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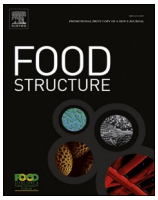

Durum wheat oil oleogels: A study on rheological, thermal, and microstructural properties

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ABSTRACT

Durum wheat oil (WO) is a by-product obtained during wheat milling process characterized by higher amount of bioactive compounds. In recent years, oleogelification, a novel technique to structure oils was developed to replace saturated and *trans* fats. The aim of this study was to evaluate the performances of WO to obtain stable oleogels using two natural waxes (beeswax BW and carnauba wax CW) at different ratio (4, 7 and 8 %, *w/w*) respect to sunflower oil (SO) used as control. Oleogels were analyzed for fundamental rheological properties, microstructure and oil loss. Results showed as a concentration below 7 %, weak networks were observed for all samples because the predominance of viscous moduli (G'') over elastic ones (G') and high oil loss. Nevertheless at 8 % of waxes, stability in terms of all analyzed parameters was highlighted for all samples (WO_BW showed the lowest). Moreover, WO samples with 7 % and 8 % of CW displayed very high stability in terms of all considered parameters, also at high temperatures, showing strong networks and reaching the optimum solid-like gel without significant differences respect to SO one. Obtained results highlighted the WO ability to be employed, as alternative to SO to develop oleogels with optimal performances and stability.

1. Introduction

In a classic semisolid fat product such as ice cream or chocolate, the solid lipids - arranged in a three-dimensional colloidal fat's crystal network - act as promoters of the crystallization representing the first step of the microcrystal network where soft matter is held similar to colloidal gels. For instance, in cake goods, saturated fats play a key role in generating the viscous foam structure, entrapping air bubbles into the fat phase of the cake batters (Kim et al., 2017). However, the negative health effects of saturated and *trans* fatty acids consume on human health were intensely discussed (Kim et al., 2017; Guo et al., 2023). Numerous studies have shown that excessive intake of saturated or *trans* fatty acids can increase the risk of cardiovascular diseases (CVDs) by lowering serum levels of high-density lipoproteins and increasing serum concentrations of low-density lipoproteins (Clifton & Keogh, 2017).

In order to reduce the content of saturated fats and *trans* fats in foods and at the same time to ensure the correct plasticity of fats, many studies have been focused on oleogels, which have similar structural characteristics as saturated hard-fat, although are characterized by higher amounts of unsaturated fatty acids and reduced amounts of saturated fatty acids. The organogelation or oleogelation is emerged as a new method of plasticization oil's technology (Öłütcü & Yilmaz, 2015). Oleogels used in foods are usually composed of a liquid vegetable oil and generally recognized as safe (GRAS) additives (da Silva et al., 2018).

From a physical point of view, oleogels are viscoelastic, anhydrous and self-supporting materials; they have rheological characteristics like a solid but are formed in the highest amount (>90 %, w/w) of a liquid matter (e.g., vegetable oil). From a thermal point of view, oleogels are structured and thermos-reversible substances. The additives or "oleogelators" lead to the formation of a three-dimensional super-molecular network (Doan et al., 2015). Therefore, based on correct melting and structuring behavior, the oleogels can provide a suitable alternative to fully and partially hydrogenated fats such as margarine or milk fat, in food production (Demirkesen & Mert, 2019; Jung et al., 2020).

Oleogels were applied to different processed foods, such as chocolate and spreads (Patel et al., 2014), ice cream (Zulim Botega et al., 2013) and biscuits (Hughes et al., 2009). In that context, the natural waxes, which are long-chain fatty acids esterified into fatty alcohols, are considered promising organogelators; since they showed great performance like texturizing agents. The physicochemical characteristics in terms of thermal and rheological proprieties were in deep investigated combining carnauba wax and candelilla wax with canola oil (Jang et al.,

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2015), sunflower oil (Mert & Demirkesen, 2016) and soybean oil (Rocha et al., 2013). Again, the effect of oleogelation on lipid digestion was recently explored. For instance, in the case of extra virgin olive oil the lipophilic oleogelators led about 40–55 % of free fatty acids release during *in vitro* digestion, while in presence of hydrophilic oleogelators, the free fatty acids release was about 100 % (Ciuffarin et al., 2023). On the other hand, Ramírez-Carrasco et al. (2024) demonstrated that in beeswax-based oleogel a reduction of about 10 % of free fatty acids released *in vitro* digestion was observed.

Moreover, oleogelation could be a useful strategy to valorize by-products and co-products, which are an interesting source of unsaturated fatty acids and different bioactive compounds. Recently, durum wheat germ oil (also called wheat oil, WO) received great attention due to its nutraceutical properties and its potential use in the food industry. WO is mainly composed of polyunsaturated fatty acids of which linoleic acid is the most representative (Cardenia et al., 2018).

However, WO due to the presence of antioxidants such as α-tocopherol, β-tocopherol and carotenoids can find application in the pharmacological, cosmetic and nutritional fields (Kumar & Krishna, 2015). WO is often used in its crude form obtained by pressing extraction, even if, the solvent extraction usually leads to an increase in yield (about 90 %) (Durante et al., 2012). On the other hand, as well reported the solvent extraction and consequent refining process improves the amount, the quality and stability of WO (Li et al., 2016), increasing its applications in the food sector (Vurro et al., 2022a; Vurro et al., 2022b).

However, due to its liquid-like behavior, its application in some food industry sectors such as the confectionery and the baking industry is limited. To overcome that limit, the oleogelation could be a useful strategy to obtain a texturized WO expanding its application. Thus, the aim of the present research was to evaluate the impact of two natural waxes used at different concentrations on the development of wheat oil-based oleogels characterizing their physical and rheological properties in order to better valorize the WO and wheat chain sustainability.

2. Material and methods

2.1. Materials

Beeswaxes (BW), carnauba waxes (CW) were provided by a local company. Refined sunflower oil (SO) was purchased from local market, while wheat oil (WO) was supplied by an Italian company (Molino Casillo, Corato, Bari).

2.2. Oleogels preparations

To assess the stability of oleogel, preliminary trials were performed employing 1.5 and 3 % of BW in the presence of SO or WO, leading to samples characterized by weak elastic moduli and poor stability as shown in Supplementary materials (S1 and S2). On the basis of these preliminary results, new oleogel samples were developed increasing the amount of BW and CW at 4, 7 and 8 %. BW oleogels were obtained by stirring waxes and oil in a water bath at 70 °C, while CW ones reaching 90 °C on the basis of their melting profiles (S3) and according with previous works of Borriello et al., (2021), Sabet et al., (2023) and Wang et al., (2024), by applying a direct method. This method does not require specific equipment being inexpensive, rapid and scalable; moreover, oleogels obtained by following this method exhibit the higher capacity to mimic the rheological properties of hard-stock fats, as they do not be sheared as a final step unlike ones obtained with indirect ones (Wang et al., 2016; Sabet et al., 2023, Valoppi et al., 2023). After stirring, samples were allowed to cool quiescently in beakers at room temperature overnight, according to Blake & Marangoni (2014) and gently removed from them by using a spatula before performing analysis. The bees and carnauba wax-based oleogels prepared with different oils and concentrations in triplicate (SO_BW; SO_CW; WO_BW; WO_CW, at 4, 7 and 8 % *w/w*) were used for further measurements.

2.3. Analytical determinations

2.3.1. Quality control of durum wheat oil

In order to determine the quality and composition of durum wheat oil, fatty acid composition (EEC Regulation no. 2568/91), carotenoids (Makhlouf et al., 2018), tocopherols and tocotrienols (Difonzo et al., 2021), phytosterols (Miazzi et al., 2020) and wax (Milani et al., 2020) were determined.

2.3.2. Fundamental rheological analysis

2.3.2.1. Frequency sweep tests. Fundamental rheological analysis was carried out in dynamic conditions by using a stress-strain rheometer (MCR 52, Physica/Anton Paar, Ostfildern, Germany) equipped with a plate-plate system (PP25) at 20 °C. Oleogel samples were transferred from the beaker into the center of the geometry with the help of a spatula, shearing as little as possible in order to avoid excessive structural damage. A strain sweep test was used to identify the linear viscoelastic region (LVR) (Glicerina et al., 2013; Penagos et al., 2023). On the basis of these results, a target strain of 0.046 % (within the linear region) was chosen for measurements. Oscillatory measurements of storage modulus (G′, Pa) and loss modulus (G″, Pa) were performed within a frequency range from 0 to 100 rad/s.

Analysis were performed with both sunflower and wheat oil-based oleogels realized with bee and carnauba waxes at the different concentrations of 4, 7 and 8 % in order to assess their stability. Three replicates for the sample were carried out.

2.3.2.2. Temperature sweep tests. Temperature sweeps were also performed to evaluate viscoelastic properties and oleogels stability during the temperature ramp. Temperature was controlled to within 0.1 °C by Peltier elements. Temperature sweep tests were performed from 0 °C to 40 °C at a linear heating rate (2.5 °C·min^{-1}). The frequency value was set at 6.28 rad/s. During heating, values of elastic modulus (G′, Pa) and viscous modulus (G″, Pa) were recorded (Tavernier et al., 2017). Three replicates were carried out on oleogels with bee and carnauba waxes, employed at the different concentrations of 4, 7 and 8 %.

2.3.3. Microstructural analysis

Microstructure of samples was analyzed by using an optical microscope (BH-2 RFCA, Olympus, Hamburg, Germany) with a 4x of magnification, in brightfield mode, in order to have a correct vision of aggregate distribution in space and not just a detail. One mg of sample was placed on a glass slide and covered with a glass slip carefully placed over the sample, parallel to the plane of the slide and centered to ensure that sample thickness was uniform. Micrographs were captured using a digital camera (Model 2.1 Rev 1; Polaroid Corporation, NY, USA). The acquired images were subsequently elaborated using the software Image Pro-plus 6.0 (Media Cybernetics Inc., Bethesda, USA) by converting them in grey scale and subsequently thresholded in order to highlight in a more accurate way samples network, especially in terms of empty and void spaces (Glicerina et al., 2015; Wang et al., 2022). Thresholded images were then processed by using the software Image J (Rasband, W. S Maryland, USA) in order to obtain the box-counting fractal dimension index (Db). These values give an indication of the spatial distribution of the crystal clusters in fat crystal networks, giving a description of their amount and homogeneity of occupied areas (Blake & Marangoni, 2014; Bouda et al., 2016). The reported fractal dimension was an average taken from 10 micrographs. Moreover, in order to better highlight crystal morphology samples were also acquired at 10x and 20x of magnifications.

2.3.4. Oil loss evaluation (OL)

Oil loss was analyzed according to Thomas et al. (2023) and Han et al. (2022). Briefly, accurately 1.000 ± 0.001 g of oleogel was weighed

into a 1.5 mL plastic centrifuge tube and immediately centrifuged at 10 x g for 15 min. After centrifugation, the 1.5 mL centrifuge tube with 1 g of oleogel was placed upside down on the desk for 24 h to remove the released liquid oil completely.

OL was calculated according to Eq. (1):

$$\mathrm{OL} = \frac{(M_1 - M) - (M_2 - M)}{M_1 - M} \quad (1)$$

where M_1 is the mass of the initial sample and centrifuge tube, M_2 is the mass of the sample and centrifuge tube after removing the excess oil, and M is the mass of the centrifuge tube. Higher is the amount of oil loss, lowest will be the ability of oleogel to entrap and so immobilizes liquid oil within its structured three-dimensional network, exhibiting lowering gelation ability. Five replicates for each sample were performed.

2.3.5. Thermal Analysis

The melting properties of oleogel samples were evaluated by using a differential scanning calorimeter (Nexta DSC 200, Alfatest, Hitachi High Test, Japan). DSC was calibrated by using indium (melting T 156.60 °C, ΔH 28.71 J/g) and tin (melting T 231.93 °C, ΔH 60.46 J/g) at a scan rate of 5 °C/min using an aluminum pan as reference. Samples (15 mg) were loaded into 40 mL capacity pans and sealed using a sample press. Pans were subjected to the following steps:

-Heating from 20°C to 110°C
-Cooling from 110°C to −20°C
-Heating from −20°C to 110°C

at the scan rate of 5 °C/min in an N_2 stream, according to Aguedo et al., (2009) with some modifications. During the thermal ramp, oleogels were heated to above their melt temperature to remove any thermal history (step 1), cooled to impart a controlled thermal history (step 2) and reheated to 110°C to evaluate the correct and stabilized melting profile (step 3).

DSC Nexta software was used to calculate respectively the crystallization and melting onset temperature (T_{onset}), the crystallization and melting maximum value (T_{peak}) and the enthalpy (ΔH) of both crystallization and melting (Gloria & Sievert, 2001; Wang et al., 2022). Each

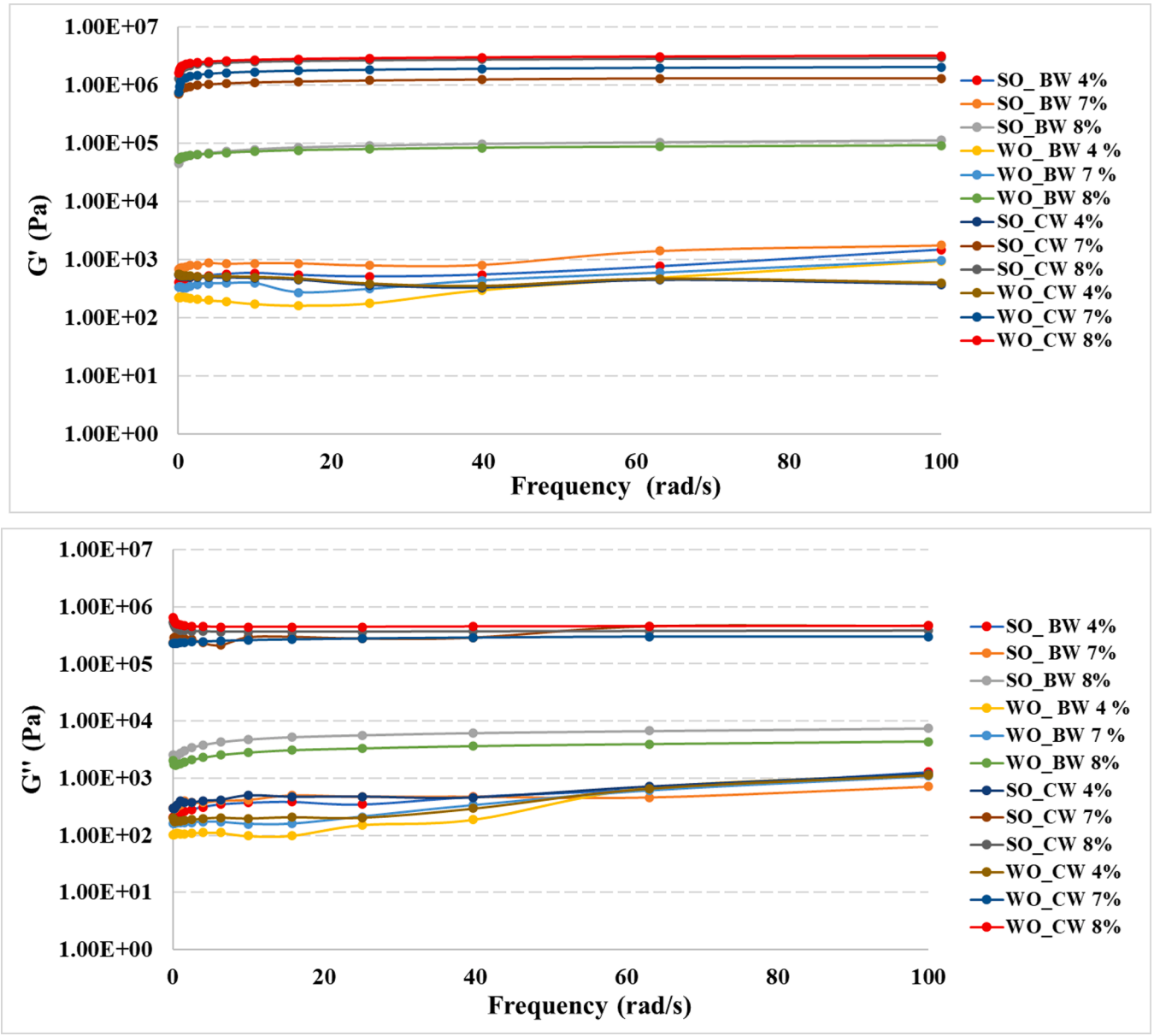

Fig. 1. (a,b). Elastic (G') and viscous (G'') moduli of sunflower (SF) and wheat (WO) oils based oleogels, realized respectively with beeswax (BW) and carnauba wax (CW) at the different percentages of 4, 7 and 8.

experiment was repeated three times.

2.4. Statistical analyses

Analyses of variance (ANOVA) and the test of mean comparison according to Fisher Least Significant Difference (LSD) were conducted on all obtained data. Level of significance was $P < 0.05$. The statistical software used was STATISTICA, version 8.0. (StatSoft, Tulsa, Oklahom).

3. Results and discussions

The rheological behavior is strictly related to the composition of oil used to generate oleogel. Thus, its composition in terms of fatty acid, tocopherols and tocotrienols, sterols and wax composition was established (S4) and resulted in line with the literature (Squeo et al., 2022).

3.1. Fundamental rheological analysis

3.1.1. Frequency sweep tests

Fig. 1(a, b) reports the results of the frequency sweep test in terms of storage (G') and loss modulus (G'') of all analyzed oleogels. Moreover, in order to better explain the results, elastic and viscous moduli of samples evaluated at 6.25 rad/s are showed in Table 1.

The response of all samples to the imposed oscillatory deformation is the stored potential energy, which give a measure of solid and liquid-like characteristics of viscoelastic materials (Bayod & Tornberg, 2011; Glicerina et al., 2015; Morales et al., 2023). As it well reported, in stable gels and oleogels the elastic component (G′) dominates over the viscous one (G'') (Patel et al., 2020; Liu et al., 2023; Thomas et al., 2023). However, in samples realized with BW, both SO and WO at 4 and 7 % the elastic modulus values ranged from around 200–850 Pa, presenting the lowest values for WO at 4 % ($1.92 *10^2$) and the highest for SF at 7 % ($8.43*10^2$). In agree with literature (Pehlivanoğlu et al., 2018; Kwon & Chang, 2022), the obtained results highlight the presence of a very weak structure characterized by low stability and a poor network. Moreover, analyzing the mechanical spectrum of samples composed of WO_BW at 4 % and 7 % two crossovers were also observed at the frequencies of 50 and 65 rad/s, respectively, which underline an increase of the viscous modulus and their low stability at higher frequencies compared to SO_BW (S5). Raising the BW amount until 8 % a clear predominance of G' with respect to G'' was observed in both oils for all the investigated frequencies, showing not significant differences between oil samples. On the other hand, CW at 4 % in both SF and WO increased the elastic modulus even if samples did not show optimal rheological values, presenting poor structured networks (Fig. 1a; Table 1a). According to the studies of Gravelle et al., (2017) and Patel et al., (2020), some rheological properties are necessary in oleogels to mimic saturated fats in specific foods such as baked, chocolate, dairy and meat products, that should be characterized by suitable properties such as high hardness, but at the same time plasticity, mouthfeel and scarce brittleness. Those peculiarities were detected in saturated fat replacers characterized by elastic moduli included in the ranges of $1*10^5$ ("soft") – $6*10^6$ ("hard"). The obtained values, in line with values reported in the literature, highlighted the potentiality of these samples to be successfully employed to mimic margarines, butter, cocoa butter, shortenings and spreads in bakery products, ice cream fillings as well as in chocolate and confectionary products (Patel et al., 2014; Zhao, 2019; Álvarez et al., 2022; Palla et al., 2021).

However, increasing CW content up to 7 % and 8 % interesting results were obtained, since G' values of $1.6*10^6$ and $2.6*10^6$ Pa*s were obtained, respectively; the presence of very strong networks and the optimum solid-like gel behavior (Patel et al., 2020; Sivakanthan et al., 2023; Thomas et al., 2023), with no significant differences ($p>0.05$) was denoted.

3.1.2. Temperature sweep tests

In Fig. 2(a, b) the behavior of elastic (G') and viscous (G'') moduli evaluated by temperature sweep tests is shown. All oleogel formulations exhibited a drop in G′ as the temperature increased, in agree with Chai et al. (2022) and Wang et al. (2024), with differences related to wax concentration and oleogel composition. However, a similar trend was observed for the frequency sweep test. In specific, CW samples displayed a better gelation behavior than BW, also at higher temperatures, remaining relatively stable with increased gelator concentration, as underlined by elastic moduli (G') values. As reported by literature (Blake, 2015; Tavernier et al., 2017; Shi et al., 2021; Tanislav et al., 2022) high elastic moduli are related to a higher gelation capacity of gelator compound; in this case, carnauba wax, that is more able to form

Table 1

a. Storage modulus of oleogel samples evaluated at 6.25 rad/s and at 20°C.

ELASTIC MODULUS (G')			
BEEWAXES CONCENTRATION (%)			
	4	**7**	**8**
SUNFLOWER	$5.35*10^2 \pm 2.65*10$ **aA**	$8.43*10^2 \pm 3.50*10$ **aB**	$7.32*10^4 \pm 1.23*10^2$ **aB**
WHEAT OIL	$1.92*10^2 \pm 3.18*10$ **bB**	$3.91*10^2 \pm 2.48*10$ **bB**	$6.89*10^4 \pm 1.04*10^2$ **aB**
CARNAUBA WAXES CONCENTRATION (%)			
	4	**7**	**8**
SUNFLOWER	$5.78*10^2 \pm 2.18*10$ **aA**	$1.07*10^6 \pm 2.54*10^2$ **aA**	$2.46*10^6 \pm 1.89*10^2$ **aA**
WHEAT OIL	$5.09*10^2 \pm 4.14*10$ **aA**	$1.64*10^6 \pm 2.89*10^2$ **aA**	$2.65*10^6 \pm 3.17*10^2$ **aA**

Table 1 b. Loss modulus of oleogel samples evaluated at 6.25 rad/s and at 20°C.

VISCOUS MODULUS (G'')			
BEEWAXES CONCENTRATION (%)			
	4	**7**	**8**
SUNFLOWER	$3.47*10^2 \pm 1.72*10$ **aA**	$4.00*10^2 \pm 1.94*10$ **aB**	$4.28*10^3 \pm 2.16*10^2$ **aB**
WHEAT OIL	$1.11*10^2 \pm 1.63*10$ **bC**	$1.70*10^2 \pm 2.92*10$ **bC**	$2.54*10^3 \pm 8.93*10$ **bC**
	CARNAUBA WAXES CONCENTRATION (%)		
	4	**7**	**8**
SUNFLOWER	$4.15*10^2 \pm 4.08*10$ **aA**	$2.13*10^5 \pm 4.58*10^2$ **aA**	$3.65*10^5 \pm 2.79*10^2$ **aA**
WHEAT OIL	$2.05*10^2 \pm 1.18*10$ **aB**	$2.55*10^5 \pm 4.47*10^2$ **aA**	$4.45*10^5 \pm 3.28*10^2$ **aA**

[a-b] Values followed by different letters differ significantly at $P < 0.05$ level between samples at the same concentration and waxes type.
[A-B] Values followed by different letters differ significantly at $P<0.05$ level between samples at the same concentration comparing both waxes.
[a-b] Values followed by different letters differ significantly at $P < 0.05$ level between samples at the same concentration and waxes type.
[A-B] Values followed by different letters differ significantly at $P<0.05$ level between samples at the same concentration comparing both waxes.

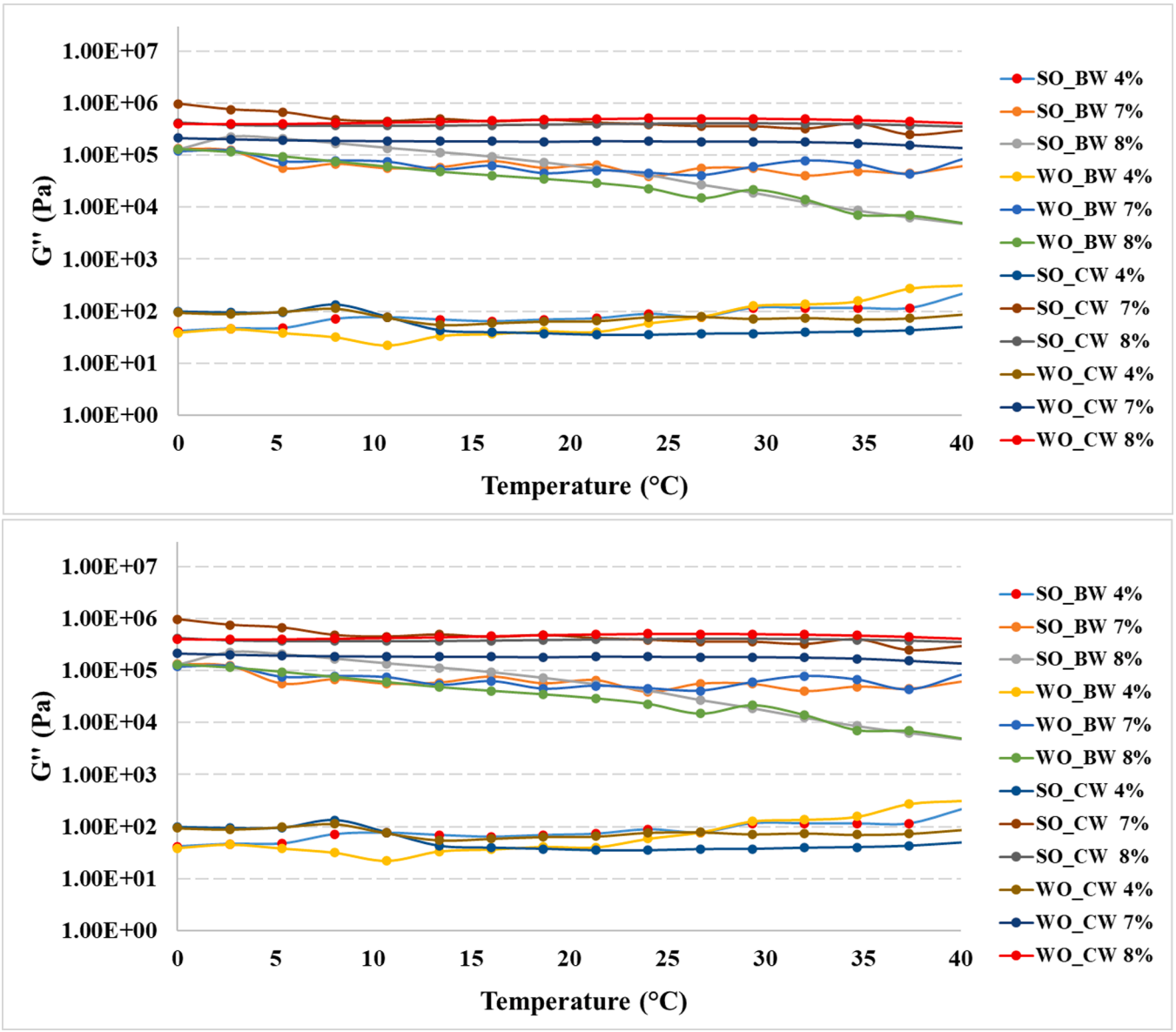

Fig. 2. (a,b). Elastic (G') and viscous (G'') moduli of sunflower (SF) and wheat (WO) oils based oleogels, realized respectively with beeswax (BW) and carnauba wax (CW) at the different percentages of 4, 7 and 8 evaluated in a temperature range comprised between 0 and 40 °C.

aggregate structures can entrap and retain oil in more strong way also at high temperatures. About beeswax samples, prevalence of viscous moduli with respect to elastic ones was observed at higher temperatures (within 30–40 °C) for both oils. In that temperature range, WO presented G'' values ranged from 1.27 $*10^2$ to 3.15 $*10^2$ and from 5.98$*10^4$ to 8.31 $*10^4$ for BW at 4 % and 7 %, respectively; whereas, SF displayed values from 1.16 $*10^2$ to 2.14 $*10^2$ at 4 % and from 5.50 $*10^4$ to 6.11$*10^4$ at 7 % of BW. However, at BW concentration of 8 %, a higher conservative modulus was highlighted than dissipative ones for both SO and WO samples. As shown in Fig. 2, SO BW samples displayed higher stability than wheat oil at lower temperature (from 0 to 20 °C). In relation to samples, WO with CW at 7 and 8 %, high stability was observed also at higher temperatures, showing no significant differences with respect to SO ones. The higher resistance to melting observed for both WO and SO samples in carnauba waxes compared to bee ones could be attributed to the different chemical compositions of these waxes in terms of esters, fatty acid and hydrocarbons chains that can interact between them giving rise to strong interactions that increase their resistance (Blake & Marangoni, 2014). As reported by Hwang et al., (2012) waxes with longer chain wax esters will exhibit superior gelation compared to waxes with shorter chain wax esters. Moreover, despite the wax characteristics, as reported by Sato (2005), Dessanaiake et al., (2012) and Choi et al., (2020), the rheological, morphology and stability properties of oleogels drastically changed with the oil used, because of the differences in triacylglycerols (TAGs) composition as well as the number of total polar materials, that involved different interaction between oil and gelator, affecting their physicochemical properties (S4) (Kim et al., 2010; Amita Devi & Khatkar, 2016; Akkaya , 2018). This behavior could explain the lowest affinity and structuring ability of WO in BW with respect to SO, but also the highest and most promising stability of wheat oil in carnauba wax, as showed also previously by frequency sweep rheological analysis (Section 3.1.1).

3.2. *Microstructural analysis*

Crystal morphologies and their arrangement were studied for better understanding the impact of gelator concentrations as well as oil characteristics on the oleogel formation and stability. In Fig. 3 the different

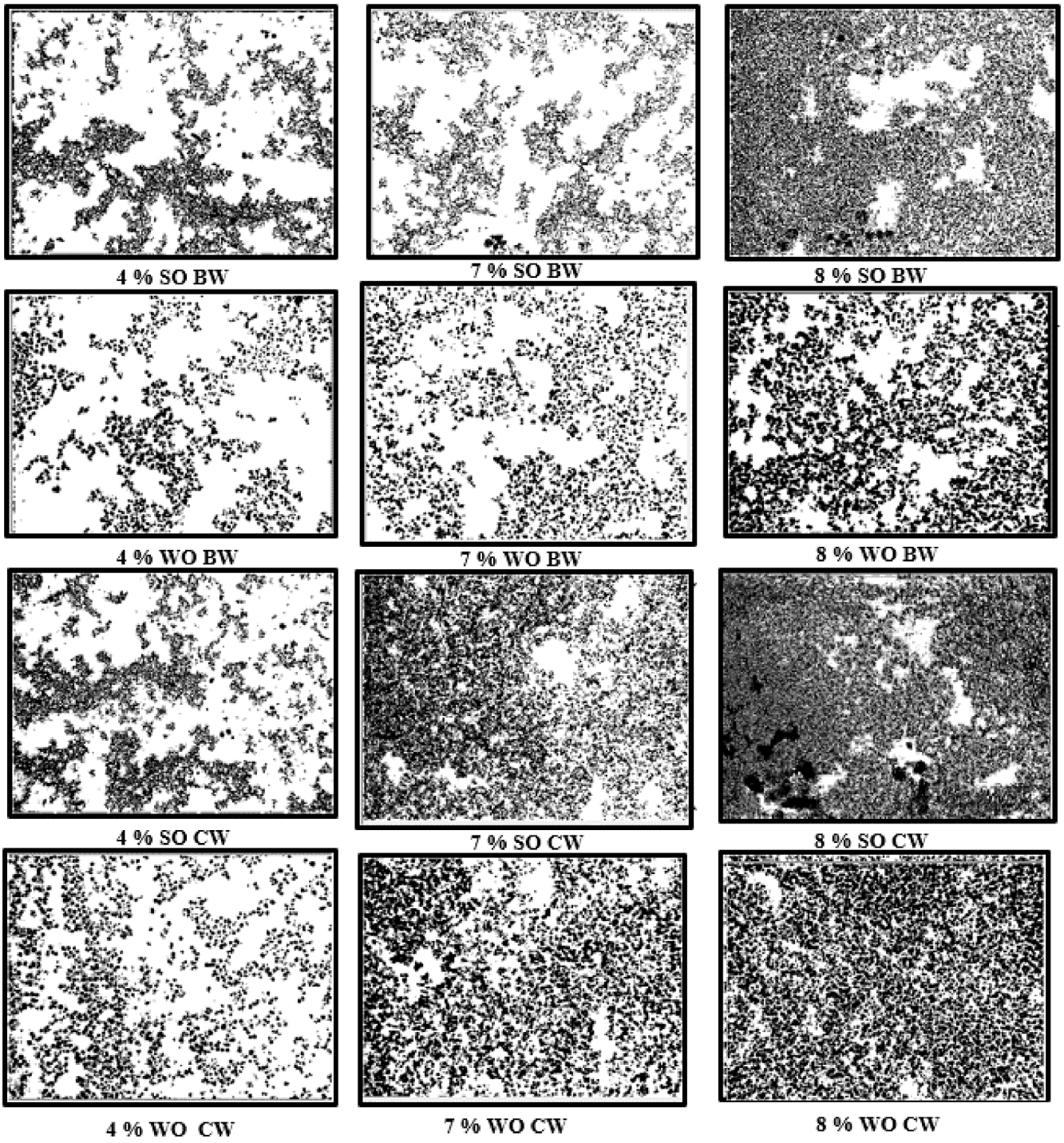

Fig. 3. Thresholded micrographs of oleogel samples acquired at 4x of magnification in brightfield mode.

micrographs of oleogel samples obtained with different oils and waxes at different ratio are displayed. As shown in Fig. 3, a progressive increase in the crystal aggregation was observed when the waxes amount for both sunflower (SO) and wheat oil (WO) increased, highlighting as the crystalline structures were also affected by the gelator concentration (Pang et al., 2020). This behavior can be reasonably attributed to the structuring effect exerted by waxes, that entrapped liquid oil into their solid matrix, increased their solid fraction volume, by reducing void spaces, made up from not binding oil, giving rise to a more compact structure, as well as to a denser network (Sagiri et al., 2015). As reported by literature, oleogelation is the process of making oil-based continuous gels in which the gelator, in this case waxes, immobilizes liquid oil within a structured three-dimensional network by oil-wax interaction stabilized through, Van der Waals interactions, hydrogen bonding and electrostatic interaction (Wijarnprecha et al., 2019; Sivakanthan et al., 2022). BW samples showed a more needle-like structure while CW a typical dendritic-spherulitic shape, as highlighted from a detail of micrographs realized with 7 % of waxes at both 10x (S6) and at 20x (S7) of magnification, that according to literature, tend to form clusters of small crystals leading to network formation as a result of aggregate overlapping (Blake & Marangoni 2014; Wang et al., 2016; Dassanayake et al., 2012; Pang et al., 2020; Silva et al., 2021). Moreover, samples

realized by dispersing oil in beeswax showed a higher amount of void space between crystals, involving the presence of a less strong network with respect to carnauba ones as also confirmed by fractal analysis, even if SO_BW samples presented a more aggregate matrix than wheat oil beeswax. On the other hand, in the presence of carnauba wax (CW) similar structures were highlighted between SO and WO, characterized by the presence of more strong networks between crystals, especially at higher wax concentrations, probably related to an increase in the contact points due to chemical and mechanical interactions between oil and waxes that reduced void spaces, as also showed by box-counting fractal dimension index (Table 2) (Servais et al., 2004; Choi et al., 2020). That value is an indicator of the spatial distribution of the solid mass in the oleogels' crystal network; allowing to numerically estimate the uniformity of the solid mass distribution in the oleogels' crystal network; greater fractal dimensions underline more homogeneously distributed mass or more uniformly filled space and so lower empty cavities and so lower pore area fraction (AFp), (Tang & Marangoni, 2006; Blake, 2015; Frolova et al., 2022). Moreover, according to literature (Narine & Marangoni, 1999; Blake & Marangoni, 2014, 2015; Shi et al., 2021; Frolova et al., 2022) this parameter can be used to describe some macroscopic properties of the oleogels, such as their oil-binding capacity strictly related with their stability and so the separation of oil from the oleogels during time, as well as to their hardness and viscoelastic properties. Higher fractal numbers values as observed for oleogel samples realized with carnauba wax at both 7 and 8 %, underlined the presence of high numbers of homogeneous small crystals evenly distributed through the material, which generated a matrix with high capacity to retain oil; small crystals provide more surface area for oil to adsorb onto compared to the larger ones (Omar et al., 2015; Palla et al., 2019). At the same time, higher fractal numbers are related to lower AFp, that highlighted the presence of a highly structured network with homogenously distributed crystals, able to bind more oil, that reducing the volume of free oil, decrease its migration and so improve structure stability (Blake, 2015; Yang et al., 2018). Studies focused on oleogels and fat networks (Vreeker et al., 1992; Marangoni & Rousseau, 1996; Litwinenko et al., 2002; Mellema et al., 2002; Palla et al., 2019; Frolova et al., 2022) highlighted as fractal analysis can be a good indicator for hardness and viscoelastic behavior. Generally, higher fractal dimensions are present in ordered, dense and compact fat networks composed of tightly packed structures with high hardness and higher elastic moduli, whereas, networks characterized by disordered, open and low-density structures, result in lower fractal values, as shown for samples realized with waxes at 4 %. In the presence of CW, WO samples displayed similar fractal values as SO ones, not significantly different ($p>0.05$) from them, and even as for 8 % WO CW, (1.89) greater than sunflowers oils (1.84), giving further evidence of the strong network and high elastic modulus characterizing this sample. In addition, the fractal approach can detect small changes in rheological properties in terms of hardness and G' of fat networks also in the presence of no significant changes in their solid fat content, as in the case of aging in which post-hardening or post-crystallisation of oils and fats frequently occur (Vreeker et al., 1992; Omar et al., 2015). However, some deflection from this trend can be observed as in the study of Blake (2015) on different oleogel matrices, because of differences in the particle morphology and particle size of the microstructural elements present in the wax.

Table 2
Box-counting fractal dimension (Db) of the different oleogels derived from brightfield micrographs.

Samples	Box- Counting Fractal Dimension (Db)
4 % SO BW	1.38±0.08c
7 % SO BW	1.61±0.06b
8 % SO BW	1.69±0.07b
4 % WO BW	1.35±0.04c
7 % WO BW	1.58±0.10bc
8 % WO BW	1.67±0.09b
4 % SO CW	1.45±0.11bc
7 % SO CW	1.81±0.10ab
8 % SO CW	1.84±0.10ab
4 % WO CW	1.40±0.11c
7 % WO CW	1.83±0.03ab
8 % WO CW	1.89±0.04a

[a-c] letters significantly differs at $p< 0.05$ for different samples at the different concentration

3.3. Oil loss evaluation

In Fig. 4 is reported the oil loss of different samples after centrifugation and 24 h of resting time. According to Blake & Marangoni (2014) and Hang et al. (2022) the long-term stability of oleogels was evaluated as the maximum amount of oil that is retained or lost by the material over a specified (usually "long'') length of time (in the case of this study, 24 h). This approach is particularly suitable in situations involving products storage, where the long-term stability of a material is of interest. Moreover, the integrity and the maintaining of the oleogels structure according to (Zulim Botega et al., 2013; Flöter et al., 2021; Li et al., 2022; Sivakanthan et al., 2022), is mostly expressed as the fraction of oil remaining in the structure after applying external forces, mostly centrifugal force and as oil loss. In our study, samples composed of the lowest percentages of waxes, both BW and CW, presented the highest oil loss percentages, being characterized by poor networks and lowest elastic moduli compared to the other samples, which tend to entrap less liquid, involving a higher oil release and so a poor integrity of the structure (Martins et al., 2016). On the other hand, oleogels showed a reduction in oil migration as wax concentration increased, presenting better performances in the presence of the carnauba one (Yang et al., 2017). Very promising results were obtained for WO samples in the presence of 7 % and 8 % of carnauba waxes, showing the significant lowest oil migration values compared to SO_CW oleogels (Fig. 4). Obtained results can be probably attributed to a very stable three-dimensional network formed during oleogelation, characterized by lower cavities and higher surface areas, as stated by microstructural analysis, that was sufficiently strong to entrap the liquid oil and to form a more physically stable gel, also after removing samples from beakers, that doesn't affect their structural characteristics (Yang, 2011; Frolova et al., 2022; Kim et al., 2022). Moreover, According to Palla et al. (2019), the oil loss and so the oil-binding capacity of oleogel samples are strictly correlated with the value of the fractal dimension, which as previously stated was higher for WO_CW.

3.4. Thermal analysis

In Fig. 5 and Table 3 the melting curve and the parameters related to thermal analysis (T_{onset}), main temperature peak (T_{peak}) and enthalpy (ΔH) of respectively melting (m) and crystallization (c) of sunflower (SO) and wheat (WO) oils based oleogels, realized respectively with

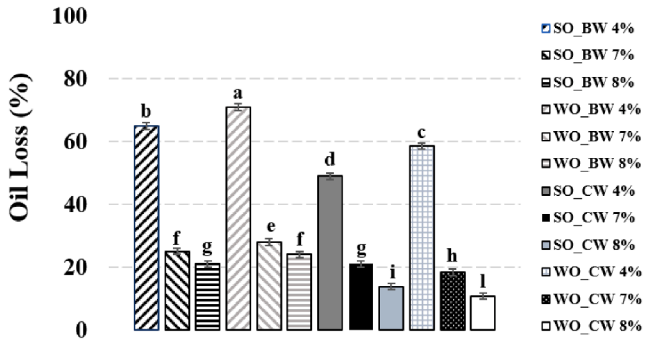

Fig. 4. Oil loss (%) of oleogel samples realized with sunflower and wheat oils in presence of respectively 4, 7 and 8 % of bee and carnauba waxes.

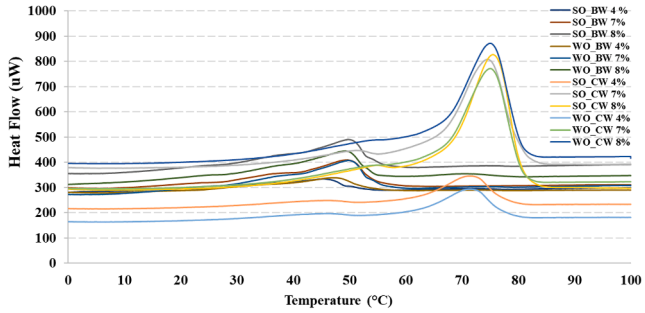

Fig. 5. Melting thermal profiles of sunflower (SO) and wheat (WO) oils based oleogels, realized respectively with beeswax (BW) and carnauba wax (CW) at the different percentages of 4, 7 and 8.

beeswax (BW) and carnauba wax (CW) at the different percentages of 4, 7 and 8 are shown.

All samples showed an increase in melting temperatures (T_{peak}) and melting enthalpies (ΔHm) with the increase of wax concentration, similar trends regarding the shifting of melting point values versus higher values by increasing wax concentration were reported by several authors (Blake & Marangoni, 2014; Martini et al., 2015; Yılmaz et al., 2015).

Carnauba wax samples showed higher onset (T_{onset}) and melting peak (T_{peak}), ranging from 55 to 84 °C, compared to beeswaxes ones (35 °C to 60 °C), in line with previous findings (Basson & Reynhardt, 1988 a, b; Aydeniz Guneser et al., 2021; Qu et al., 2024) probably due to their different chemical compositions. Carnauba wax is mostly constituted by wax esters and free fatty alcohols, while beeswax is high in wax esters and hydrocarbons. In specific, CW waxes are characterized by higher amounts of long-chained wax ester as reported by Davidovich-Pinhas, (2018) and Brykczynski et al., (2022) and high amount of long chain free fatty alcohols especially C_{32} and long chain fatty alcohols moieties, that need high temperatures to melt their structures exhibiting also higher gelation ability (Hwang et al., 2012; Doan et al., 2017; Lorenzo et al., 2023). In addition, the microstructural analysis highlighted the presence of higher dense and aggregate structure when carnauba wax at 7 and 8 % was used, both in the presence of sunflower and wheat oil, with respect to beeswax, as also confirmed by rheological analysis that being able to bind more oil needs more energy to melt, as also highlighted by fractal number and oil binding capacity results.

Moreover, in the temperature sweeps part differences in oil's TAGs composition affect the rheological and thermal properties of samples. In WO, the presence of higher amount of saturated fatty acids (S4) compared to SO Kim et al. (2010) and Akkaya (2018) led to a slightly higher melting point, that positively affected oleogels oxidation stability; in addition, it has to be considered the presence of antioxidants such as α-tocopherol, β-tocopherol. On the other hand, a higher level of unsaturated fatty acids is correlated to a lower melting point (Amita Devi & Khatkar, 2016; Perța-Crișan et al., 2023). Moreover, according with literature the choice of structuring agent with high melting points, as highlighted from carnauba wax, then those with lower melting points can provide better oxidative stability to oleogels (Hassim et al., 2022; Perța -Crișan et al., 2023).

In both cases (beeswax and carnauba wax) a shoulder before the main melting peak was highlighted, in relation to the presence of another peak, as showed also for pure wax, but in the former in a less enunciated way probably due to the presence of oils that modify thermal properties of waxes. Double or several peaks can be related to the co-existence of different chemical and molecular compounds, with different thermal properties (Blake & Marangoni, 2014; Martini et al., 2015). Crystallization profiles (S8) underlined the co-existence of several different molecular compounds (several crystallization peak), as well as different crystals populations with different crystallization temperatures in relation to their fractionated degree (Martini et al., 2015). Moreover, as observed by several authors (Toro-Vazquez et al., 2010; Blake & Marangoni, 2014; Dassanayake et al., 2012; Martini et al., 2015; Sivakanthan et al., 2022), the presence of oil with different fatty acid and fatty alcohols compositions dependent on the length of their chemical chains, affect oleogel crystallization, in terms of polymorphic crystal types and its thermal behavior. At last, also for crystallization parameters, a linear relationship between enthalpies and rheological, as well as microstructural parameters was observed, strengthening our previous findings (Table 3).

4. Conclusions

Overall results showed the potentiality of wheat durum oil to be employed for developing stable oleogels. In particular, fundamental rheological analysis both frequency and temperature sweeps, highlighted the presence of a very firm structure, with a predominance of elastic modulus also at high temperatures for samples of wheat durum oil-based containing up to 7 % and 8 % of carnauba wax, without significant differences with respect to samples obtained with sunflower oil. Again, the lowest stability was observed for both oils (WO and SO) in the presence of beeswax, probably in relation to its lowest gelation ability strictly related to its chemical composition. Microstructure evaluation also underlined the presence of very strong networks for WO and SO in the presence of carnauba waxes. On the other hand, the fractal analysis dimension also highlighted significant higher values for WO samples than SO, corroborating the high oil binding capacity of WO samples at 7 % and 8 % of CW. Obtained results, confirm the suitability of WO-

Table 3
Peak onset (T_{onset}), main temperature peak (T_{peak}) and enthalpy (ΔH) of respectively melting (m) and crystallization (c) of sunflower (SO) and wheat (WO) oils based oleogels, realized respectively with beeswax (BW) and carnauba wax (CW) at the different percentages of 4, 7 and 8.

	Melting			Crystallization		
	Tm_{onset} (°C)	Tm_{peak} (°C)	ΔH_m(mJ/mg)	Tc_{onset} (°C)	Tc_{peak} (°C)	ΔHc (mJ/mg)
4 % SO_BW	37.89±1.04 cd	47.85±0.89 cd	0.80±0.04d	46.17±1.18d	43.04±1.78bc	−1.12±0.09c
7 % SO_BW	41.30±1.10c	49.55±0.59c	1.17±0.09c	48.91±2.14d	46.19±1.22b	−1.22±0.19c
8 % SO_BW	42.19±1.03c	49.83±1.18c	3.97±0.47b	48.43±1.07d	45.22±2.09b	−3.18±0.67b
4 %WO_BW	36.48±1.09d	46.05±0.52d	0.94±0.04d	43.28±0.87e	39.09±1.18c	−0.61±0.05d
7 %WO_BW	39.20±0.82c	49.30±1.12c	1.47±0.18c	44.21±2.07de	41.81±0.79c	−1.03±0.11c
8 %WO_BW	41.52±1.02c	49.55±1.31c	3.74±0.28b	55.05±1.12c	47.28±1.44b	−4.18±0.65b
4 % SO_CW	54.74±1.12b	69.50±1.14b	1.09±0.19d	74.92±1.84b	63.44±2.17a	−1.13±0.12c
7 % SO_CW	56.71±0.29b	74.71±2.24a	6.11±0.64a	74.37±1.48b	62.40±1.46a	−5.84±0.87a
8 % SO_CW	57.87±1.18ab	75.02±1.74a	6.62±0.78a	77.93±1.07a	63.57±1.32a	−6.37±0.93a
4 %WO_CW	54.58±1.07b	68.21±1.03b	0.98±0.08d	74.74±1.18b	63.46±1.89a	−1.05±0.08c
7 %WO_CW	58.37±1.06a	74.4±2.18a	7.16±0.89a	73.64±1.74b	63.29±2.09a	−6.43±0.89a
8 %WO_CW	58.66±1.01a	75.31±1.09a	6.78±0.74a	78.19±1.49a	62.39±2.40a	−7.14±1.11a

[a-e] Values followed by different letters differ significantly at $P < 0.05$ level between samples at different concentration and waxes type for each different thermal parameter.

based oleogel to be successfully employed as fat-mimic matter; however, a deeper study focused also on the sensory aspects of the stabilized and developed oleogels is required in order to better define its applications in the food industry.

In conclusion, it is possible to highlight the promising ability of wheat oil a by-product obtained from wheat milling processing, rich also in bioactive compounds, to be employed in the food sector, as an alternative to sunflower ones, to develop oleogels with optimal performances and characteristics in terms of rheological and structural stability.

Declaration of Competing Interest

We like to declare that the authors have no conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.foostr.2024.100397.

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