW and 10% SW+MGs, which have approximately the same amount of wax, exhibited crystallization at the same temperature. This implies that the observed peak is associated with the crystallization of wax. The same melting temperature were reported by the Doan *et al.* [40], who concluded that the oleogels with 5% SW in rice bran oil had temperature crystallization 60.42 °C and temperature melting 62.76 °C and as the concentration decreased, the crystallization and melting temperature also decreased. Concerning the samples containing wax and monoglycerides, they displayed a second exothermic peak at 37.8 and 42.4 °C and a third at 11.5 and 12.0 °C for 6% and 10% SW+MGs, respectively. These peaks were associated with the structures of monoglycerides and correspond to α - and sub- α crystals, respectively [42,43,48]. Specifically, when MGs were dissolved in oil (at high temperature) and the system was cooled at room temperature, an inverted lamellar state, α -crystal network, was formed. Upon further cooling to 5 °C, a part of the α -crystal network was transformed to sub- α ; this transition temperature corresponded to the crystallization of fatty acids aliphatic chains in the lamella [49]. The α - and sub- α crystal network are considered metastable phases which transformed into the more thermodynamically stable β -crystals during a storage period of approximately two to three days [8,44,49]. Hence, the temperature peak at approximately 40 °C was linked to α -crystals, while the peak ranging from 11.5 to 12.0 °C was linked to sub- α crystals [8,42,48].

Upon the second heating cycle, the oleogels with pure SW showed a single endothermic peak at 60.4 and 63.6 °C for 6 and 10% SW respectively, values corresponding to those observed in the initial

heating cycle. On the other hand, five peaks were present for the oleogels consisting of SW and MGs, corresponding to sub- α_2 , sub- α_1 , α - and β -crystal forms [42,48] and SW crystals. The sub- α_2 crystals form at 2.2 °C [44], while sub- α_1 crystals form at 13.7 and 14.4 °C [48] for 6 and 10% SW+MGs respectively. The α -crystals of MGs exhibited a peak at around 44 °C, while the endothermic peak attributed to SW crystals was at 53.6 and 57.2 °C for 6 and 10% SW+MGs, respectively. In addition, as illustrated in Figure 4, a shoulder was detected at 58.5 and 65 °C for oleogels formed with 6 and 10% SW+MGs which was attributed to the β -crystal forms. Regarding the melting enthalpy values, the SW+MGs oleogels showed lower ΔH values in comparison to oleogels formulated exclusively with SW at the same total concentration. Moreover, higher ΔH values were noted as the concentration of gelling agents increased. In general, the lower melting enthalpies suggest reduced energy requirements for the organization of the crystalline network. Therefore, for the same concentration of gelators, SW+MGs require lower energy to form the crystalline network, which is also harder according to measurements from texture analysis presented in Section 2.4.

When stored at 5 °C, there were no observable changes in the melting temperatures and melting enthalpies both for oleogels containing solely SW and for those containing MGs and SW. These findings are in agreement with Doan *et al.* [40] who noted that the storage of oleogels for 4 weeks at 5 °C did not affect the melting temperature of the primary peak of 5% SW (62.66 °C). Instead, after 4 weeks they observed a new peak at around 21 °C, attributing it to the formation of a new crystalline form, i.e., spherulite clusters. Additionally, Zampouni *et al.* [20] reported that the melting point of oleogels with 15% MGs and 15% MGs plus 5% phytosterols did not change after 14 days at different storage temperatures.

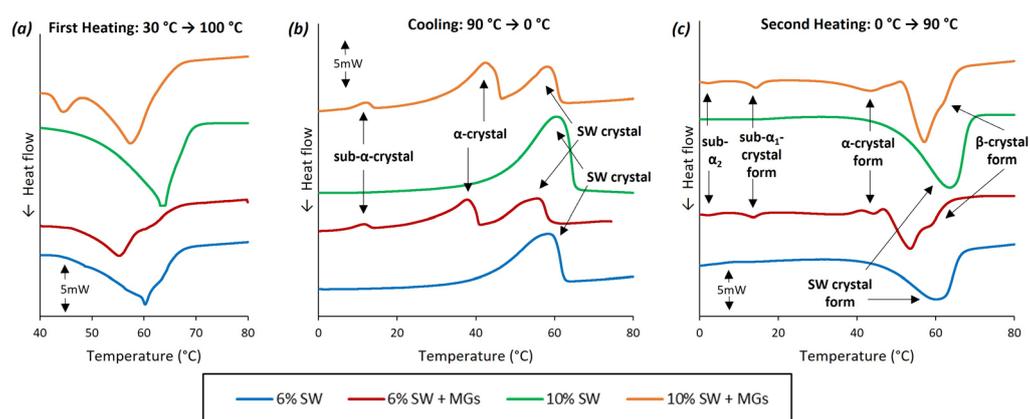


Figure 4. μ DSC thermographs of olive oil oleogels prepared with 6 and 10% (w/w) of sunflower wax (SW) and sunflower wax with monoglycerides (SW+MGs) in a 1:1 ratio; (a) first heating run from 30 °C to 100 °C; (b) cooling from 100 °C to -10 °C; (c) second heating run from -10 °C to 90 °C. .

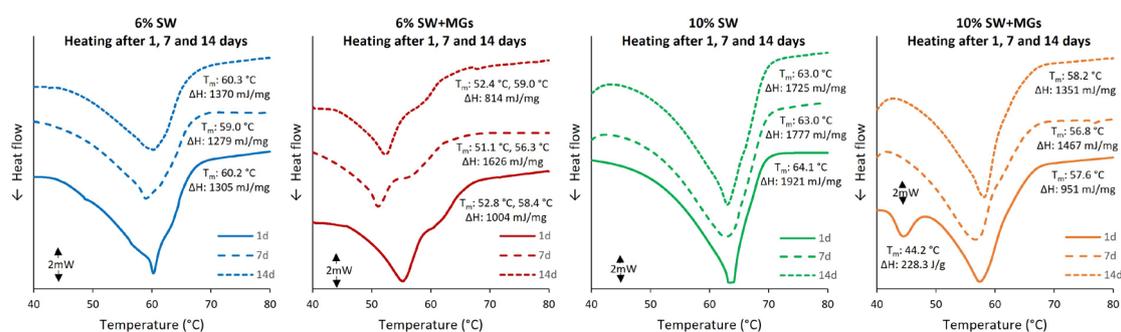


Figure 5. μ DSC thermographs of olive oil oleogels prepared sunflower wax (SW) and sunflower wax with monoglycerides (SW+MGs, in a 1:1 ratio) stored at 5 °C for 1, 7 and 14 days; heating run from 30 °C to 100 °C; heating rate: 1 °C/min.

2.4. Texture Analysis

Texture properties, particularly hardness, are essential functional aspects of oleogels that determine their suitability for use in various food products [19,36,41]. In oleogels formed by both plain SW and a combination of SW and MGs, the hardness increased proportionally with the concentration of structurants (Table 1). This finding is in agreement with the conclusions drawn by Hwang *et al.* [50] and Ögütçü and Yılmaz [41], who observed increased hardness values with the increase in SW concentration, ranging from 3% to 7% in soybean oil and from 3 to 10% in hazelnut oil, respectively.

The oleogels formed by combining MGs with SW led to different crystal structure, directly affecting the textural properties of oleogels. Specifically, at the concentration level of 10 and 12%, the hardness of the mixed component oleogels was 25-30% greater compared to those formed solely by SW, while at lower concentrations (6-8%), the opposite behavior was observed. We believe that the difference in this behavior is related to the concentration of the components; that is, monoglycerides in low concentration are not sufficient to strengthen the crystalline network, and they eventually weaken it by disrupting SW crystallization. This critical concentration of MGs is believed to be at 4%. Above this critical concentration, the combination of SW and MGs gives higher hardness compared to the same concentration consisting only of wax. Moreover, as depicted in Figure 2, in the MGs and SW oleogels containing > 8% w/w (4% SW and 4% MGs), the length of the crystals and aggregates was much smaller, and therefore, the network was firmer than the oleogels with 6% and 8% SW and MGs. These results align with our previous study where the concentration of structurants remained constant at 15% and it appeared that the combination of SW with MGs in a ratio 1:1 gave a higher hardness than the oleogels from the individual components [25].

2.5. FTIR Analysis

FTIR spectroscopy has been used in order to provide insights into the intermolecular interactions and the chemical groups that significantly contribute to the development of the oleogel network.

The pure MGs and oleogels containing MGs showed a broad double peak in the region of 3100 – 3400 cm^{-1} (at ~ 3240 and ~ 3306 cm^{-1}) which corresponds to hydrogen bonding between 2-OH and 3-OH of polar groups [36,43]. These hydrogen bonds are associated with the formation of the inverse lamellar phase and the creation of the stable β -crystal polymorph [20,43] and therefore they contribute to the establishment of the crystal network in oleogel formation [42]. On the contrary, in solely SW-based oleogels, these two peaks were absent because the formation of such hydrogen bonds did not occur. In the oleogels containing both SW and MGs, as the concentration of MGs in the system increased, these peaks became more intense (Figure 6). These results are in agreement with Ögütçü and Yılmaz [37] who observed the presence of weak intermolecular -OH hydrogen bonds exclusively in MG oleogels because of the existence of hydroxyl groups, while such bonds were not observed in oleogels with carnauba wax.

The two absorbance peaks observed at ~ 2917 and ~ 2850 cm^{-1} were related to the C-H stretching vibration [43] and the intensity was higher in pure SW-based oleogels because waxes contain a long-chain alkane backbone [51]. These two peaks are related to the van der Waals interactions between long alkyl chains or fatty acid tails, and therefore affect the formation of the oleogel network [36].

The absorbance peak at 1743 cm^{-1} associated with the stretching vibration of the carbonyl group C=O [52] was noted in all samples. In case of oleogels formed with MGS and SW the peak intensity was higher compared to the oleogels with SW at the same total concentration, while a shoulder at ~ 1730 cm^{-1} was observed (Figure 7). The peak at ~ 1730 cm^{-1} was also reported in our previous study [25]. This peak is characteristic for MGs, and it decreased as the concentration of MGs in the system decreased. This peak corresponds to the carbonyl group of ester bond between glycerol and fatty acids [20]. The same observation was mentioned by Pakseresht *et al.* [36], who reported that the peak intensity was more pronounced in MGs compared to carnauba wax, and decreased as the concentration of wax in the system increased.

The absorbance peaks in the range of 1000 – 1300 cm^{-1} is mainly related to C-O stretching vibrations in the ester group and C-H bending vibrations [25,42]. Moreover, the peaks at ~ 1345 cm^{-1}

and 1453 cm^{-1} correspond to the stretching vibration of C-H in CH_2 and CH_3 groups [53]. These two peaks signify the van der Waals interactions of adjacent aliphatic tails of MGs and long alkyl chains of waxes [42]. Additionally, there are differences in the spectrum of different oleogels, suggesting disparities in the chemical composition between SW and MGs. Specifically, a peak at 1179 cm^{-1} represents the stretching vibration of non-hydrogen-bonds of C-OH groups, a peak at 1161 cm^{-1} relates to the stretching vibration of C-OH groups involved in hydrogen bonding, and peaks at 1048 and 1062 cm^{-1} correspond to the stretching vibration of C-O bonds [42,53]. These peaks are shown only in the oleogels containing MGs, and they might indicate the organization of hydrophilic groups in the crystal network. The absorbance peak at 940 cm^{-1} denotes the bending vibration of hydrogen bonds between carboxylic acids. This peak was observed for MGs and oleogels with MGs [52], while the peak was absent in SW oleogels [36].

The FTIR spectra of oleogels stored at $5\text{ }^\circ\text{C}$ for two weeks are depicted in Figure 7. In the case of oleogels containing only SW, the spectra show no significant variations during their storage for 14 days. There are very slight differences at 956 , 1058 , 1164 , 1207 , and 1226 cm^{-1} , but they are minimal. These findings are aligned with the observed crystals and DCS results, as the wax crystals maintain their form without undergoing changes during the storage period. In the case of oleogels containing MGs, the absorbance peak at $\sim 3230\text{ cm}^{-1}$ becomes more distinct during the storage of 7 and 14 days. According to the literature [20,54], the formation of this peak is linked to the transition of α - to β -crystals. Moreover, some modifications in terms of peak creation and intensity are shown at 1393 , 1178 , 1193 , 1178 , 1062 , 1048 and 942 cm^{-1} , which may be related to the changes in crystal morphology observed by microscopy.

These observations led to the hypothesis that in oleogels containing MGs with SW, hydrogen bonding interactions are probably the primary mechanism enhancing the physical attributes of oleogels, followed by van der Waals interactions. On the other hand, in SW oleogels the gel formation mainly arises from the synergistic effects of van der Waals forces, crystal morphology, and their spatial arrangement [55].

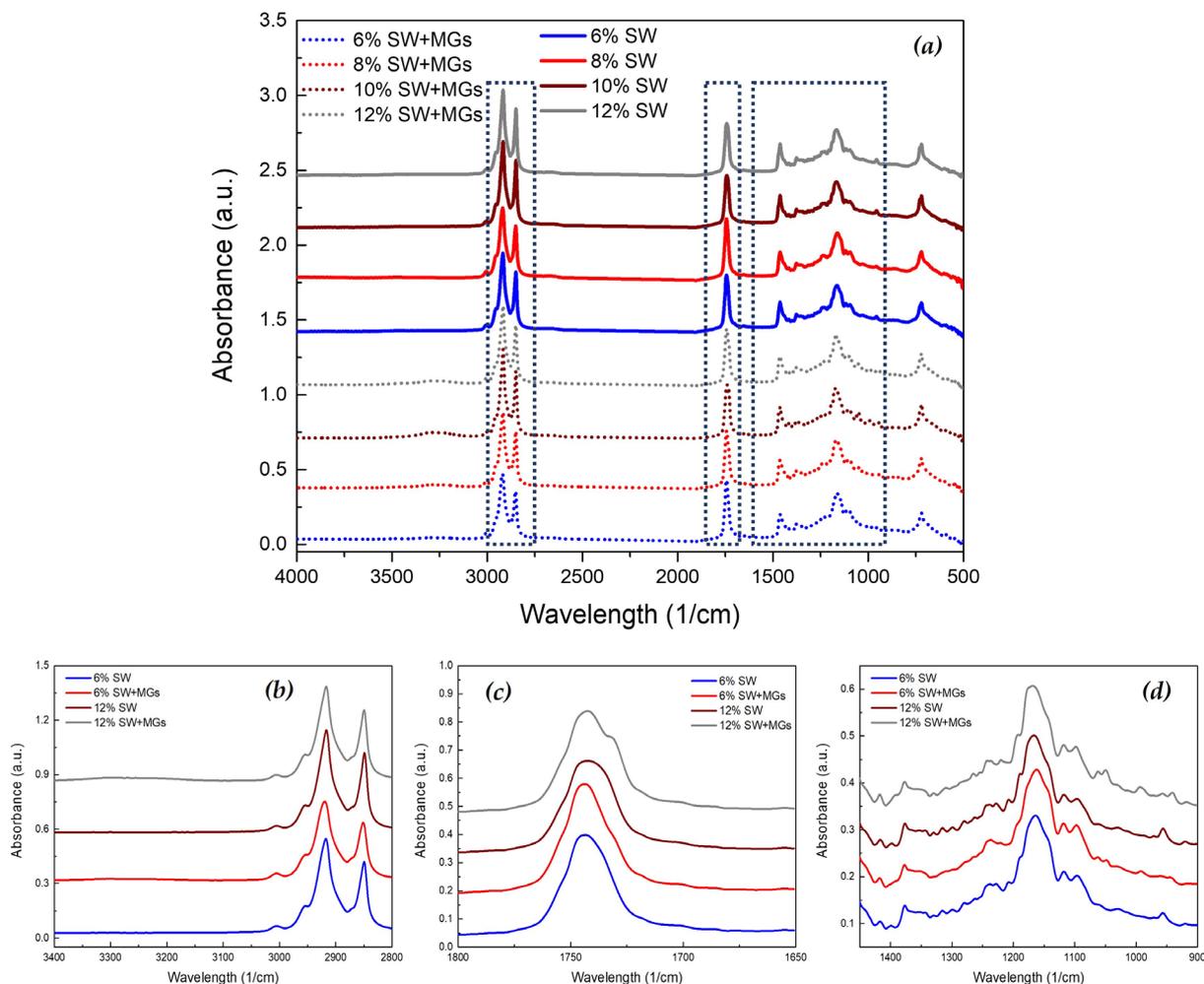


Figure 6. FTIR spectra of olive oil oleogels created with a variety of concentrations of sunflower wax (SW) or sunflower wax with monoglycerides (SW+MGs) in a 1:1 ratio (spectral regions: (a) 4000 – 500 cm^{-1} , (b) 1800 – 1650 cm^{-1} , (c) 1450 – 900 cm^{-1}).

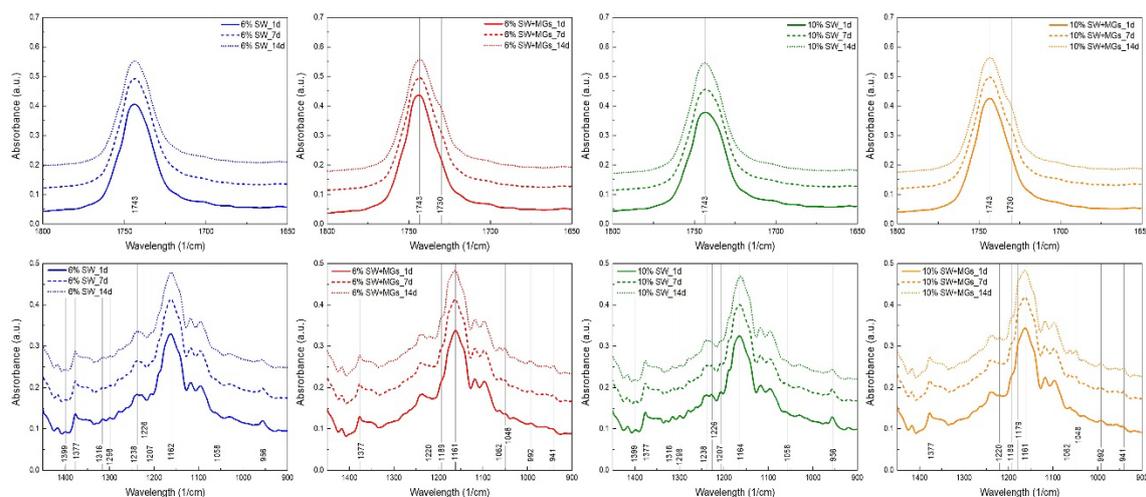


Figure 7. FTIR spectra of olive oil oleogels, prepared with 6 and 10% (w/w) of sunflower wax (SW) and sunflower wax with monoglycerides (SW+MGs) in a 1:1 ratio, stored at 5 °C for 1, 7 and 14 days (first row: spectral region 1800 – 1650 cm^{-1} , second row: spectral region 1450 – 900 cm^{-1}).

2.6. Oxidative Stability

Lipid oxidation occurs in three phases, namely initiation, propagation, and termination. During this process, in the initiation and propagation stages, primary oxidation products, such as superoxides, are formed, which subsequently react with fatty acids and other substances and form the secondary oxidation products, like aldehydes, ketones, alcohols and hydrocarbons [56,57]. The products formed during lipid oxidation lead to the development of unacceptable flavor, and furthermore, some of these oxidation products are toxic [57]. In order to determine lipid oxidation of olive oil oleogels, peroxide values (PV), which measure primary oxidation products, and thiobarbituric acid reactive substances (TBARS) corresponding to secondary oxidation products, were examined. The storage of the samples was performed at two high temperatures, 25 and 35 °C, in order to accelerate the lipid oxidation and to monitor their oxidative stability. The changes in PV and TBARS of olive oil oleogels created by either 10% SW or 10% SW+MGs, as well as liquid olive oil, which was heated simulating the processing conditions of the oleogels, during the storage period of 28 days are depicted in Figure 8.

The PV of the heated olive oil were consistently higher throughout the storage period compared to those of oleogels except for the first day (Figure 8.a). These results indicate that oleogels, which entrap the oil in a semi-solid structure, resulted in an increased resistance to oxidation compared to liquid olive oil and therefore the samples are more stable to deterioration. Moreover, in most cases the PV of the samples stored at 35 °C were slightly higher than those stored at ambient temperature without being statistically significant. These results are in line with the literature, as the higher temperature favors the formation of radicals which are responsible for the initiation and propagation of lipid oxidation [58]. These are aligned with Samui *et al.* [57] who reported that the oxidation rate of canola oil was higher than oleogels formulated by glycerol monostearate and lecithin throughout the storage period of 30 days at different storage temperatures, 4, 25, and 40 °C.

The PV of oleogels increased over time, with a more pronounced increase was noted in samples stored at 35 °C ($p > 0.05$). Concerning the oleogel composition, it appears that oleogels formed solely with SW exhibited slightly higher PV values than those containing SW and monoglycerides, although these differences were not statistically significant. It is worth noting that PV of oleogels throughout the storage of 4 weeks are below the upper limit which is 10 mEq/kg of oil, according to the Codex standard for edible fats and oils [59]. In general, PV values in the range of 1 to 5 mEq/kg indicate a low level of oxidation development, values between 5 and 10 mEq/kg are considered moderate level of oxidation, whereas those exceeding 10 mEq/kg signify a high level of oxidation [60]. According to the above, the oleogels exhibited oxidative stability when stored for 4 weeks at 25 and 35°C. These results are in agreement with Ögütçü and Yılmaz [41] who mentioned that oleogels formed with SW and carnauba wax in hazelnut oil were very stable against oxidation during three months storage at 4 and 20 °C. Additionally, Hwang *et al.* [61] observed that the oxidative stability of oleogels is affected by the wax type, and the storage temperature. Specifically, the authors studied the oxidative stability of fish oil oleogels formed with rice bran wax, sunflower wax, candelilla wax, and beeswax. On the contrary, Orhan and Eroglu [62] showed higher PV of oleogels prepared with beeswax, SW and carnauba wax in black cumin oil during the storage period of eight weeks. The decrease in PV values observed at the 28th day is expected as hydroperoxides, which are the primary oxidation products, further oxidize to aldehydes and ketones, which are the secondary oxidation products measured as TBARS.

The TBARS values of oleogels during the storage period of 28 days are illustrated in Figure 8.b. Oleogels, prepared with SW or a combination of SW and MGs, and liquid oil had very low TBARS values throughout the storage. An increase was noted for all samples stored at 35 °C compared to 25 °C, while the values increased over time. Similar low TBARS values were observed by Samui *et al.* [57] for oleogels composed of glycerol monostearate and lecithin in canola oil, and they were stored at 25°C.

Considering both PV and TBARS values, the oleogels formulated with either SW or SW and MGs show oxidative stability for at least one month at ambient temperature. This suggests that a further extension of their shelf life could be achieved by storing them at refrigerated temperatures.

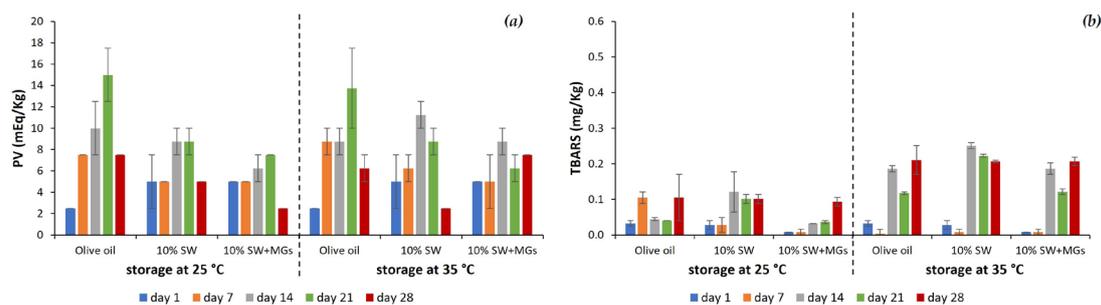


Figure 8. Evolution of Peroxide (a) and TBARS (b) values in liquid olive oil, SW-based oleogels, and SW plus MGs-based oleogels during storage at 25 and 35 °C over time.

3. Conclusions

In this study, olive oil oleogels created by either pure SW or a combination of SW and MGs in a 1:1 ratio, at different concentrations, were examined, and the synergistic behavior of the two components was assessed. All the oleogels remained shelf-stable at ambient temperature, with increased hardness observed as the total concentration of gelators increased. Furthermore, a positive interaction between SW and MGs was observed above the 4% w/w of concentration of MGs, contributing to the increased hardness of oleogels. The crystals of SW oleogels were long needle-like, while the combination of SW and MGs resulted in the formation of crystal aggregates and rosette-like crystals. Microscope images revealed changes in crystalline structure due to the use of different gelling agents and during storage at refrigeration temperature for 2 weeks. These changes were further confirmed by the results of DSC and FTIR analyses. The findings suggest that hydrogen bonding and van der Waals forces predominantly govern the SW and MG oleogels, while van der Waals interactions are responsible for SW oleogels. Additionally, oleogels formulated with SW and a combination of SW plus MGs exhibited high stability in terms of oxidative stability during a 4-week storage period at ambient temperatures. Therefore, we can conclude that using a blend of two economic gelling agents provides several benefits, including a reduction in the overall concentration of gelling agents and the avoidance of a pronounced waxy mouthfeel. Hence, the developed oleogels could serve as an alternative hard fat source in various food products.

4. Materials and Methods

4.1. Raw Materials and Oleogels Preparation

Sunflower wax (SW) (Daraveli and Co., Ltd, Athens, Greece) and monoglycerides (MGs) (HARI 95 Riketa SDN BHD, Johor Bahru, Malaysia) were employed in the formulation of different oleogels. MGs exhibited at least 95% monoester content, with the acid value not exceeding 3%, the iodine value capped at 2%, and the free glycerine value limited to 1%. According to the manufacturer's specifications, SW presented an acid value of 2.3 mg KOH/g and a saponification value of 91.6 mg KOH/g. The melting points for the structuring agents were reported at 75 °C and 71 °C, for SW and MGs, respectively.

Different amounts of SW (6, 8, 10, and 12% w/w) or a mixture of SW and MGs in a 1:1 ratio (6, 8, 10, and 12% w/w) were studied in order to form shelf-stable oleogels. For oleogel preparation, appropriate quantities of olive oil (Minerva SA, Metamorphosi, Greece) were weighed and preheated at 85 °C with continuous stirring. Following that, the structuring agents were gradually added, fully dissolved, and the mixtures underwent stirring for 30 minutes at a temperature of 90–95 °C [21,25]. The resulting liquified oleogels were subsequently transferred into plastic containers (polypropylene, 10x10 cm), followed by cooling at room temperature for 40 minutes. Following this, the oleogels were stored at 5 °C for 1, 7 and 14 days. Measurements were carried out at room temperature, with the oleogel samples first being allowed to reach equilibrium at 25 °C for 3 hours. All the measurements were conducted in duplicate using distinct batches of oil.

4.2. Color Measurement

Color measurements were conducted using a Chroma Meter CR-400 (Minolta, Osaka, Japan), utilizing a D 65 light source. The color of the oleogels was assessed by recording the L^* (brightness), a^* (+/-, red to green spectrum), and b^* (+/-, yellow to blue spectrum) values after calibrating the colorimeter with a supplied white tile. For each oleogel sample ten measurements were obtained, with the outcomes reported as mean \pm standard deviation.

4.3. Polarized Optical Microscopy

The microstructural images of the oleogels were captured using an Olympus BX43 polarizing microscope (Olympus Optical Co Ltd, Tokyo, Japan), which was equipped with a digital microscope camera (Basler USB3 Vision, Ahrensburg, Germany). Specifically, one drop of liquified oleogels was placed on a preheated microscope slide and was covered by a glass coverslip. Subsequently, the samples were cooled at 5 °C for the predetermined period mentioned earlier. The morphological characteristics were noted at 25 °C, employing a 20x magnification objective (NA 0.75), and images of the oleogels were captured utilizing Basler Microscopy Software (version 2.1) (Basler, Ahrensburg, Germany).

4.4. Differential Scanning Calorimetry (DSC)

The investigation of melting and crystallization behavior of oleogels was conducted by a microcalorimeter (microCalvet μ DSC 7 Evo-1A, Setaram, Caluire-et-Cuire, France), equipped with two parallelly positioned 1mL capsules. One capsule contained the sample, while the other contained olive oil and was used as a reference sample. The samples were heated from 30 °C to 100 °C (first heating run), remained at this temperature for 5 min to erase the crystal memory of the samples, then the oleogels were cooled to -10°C and remained at this temperature for 5 min. Afterwards, the samples were reheated to 90 °C (second heating run). Throughout the measurements, there was a continuous flow of nitrogen gas (0.8 bar). The heating and cooling rate was set at $\pm 1^\circ\text{C}/\text{min}$. The sample quantity was 400 mg \pm 10 mg. The μ DSC was calibrated using a standard sample of pure naphthalene. The peak melting temperature (T_m), peak crystallization temperature (T_c), and apparent melting/crystallization enthalpy (ΔH) of the structured emulsions were defined from the endothermic and exothermic peaks of the μ DSC scans, respectively, using the CALISTO software (Setaram, Caluire-et-Cuire, France). The measurements were carried out one, seven and fourteen days after oleogels' preparation. All μ DSC experiments were conducted in triplicate.

4.5. Texture Analysis

The texture properties of the olive oil oleogels were evaluated by texture profile analysis (TPA), employing a double compression cycle test [21] with a Universal TA.XT plus Texture Analyzer (Stable Micro Systems, Godalming, Surrey, UK) equipped with a 5-kg load cell. Following a 3-hour equilibration at 25 °C, the samples were cut into cubes of 20 mm. The test speed was set at 1.0 mm/s, compressing the samples to 75% of their initial height using an SMS P/100 probe (with a plate probe diameter of 100 mm). The TPA parameters assessed were hardness (N) (the maximum force required during the initial compression) and the cohesiveness (the ratio of the two areas under the first and the second compression curves). Each treatment was subjected to six assessments, with outcomes presented as the mean \pm standard deviation.

4.6. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the oleogels were acquired using an FTIR 6700 series spectrometer (JASCO, Japan) equipped with 3-reflection ATR diamond (MIRacle ATR, Pike Technologies, U.S.). Following a 3-hour equilibration at 25 °C, the oleogel samples were placed on the ATR plate and the spectra were recorded across a wavenumber range of 4000 to 500 cm^{-1} , with a spectral resolution of 4 cm^{-1} , and 32 scans. A background spectrum of air was captured and subtracted from each sample's spectrum before measurements. For each treatment, five spectra were acquired, and the average of

these spectra was used for analysis. The analysis of the spectra was carried out using Spectra manager (V.2, Jasco, Tokyo, Japan).

4.7. Oxidative Stability of Oleogels

For the assessment of oxidative stability, the oleogels were stored at room temperature (25 °C) and at 35 °C in order to accelerate the lipid oxidation. The oxidative stability of oleogels was assessed by determining the primary oxidation products, i.e., peroxide values (PV) and secondary oxidation products, i.e., thiobarbituric acid-reactive substances (TBARS). The measurements were performed on 1, 7, 14, 21, and 28 days.

The PV were assessed following AOAC Official Method 965.33, with minor adjustments. In summary, 5 g of sample were combined in an iodine flask with 25 ml of a 3:2 acetic acid-chloroform solution and 1 ml of saturated KI solution. Then, the mixture was shaken and left in dark conditions for 1 min. Following that, 75 ml distilled water and 2 ml starch indicator (1% w/w) were added, and the solution was titrated against 0.05 N sodium thiosulphate solution until the disappearance of the blue color. At the same time, a blank test was measured without oleogel sample. PV were calculated with the equation provide below:

$$PV = \frac{N \cdot (V - V_0)}{w} \cdot 1000 \quad (1)$$

where N is the normality of the sodium thiosulphate solution, V and V_0 is the volume (ml) of sodium thiosulphate solution used for titration of the samples and blank test, respectively, and w in the samples weight (g). The determination of PV was performed in duplicate and the results were expressed as mEq/Kg.

The TBARS were assessed following the method described by Katsanidis and Zampouni [63] through the steam distillation process. TBARS concentration was measured by absorbance measurements at 532 nm (UV-1700 spectrophotometer, Shimadzu Europe GmbH, Duisburg, Germany). Duplicate samples were examined, and the results were presented as mg of malonaldehyde (MA)/kg of sample.

4.8. Statistical Analysis

The gathered data underwent analysis through ANOVA, employing the general linear model with a significance threshold set at $\alpha=0.05$. To discern differences between treatments, Tukey's test was applied. This statistical evaluation was executed utilizing MINITAB v.16 software (Minitab, Inc., State College, PA, USA).

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