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Rheological and thermal properties of reinforced monoglyceride-carnauba wax oleogels

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Abstract

BACKGROUND: Oleogels can be used in the food industry to reduce the consumption of solid fat in the human diet and diminish some of the industrial–technological issues of using oil instead of fat. Regarding the structural weakness of neat monoglyceride oleogel and the waxy mouthfeel of pure carnauba wax oleogel, as a result of the high melting and crystallization points, the present study aimed to diminish these defects.

RESULTS: Carnauba wax (CBW) was used as a co-gelator with distilled monoglyceride (DMG) at different weight ratios (100:0, 85:15, 70:30, 55:45, 40:60, and 0:100) (DMG: CBW) and two total gelator concentrations (50 and 100 g kg^{-1}) to improve the DMG oleogel characteristics. The addition of CBW strengthened the DMG network and decreased the polymorphic transition. Thermal analysis showed just co-crystallization at the 85:15 ratio, whereas, in the other combinations, high melting components of CBW crystalized at first. As a result of the crystal homogeneity and long-time development, the oleogel properties improved at the 85:15 ratio. The low concentration of CBW and the formation of the eutectic system were efficient in the waxy mouthfeel reduction of oleogel at the 85:15 ratio in food applications.

CONCLUSION: The DMG/CBW oleogel at the 85:15 ratio, with better structural and sensorial properties than DMG and CBW oleogels, respectively, has the potential for use instead of fat in food formulations.

Supporting information may be found in the online version of this article.

Keywords: multi-component oleogel; frequency sweep; temperature sweep; DSC analysis

INTRODUCTION

Efforts have been made to structure edible liquid oil with oleogelators to reduce the consumption of solid fat in the human diet and diminish some of the industrial–technological issues of using oil instead of fat. Accordingly, the potential of oleogels to act as delivery systems[1] and as a deep-fat frying medium,[2] as well as their application in breakfast spreads,[3] bakery and confectionary,[3-5] meat,[6] and dairy[7] products, has been investigated. Researchers have suggested the combination of gelators as an effective way to satisfy some of the legal and industrial requirements on gelator concentration, food-grade status, price, availability, and oleogel quality.[8]

Carnauba wax (CBW), as the hardest wax, is extracted from *Copernicia prunifera* leaves. Aliphatic esters and di-esters of cinnamic acid are the main components of CBW. The Food and Drug Administration considers CBW as generally recognized as safe (i.e. GRAS) without any limitation on the conditions of good manufacturing practices.[9] However, the development of waxy mouthfeel at high CBW concentrations restricts its application in the food industry.[8]

The 17th report of the joint Food and Agriculture Organization/World Health Organization committee on food additives has announced that, because the differences between mono- and diglycerides and food are little, they can be used without limitation.[10] The safety and non-toxicity of monoacylglycerols (MAGs) lead to their wide usage as food emulsifiers (around 75% of total emulsifiers).[11] Moreover, they have the potential to structure liquid oil; thus, they are some of the most promising low molecular weight gelators.[5]

Although the critical gelation concentration of MAGs is low, the strength of their oleogel is lower than commercial shortening[12] and even than some other oleogels. According to Ogutco and Yilmaz,[13] the oil binding capacity (OBC), hardness, and oxidative stability of CBW organogel are higher than those of MAG organogel. Chen and Terentjev[14] reported that MAG-based structure was not stable during storage, damaging the OBC, thermal, and mechanical features of oleogel. However, the textural parameters

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of CBW oleogel were more stable during the 3 months of storage.[15] Accordingly, to improve the MAG oleogel quality, the combination of monoglycerides and phytosterols,[16] fatty alcohols,[17] ethylcellulose,[18] and candelilla wax (CLW), berry wax (BW), and sunflower wax (SFW)[19,20] was investigated. da Silva *et al.*[20] reported that CLW, MAG, and hard fat combination improved the rheological properties, shear stability, and OBC of oleogel. Barroso *et al.*[19] stated the contrary effect of BW or SFW with glycerol monostearate (GMS). According to their report, although the negative interaction of BW/GMS lowered the dynamic moduli and OBC of oleogel, GMS addition improved the SFW gel properties. More information about the advances in multi-component oleogels is presented in a recent study.[8] Li *et al.*[12] compared the properties of a combination of waxes and monoglyceride oleogels. They reported that CBW demonstrated notably more desirable physical properties. However, they considered 50 g kg^{-1} as the minimum wax level for comparison and did not determine the effective combination of gelators.

The present study aimed to determine the best combination of DMG and CBW for the first time. The plan was to achieve the multi-component oleogel with better rheological properties than DMG and lower crystallization and melting temperatures, a reason for the waxy mouthfeel, than CBW.

MATERIALS AND METHODS

Materials

Canola oil was supplied by Segol (Nishabour, Iran). Commercial food-grade Monoglyceride (product code DMG 0093) (Palsgaard, Malaysia) was received as a gift from the Pishgaman Company (Tehran, Iran). According to our analysis by gas chromatography, its fatty acid composition was stearic acid (41.33 ± 0.57%), palmitic acid (56.91 ± 0.32%), and other fatty acids (1.75 ± 0.1%). CBW was purchased from Sigma-Aldrich Pte Ltd (Singapore).

Preparation of oleogels

Different ratios of DMG to CBW (100:0, 85:15, 70:30, 55:45, 40:60, and 0:100) with a gelator concentration (GsC) of 50 and 100 g kg^{-1}, dispersed in canola oil, were used. The mixtures were heated to 80 °C under stirring conditions (10.47 rad s^{-1}). When clear solutions were obtained, the dispersions were cooled to room temperature (25 °C) under static conditions. The corresponding oleogels were coded as D_{100}-50, D_{85}-50, D_{70}-50, D_{55}-50, D_{40}-50, and D_0-50 for 50 g kg^{-1} GsC and D_{100}-100, D_{85}-100, D_{70}-100, D_{55}-100, D_{40}-100, and D_0-100 for 100 g kg^{-1} GsC, respectively. The subscript numbers indicate the ratio of DMG in total GsC. Oleogels were stored at 25 °C for 120 h before the experiments.[21]

Dynamic rheological analysis

Rheological properties were assessed using a rheometer (MCR-302; Anton Paar, Graz, Austria) at 25 °C. Initially, the linear viscoelastic region (LVR) was determined by the strain sweep test (strain = 0.01–100% and frequency = 1 Hz). The first point where there was a 10% difference between the storage modulus (G') and G'_{LVR} values was marked as the end of the LVR.[22] The corresponding strain, stress, G', and loss modulus (G'') were referred to as critical strain (γ_L), yield stress (τ_{yLVR}), G'_{LVR}, and G''_{LVR}, respectively.

Then the frequency sweep test was performed (frequency = 0.01–100 Hz and strain = 0.01%). The frequency dependence of oleogels was evaluated via curve fitting of G' by the power-law model (1):

$$G' = a\omega^b \tag{1}$$

where ω represents the angular frequency (rad s^{-1}), a is a constant ($pa.s^b$), and b is the flow behavior index (dimensionless). The b value is the slope of G' *versus* the ω plot in the logarithmic scale and can be used to determine the frequency dependency of G'.

Finally, the temperature sweep test in three cycles (heating–cooling–heating) was conducted between 20 and 90 °C, at 5 °C min^{-1} (frequency = 1 Hz, strain = 0.01%). The holding time between each cycle was 10 min.[4,23]

Thermal properties

The thermal behavior was determined by differential scanning calorimetry (DSC) (model DSC1; Mettler Toledo, Greifensee, Switzerland). Samples were heated from room temperature to 140 °C, cooled to −20 °C, kept in isothermal condition for 3 min, and finally heated to 100 °C. The cooling and heating rate was 10 °C min^{-1}.[15]

Statistical analysis

Twelve oleogel treatments in three replicates (36 total samples) were prepared for all experiments. Data were analyzed by analysis of variance using the general linear model. $P \leq 0.05$ (Tukey's test) was considered statistically significant. Minitab, version 16 (Minitab, LLC. State College, PA, USA) was used for data analysis.

RESULTS AND DISCUSSION

Dynamic rheological analysis

Strain sweep tests

The GsC, ratio, and their interactions influenced the strain sweep test parameters ($P < 0.01$) (see Supporting information, Table S1). In general, because of the acceleration of nucleation at high concentration and, subsequently, the existence of a stronger gel network, augmenting the GsC increased the γ_L, τ_{yLVR}, τ_f, G_f, and G' values ($P < 0.01$) (see Supporting information, Table S1). The lowest and highest γ_L values were found for DMG and CBW oleogels, respectively, implying that DMG oleogels were more flexible[24] and CBW oleogel had high stability under the strain sweep test.[25] The differences in crystal nature of CBW and DMG, the homogeneous and small-size crystals *versus* the non-homogeneous and large-size crystals, lead to fewer contact sites, loose entanglement of crystals, and, subsequently, higher deformability of the DMG oleogel.[12,22] On the other hand, as a result of the denser crystal network, CBW oleogel demonstrated the highest G'_{LVR}, τ_{yLVR}, and τ_f values. Because G'_{LVR}, τ_{yLVR}, and τ_f values in multi-component oleogels were higher than DMG oleogel ($P < 0.01$), we concluded that the addition of CBW improved the crystalline network of DMG oleogel.[19] Among the multi-component oleogels, the 85:15 ratio was placed after the 0:100 ratio. According to the DSC analysis, in the 85:15 ratio, only DMG/CBW mixed crystal was formed; in contrast, in the other ratio, both CBW crystals and mixed crystals were presented in the final oleogel. Thus, the crystal homogeneity in the 85:15 ratio improved the oleogel properties. According to the strain sweep test results, the strain of 0.01% for the frequency and temperature sweep test was well within the LVR, where the network was not damaged by strain.

As shown in Fig. 1, above the yield stress, the stress values of D_0-50 and D_0-100 revealed a more sudden drop, indicating a more brittle-like behavior. The other samples, which showed a more

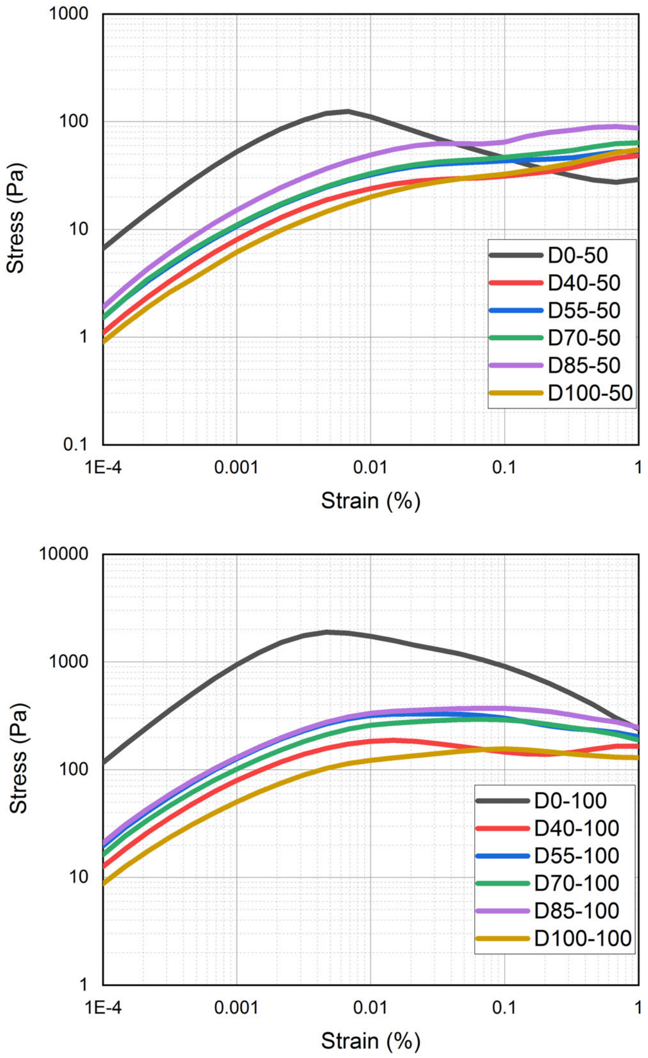

Figure 1. Stress–strain curves, obtained from the strain sweep test. The numbers to the right and left of the dashes show the total gelator concentration and the ratio of monoglyceride, respectively.

plastic-like response, demonstrated adequate flow during yielding.[26] This behavior was probably a result of the localized crowding of aggregated crystalline particles, leading to the heterogeneous bonding strength in CBW oleogel, which increases the network strength in a certain region. However, the broken structure does not recover because the shear forces conquer the Brownian motion. By contrast, the bonding strength in other samples was more uniform.[22]

Frequency sweep tests

Based on the classical theories of viscoelastic behavior, the results of the frequency sweep tests can be used to describe the structural properties of gelling systems.[25] In all samples, the elastic component (G') dominated over the entire frequency range (see Supporting information, Fig. S1). Thus, all gels could withstand deformation, so they were true gels. Additionally, the G' and G'' curves had a positive, gentle slope. This behavior results from the characteristic of the weak gels at low frequency and shows the presence of non-covalent (physical) crosslinks in the oleogel network.[24,27]

The G', G'', and complex viscosity (η^*) values were significantly affected by the GsC, ratio, and their interactions ($P < 0.01$). In comparison with the CBW oleogel, the higher crystal size of DMG oleogel decreases the crystal–crystal interactions, which subsequently reduces the sustainability of gel against applied stress.[15,22] Accordingly, CBW-based oleogels had the highest G', G'', and η^* values at each concentration (Table 1) ($P < 0.05$). Based on the structural difference, D_0-50 demonstrated the higher G' and η^* than D_{100}-100 ($P < 0.05$), whereas the other oleogels, prepared at 100 g kg^{-1} GsC, displayed higher G' and η^* than those at 50 g kg^{-1} GsC. This phenomenon was a result of the accelerated nucleation at a higher concentration that subsequently caused the formation of smaller crystals,[28] with a high contact surface and the possibility of crystal–crystal interactions. The high gelator content also increases the crystals' packing density and the oleogel matrix strength.[1] The tanδ values were between 0.16 and 0.27, indicating that the elastic component dominated the viscous component. The lower tanδ value at 0:100 ratio indicated that the gel network was more stable in CBW-based oleogels.[19]

Table 1. Storage modulus (G'), loss modulus (G''), complex viscosity (η^*), loss tangent (tanδ), and slope of complex viscosity of monoglyceride (DMG)/carnauba wax (CBW)-based oleogels, as determined by the frequency sweep test (strain = 0.01%, frequency = 0.01–100 Hz, and temperature = 25 °C)

Concentration (g kg^{-1})	Ratio (DMG:CBW)	G' (kPa)	G'' (kPa)	η^* (kPa)	tanδ	Slope of η^*
50	0:100	77.8 ± 0.09 f	12.5 ± 0.07 g	31.5 ± 0.04 f	0.161 ± 0.004 f	−0.927 ± 0.010 e
50	40:60	8.41 ± 0.01 l	2.16 ± 0.03 k	3.47 ± 0.04 l	0.257 ± 0.004 abcd	−0.879 ± 0.004 a
50	55:45	10.3 ± 0.03 j	2.64 ± 0.02 j	4.24 ± 0.02 j	0.257 ± 0.005 abcd	−0.875 ± 0.005 a
50	70:30	13.6 ± 0.01 i	3.56 ± 0.03 i	5.62 ± 0.03 i	0.262 ± 0.00 8abc	−0.898 ± 0.010 b
50	85:15	16.8 ± 0.05 h	4.52 ± 0.01 h	6.95 ± 0.03 h	0.270 ± 0.00 4 ab	−0.874 ± 0.00 4a
50	100:0	9.18 ± 0.02 k	2.50 ± 0.04 j	3.80 ± 0.03 k	0.272 ± 0.004 a	−0.861 ± 0.006 a
100	0:100	598 ± 0.13 a	111 ± 0.11 a	243 ± 0.10 a	0.187 ± 0.004 e	−0.922 ± 0.007 de
100	40:60	103 ± 0.06 e	25.3 ± 0.11 e	42.3 ± 0.07 e	0.246 ± 0.003 d	−0.908 ± 0.007 bcd
100	55:45	133 ± 0.08 c	33.4 ± 0.08 c	54.8 ± 0.05 c	0.251 ± 0.006 cd	−0.924 ± 0.005 de
100	70:30	118 ± 0.11 d	29.9 ± 0.06 d	48.5 ± 0.06 d	0.255 ± 0.004 bcd	−0.927 ± 0.003 e
100	85:15	187 ± 0.09 b	47.4 ± 0.06 b	77.2 ± 0.08 b	0.253 ± 0.006 cd	−0.921 ± 0.006 cde
100	100:0	64 ± 0.05 g	16.7 ± 0.06 f	26.6 ± 0.04 g	0.259 ± 0.008 abcd	−0.903 ± 0.003 bc

Note: Different lowercase letters in the same column show significant differences among mean values by Tukey's test ($P < 0.05$).

Increasing the CBW ratio in the mixed-component oleogels decreased the G', G'', and η^* values ($P < 0.05$). In comparison with the DMG oleogel, the G' values of D_{85}-50 and D_{85}-100 oleogels had a 1.8 and 2.9-fold increase, respectively, indicating that the positive interaction which occurred between DMG and CBW strengthened the network by increasing the physical crosslinks and network density which, subsequently, improved the G', G'', and η^* values ($P < 0.05$).[26,27] In other ratios, this positive effect was lower, which might probably be a result of the differences in the crystal morphology and distribution. Additional discussion is given further below. According to Li *et al.*,[12] the smaller crystal size and higher network density in the monoglyceride/wax combination improved the oleogel mechanical strength.

The evaluation of the shear-dependent flow behavior of oleogels was performed by investigating the η^* *versus* frequency. As shown in Fig. 2, η^* increased as the GsC increased, which indicated that the strong gel network was formed at a higher concentration.[27] It was also decreased linearly with frequency, demonstrating the non-Newtonian shear-thinning behavior of oleogel. This behavior was also found for other oleogels.[1,22,27] At high frequency, the viscoelastic response of monoglyceride and mixed component oleogels with 50 g kg^{-1} GsC changed into Newtonian behavior. On comparing these curves with frequency sweep curves (see Supporting information, Fig. S1), it can be seen that in these oleogels, although G' was higher than G'' over the entire frequency range, G'' neared G' at high frequency, which probably caused the behavior change. The η^* slope was also used to evaluate the gel strength. The gelator ratio and concentration significantly affected the crystal–crystal interactions and, subsequently, the η^* slope ($P < 0.01$). The highest and lowest slope were found at 0:100 and 100:0 ratios, indicating that the DMG oleogels had the lowest gel strength.

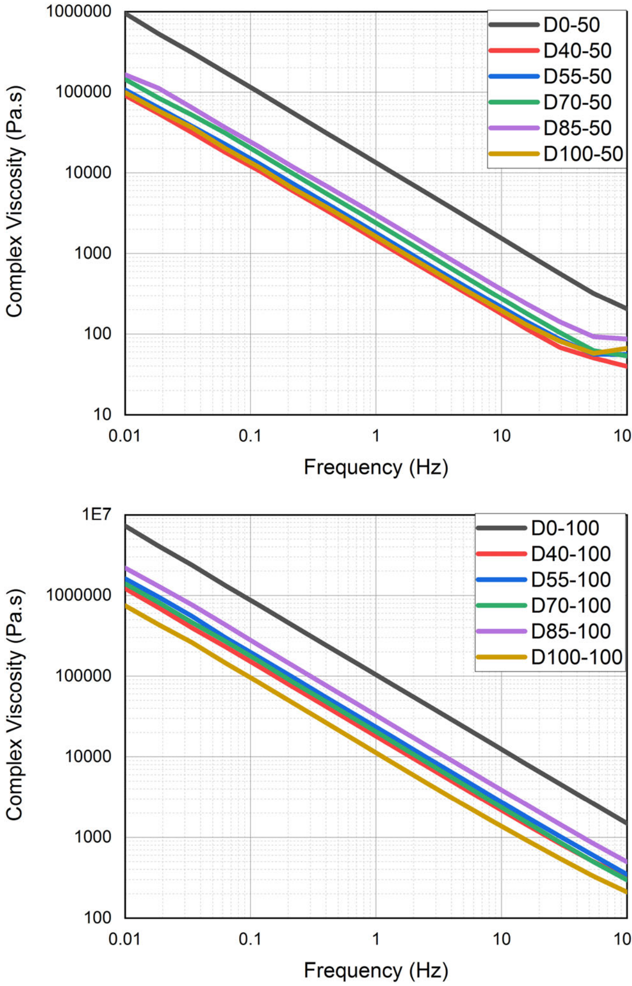

Figure 2. The effect of frequency on complex viscosity of the oleogel samples (strain = 0.01%, frequency = 0.01–100 Hz, and temperature = 25 °C). The numbers to the right and left of the dashes show the total gelator concentration and the ratio of monoglyceride, respectively.

Because of the high value of R^2, the power-law model is suitable to describe the frequency dependency of G'. The low b values (0.07–0.14) show that the elastic behavior dominated the viscous behavior, and the oleogels exhibited less frequency dependence (Table 2). The GsC and ratio significantly influenced the shear properties of oleogels ($P < 0.01$). In accordance with the results for G' and η^*, lower b values of oleogels prepared at 100 g kg^{-1} GsC indicated that the changes of G' values with frequency were lower and the strength of oleogels was higher than 50 g kg^{-1} ($P < 0.01$). Because of the structural weakness, the 100:0 ratio demonstrated the highest frequency dependency ($P < 0.05$). As expected, the strongest structure, the 0:100 ratio, displayed the lowest frequency dependency ($P < 0.05$).

The higher a values at 100 g kg^{-1} GsC ($P < 0.01$) indicated the formation of a stronger network at higher concentration. In each concentration, because of the formation of a stronger elastic structure, the highest a value was obtained for CBW-based oleogel, followed by the 85:15 ratio. Similar to G', the a value decreased with the increase in the CBW ratio ($P < 0.05$), which was probably because of the differences in crystal morphology and distribution.

Temperature sweep tests

Figure 3 present the changes in G' and G'' during the first heating cycle (20–90 °C). Because of the differences between the holding time of oleogels in the first and the second heating process, 120 h for the first stage against 10 min for the second stage, the results of these two stages were not similar. However, because the recovery of the structure, as a result of a higher possibility of crystal–crystal interaction, was fast at high concentration, these differences at 100 g kg^{-1} GsC were lower than 50 g kg^{-1} GsC. Borriello *et al.*[29] stated that a perfect 3D network of CBW-based oleogel, at 40–80 g kg^{-1} wax concentration, formed in 60 min of setting time at 25 °C.

Three different regions of the cooling curves (Fig. 4) are a liquid-like region, a transition region, and a solid-like region. Accordingly, all oleogel samples displayed thermo-reversible properties. The phase transition, cluster formation, and gelator crystallization started in the second region. In this region, the sol–gel transition began at the crossover point ($G'' = G'$), where changes in the G'' and G' values occurred suddenly.[19,23,29] The GsC and ratio affected the formation of the three-dimensional network at the end of the cooling step ($P < 0.01$) (Table 3). Before the holding stage, due to the formation of non-homogeneous and large-size crystals,[12] G' reached 58% and 64% of its final values for D_{100}-50 and D_{100}-100, respectively, which were the lowest values at concentrations of 50 and 100 g kg^{-1}. Apart from D_{100}-100, during the holding stage, the maximum change in the G' value of oleogels, prepared at a concentration of 100 g kg^{-1}, was 10%, which indicated that, because of the accelerated nucleation at higher gelators' mass, the network formation was nearly finished in this

Table 2. Power-law parameters for the storage modulus of monoglyceride (DMG)/carnauba wax (CBW)-based oleogels

Concentration ($g\ kg^{-1}$)	Ratio (DMG:CBW)	$G' = a\omega^b$ a	b	R^2
50	0:100	72 291 ± 106 f	0.071 ± 0.0001 f	0.995
50	40:60	7354 ± 52 j	0.117 ± 0.008 b	0.932
50	55:45	8845 ± 48 j	0.124 ± 0.000 b	0.907
50	70:30	11 859 ± 262 i	0.100 ± 0.000 c	0.946
50	85:15	14 564 ± 166 h	0.132 ± 0.007 ab	0.907
50	100:0	8038 ± 9 j	0.142 ± 0.003 a	0.833
100	0:100	556 554 ± 907 a	0.079 ± 0.002 ef	0.999
100	40:60	93 206 ± 698 e	0.094 ± 0.007 cde	0.992
100	55:45	122 746 ± 650 c	0.078 ± 0.009 ef	0.994
100	70:30	106 442 ± 856 d	0.078 ± 0.009 ef	0.984
100	85:15	171 174 ± 651 b	0.083 ± 0.003 def	0.990
100	100:0	58 057 ± 663 g	0.097 ± 0.001 cd	0.983

Note: Storage modulus (G') (Pa), angular frequency (ω) (rad s^{-1}), a is a constant ($pa.s^b$) and flow behavior index b (dimensionless). Different lowercase letters in the same column show significant differences among mean values by Tukey's test ($P < 0.05$).

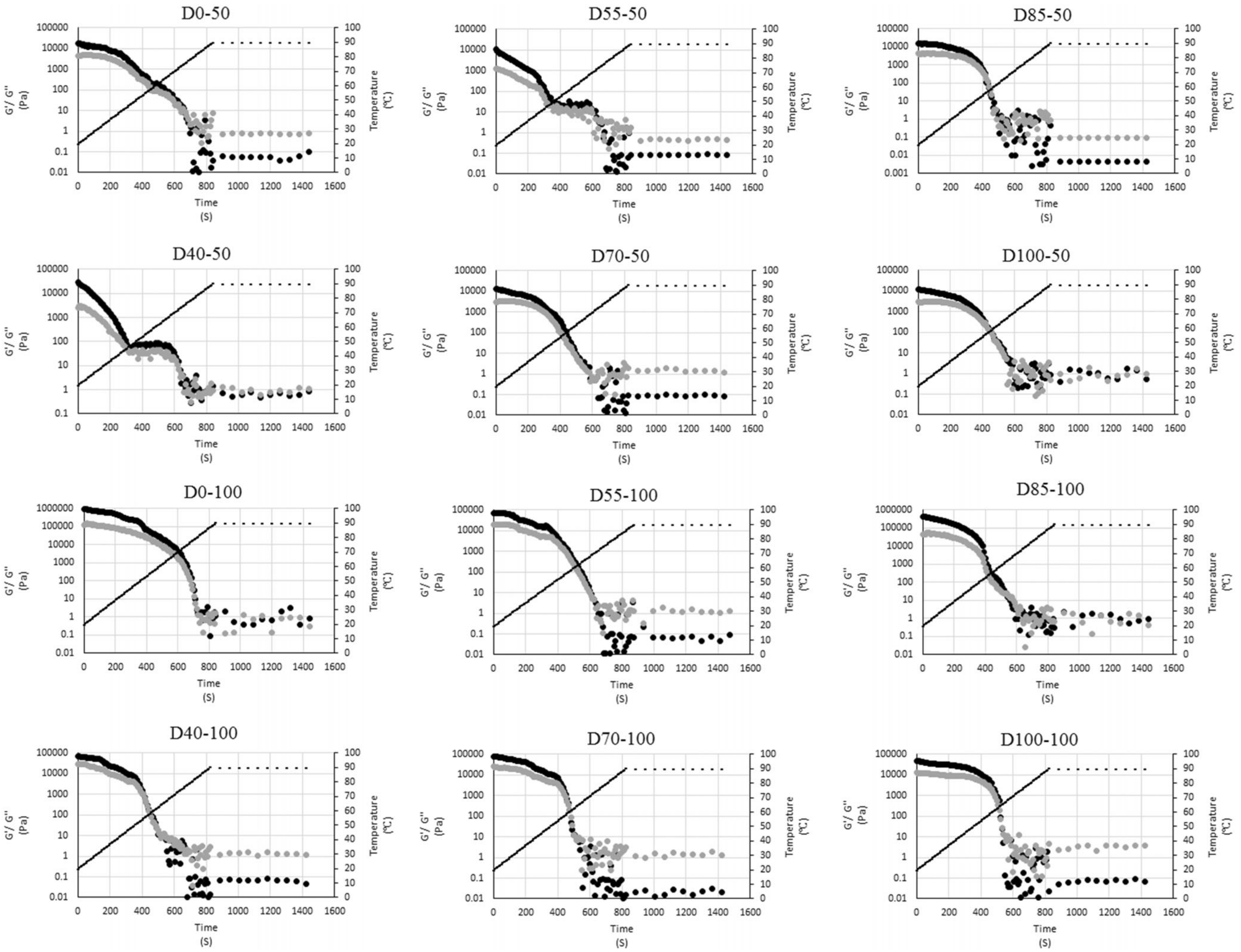

Figure 3. Gel–sol transition, during the heating stage of temperature sweep test, followed by a setting stage (90 °C, 10 min) of the oleogel samples. The numbers to the right and left of the dashes show the total gelator concentration and the ratio of monoglyceride, respectively. The black and gray curves show the storage (G') and loss (G'') modulus, respectively.

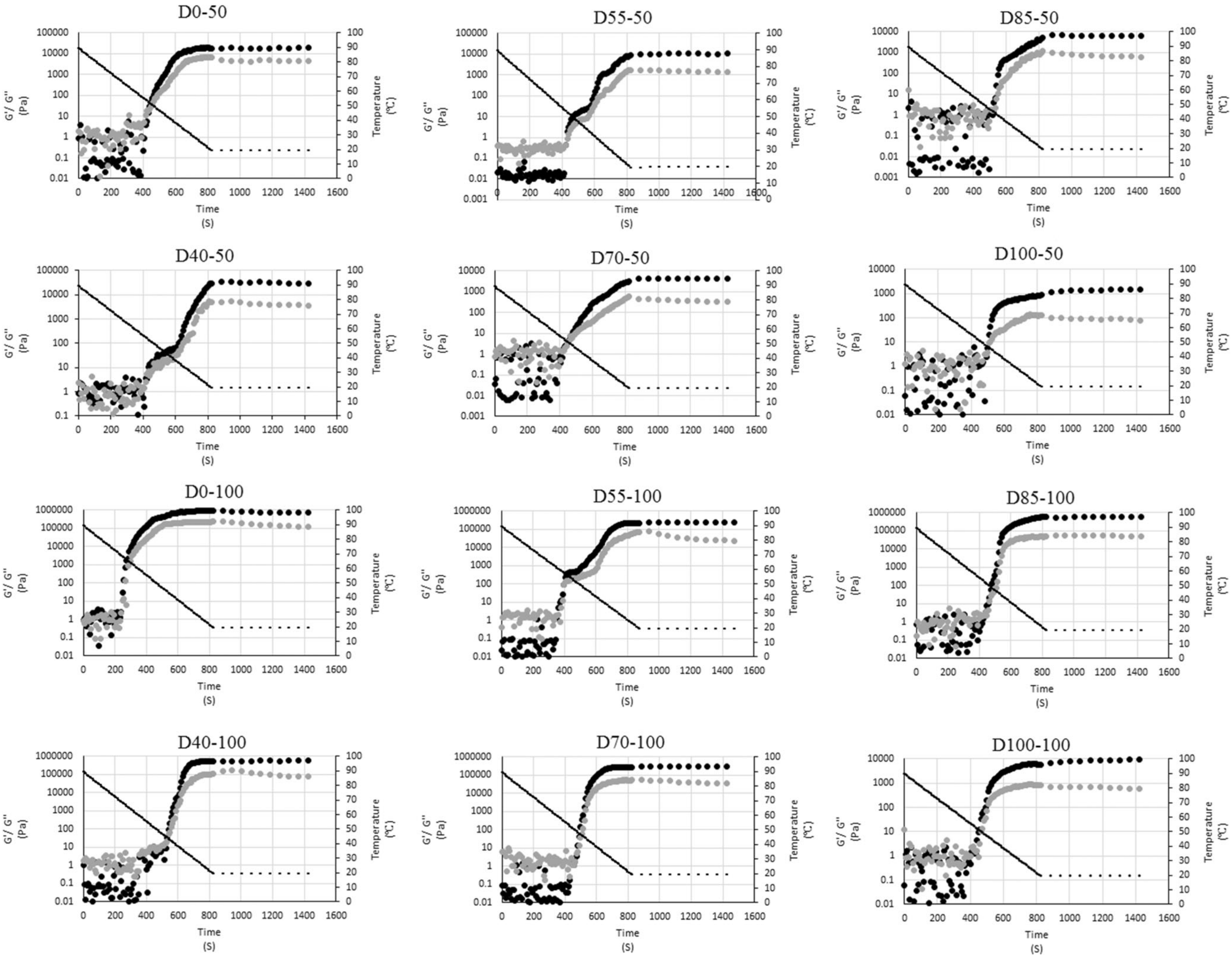

Figure 4. Sol–gel transition, during the cooling stage of temperature sweep test, followed by a setting stage (20 °C, 10 min) of the oleogel samples. The numbers to the right and left of the dashes show the total gelator concentration and the ratio of monoglyceride, respectively. The black and gray curves show the storage (G') and loss (G'') modulus, respectively.

Table 3. Temperature sweep test parameters of monoglyceride (DMG)/carnauba wax (CBW)-based oleogels (temperature: 20–90 °C, heating rate: 5 °C min^{-1}, frequency: 1 Hz, and strain: 0.01%)

Concentration (g kg^{-1})	Ratio (DMG: CBW)	Onset of crystallization temperature (T_O) (°C)	Gelation temperature (T_g) ($G' = G''$) (°C)	Gelation time (s)	Final storage modulus (T = 20 °C) (kPa)	Melting temperature (tanδ = 1) (°C)
50	0:100	55.1 ± 0.69 def	52.9 ± 0.34 d	432 ± 4.16 bcd	19.8 ± 0.27 g	72.5 ± 0.50 b
50	40:60	57.9 ± 0.71 cd	54.3 ± 0.23 c	416 ± 31.3 d	28.5 ± 0.30 f	73.6 ± 0.37 b
50	55:45	55.1 ± 1.87d ef	53.6 ± 0.37 cd	424 ± 16.0 cd	10.9 ± 0.13 h	73.6 ± 0.34 b
50	70:30	56.5 ± 0.68 de	50.5 ± 0.35 e	461 ± 4.0 b	4.41 ± 0.06 i	65.7 ± 0.38 c
50	85:15	46.6 ± 1.43 g	45.5 ± 0.36 g	520 ± 4.0 a	6.33 ± 0.01 i	55.9 ± 0.35 d
50	100:0	54.4 ± 0.51 ef	47.3 ± 0.72 f	499 ± 8.50 a	1.53 ± 0.00 j	55.9 ± 0.34 d
100	0:100	69.9 ± 1.37 a	69.2 ± 0.47 a	241 ± 13.0 f	716 ± 2.04 a	78.2 ± 0.77 a
100	40:60	60.7 ± 1.37 bc	55.9 ± 0.69 b	374 ± 8.00 e	580 ± 2.23 c	75.6 ± 1.78 ab
100	55:45	60.7 ± 0.68 bc	57.6 ± 0.36 b	401 ± 4.50 de	252 ± 0.22 e	74.3 ± 1.07 b
100	70:30	63.2 ± 0.37 b	50.8 ± 0.69 e	457 ± 8.50 bc	315 ± 0.54 d	64.7 ± 3.05 c
100	85:15	54.0 ± 0.34 ef	52.6 ± 0.37 d	437 ± 4.00 bcd	599 ± 0.27 b	64.4 ± 0.33 c
100	100:0	53.3 ± 0.34 f	52.9 ± 0.23 d	433 ± 7.44 bcd	9.38 ± 0.06 h	65.1 ± 0.34 c

Note: Different lowercase letters in the same column show significant differences among mean values by Tukey's test ($P < 0.05$).

concentration. A plateau region with roughly equal values of G' indicated that the oleogel structure was completed. The final G' values, at a CBW concentration of 40 and 80 g kg^{-1}, were reported to be 55.4 and 88.1%, respectively.[29] As expected, at the end of the cooling step, the G' value of oleogels, prepared at a concentration of 100 g kg^{-1}, was higher than that at 50. Interestingly, the G′ values of D_0-50 and D_{40}-50 were higher than that at D_{100}-100 ($P < 0.05$). Once again, these results revealed that CBW could induce an effective interconnected 3D network. Another impressive result was the considerable increase (63-fold) in the G' value of D_{85}-100 oleogel compared to D_{100}-100, although the replacement value was equal to 15%. This result indicated that the presence of CBW strengthened the network by increasing the physical crosslinks.[26] During the holding stage, the rheological behavior of DMG-based oleogel was related to the presence of a mixture of sub-α and β crystals.[30]

Because G' did not increase or decrease continuously during the cooling or heating process, we concluded that the conformational transition or the formation of the secondary structures occurred in the gelation process.[26] This phenomenon could also be a result of the separate crystallization of high and low melting components in chemically heterogeneous CBW.[29] This opinion was confirmed by DSC results because the oleogel thermograms showed more than one peak. A high correlation was observed between the point where the slope of the curve changed in the temperature sweep tests and the peak position in DSC measurements. According to Barroso *et al.*,[19] different crystalline structures caused different slopes, between 20 and 40 °C, in temperature sweep curves of GMS/berry wax-based oleogels, and their detection in the heating cycle was more accessible than the cooling step. Overall, because of the presence of several transition points, the rheology was less sensitive in the detecting of the polymorphic transition points. In this case, the DSC test was more effective.[31]

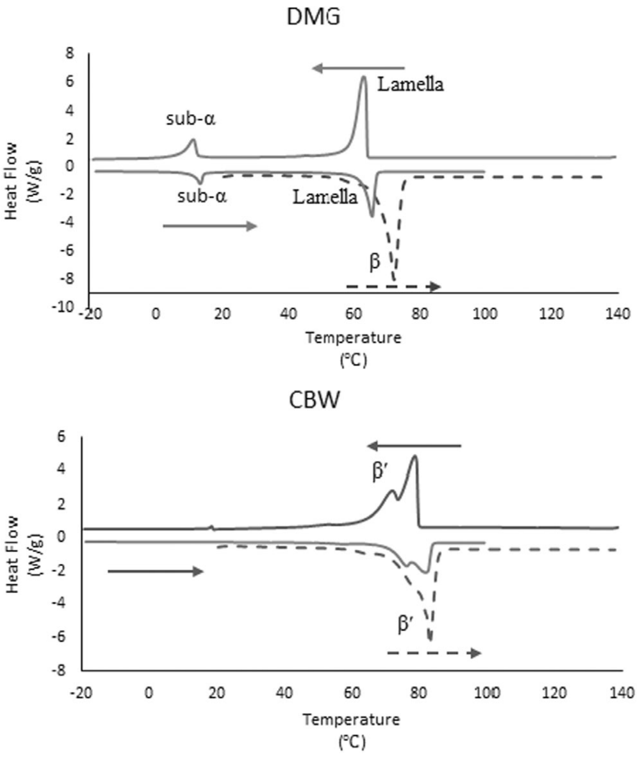

Figure 5. Differential scanning calorimetry (DSC), thermograms of distilled monoglyceride (DMG) and carnauba wax (CBW). Dashed lines show the first step of heating.

Temperature sweep test parameters of DMG/CBW-based oleogels are listed in Table 3. The onset of gelation was defined as the point where the G' and G'' values were equal or $\tan\delta = 1$. The corresponding temperature and time were coded as T_g and t_g, respectively. The onset of crystallization temperature (T_O) was determined as the temperature at which a quick increase in the G' value or an abrupt decrease in the G'' value was observed.[23,31]

The formation of the three-dimensional network was strongly influenced by the gelators' concentration, ratio, and their interactions ($P < 0.01$). Because of the crystallization of a large number of high melting components of CBW-based crystals with a strong possibility of crystal-crystal interaction, D_0-100 demonstrated the highest T_O and T_g values. The high percentage of DMG in the 85:15 and 100:0 ratios, with lower melting and crystallization temperature, decreased the T_O and T_g values significantly ($P < 0.05$). It is worth noting that there was a big difference between T_O and T_g for D_{70}-100, which demonstrated that, although the crystal formation started at a high temperature, the gel formation was delayed. As mentioned later below, this effect is a result of the release of great heat during the crystallization process of D_{70}-100, which increases temperatures that subsequently dissolved the already-formed crystals. According to Perez-Monterroza *et al.*,[32] the beginning temperature and the crystallization time were affected by the number of saturated components, which were dependent on the chemical composition of organogelators.

The gelator ability to form organogel can be evaluated by the crystal formation time.[21] Increasing the GsC and CBW ratio decreased the onset of gelation time (t_g) ($P < 0.05$). However, the t_g values of D_0-50, D_{40}-50, and D_{55}-50 were not significantly different from those of D_{85}-100, and D_{100}-100, implying the CBW quantity in total gelator mass was highly efficient in the t_g value. The presence of different carboxylic acids, esters, and alcohols, with a high melting point, in the chemical composition of CBW probably facilitated the formation of intermolecular hydrogen bonds and, thus, reduced the gelation time. Lupi *et al.*[31] also showed that the fatty alcohols (policosanol) promoted faster gelation than MAGs.

Thermal properties

Thermal properties of DMG, CBW, and oleogels were investigated by DSC analysis. At the first melting step, which was used to erase the thermal history, neat DMG thermograms indicated one melting peak at 72.3 °C, associated with the melting of the stable β-polymorph. After crystallization, the second melting peak demonstrated two endotherms associated with sub-α and lamella structures (Fig. 5). The sub-α phase with a low-ordered structure and less densely packed crystal was metastable and converted into a better-ordered β-polymorph during storage. Because the second melting pattern was the same as the crystallization pattern, the polymorphic behavior of these two steps was similar.[14,18,23] However, Lopez-Martinez *et al.*[30] identified three peaks in GMS thermograms associated with the sub-α2, sub-α1, and lamella structures. These different peak positions and quantities might be relevant to the monoglyceride source[5] and crystal states.[30]

The pure CBW thermograms exhibited three crystallization (two small and one overlapped) and two melting (one small and one overlapped) peaks (Fig. 5; see also Supporting information, Table S2). This pattern indicated that some CBW molecular species crystallized separately, and others co-crystallized. Moreover, because of the heterogeneous chemical composition, the DSC thermograms of CBW, SFW, and BW demonstrated more than a single peak.[19,29]

Figure 6 shows the endotherms of oleogels at the first step of heating at 100 g kg^{-1} GsC. A similar trend was observed in 50 g kg^{-1} GsC. In all oleogels, with the increase in the CBW ratio, the first peak shifted toward lower temperatures and enthalpies, which expressed the formation of CBW/DMG mixed crystal (co-crystallization).[20] Molecular interactions between CBW and DMG might likely occur through interactions between polar moieties or aliphatic chains of two gelators.[19,20] The presence of one melting/crystallization peak at the 85:15 ratio indicated that just the DMG/CBW mixed crystal was formed in this ratio. Nevertheless, in other ratios, because of the melting of high melting components in CBW, there was a new peak at temperatures above 70° C, which shifted toward higher temperatures with the increase in the CBW ratio. These results indicated that different crystals existed in these oleogels. Accordingly, we concluded that the presence of 15% CBW was sufficient to form mixed crystals, and the excessive amount of CBW crystallized separately.

In the second heating step, the first and second peaks were observed in DMG containing oleogels (Fig. 7). Because DSC analysis started from 20 °C and the first peak was between 10 and 14 ° C, it was not detected in the first step. This peak was associated with the sub-α polymorphic transition. The second peak, which was located at 42–53 °C, was not detected in the first step, indicating that these non-stable polymorphs were converted into stable types during storage. The third was detected in all oleogels at 52–63 °C. The corresponding temperature and enthalpy of peak decreased with the increase in the CBW ratio. D_{85}-100 demonstrated the highest enthalpy indicating the presence of high crystalline mass, which causes high stability.[1,33] The last, as also detected in the first step, was associated with the stable polymorphs and was observed in samples containing a 45% CBW ratio and above. This peak shifted toward higher temperature and enthalpy with the increase in the CBW ratio. High melting enthalpy, resulting from the high crystalline mass, increased the oleogel stability.[1,33]

The first crystallization peak of oleogels, which shifted toward lower temperatures with the increase in the DMG ratio, was associated with the crystallization of CBW components. This peak closed the second peak at the 70:30 ratio with the temperature differences equal to 0.28 °C and was deleted in 85:15 ratio (Fig. 8). Moreover, the peak enthalpy reduced with the decrease in the CBW ratio. These results indicated that below the 85:15 ratio, the onset of crystallization temperature ($T_{C\text{-}on}$) and enthalpy were handled by CBW concentration. The temperature and enthalpy of the second, located at 45–50 °C in all exotherms, decreased with the increase in the CBW ratio. As mentioned before, this reduction indicated the co-crystallization between the CBW and DMG.[20] Similar to the heating step, the 85:15 ratio demonstrated the highest enthalpy indicating the formation of high crystalline mass, which causes high stability. Because the third peak, located between 9 and 12 °C, was not detected in pure CBW oleogels, it was associated with DMG sub-α polymorphic transition. With the increase in the CBW ratio, the $T_{C\text{-on}}$ in the second and third peaks decreased, whereas the first peak increased. The increase in the $T_{C\text{-}on}$ and peak crystallization temperature ($T_{C\text{-}peak}$) indicated the acceleration of the crystallization at first.[34]

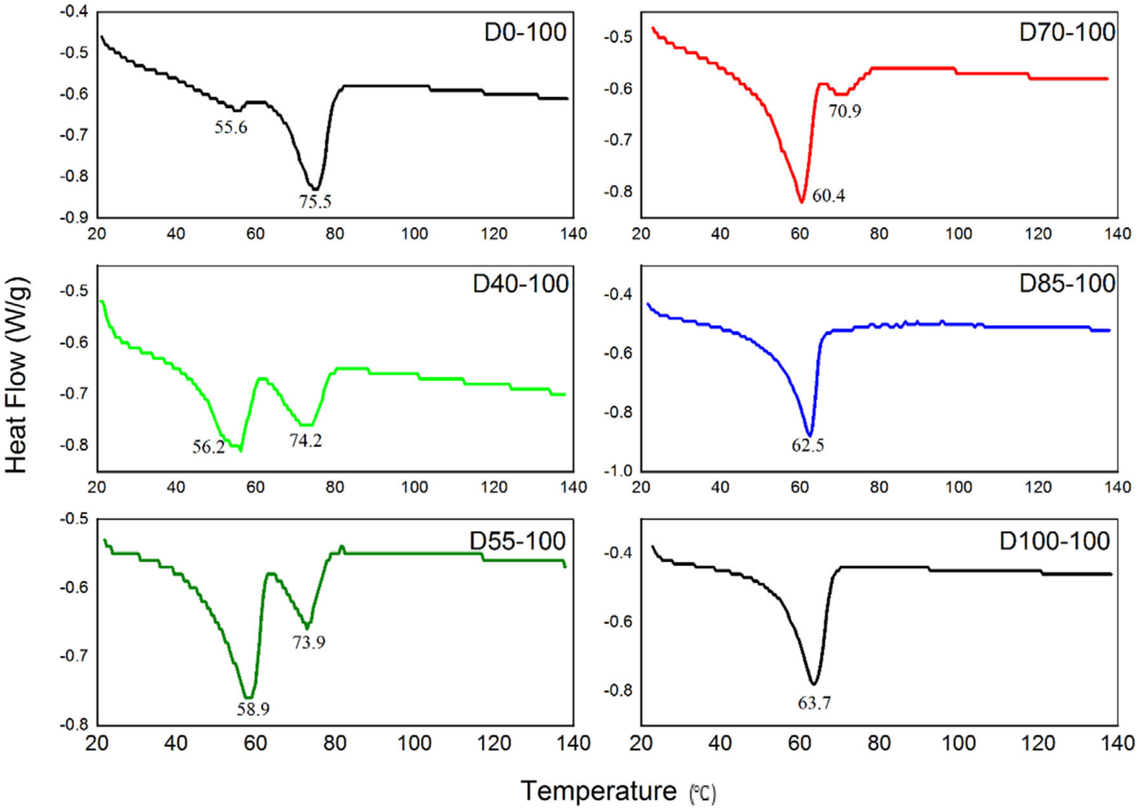

Figure 6. The first step of heating endotherms of the oleogel samples at 100 g kg^{-1} gelator concentration. The numbers to the left of the dashes show the ratio of monoglyceride.

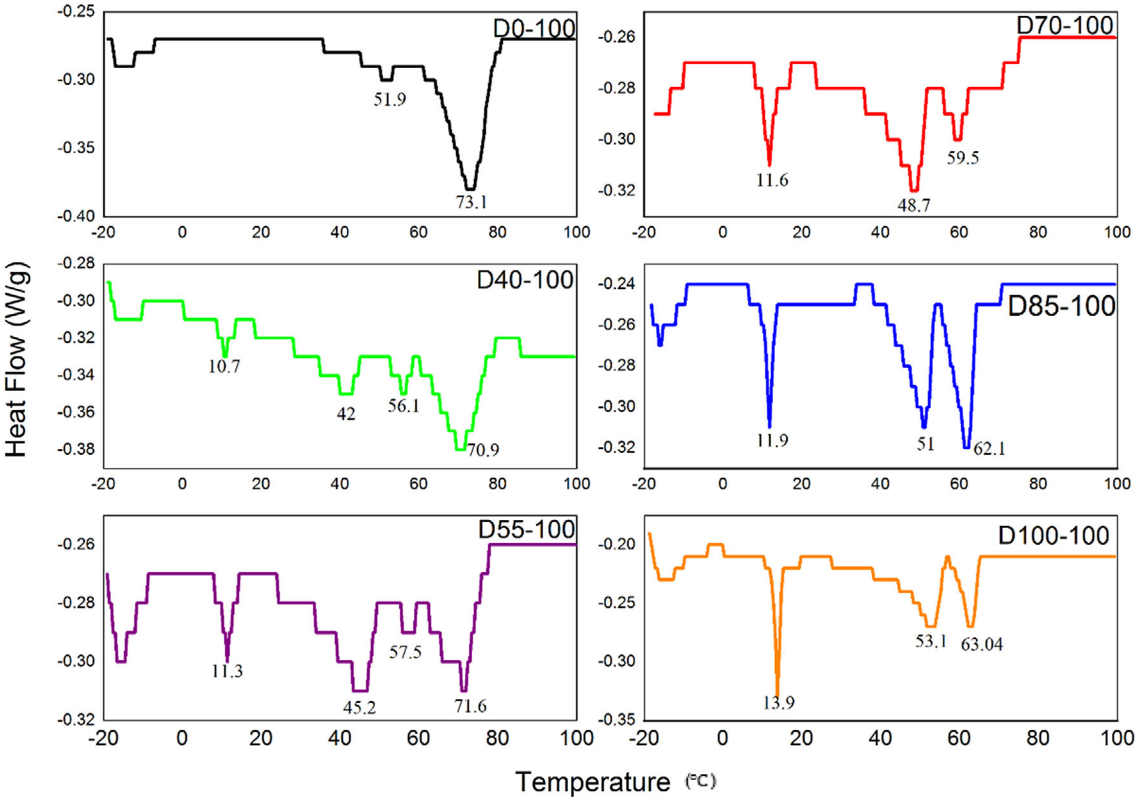

Figure 7. The second step of heating endotherms of the oleogel samples at 100 g kg^{-1} gelator concentration. The numbers to the left of the dashes show the ratio of monoglyceride.

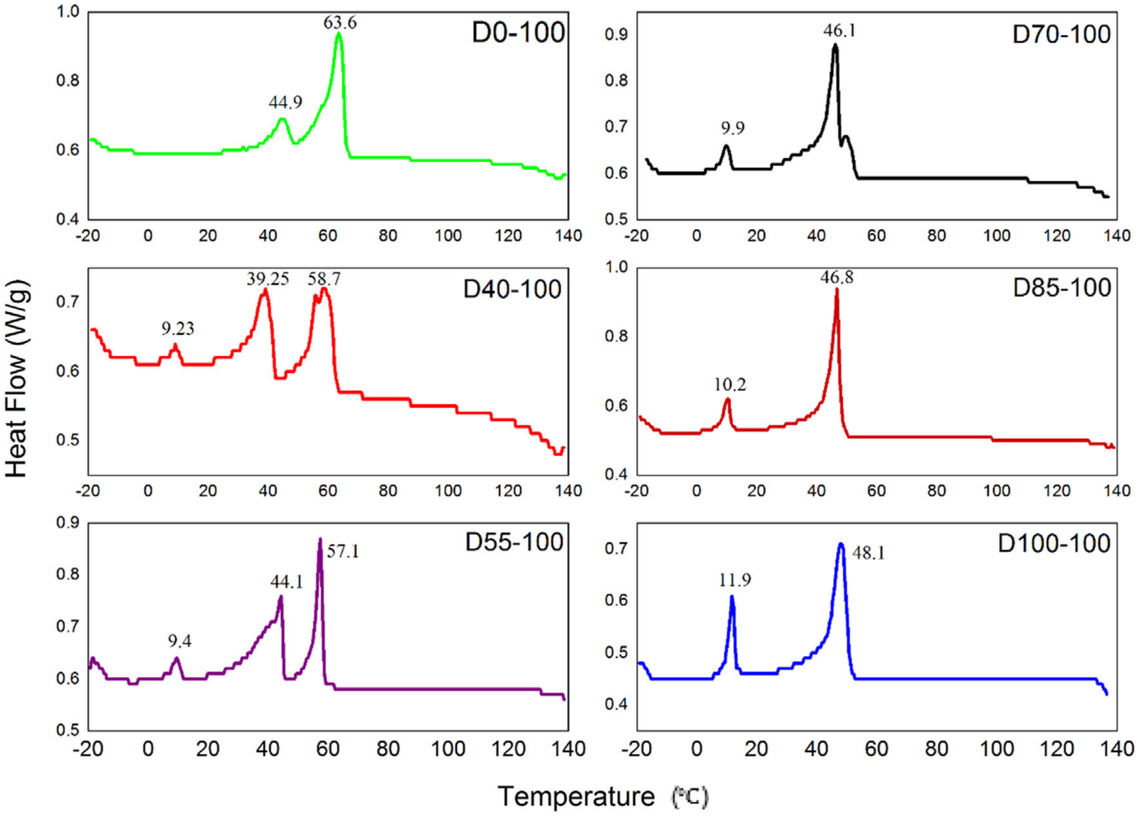

Figure 8. The crystallization exotherms of the oleogel samples at 100 g kg^{-1} gelator concentration. The numbers to the left of the dashes show the ratio of monoglyceride.

By contrast, the decrease in the $T_{C\text{-}on}$ indicated the inhibition of polymorphic transition because of the presence of CBW.[12] However, in comparison with the first, the second peak enthalpies were high in 70:30 and 55:45 ratios (about 0.76, 5.4, 1.97, and 2.95 J g^{-1} for D$_{70}$-100, D$_{55}$-100, D$_{70}$-50, and D$_{55}$-50 respectively, in the first peak *versus* 4.75, 8.73, 4.8, and 3.4 J g^{-1} in the second peak). This indicated that, during the crystallization process of 70:30 and 55:45 ratios, the release of immense heat might increase temperatures that subsequently dissolved the already-formed crystals.[34] As seen before, this phenomenon affected the mechanical and rheological properties of these oleogels. Because the highest difference between the first and the second peak enthalpies (> 6-fold) was obtained for D$_{70}$-100, as mentioned before, a noticeable reduction in the T_g value was observed. By contrast, as mentioned above, the first peak did not develop in the 85:15 ratio. This benefited the oleogel properties because the crystals did not form before so as to melt now. Moreover, in the 85:15 ratio, the formation of the DMG/CBW mixed crystal, which was the only crystal existing above 25 °C, and lower crystallization and melting end temperatures than for the 100:0 and 0:100 ratios ($P < 0.05$), indicated the formation of the eutectic system. This process is efficient in the reduction of the waxy mouthfeel of oleogel.[35] The higher crystallization and melting temperatures indicate the presence of significant solid contents corresponding to the waxy mouthfeel. Additionally, a significant difference between the two crystallization enthalpies (11.18 ± 0.14 J g^{-1} *versus* 1.70 ± 0.05 J g^{-1}) indicated that the development of the crystals took a long time at this ratio, which could improve the oleogel properties.[19]

A one melting peak higher than the crystallization peaks in all oleogels was probably a result of the co-crystallization (formation of DMG/CBW mixed crystal) of different crystalline structures. These conformations were more clearly identified during heating.[19,31] According to Ferro *et al.*,[23] the presence of different crystallization and melting peaks in GMS thermograms indicated the polymorphic instability of gelators during processing conditions.

CONCLUSIONS

In the present study, canola oil was structured by DMG/CBW mixture. It was observed that the monoglyceride oleogel showed the highest loss tangent and frequency dependence. At 100 g kg^{-1} GsC, the oleogel samples demonstrated non-Newtonian shear-thinning behavior, whereas, at high frequency, the Newtonian behavior was the predominant feature in mixed component oleogels at 50 g kg^{-1} GsC. Our results revealed that CBW could induce an effective interconnected 3D network, so that the network formation rate was increased. The formation of the eutectic system, the crystal homogeneity, and the development of the crystals over a long time improved the oleogel properties at the 85:15 ratio. This specific ratio, with the best structural properties and lowest waxy mouthfeel, is suggested as a saturated fat replacer. These findings are valuable for higher applications of monoglycerides and carnauba wax as the co-structuring agent of edible liquid oil.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data will be made available on request.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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