

Wax-Based Oleogels—Properties in Medium Chain Triglycerides and Canola Oil

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The non-triglyceride structuring of liquid oils, so-called oleogelation, enables new and more beneficial product designs. Natural waxes have proven to be excellent oleogelators due to their wide availability and low inclusion levels. However, waxes vary greatly in their compositions and contain different proportions of major components: wax esters (WE), fatty acids (FA), fatty alcohols (FaOH), and hydrocarbons (HC). In this study six waxes (bees (BW)-, sunflower (SFW)-, ricebran (RBW), carnauba (CRW)-, candelilla (CLW)-, and sugarcane wax (SCW)) are selected to develop a pairwise assessment regarding the major components. Commercial canola oil, rich in minor and polar components, and medium-chain triglycerides (MCT), as a “clean” saturated solvent, are used to elucidate the effect of solvent type on the gel forming behavior of 10% w/w oleogels. The gels are analyzed rheologically, penetrometrically, microscopically, and by calorimetry. It can be shown that the solubility and presence of polar minor components are crucial factors in oleogelation.

Practical applications: Useful areas of application can be found in products with high proportions of saturated and trans fatty acids, a high potential of substitution, and can for instance include bakery-, meat-, culinary- and confectionary products.


are closely related to cardiovascular diseases. Far more physiologically valuable vegetable oils, such as canola oil, have an improved, beneficial fatty acid profile. However, in many products, the substitution of fat phases with increased amounts of hardstock fats with straight oils is not possible due to their liquid state. Properties important for products, such as texture, foam, or emulsion stabilization, cannot be achieved by oils. For that reason, the gelation of oil, so-called organogelation/oleogelation can be used to transform liquid oils into gels delivering required functionalities. The production of the oleogels is possible with a wide range of structuring agents such as cellulose derivatives,^[1,2] proteins,^[3,4] phytosterols and phytosterolesters,^[5] and waxes.^[6] Potential structurants should be food grade, affordable, deliver similar organoleptic characteristics, variable in techno-functional properties and noninterfering with other ingredients.^[7,8] Waxes fulfill almost all criteria which is why they are supposedly the most promising structurants currently.^[6]

Natural waxes differ widely in proportions of wax esters (WE), hydrocarbons (HC), fatty acids (FA), and fatty alcohols (FaOH) present. The wax composition strongly depends on the organism (animal or plant based) and geography of origin. The term waxes covers a wide range of materials relating to the various natural functionalities they fulfill. The excellent oil structuring abilities some waxes exhibit is mainly attributed to the presence of long chain wax esters. However, the structuring is highly dependent on overall wax composition and WE concentration,^[9–11] cooling rate,^[12,13] applied shear,^[14,15] and oil quality. The capacity of a wax to gel is often expressed as minimal or critical gelling concentration (CGC). On one hand the CGC, mostly regarded as the concentration above which the oil does not flow under gravitational force, is not well defined since it depends on the crystallization process. On the other hand, this observation is primarily depending on the solubility of the structurants and second on the ability of the existing crystals to form a network. Since the term waxes covers a quite diverse group of multicomponent systems, studying these at CGC is at risk to overemphasize the role of the components dissolving only at the highest temperature in the respective system studied. Hence, the use of CGC results in structure formation by only a minute fraction—material with apparent composition higher

1. Introduction

In many foods fat phases are structured by high melting triacylglycerides (TAGs), so-called hardstock fats. These provide the necessary product properties. They consist in high amounts of esterified saturated fatty acids, if not small amounts of *trans* fatty acids are still present due to insufficient hydrogenation. These

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than the solubility that supplies structure—of the structuring material. Consequently, this type of assessment excludes other components that do contribute to structure formation if either temperature is lower or structurant concentrations are higher, resulting in different compositions of the solid phase. After all, the sequential crystallization of saturated TAGs plays a major role in traditionally TAG structured lipid phases. The area of wax-based oleogels has already been studied quite excessively. However, the works by Doan et al.,^[10] are laudable because the detailed compositional analysis of various waxes is a necessary prerequisite to a better understanding of the underlying mechanisms of wax-based oil structuring. This combines well with the two systematic studies on oleogels covering several waxes originating from the same lab,^[16,11] so that already some insights for the contribution of different molecule classes to structure have been formulated.^[10] In contrast to the different waxes, the effect of the oil to be structured has been addressed less systematically. Despite the fact, that waxes have been used to structure different oils it remains difficult to compare the results originating from different labs. The contribution of oil Hwang et al., studied combinations of sunflower wax with thirteen different vegetable oils.^[17] The variations found could unfortunately neither be explained to oil quality nor fatty acid composition of the respective oils. S. Jana and S. Martini examined the properties of bees wax (BW) in six different oils. The focus of this work was however the application of high intensity ultrasound (US) during crystallization. Consequently, mainly differences between treated (US) and untreated samples were discussed.^[12] However, to explain differences between different oils minor components and solubility differences were mentioned. In an earlier contribution from our lab it was revealed that the gel–sol transition temperature in sitosterol/oryzanol oleogels does practically not change with oil quality: fatty acid composition, minor components.^[5] In another manuscript of ours it appeared that the gel–sol transition temperatures of sunflower-wax oleogels can reasonably well be described by ideal solubility calculations.^[18] The body of studies concerning the characteristics of the oil to be structured indicate that the oil matters but does not allow to draw solid conclusions. Elucidation of the role of oil quality in wax-based oleogels appears to be crucial for future product applications. To this end, the work presented here aims to systematically investigate the effect of different oils in combination with waxes that differ in their molecular compositions. The investigation covers the respective combinations of six natural waxes with either canola oil—rich in monounsaturated fatty acids (C18:1)—or a medium-chain triglycerides oil (MCT). The latter is a “synthetic” oil composed of saturated C8 and C10 fatty acids.

2. Experimental Section

2.1. Material

Canola oil (refined) was provided by Brökelmann+Co—Oelmühle GmbH+Co (Hamm, Germany) and exhibited a typical composition (64% oleic acid, 19% linoleic acid). MCT-oil (Miglyol 812) was obtained from Caesar & Loretz GmbH (Mainz, Germany) and was composed of 56.4% caprylic acid and 43.6% capric acid. Polarities were determined by Testo 270 cooking oil tester (Titisee-Neustadt, Germany) (4.5%TPC Canola,

0%TPC MCT oil). Sunflower wax (6607L, Lot.nr. F1911020-0010) (SFW), beeswax (8108LM, Lot.nr. F1727017-001) (BW), Ricebran wax (2811, Lot.nr. F1851015) (RBW), Candelilla wax (2039L, Lot.nr. F1915044-001) (CLW), and Carnauba wax (2442L, Lot.nr. F1806007-001) (CRW) were kindly supplied by Kahlwax GmbH & Co KG (Trittau, Germany). Sugarcane wax (SCW) (X 5217M, Lot. Nr.: 20-092) was supplied by Deurex AG (Elsteraue, Germany). All materials were used without further modification.

2.2. Methods

2.2.1. Preparation of Gels

Oleogels with a constant wax concentration of 10% w/w were produced to ensure consistently clear signals throughout the different analytical procedures. Building on data of CGC for different waxes after storage at 5 °C,^[16] it appeared necessary to use this relatively high concentration such that wax crystallization also occurs on stabilization at room temperature. The commercially available waxes (SFW, RBW, BW, CLW, SCW, and CRW) were used without any further treatment. Likewise, the canola and MCT-oil were used as received.

To ensure complete dissolution of the waxes the wax-oil mixtures were heated up to and kept at 90 °C for 30 min. These solutions (100 mL in a glass beaker, heating plate (MR Hei-Tech, Hei-dolph Instruments GmbH & Co.KG, Schwabach)) were stirred in the meanwhile with a magnetic stirrer at 200 rpm. Samples were prepared by carefully pouring the solution into petri dishes, sample size 40 g (\pm 1 g). The glassware was preheated (95 °C) to prevent instantaneous crystallization on the containers surface. To allow controlled sol–gel transitions the samples were stored for 48 h at 20.5 °C (\pm 1.5 °C) prior to any analysis. To avoid any changes of the gels due to sample preparation the samples for calorimetric, rheological, and microscopical analysis were prepared directly out of the hot solution into the respective measurement environment.

2.2.2. Thermal Behavior

Differential scanning calorimetry (DSC) was performed using a 214 Polyma (Netzsch, Selb, Germany) calorimeter. The sample size was 6 mg (\pm 1 mg). The samples were conditioned before each measurement. The crucibles were heated from 20 to 105 °C with a heating rate of 5 K min⁻¹ and kept isothermally for 5 min. The samples were then cooled down to 20 °C at a rate of 5 °C min⁻¹. The samples were subsequently stabilized for 48 h at 20.5 °C (\pm 1.5 °C). Once again in the DSC, the crucibles were heated from 20 to 105 °C with a heating rate of 5 °C min⁻¹. After holding for 2 min, samples were cooled down from 105 to 5 °C with a rate of 5 °C min⁻¹. They were kept at 5 °C for 20 min. The same procedure (5–105 °C; 2 min at 105 °C; 105–20 °C; scan rates 5 °C min⁻¹) was repeated on the same sample.

2.2.3. Microscopy

Brightfield light microscopy (BFM) and polarized light microscopy (PLM) images were taken with a Axio Scope.A1 KMAT

microscope (Zeiss, Jena Germany) equipped with a AxioCam ICm1 Rev.1 camera. Both BFM and PLM images were taken of all samples to allow for comparison. Sample preparation was as reported earlier.^[18]

2.2.4. Image Analysis

Micrographs (brightfield) were processed with ImageJ 1.52a. Due to various morphologies it was not possible to establish an automated image analysis. After scaling on the scale bar (100 μm), digital zoom of 200% was applied and only single non-superimposed objects were characterized by their maximum diameter. This was done 40-times in two images, respectively.

2.2.5. Firmness

The firmness measurements were performed with a zwickiLine universal testing machine from Zwick Roell (Ulm, Germany) equipped with a 1 kN load cell (trigger force 0.02 N). The samples in the petri dishes were penetrated for 30% of the sample height (2.9 ± 0.2 mm). The penetration speed was 200 mm min^{-1} and the probe head was a 12 mm diameter stainless steel cylinder. Each sample (prepared twice) was subject to 5 penetrations, at sufficient distance from each other. Values of maximum force determined are averages of 10 independent values though.

2.2.6. Viscoelastic Properties

The viscoelastic behavior was analyzed with a MCR 302 rheometer (Anton Paar GmbH, Austria) using a parallel plate geometry. To avoid any slip a sandblasted PP25 ($d = 25$ mm) was used. To detect the sol–gel and gel–sol transitions both temperature and amplitude-strain-sweeps were performed. To distribute the samples on the geometry the hot liquid sample (≈ 5 mL) was poured onto the preheated Peltier Plate ($T = 90$ °C). Final gap distance was 0.2 mm. For stabilization purposes the sample was kept for 10 min under shear ($\dot{\gamma} = 1/\text{s}$). After 2 min under quiescent conditions, the samples were cooled down to 5 °C at a rate of 5 °C min^{-1} and kept isothermally for 30 min. After that, a heating scan up to 90 °C was performed. After a 2 min holding time, a cooling scan was performed again. Once the target temperature of 5 °C was reached, samples were stabilized isothermally for 30 min. Finally, the samples were subjected to a strain sweep ranging from 0.01% to 100% at an angular velocity of 10 rad s^{-1} . During temperature and time scans, a constant strain of 0.1% and a constant angular velocity of 10 rad s^{-1} was applied. The gap distance was allowed to compensate sample contraction since the normal force was set to be zero.

3. Results and Discussion

3.1. Calorimetry (DSC)

Regarding the functionality of the fat phase, knowledge of the solubility and crystallization kinetics are crucial for application

in products.^[19] The thermal behavior of the oleogels was determined using Differential Scanning Calorimetry, DSC. **Figure 1** shows the heating and cooling thermograms of 10% w/w oleogels in MCT-oil (gray line) and in canola oil (black line). Comparing the thermograms gathered quantitatively with the data presented elsewhere,^[16] which report on 5% w/w wax gels in ricebran oil, one finds quantitative agreement, in particular for the waxes predominantly composed of WE's. As anticipated the higher wax inclusion level results in additional identifiable solid phases.

For canola oil-based oleogels the different waxes reveal qualitatively distinguishable thermograms with varying number of thermal events. On heating two distinct peaks were identified in BW- (41.4 ± 0.1 , 53.0 ± 0.1 °C), CRW- (50.1 ± 0.2 °C, 74.8 ± 0.1 °C), and SFW-samples (57.4 ± 0.2 °C, 64.2 ± 0.1 °C). In contrast, RBW exhibited only a single crystallization event at 68.7 ± 0.3 °C with significant fronting starting at 38 °C. The two remaining waxes, CLW and SCW, yield oleogels characterized by multiple distinct thermal events; 48.1 ± 0.1 , 61.6 ± 0.1 , 68 ± 0.1 °C for CLW and 34.2 ± 0.3 , 60.9 ± 0.1 , and 71.3 ± 0.4 °C for SCW. Considering the major components listed in Table 1 it is fair to assume that the major peak found in the SFW (96.3% WE) and RBW (93.5% WE) based samples, which both contain predominantly WE, is due to wax ester dissolution. Despite the expansion of the peak over a broad temperature range, which is expected because of the continuous change in the wax solubility on temperature increase, the peaks do reveal shoulders. These shoulders are either, due to other components crystallized as well (see also)^[10] – this however, is unlikely due the very high concentration in wax esters – or to the presence of more than one crystalline wax ester phase. Such a presence of multiple coexisting solid phases is a well-established fact in triglyceride crystallization, e.g., in palm oil.^[20] For the RBW-sample this is already indicated by the pronounced second crystallization event depicted in the cooling thermogram. Regarding the CRW-sample the cooling curve showed three delimited peaks. These are found back, less pronounced though, in the heating thermograms. Considering the composition displayed in Table 1, these relate most likely to crystals of FaOH and two different WE crystalline phases. In sugar cane wax (SCW) the similarly high level of FaOH (32%) is accompanied by high levels of fatty acids (FA, 56.5%). Even though the cooling curve essentially shows a single crystallization peak, the heating thermogram reveals multiple events that partly overlap. BW, which contains a similar portion of WE as CRW, exhibited two distinct peaks on cooling. On dissolution, these solid phases seem to be found back in the canola oil-based sample. This is in agreement with earlier findings.^[21,22] Surprisingly, the heating thermogram of BW in MCT-oil (gray line) shows at least three events. At this stage, it remains unresolved if the qualitative differences between BW and CRW are due to the secondary component in the wax, 26.8% HC in BW and 30.7% FaOH in CRW^[21] assigned the lower melting peak of BW to HC though. Reported dissolution temperatures of oleogels based on behenyl- or stearyl-alcohol are reported to be 54.9 °C (10% w/w inclusion level)^[23] and 37.8 °C (5% w/w inclusion level),^[24] respectively. This renders the more than 2% dotriacontanol (C32-OH) in CRW a likely minor crystalline phase. CLW and SCW are characterized by exceptionally low levels of WE (15.8% and 6.8%). CLW, having a high level of HC, shows similarly to SCW a single clear

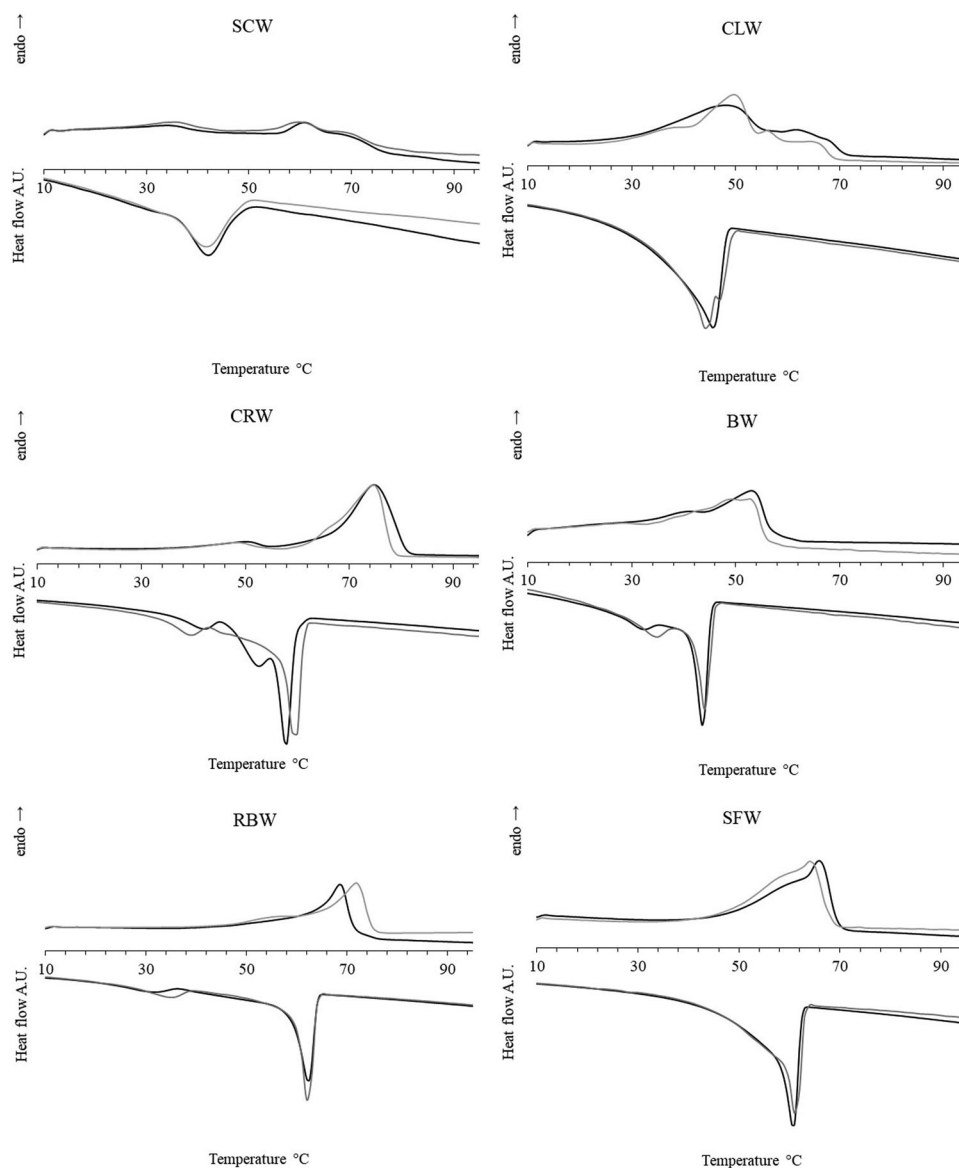


Figure 1. Heating and cooling thermograms (DSC) of oleogels with 10% w/w wax concentration in canola (black lines) and MCT-oil (gray lines). The arrangement corresponds to the increasing proportion of wax esters (left to right, up to down). Curves represent mean values of 3 independent measurements and are shifted on y-axis for convenience. First cooling and second heating data are shown.

crystallization event in canola oil. During crystallization in MCT-oil surprisingly two distinct adjacent peaks are found. Even though some differences are found in the respective dissolution curves, these clearly indicate the presence of multiple solid phases.

Comparing canola oil based and MCT-oil-based samples some differences occur. MCT-oil caused in practically all oleogel samples more distinct and better identifiable peaks. For RBW, CLW, and CRW in MCT-oil additional dissolution peaks were identified at 56.9 ± 1.9 , 35.8 ± 0.8 , and 65.6 ± 0.1 °C, respectively. BW showed even greater diversity with three additional events (29.3 ± 1.9 , 43.3 ± 1.2 , 49.8 ± 0.8 °C) in MCT-oil. Similar effects can be observed during crystallization. SFW (61.4 ± 1.8 °C), CRW (39.6 ± 0.0 °C), and CLW (44.4 ± 0.1 °C) showed one extra peak com-

pared to canola oil-based systems. In the RBW, SCW, and BW solutions only marginal changes between systems based on different oils could be observed.

As stated by Hwang et al., who studied the melting behavior of SFW in various plant oils, it remains an insurmountable task to elucidate the underlying mechanism for variations due to number of obvious and hidden factors.^[17] However, the detailed composition of waxes, the solubilities of different solutes, and the distinction of kinetic effects and equilibrium should be considered during the interpretation of experimental evidence.

Since waxes are already multicomponent within each characteristic classes of molecules, such as wax esters, it is difficult to find a relevant characteristic property. The simple reduction to the wax ester content does not lead to a satisfying description that

Table 1. Normalized composition of natural waxes in%, categorized in major groups (main wax components). CN = carbon number.

	CLW ^a	BW ^a	CRW ^a	SCW ^{a, b}	RBW ^a	SFW ^a
HC	72.92	26.84	0.41	4.8	0.29	0.17
WE	15.76	58.00	62.05	6.8	93.49	96.23
FA	9.45	8.75	6.80	56.5	6.00	3.29
FaOH	2.20	6.42	30.74	31.9	0.22	0.30
CN _{WE}	34–52	40–48	43–56	40–58	44–52	44–50

^a Doan et al. 2017 ^b Attard et al. 2015, Rind.

corresponds with the crystallization behavior. In an earlier contribution of ours,^[18] it was however shown that for specific waxes, such as SFW, the approach to consider WE concentration and ideal solubility can yield meaningful results. In waxes with more complex compositions, the significant fractions of FA, FaOH, and HC cannot be ignored because it is proven that these either individually or in adequate mixtures do structure liquid oils as well. After all, wax esters remain the most prominent component in most waxes and drive oleogel microstructure and hence the macroscopic properties. Comparison of RBW and SFW reveals that both waxes contain a very high fraction of WE (94% and 96% w/w) with a similarly spread carbon number distribution (44–52 and 44–50 carbons) within the WE fraction. However, regarding oleogel performance, SFW is clearly more effective than RBW. Building on the data given by Doan et al.,^[10] the differences between these two waxes becomes apparent. Compared to SFW the RBW has a flatter distribution of the chain length in both fatty acids and fatty alcohol moieties: 55/25/7% and 38/30/12% versus 28/27/26% and 33/25/14%. This results in a much broader distribution of WE configurations. Consequently, RBW contains more WE with equal chain length but different position of the ester bond. It is well established that at least in pure WE this feature influences the crystallization behavior.^[25] Even though little is known about effects in mixed solid phases, this possibly is the root cause for the differences observed.

Combining the thermal data gathered and the compositions given in **Table 1**, a relation describing the undercooling found as a function of WE concentration and composition of the WE-fraction was sought. It was found that the latter can conveniently be expressed as chain length disparity ΔCN_{WE} . It is determined according to Equation (1)

$$\Delta CN_{WE} = CN_{max} - CN_{min} \quad (1)$$

Where CN_{max} is the longest and CN_{min} the shortest reported occurring chain length. It was found that it is necessary to scale this disparity with the concentration of the individual WE and the overall WE concentration. These considerations resulted on the definition of a wax ester concentration scaled degree of homogeneity, DoH:

$$DoH = \frac{x_{WE}^2}{\sum (x_n^2)} \cdot \frac{100}{\Delta CN_{WE} + 1} \quad (2)$$

Where x_{WE} is the WE fraction (w/w) in the wax, x_n is the incidence of wax component (n). The main components considered are WE, HC, FA, and FaOH. Calculations were based on data ob-

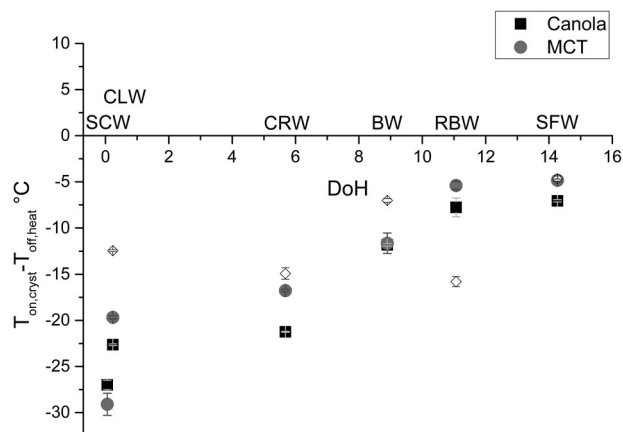


Figure 2. Undercooling of 10% w/w wax-oleogels as a function of calculated degree of homogeneity (DoH). Gray symbols = MCT-oil, black symbols = canola oil, diamonds = external data (5% w/w inclusion level).^[16]

tained by Doan et al.^[10] and Attard et al.^[26] The resulting DoH values are as follows: SCW: 0.06, CLW: 0.23, CRW: 5.68, BW: 8.89, RBW: 11.07, and SFW: 14.27. Low DoH values are computed for either low WE concentrations or broad WE chain length spread. A DoH 100 is characteristic for a pure wax ester.

Despite acknowledging that the undercooling derived from DSC thermograms is not a well-defined material characteristic but also a function of the cooling rate, it is plotted as a function of DoH in **Figure 2**. In the above-mentioned contribution,^[16] the temperature differences between sol–gel and gel–sol transition for different waxes at 5% w/w dosage in ricebran oil were reported. Surprisingly, the values reported are consistently smaller despite the lower wax concentration studied. Additionally, the data reported do not follow the trend revealed in **Figure 2** (diamonds).

Due to the multicomponent character of waxes and resulting complexity of the thermograms, the undercooling is defined here as the difference between the melting offset ($T_{m,offset}$) and crystallization onset ($T_{c,onset}$). The data shown indicate that the undercooling is lowest for highest DoH's, hence SFW. Furthermore, the data suggest that there is a linear relationship between undercooling and DoH. The relation formulated clearly outperforms efforts to correlate the undercooling with either, concentration or homogeneity of the WE present in a wax. Regarding the definition of DoH, it is quite surprising that the waxes with low WE-content also seem to follow the relation formulated.

Regarding the effect of the two oils compared in this study, Figure 2 reveals that the basic finding holds for both oils. It indicates that despite the shift in transition temperatures displayed in Figure 1 the undercooling found is similar for both oils. If any, there is a tendency that MCT-oil-based samples show smaller undercooling. This could possibly relate to the purity of the oils with respect to the presence of minor components.

As mentioned before, the thermograms in Figure 1 show some changes when the waxes are combined with the different oils. Assuming ideal solubility, one has to take into account that the molecular weight distribution of canola and MCT-oil differ significantly. Taken an average chain length for the fatty acids of C18 in canola oil and of 9 in MCT-oil, substantial differences in the molecular concentration of the solutes emerge. Reducing SFW to a WE with 47 carbons, the 10% w/w dosage yields a molar wax fraction of 0.12 in canola and 0.073 in MCT-oil samples. Computing the gel–sol transition temperatures as described earlier,^[18] respective values of 66.5 and 64 °C are found. This shift in molar compositions between the samples based on different oils is also influencing the changes in relative positions of peaks observed. The actual data, however, prove the assumption of ideal solubility at least questionable. The evolution of onset crystallization temperatures and in particular the gel–sol transition temperatures found for RBW clearly indicate nonideal behavior. Preliminary studies on the “molar” – which is for the highly mixed system present approximately correct – solubility of SFW showed, that the wax has a significantly higher solubility in canola than in MCT-oil. This finding warrants a more detailed study on the interaction of wax esters and oils.

The solubility is an important characteristic as it predominantly defines the gel–sol transition and the presence of solid material, the solid wax content (SWC), and consequently the formation of a 3D network.

Content of solid matter is important for the interpretation of the macroscopic properties by indicating the structural efficiency. Solid wax content data in oleogels reported^[21,27–29] are based on pNMR measurements. The methods applied appear to be specific for solid TAGs and therefore the actual solid phase of oleogelators cannot be determined without data transformation.^[19] The determination of solid materials by DSC is a method independent of sample calibration,^[30–32] which makes it attractive for wax-based oleogels. This method assumes that the heat of fusion determined for the pure solute is pro rata expressed for the solid matter dissolving in mixed systems (Equation (3)). This is certainly applicable for a pure solid which does not undergo polymorphic transitions. Taking the complexity of wax crystallization with co-existing solid phases this certainly deserves further verification.

$$\text{SWC } (\%) = \frac{dh_{\text{oleogel}} \cdot 100}{dh_{\text{wax}}} \quad (3)$$

Figure 3 depicts the solid material content according to Equation (3) derived from DSC-curve integration of thermograms from pure waxes and oleogels over the temperature range from 20 to 90 °C. First, it has to be noted that a break in the y-axis was inserted to emphasize the differences between the samples. According to the method outlined, BW in canola oil had the lowest solid wax content (SWC) of 7.1%. This corresponds to a solubility at 20 °C to be 2.9% w/w. The data for BW-based gels

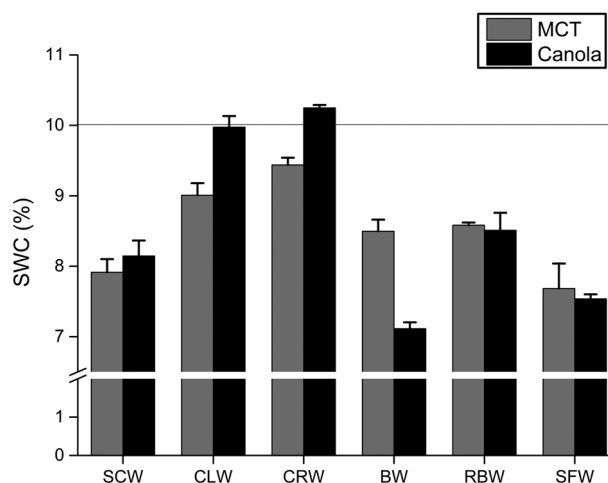


Figure 3. SWC (%) according to Equation (3) for 10% w/w oleogels (mean out of $n = 3$) sorted by increasing DoH. Horizontal black line indicates 10% solid (100% added material). Gray pillars = MCT oil, black pillars = canola oil.

also show largest difference between the samples with different oils; a much lower solubility in MCT-oil (1.5%). For SCW, RBW, and SFW the solubilities determined in the two oil are practically identical. CLW and CRW are found to have the lowest solubilities. There, data for canola-based samples are peculiar, since these indicate the waxes insoluble. Figure 3 illustrates that no relation between solubility and DoH could be established.

The literature data on solubilities of waxes and critical concentrations are not univocal as recently published.^[33] For example, the solubilities reported for CLW vary in a range from 0.75% to 2% w/w covering the solubility in MCT-oil determined here (1.0%). Also the RBW solubility found here (1.4%) fits into the reported range from 1% to 5% w/w.^[33] The same holds for two solubilities of BW determined (2.9% in canola, 1.5% MCT) compared to literature values between 1.0% and 4.0% w/w. In summary, the approach followed appears promising but still shows some weaknesses. The solubility values are within the range of those reported earlier. Nevertheless, the disadvantage that possible differences in the solid matter between the 100% solute reference data and the actual oleogel data are believed to be the source of variations and unrealistic data, as obtained for CLW and CRW in canola oil might result from this flaw. The data furthermore emphasize that the solubility of waxes cannot be described by assuming ideal solubility because the solubility values in MCT-oil were not found to be consistently higher than those for canola-based samples.

3.2. Microstructure

The PLM micrographs of 10% w/w oleogels produced with MCT and canola oil are shown in Figure 4. In canola oil (upper row) CLW, BW, and SFW show needle-shaped aggregates. CRW forms dendritic and omnidirectional growing particles; the RBW oleogel is characterized by less branched aggregates. Some of these aggregates are quite extended while most of them appear small and bulky. SCW exhibited small grain-like particles sporadically agglomerated. These observations are

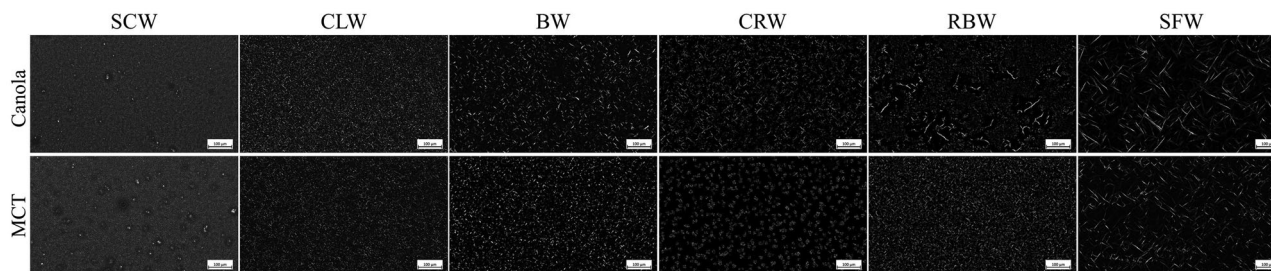


Figure 4. PLM micrographs of 10% w/w wax-based oleogels in canola (upper row) and MCT-oil (lower row) at 200x magnification. Images are sorted from the lowest (left) to highest share (right) of wax esters.

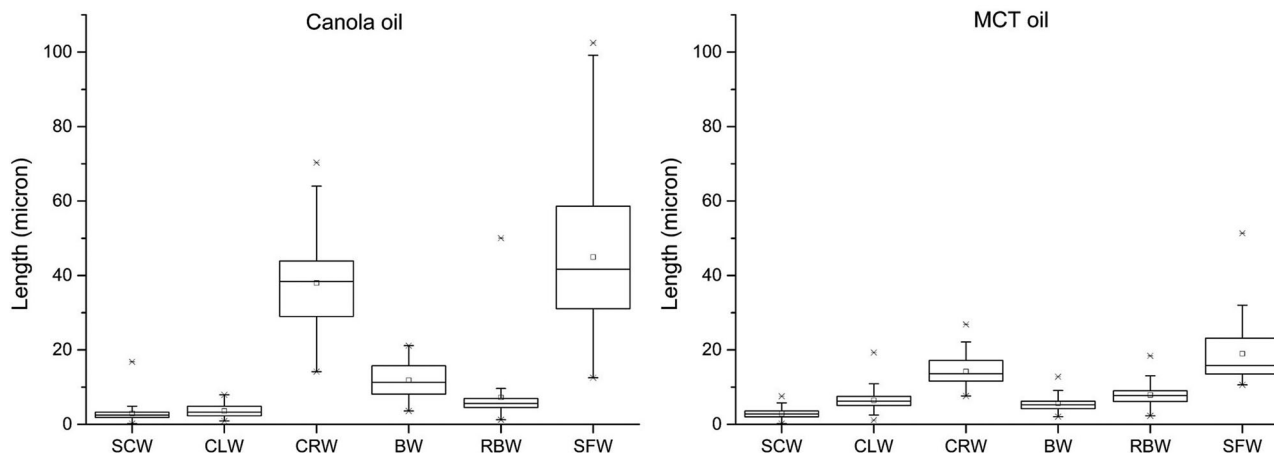


Figure 5. Boxplots of aggregate size, ferret max. diameter, based on 80 individual particles per sample. Square = mean value, cross = min and max, respectively. Left side = canola oil, right side MCT oil.

in broad terms in agreement with characterizations reported elsewhere.^[22,34,35]

However, if MCT-oil is used as continuous phase, different microstructures seem to emerge (Figure 4, bottom row). Except for CRW, which shows round and grain-like instead of dendritic particles, the wax crystals maintained their basic morphologies. Nonetheless, differences in particle or agglomerate size are found for the two oils. To quantitatively characterize these systems, particle sizes were determined using ImageJ software. Due to the absence – or lack of resolution – of single crystals, rather crystal agglomerates, hence solid entities were characterized by the Feret max. diameter. **Figure 5** depicts the processed data obtained. The crystal aggregate length distribution derived from BFM micrographs of 10% w/w wax oleogels is depicted as boxplots. Samples based on canola oil are shown on the left, those with MCT-oil on the right. For both oils the tendency for increased aggregate sizes with increasing DoH (*x*-axis) can be seen. Only CRW does not follow this trend.

When comparing gels based on the different oils, there is a tendency toward smaller aggregates for samples based on MCT-oil. This impression is most convincing considering CRW, BW, and SFW. The characteristic lengths discussed here are not the results of crystallization exclusively but account mostly agglomerates and hence agglomeration processes. Due to this fact, the data gathered will not be discussed in terms of supersaturation, nucleation, and growth.

CRW shows dense agglomerates with a grain-like morphology. Both, Dassanayake et al.^[36] and Ögütçü,^[37] found similar structures when gelling olive oil with CRW. This compact agglomeration possibly relates to the substantial fraction of FaOH (>30% in wax) present. The fact that also SCW, a wax with a similar level of FaOH but a different major component (FA), shows similar structures supports this conclusion. This is in line with the agglomeration behavior of mixtures of lecithins with FA and FaOH originating from fruit wax.^[38]

3.3. Structure Efficiency

Comparing the gel hardness of the different waxes at an arbitrary inclusion level – here 10% w/w – is certainly meaningful but ignores effects of solubility and changes of gel hardness as a function of varying concentration. To address this issue, the data on gel firmness, measured by penetration tests as described above, and amount of solid wax (SWC; Equation (3)) are combined to calculate the structural efficiency (S.E.) of the wax according to Equation (4). The values obtained for structural efficiency are shown in **Figure 6**

$$S.E. \left(\frac{N}{\% \text{solid}} \right) = \frac{F_{\max}}{SWC} \quad (4)$$

It can be seen that structural efficiency varies between the different waxes and different oils. SFW shows in both oils

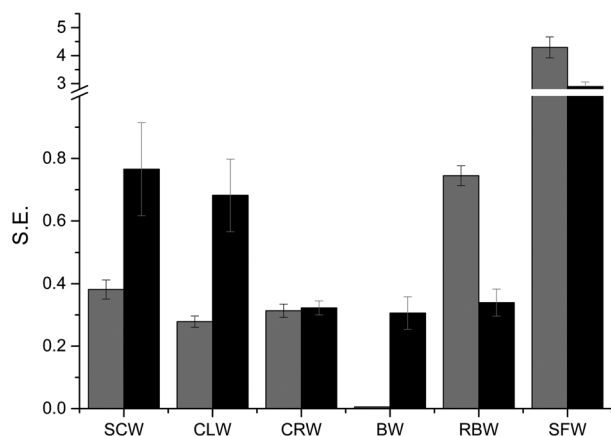


Figure 6. Structure effectiveness of waxes in 10% w/w oleogels. Mean values and standard deviations originate from $n = 10$ measurements. Gray pillars = MCT-oil, black pillars = canola oil. Waxes are ordered with increasing DoH.

exceptionally high structure efficiency with values of 2.9 ± 0.16 N/%solid in canola oil and 4.3 ± 0.38 N/%solid in MCT-oil. Ignoring the outstanding SFW performance, the structural efficiency varies between 0.3 and 0.8 with most data in the range 0.3–0.4 N/%solid. The gels based on CRW showed practically the same values irrespective of the oil immobilized. However, some dramatic difference between MCT- and canola oil-based gels were found. For RBW gels with MCT-oil show twice the value of canola-based gels. The analysis of the CLW and SCW-based gels indicate a structural efficiency of canola systems twice as high as for MCT oils. The value found for BW in MCT-oil is exceptionally low, 0.01 ± 0.001 N/% solid. This is the more so surprising because BW structures canola oil similar to the other waxes.

To discuss the structural efficiency over all structuring systems, it is fair to conclude that except for SFW and BW in MCT-oil, the values remain in the range given above. Even though the data available are not abundant Figure 6 suggest that in MCT-oil the waxes with higher DOH are more efficient. For waxes with low DoH this is effect seems inverted. Ignoring the DOH, but considering the actual wax composition it appears that waxes with very high WE concentrations ($> 90\%$) seem to be more efficient structurants in oils without minor components. On the other hand, the minor components present in canola seem to promote structure build up in SCW and CLW which predominantly contain fatty acid and hydrocarbons, respectively. Even though in another study comparing sterol/sterolester-based gels with either canola as usually used or purified canola oil, it was found that the oil depleted of minor polar components results in weaker structures this offers no explanation.^[5] The fact that it is shown that the minor components matter, does not offer any explanation for the differences observed.

3.4. Viscoelastic Properties

To investigate the sol–gel and gel–sol transitions of the gels different rheological experiments were carried out. To gather a most comprehensive data set these were temperature-, time- and

amplitude-strain sweeps. Figure 7 shows the cooling scans from 90 to 5 °C.

At first instance it is obvious that the six different systems behave quite differently. This holds for the general development of G' and G'' on cooling as well as the effects of the different continuous phases. To support the interpretation data temperatures extracted from the thermograms (Figure 1) are displayed in the x -axis as well. Here the squares mark crystallization onset temperatures and triangles peak temperatures. Additionally, the compositional data displayed in Figure 8 are considered supportive for the interpretation. First considering SFW, a dramatic increase in both G' and G'' is found in the temperature range defined by the onset of crystallization and peak temperature derived from DSC thermograms. In line with the DSC assessment no effect of the difference in oil used was detectable. Despite the fact that the melting thermograms indicate a second solid phase the change in rheological properties appears to relate to a single crystallization event. This observation appears to correspond well with the composition of more than 95% WE with a limited disparity in carbon numbers (highest DoH) suggesting mixed crystal formation. RBW has in the first place a composition that is similar to that of SFW, very high levels of WE. Despite similar DSC thermograms the rheological data of the two waxes differ significantly. For RBW, G' and G'' increase dramatically once the crystallization temperature as identified by DSC is reached. In MCT-oil this results in a step change which is followed by another increase at lower temperatures. The temperature of this second increase coincides with the second crystallization event identified during DSC. In the canola oil-based system the initial crystallization results in a less clean step but rather into a smooth increase after an initial step change. Also in this system another event is detected at the temperature of the second DSC crystallization peak. Considering the composition of RBW it is unlikely that this second crystallization peak is due to the small amount of fatty acids present (6%). It appears far more likely that the wider span of carbon numbers reported for RBW compared to SFW results in the coexistence of two solid WE phases of different composition. Even though CLW and SFW differ significantly in their composition, their basic rheological behavior on cooling is quite similar. CLW, which is mainly composed of hydrocarbons showed a step change in G' and G'' once the crystallization as indicated in the DSC thermograms is reached. Also in this case, no additional effects could be observed despite the identification of several solid phases during melting in the DSC. Further, no differences as a function of the oil type could be detected. SCW is similar to CLW in the way that it has a low concentration of WE. It contains significant portions of FA and FaOH. It is known that FA and FaOH show synergistic effects in oil structuring in case identical chain lengths are found. The temperature at which increasing values of G' and G'' occur in the SCW sample is slightly lower than the crystallization temperature identified in DSC. The increase in these two characteristics is much less a step change than in the other systems. The continuous increase appears much more related to a continuously decreasing solubility. Finally, also for SCW, which shows multiple melting events in DSC, the crystallization on cooling in the rheometer does not seem to vary with oil type. Finally BW and CRW both have a high WE content, 58% and 62% w/w, respectively. Both have

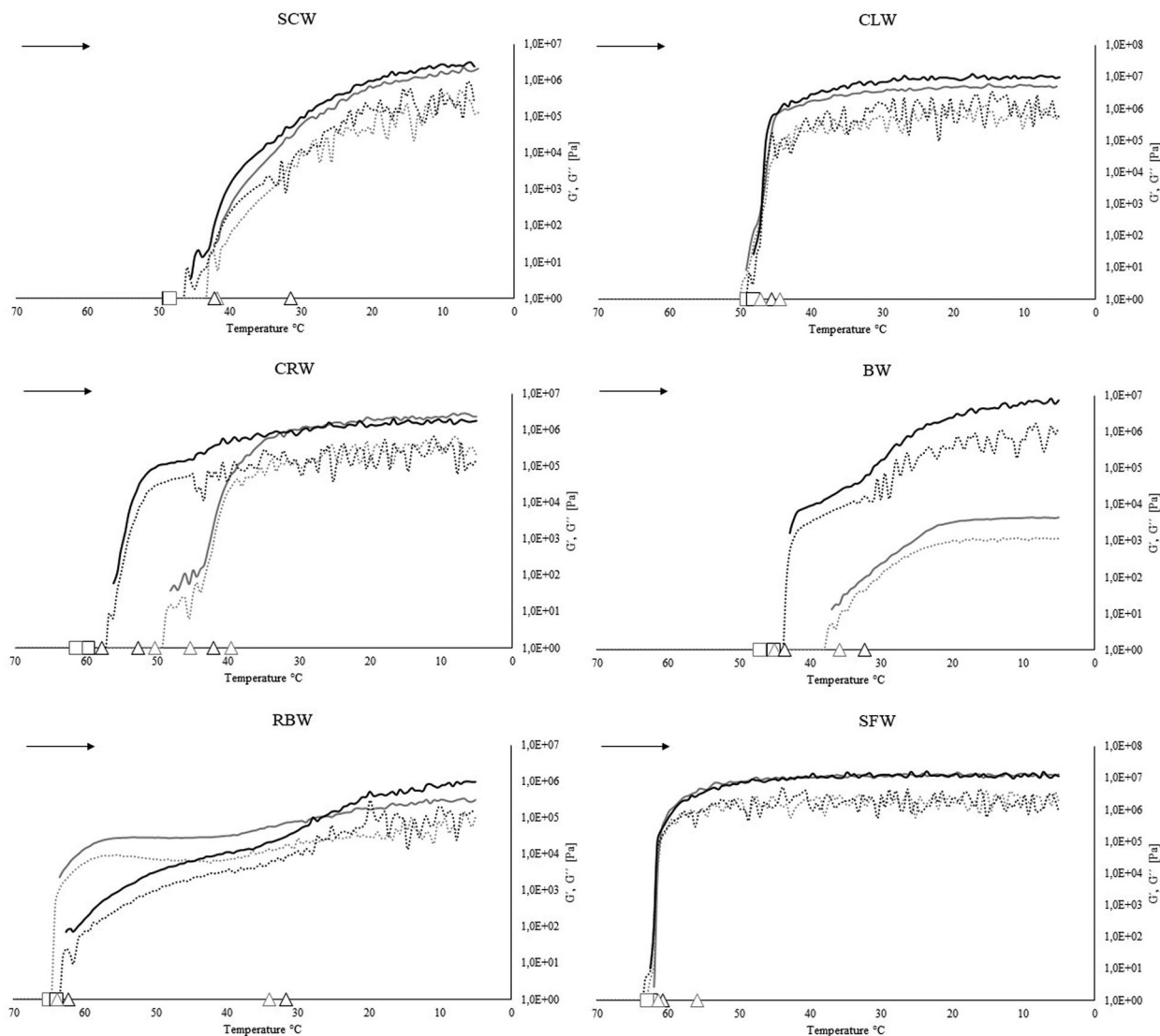


Figure 7. Temperature Sweeps of 10% w/w oleogels. Solid lines = G' , dotted lines: G'' . Black = canola, gray = MCT. Arrow indicates direction of scan. Mean values of 2 repetitions are represented and sorted from left to right and up to down with increasing DoH. DSC crystallization data are 1D projected on x-axis (squares = T_c , onset; Triangles = peak crystallization temperatures).

a different second main component, hydrocarbons in BW and FaOH in CRW. In both cases, once the crystallization temperature, determined by DSC, is reached, a step increase in G' and G'' is observed in the canola oil systems. Different to the DSC data, the cooling crystallization data in the rheometer reveals differences between canola- and MCT-oil systems. In the MCT system an increase of the moduli is observed at temperatures as much as 10 °C lower. For CRW the effect of the different oils appears almost as a parallel shift to lower temperatures. The second crystallization event, which is also found in the DSC data, is more pronounced in MCT-oil. This is somewhat surprising considering that the second crystallization event during DSC is more pronounced in canola oil. Even though speculative, one could argue that the first crystallization is related to FaOH and that these crystals possibly function as heterogeneous nuclei for the WE crystallization. The data for BW are most unexpected.

Not only is the initial step change in the moduli very different for the two oils, in MCT-oil the moduli at the end of the experiment reach a value three dimensions smaller than in canola oil. The data gathered actually show a similar development but in MCT-oil the initial steep increase of the moduli is absent. Following the reasoning applied to the CRW system, the initial crystallization in the rheometer could be assigned to the HC fraction. Even though no data are available currently it is fair to assume that the hydrocarbons (HC) have a higher solubility in MCT-oil than in canola oil. The question if this causes lack of a second solid fraction interfering with aggregation or reduces mixed crystal formation remains unanswered here.

The rheological data reveal significant differences between the crystallization behavior of different waxes. In most cases, the effect of using different oils is limited. However, in particular for BW the change from canola to MCT-oil has a dramatic effect.

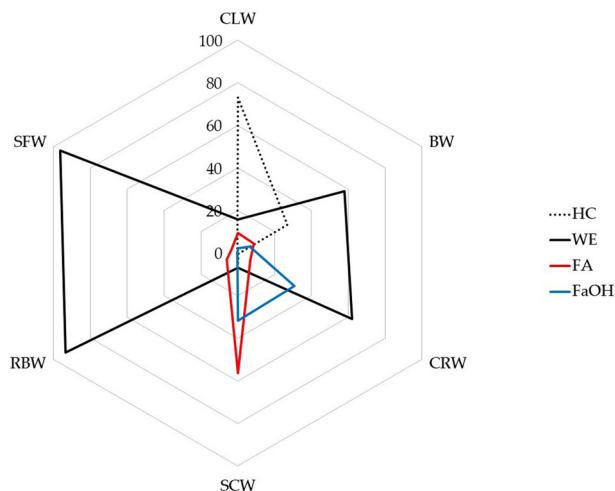


Figure 8. Illustration of the normalized major components (%) of the used waxes.

Data from monitoring cooling crystallization at identical cooling rates in either DSC or rheometer were in good agreement. The development of the moduli in the course of the experiments corresponds well to interpretations based on the composition of the different waxes.

Following the cooling crystallization under mild shear, the gels were kept for 30 min isothermally (5 °C). It was monitored, if the samples underwent any postcrystallization. Tavernier et al., have already reported on postcrystallization behavior in combined waxes' oleogel systems.^[18,39] Linear fitting of the data gathered isothermally ($\gamma = 0.05\%$, $\omega = 10 \text{ rad s}^{-1}$) revealed different slopes. The results are basically in line with the data displayed in Figure 7. The SFW and CLW systems appear to have completed the crystallization process already during the cooling process and do not show any further increase of the moduli. As suggested by Figure 7, BW in canola, RBW, and SCW revealed significant further increases in the moduli. In the other systems, moderate increases were observed. Hence, an isothermal step should always be performed with wax gels a priori to measure equilibrated samples in, e.g., amplitude sweeps.

As described above, the stabilized samples, 30 min at 5 °C under mild oscillation, were further characterized. The end of the linear-viscoelastic region (LVR) is the maximum deformation without changes of the network characteristics. It hence is a measure for elastic nature of the gel. The LVR data (10% threshold) are depicted in Figure 9. First of all, it is astonishing that SCW-canola oil gel withstands an exceptional large deformations at 0.33% strain ($\pm 0.002\%$). This is more than fourfold the value obtained for SCW-MCT-oil combination. The deformation limit of the linear viscoelastic region is quite similar for the gels SCW-MCT-oil, RBW with either oil, SFW with either oil, and BW in canola oil. Recent data have further supported the hypothesis the SFW gels are the results of sintered crystalline structures.^[18] Consequently, the data presented here suggest to draw the conclusion that the systems listed are also subject to sequential crystallization with resulting sintered structures. Irrespective of the oil type the CRW-based gels showed clearly longer LVR values. How this can be linked to the exceptional behavior of SCW in canola oil re-

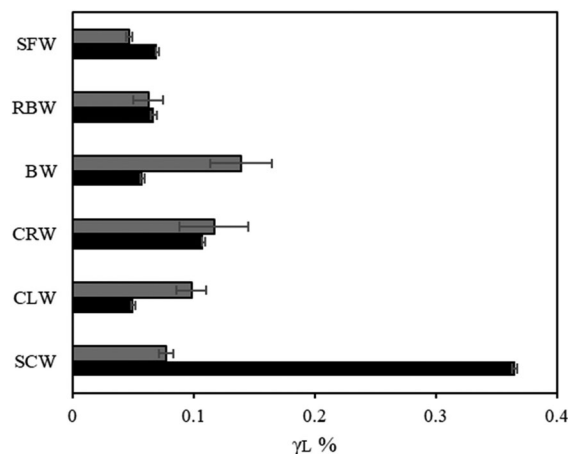


Figure 9. Linear-viscoelastic region (LVR) of 10% w/w wax gels based on MCT (gray) or canola oil (black). Data shown represent mean values of two measurements. Threshold was set to be 10%.

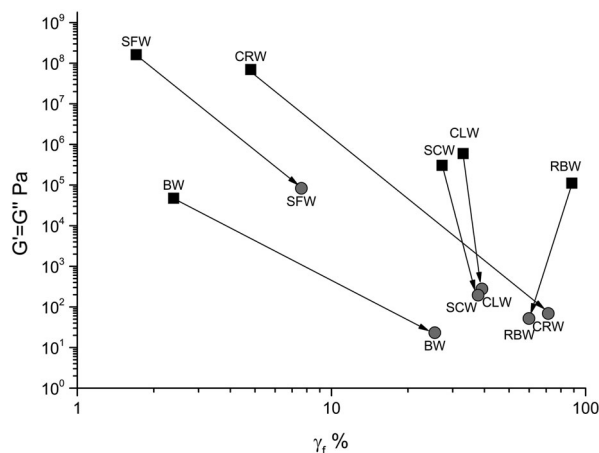


Figure 10. Comparison of the mean ($n = 2$) flow points ($G' = G''$) of 10% w/w wax gels produced with canola oil (black squares) and MCT-oil (gray circles). Deviations removed for clarity. Arrows indicate the shift of flow point when MCT-oil is used instead of canola oil for the corresponding wax.

mains unclear. In both waxes, the secondary component (>30%) is fatty alcohol (FaOH). The fact that both BW- and CLW-gels with MCT-oil have a higher tolerance to deformation corresponds with the high levels of hydrocarbons present in these waxes. That solubility affects the structure in terms of sintering in these systems appears likely taking also the data on structure efficiency in Figure 6 into account. Even though not really consistent throughout the data it appears that at least for a single structural brittle networks are more structure efficient. This is in line with expectation and well established for fat crystal networks.^[40]

The crossover point ($G' = G''$) of a gel indicates the deformation that mechanically induces a gel-sol transition. Figure 10 illustrates that the yield points determined for the different gels strongly depend on the continuous phase. Here, either canola- or MCT-oil. The figure shows for all waxes studied, both yield point deformation as well as the value of the moduli change when the oil type is changed. Even though the optical impression might

suggest that the deformation is similar for all gels concerning MCT-oil this is not the case, see logarithmic axis. The data clearly show that gels based on canola oil experience critical changes already at smaller deformations than those based on MCT-oil. Not unexpectedly the corresponding moduli are higher for canola oil variants. Lower critical moduli are found without exception for all MCT-based gels. The critical deformation however dramatically increases in the SFW, CRW, and BW systems. For the three other systems, the change is less clear. In broad terms, these findings correspond to results on structural efficiency, Figure 6.

4. Conclusion

In this work, in total 12 oleogel systems were studied in detail. The systems were composed of six different waxes combined with two oils. Commercial canola oil and MCT-oil were selected to represent both a common oil with typical minor components and unsaturated fatty acids, and a clean “synthetic” oil without minor components and saturated fatty acids exclusively. In particular, the latter is of interest because the fatty acid moieties in the waxes are predominantly saturated. Waxes were selected such that effects of different molecular species could possibly be assessed pairwise. SFW and RBW represent very high levels of WE. CRW and BW show intermediate levels of WE. BW and CLW show intermediate and high levels of HC. CRW and SCW show intermediate and high levels of FAOH. SCW and CLW have main components different from WE, namely FA and HC, respectively. These gels were characterized in terms of calorimetry, polarized light imaging, penetrometry, and rheology.

Calorimetric measurements revealed more distinct peaks in the melting and crystallization thermograms of MCT-based oleogels. The cooling thermograms were in general characterized by a major peak which in some cases revealed a shoulder or one additional peak. The heating thermograms reflected the compositional differences of the waxes expressed in quite different thermograms with sometimes several peaks. The latter is a clear indication for the existence of multiple solid phases. Postulating WE as main component, further data processing allowed to formulate a linear relation between undercooling and the homogeneity of the wax compositions, expressed as degree of homogeneity, DoH. In general undercooling was less pronounced in MCT-oil-based samples. This could be an indication for the effect that the minor components in canola oil have on the nucleation or due to differences in solubility. The calculation of the solid wax content based on the relation of the enthalpies of fusion in the gel versus the pure wax revealed significant differences in the solubilities depending on wax and oil type. Combining these data with those from penetrometry allowed to compute the structure efficiency (S.E.). Except for SFW with exceptionally high S.E.s, the values of the other systems are similar. Waxes high in WE, SFW, and RBW, exhibit a high S.E. value. However, depending on the type of wax clear differences with respect to the oil variation were found. RBW is the only structurant that is more structure efficient in MCT-oil than in canola oil. SCW, CLW, and BW structure MCT-oil dramatically less efficient than canola oil.

The rheological measurements revealed more information on crystallization behavior of the waxes and the structure of the gels. Significant differences between waxes and oil type could be identified. Effects of the oil type were most pronounced in the gels

based on BW and CRW which show clearly retarded sol–gel transition of crystallization in MCT-oil. By combining DSC, compositional data and the rheological observations rather comprehensive interpretations with respect to the sequence of crystallization events could be formulated. Beyond the cooling scan the rheological assessment was also applied to characterize the LVR and the flow point. In most systems the LVR was found at a strain $>0.05\%$. SCW had somewhat elevated values. Interestingly, for BW and CLW the LVR of gels appears in MCT-oil at twice the strain compared to canola oil-based gels. The determination of the flow point of the stabilized gels revealed a similarly complex image. For most structurants the deformation at the flow point is clearly larger in MCT-oil-based gels. At the flow point the moduli of the gels with MCT-oil are clearly smaller than those of canola oil-based gels.

Any detailed explanation of the observations made comprehensively remains speculative at this state due to the limited availability of data. In the first place, the different observations in phase transitions observed in DSC correspond quite well with the compositional data of the waxes studied. It is however difficult to assign crystallization events with certainty to specific fractions. To possibly do so, better characterization of the species present is necessary to estimate specific solubilities. The data furthermore indicate that sintering, sequential crystallization supporting the primary 3D network, plays a major role in wax-based oleogelation. In this context, it is of relevance if structuring, the sol–gel transition, happens under shear or quiescent conditions. However, this distinction is not as easy as it might sound because the actual situation is a result of superimposing process and kinetics. In addition to these structural considerations based on the different molecular species added as waxes, the continuous oil phase also appears to have a profound effect on gel properties. For the two oils considered in this work three major attributes are different. At first, MCT-oil is at equal weight fractions, due to the differences in average molecular weight, present in significantly higher molar fractions than canola oil. This should already have significant effects on the solubilities of the different species. Preliminary results on the dissolution behavior of waxes in the oils studied considering molar compositions, indicate a higher wax solubility in canola oil than in MCT-oil. This is not contradicting the fact that samples with canola oil studied have been more structure efficient. However, more detailed thermodynamical considerations using molar compositions will be reported soon. Second, are the saturated fatty acid chains in MCT-oil supposed to interact differently with the mainly saturated fatty acids moieties of the solutes (waxes) than the predominantly unsaturated fatty acid chains in canola oil. Third, the oils differ in the presence of minor components. MCT is “synthetic” and free of minor components and polar oxidation products, while the canola oil contains significant amounts of polar components, for example FA. These minor components could influence the gel formation and structure in different ways. This was already disclosed elsewhere.^[5,33] Latter authors revealed that native canola oil compared to canola oil stripped from its polar components results in harder BW and RBW-based oleogels. The authors furthermore documented that the CGC is, particular for these waxes, higher in stripped oils. Taking thus into account that MCT-oil resembles the stripped canola oil the following hypothesis emerge. Initial effects of crystallization in MCT-oil might

not be detected by rheology because there is no contribution of minor components in aggregate/floc stabilization. The presence of FA in canola oil might influence the crystallization and structuring when structurants rich in FA or FaOH are present. Solubility of hydrocarbons in MCT-oil could be the basis for the structural underperformance of BW and CLW because secondary components might not contribute to a sintered network.

In conclusion, the data gathered appear fairly consistent and illustrate that the specific composition of waxes and the characteristic of the oil to be gelled are important parameters for both the gelling process and the characteristics of resulting gels. The observations made after all leave us at a level of understanding that necessitates further research into wax-based oleogelation.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

canola, MCT oil, minor components, oleogels, waxes

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