Food Chemistry: X 25 (2025) 102067

Contents lists available at ScienceDirect

Food Chemistry: X

journal homepage: www.sciencedirect.com/journal/food-chemistry-x

Characterization of the sunflower oil-based oleogel developed by the ferulic acid/monoglyceride mixture and its application in chocolate preparation

Sheng Zhang, Sheng Geng, Hanjun Ma, Benguo Liu *

School of Food Science, Henan Institute of Science and Technology, Xinxiang 453003, China

ARTICLE INFO

Keywords:
Oleogel
Ferulic acid
Monoglyceride
Characterization
Chocolate

ABSTRACT

The ferulic acid (FA) / monoglyceride (MG) mixture could act as a gelator to structure sunflower oil at the gelator concentration (c) ≥ 4 % and the FA/MG ratios (r) of 0:100, 25:75, 50:50 and 75:25. The rectangular FA and needle-shaped MG crystals in the oleogel interlock with each other to form a 3D network, restricting the flow of oil. The gel strength and rheological performance of the oleogel were positively correlated with c and negatively correlated with storage temperature (t). Its gelation temperature was determined by c and r. Its β-carotene protective ability against ultraviolet irradiation was proportional to the FA concentration. The oleogel with r = 25:75, c = 5 % and t = 4 °C could partially substitute cocoa butter for chocolate production. With the increasing substitution rate (W_{CBS}), the appearance, texture properties and enthalpy change of chocolate gradually deteriorated. But when $W_{CBS} \leq 40$ %, the oleogel had no significant effect on the sensory characteristics.

1. Introduction

Lipids are not only an important source of energy, but also an important carrier for nutraceuticals, which determine the functionality, texture, and taste of food (Pinto, Martins, Pastrana, Pereira, & Cerqueira, 2021). Oleogel is a gel-like structure formed by encapsulating liquid oil within a 3D gel network using a certain amount of gelator, thus possessing the characteristics of solid fat (Pehlivanoglu et al., 2018). During the preparation process of edible oleogels, the gelator first undergoes random and non-directional aggregation to form a primary structure. Then, through self-assembly or crystallization, the gelator forms secondary structures such as fibrous or lamellar aggregates. These aggregates further form a three-dimensional network structure, preventing the flow of oil and resulting in the gelation of the entire system (Puscas, Muresan, & Muste, 2021). In recent years, researchers have shown great interest in the development of oleogels due to the fact that common plastic fats, such as lard, beef tallow, butterfat, coconut oil, margarine, vegetable shortening, contain high levels of saturated fatty acids and significant amounts of *trans*-fatty acids. Although these fats can provide unique functional properties to food, excessive consumption can increase the risk of coronary heart disease, cardiovascular disease, metabolic syndrome, obesity, diabetes, and cancer (Pehlivanoglu et al., 2018). In addition, when liquid oil is directly added to food as a substitute for plastic fats, adverse phenomena such as oil leakage and even shortened shelf life of the product may occur (Pakseresht & Tehrani, 2022). Since the construction of food-grade oleogels only requires the participation of edible vegetable oil and gelators, oleogels are a new strategy for constructing zero-*trans*, low-saturated fatty acid plastic fat substitutes.

Currently, oleogels can be classified into single-component and multi-component oleogels based on the type and quantity of gelator used. Common single-component gelators include monoglyceride, wax, ethyl cellulose, etc. (Davidovich-Pinhas, Gravelle, Barbut, & Marangoni, 2015). Although these gelators can form edible oleogel by themselves, they show some limitations under shear, heating and processing conditions. The mixture of various gelators can play a synergistic effect to enhance the strength of the gel, such as monoglyceride/diglyceride (Wang et al., 2022), stearic acid/stearol (Gravelle, Blach, Weiss, Barbut, & Marangoni, 2017), β-sitosterol/phytosterol and γ-oryzanol (Okuro, Malfatti-Gasperini, Vicente, & Cunha, 2018), β-sitosterol/lecithin (Li, Wan, Cheng, Liu, & Han, 2019), lecithin/tocopherol (Bin Sintang et al., 2017), etc. In addition, the application of oleogels in food has been gradually increasing, such as in chocolate (Espert, Hernández, Sanz, & Salvador, 2021), spreads (Bascuas et al., 2021), artificial cream (Moriano & Alamprese, 2017), meat products (Wolfer, Acevedo, Prusa, Sebranek, & Tarté, 2018), and baked goods (Jang, Bae, Hwang, Lee, & Lee, 2015). Li and Liu used different types of corn oil-based oleogels developed by monostearin glycerol ester, sitosterol/lecithin, ethyl

* Corresponding author.
E-mail address: liubenguo@hist.edu.cn (B. Liu).

https://doi.org/10.1016/j.fochx.2024.102067
Received 22 September 2024; Received in revised form 12 November 2024; Accepted 2 December 2024
Available online 4 December 2024

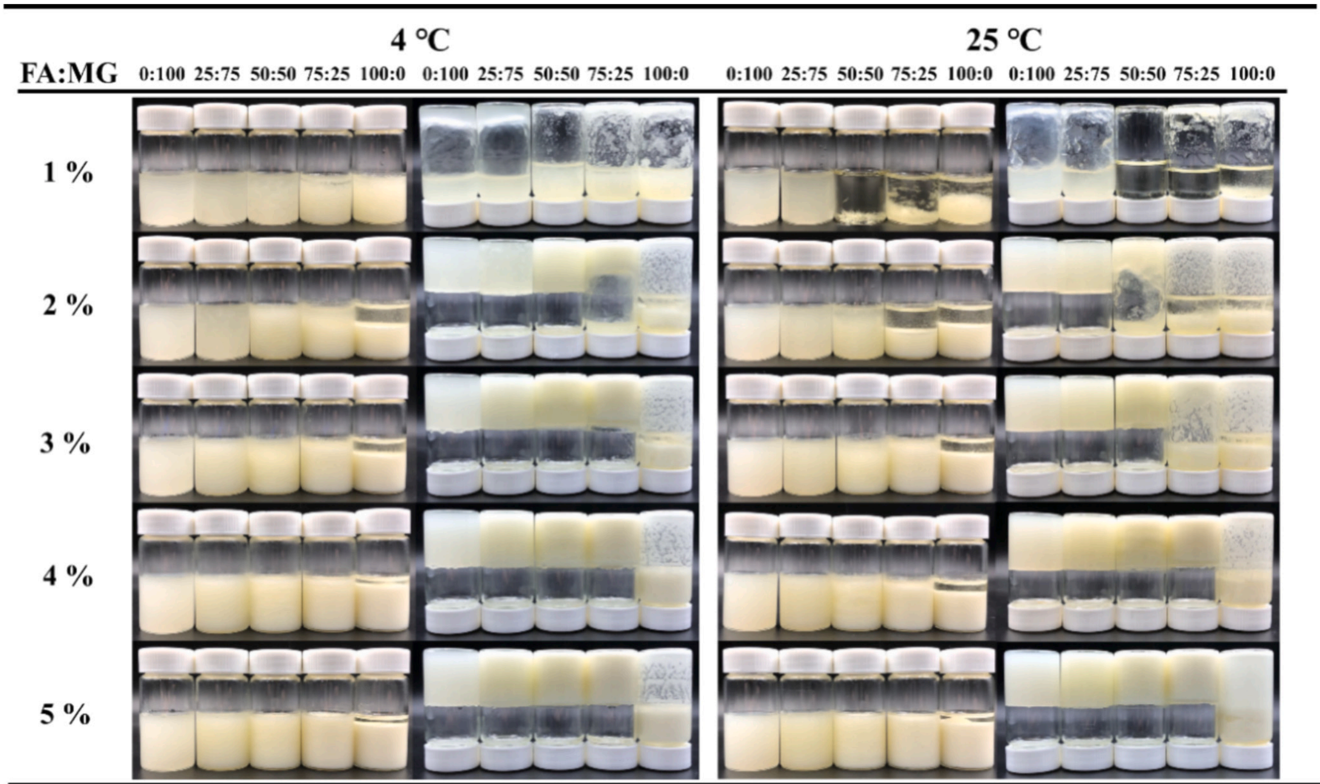

Fig. 1. Effect of gelator concentration, storage temperature and FA/MG ratio on the formation of the sunflower oil-based oleogel.

cellulose to replace cocoa butter in dark chocolate, and found that the thermodynamic behavior and morphology of chocolate prepared with a certain amount of oleogels were similar to traditional dark chocolate (Li & Liu, 2019). Bascuas et al. partially or completely replaced coconut oil with oleogels in chocolate spread, and found that partial substitution improved the spreadability of the chocolate spread, while complete substitution resulted in uneven spreading. Furthermore, chocolate spreads with 50 % oleogel substitution exhibited similar sensory characteristics to those made with coconut oil (Bascuas et al., 2021). Oh et al. used the oleogel developed by hydroxypropyl methylcellulose to replace butter in the meat patty, which significantly reduced the content of saturated fatty acids. The addition of oleogel also reduced the cooking loss of the meat patty, resulting in a more tender texture, while the sensory characteristics remained unaffected (Oh, Lee, Lee, & Lee, 2019).

Ferulic acid (FA) is a phenolic compound widely found in plants, exhibiting multiple functions such as antioxidant activity, free radical scavenging, antitumor effects, and the maintenance of cardiovascular and cerebrovascular health (Zhai et al., 2023). Monoglyceride (MG) is a commonly used emulsifier in food and extensively employed in the production of oleogels. Palla et al. used MG as a gelator to produce oleogels with a texture similar to butter by controlling the production conditions (Palla, Giacomozzi, Genovese, & Carrín, 2017). However, when MG is used as a gelator alone, the internal crystals in the oleogel rapidly transform into the β-crystalline form with prolonged storage time, leading to a decrease in the oil-holding capacity of the crystals (Chen, Van Damme, & Terentjev, 2009). However, the crystalline transformation of MG can be effectively controlled and the stability of oleogels can be improved by complexing with other gelators such as ethyl cellulose and beeswax. In this study, the sunflower oil-based oleogel developed by the ferulic acid/monoglyceride mixture was first reported. The effects of the composition and amount of FA/MG mixture and storage temperature on the formation, structure, mechanical properties and β-carotene protective capacity of oleogel were investigated, and the feasibility of replacing cocoa butter in chocolate production was also evaluated. The obtained results can provide reference for the development of new oleogel and promote the application of oleogel in food industry.

2. Materials and methods

2.1. Chemical

FA, MG and β-carotene were from Aladdin (Shanghai, China). The sunflower oil was the product of COFCO Excel Joy Co., Ltd. (Tianjin, China). Soybean lecithin was purchased from Sangon (Shanghai, China). Cocoa butter was bought from Jiangsu Shengyi Cocoa Food Co., Ltd. (Zhenjiang, China). Cocoa powder was the product of ChocZero Inc. (Pleasanton, CA, USA).

2.2. Preparation of oleogel

The sunflower oil-based oleogel was prepared according to the method of Gravelle et al. (Gravelle, Barbut, & Marangoni, 2012). FA and MG were mixed and added to sunflower oil according to a certain FA/MG ratio (0:100, 25:75, 50:50, 75:25, 100:0), so that the final concentration of the mixture in sunflower oil reached 1 %, 2 %, 3 %, 4 % and 5 %, respectively. Then the oil was incubated at 120 °C, and stirred at 500 rpm for 15 min (ZNCL-BS180*180, Henan Yuhua Instrument Co., China). After heating, the samples were stored at 4 °C and 25 °C for 24 h, respectively. The formation of oleogel was determined by the inverted-tube method.

2.3. Polarizing microscopic observation

The 20 μL sample prepared at different FA/MG ratios (0:100, 25:75, 50:50, 75:25) and gelator concentration of 4 % and 5 % was dripped onto the glass slide, covered with the cover glass, and observed with a Hengping BH200P polarizing microscope (Shanghai, China).

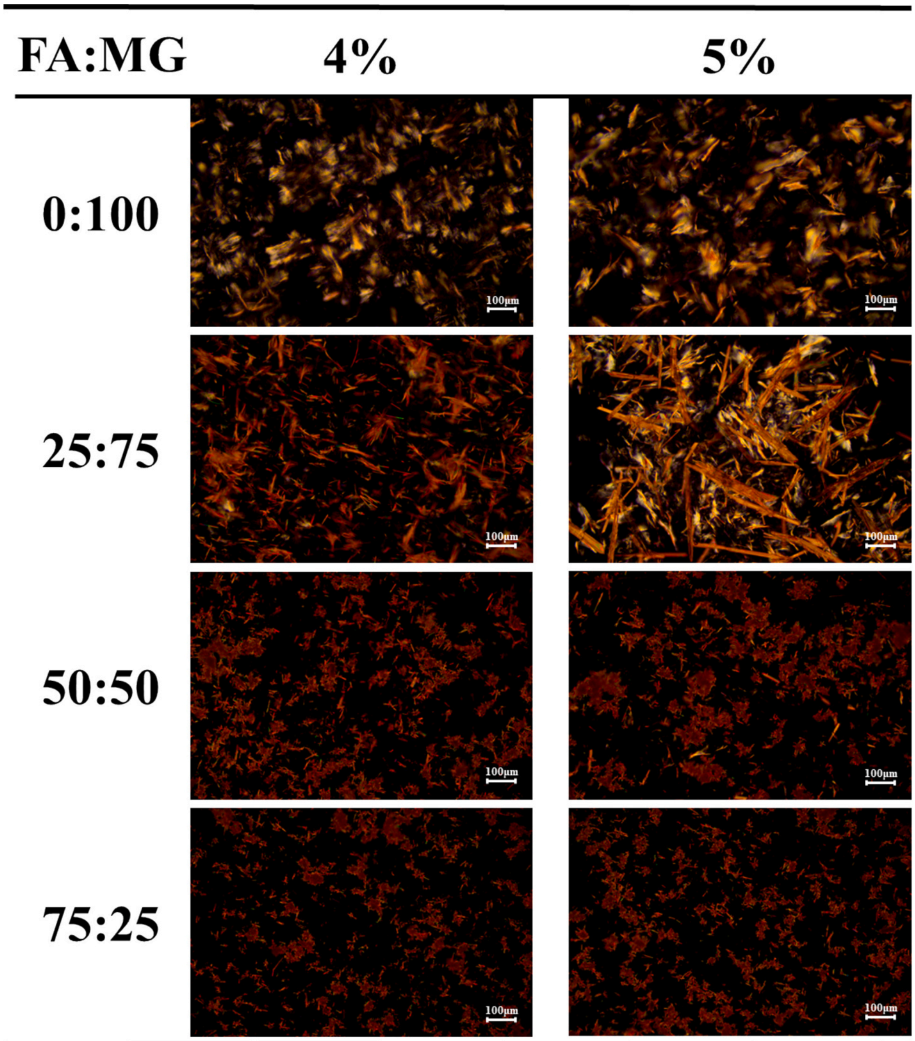

Fig. 2. Effect of gelator concentration, storage temperature and FA/MG ratio on the microstructure of oleogel.

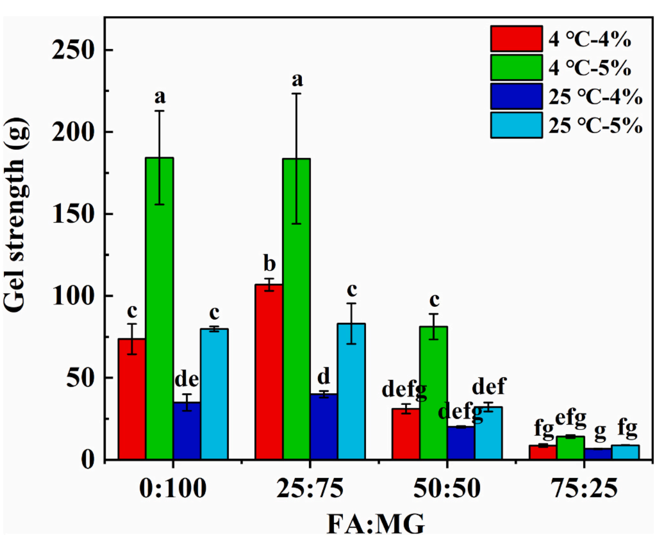

Fig. 3. Effect of gelator concentration, storage temperature and FA/MG ratio on the gel strength of oleogel.

2.4. Determination of gel strength

The gel strength values of the oleogels developed at different FA/MG ratios (0:100, 25:75, 50:50, 75:25) and gelator concentration of 4 % and 5 % were determined by a TA-XT Plus texture analyzer (Surrey, UK). The test temperature was consistent with the storage temperature of the oleogel, and the analysis was carried out in the GMIA Gelation mode using the P/0.5 probe. The probe speed was 1.0 mm/s. The insertion distance was set at 4 mm with the trigger force of 3.0 g (Zhou et al., 2020).

2.5. Measurement of texture properties

The texture properties of the samples were also measured by a texture analyzer with a P/0.5R probe at storage temperature. The test was conducted based on the TPA mode, with two compressions performed on the sample. The probe speed of the probe was set at 1 mm/s. A 5-s pause was introduced between compressions, with a compression ratio of 75 % and a trigger force of 3 g (Davidovich-Pinhas et al., 2015).

2.6. Determination of rheological properties

The rheological properties of the sample were tested using a HAAKE MARSIII rotational rheometer (Thermo Scientific Co., Ltd., Waltham, MA), with a P35TiL parallel plate probe and a gap of 1.000 mm. During

Table 1
Effect of gelator concentration, storage temperature and FA/MG ratio on the texture properties of oleogel.

Storage temperature	Gelator concentration	FA/MG ratio	Hardness (g)	Adhesiveness (g.*sec*)	Gumminess (g)	Chewiness (g)
4 °C	4 %	0:100	103.17 ± 10.13^{d}	−365.58 ± 57.61^{de}	19.36 ± 1.43^{d}	18.48 ± 1.54^{de}
		25:75	156.18 ± 12.45^{b}	−403.75 ± 90.93^{de}	18.88 ± 0.32^{d}	17.17 ± 0.16^{def}
		50:50	52.09 ± 3.44^{e}	−229.54 ± 30.55^{bc}	13.40 ± 1.49^{e}	12.97 ± 1.72^{f}
		75:25	14.61 ± 0.64^{g}	−46.25 ± 2.07^{a}	6.19 ± 0.34^{f}	6.13 ± 0.35^{g}
	5 %	0:100	239.31 ± 13.78^{a}	−596.85 ± 177.69^{f}	38.67 ± 0.95^{a}	35.57 ± 6.22^{a}
		25:75	226.50 ± 18.02^{a}	−441.13 ± 109.42^{e}	25.38 ± 6.77^{b}	24.09 ± 5.15^{bc}
		50:50	123.02 ± 5.26^{c}	−315.59 ± 12.59^{cd}	18.52 ± 0.94^{d}	17.67 ± 0.96^{def}
		75:25	19.55 ± 1.06^{g}	−76.14 ± 6.85^{a}	7.33 ± 0.34^{f}	7.23 ± 0.35^{g}
25 °C	4 %	0:100	53.48 ± 2.91^{e}	−341.76 ± 15.79^{cde}	18.54 ± 1.83^{d}	17.82 ± 2.61^{def}
		25:75	63.04 ± 6.19^{e}	−313.45 ± 58.90^{cd}	20.47 ± 3.05^{cd}	20.20 ± 3.14^{cd}
		50:50	35.25 ± 0.89^{f}	−186.34 ± 10.57^{b}	13.39 ± 0.34^{e}	13.24 ± 0.36^{ef}
		75:25	12.40 ± 0.97^{g}	−22.30 ± 2.50^{a}	5.75 ± 0.32^{f}	5.70 ± 0.32^{g}
	5 %	0:100	97.56 ± 3.65^{d}	−444.21 ± 52.74^{e}	24.36 ± 3.41^{bc}	24.22 ± 3.39^{bc}
		25:75	124.01 ± 8.98^{c}	−378.42 ± 63.65^{de}	27.96 ± 4.28^{b}	26.42 ± 5.78^{b}
		50:50	52.68 ± 1.56^{e}	−329.45 ± 14.86^{cde}	20.63 ± 0.63^{cd}	20.48 ± 0.62^{cd}
		75:25	16.48 ± 0.65^{g}	−63.85 ± 6.42^{a}	7.26 ± 0.49^{f}	7.12 ± 0.51^{g}

the measurement, a 1 g sample was placed on the temperature-controlled test platform and allowed to equilibrate for 10 min at the test temperature. The shear rate scanning experiment of the sample was conducted at the shear rate range of 0.1–100 s^{-1} and shear stress of 1 Pa. The curve depicting the variation of apparent viscosity with shear rate was recorded, and fitted using the Ostwald equation (Zhang & Qin, 2016). Subsequently, stress scanning test was performed within a shear stress range of 0.1–100 Pa at a frequency of 1 Hz to determine the linear viscoelastic region (LVR) of the sample (Liu et al., 2019). Finally, the temperature sweep test was carried out to determine the gelation temperature of the sample. The sample was heated to 120 °C and held for 10 min to remove crystalline memory. It was then cooled from 120 °C to 0 °C at a cooling rate of 3 °C/min. Throughout the entire testing process, the frequency was fixed at 1 Hz and the shear stress was set at 1 Pa (Zhang & Qin, 2016).

2.7. Evaluation of β-carotene protective capacity

The sunflower oil-based oleogel containing 2.0 mg/mL β-carotene was prepared according to Section 2.2 and placed in an incubator at 30 °C with a UV lamp 15 cm above it (power, 6 W). Every 48 h, 50 mg of sample was mixed with 10 mL of ethanol/n-hexane mixture (2:1, *v*/v) and centrifuged at 1000 rpm for 10 min. The absorbance of supernatant at 450 nm was read and the β-carotene retention was calculated. Sunflower oil with the same β-carotene content was used as a control (Li, Geng, Zhen, Lv, & Liu, 2022).

2.8. Preparation of chocolate

According to a previous report (Espert et al., 2021), the oleogel developed at the FA/MG ratio of 25:75, gelator concentration of 5 %, and storage temperature of 4 °C was used as cocoa butter substitutes in chocolate preparation. The cocoa butter substitution rates (W_{CBS}) were 0 %, 20 %, 40 %, 60 %, 80 %, and 100 %, respectively. The corresponding chocolates were respectively named as Chocolate-O0, Chocolate-O20, Chocolate-O40, Chocolate-O60, Chocolate-O80, and Chocolate-O100. According to **Table S1**, a certain amount of cocoa butter and oleogel were mixed and melted at 80 °C. Lecithin was added and stirred until dispersed in the liquid fat. Gradually, cocoa powder and sifted powdered sugar were added and mixed until a smooth consistency was obtained. Then, the mixture was tempered in three stages (50 °C, 28 °C, and 32 °C). Finally, the resulting mixture was placed in a mold (30 mm × 30 mm × 20 mm), chilled at 4 °C for 24 h. The obtained chocolate was collected and reserved for the following test.

2.9. Evaluation of color of chocolate

The color of chocolate was determined by a Konica-Minolta CR-400 colorimeter (Osaka, Japan). The color difference of the sample was reflected by CIE-L*a*b model.

2.10. Determination of texture properties of chocolate

With reference to a previous report (Li & Liu, 2019), the texture properties of chocolate were determined using a texture analyzer. The chocolate of 30 mm × 30 mm × 20 mm was placed on the loading table of the texture analyzer for TPA mode determination. The test parameters were set as follows: probe speed, 1.00 mm/s; strain, 30 %; strain time, 3 s; trigger force, 10.0 g.

2.11. Determination of thermodynamic properties of chocolate

Following the method proposed by Li et al. (Li, Liu, & Lin, 2021), the thermodynamic properties of the sample were determined using a TA Q20 differential scanning calorimetry (Newcastle, DE, USA). The sample (10–15 mg) was sealed in an aluminum crucible, with an empty sealed aluminum crucible used as a reference. The measurement was conducted using a heating-cooling cycle, with a 30-min hold at the end of the first heating program to eliminate any crystalline memory, followed by data recording and analysis of the second heating curve. The temperature program for heating/cooling of the chocolate ranged from −20 °C to 60 °C, with a heating/cooling rate of 5 °C/min. The flow rate of nitrogen gas was set at 40 mL/min.

2.12. Sensory evaluation of chocolate

Fifteen trained students familiar with chocolate characteristics and descriptive analysis methods were selected as assessors for this experiment. Chocolate samples were placed in white plastic cups with random three-digit codes, arranged randomly. Assessors were required to evaluate the appearance and aroma of the samples by observing them, and evaluate the flavor and texture of the samples after tasting them. The scoring criteria were based on the method of Sim et al. (Sim, Ng, Ng, Forde, & Henry, 2016), evaluating the appearance, color, hardness, flavor, melt, and overall acceptance of the chocolate. Assessors were instructed to taste a piece of chocolate, then drink water to rinse the taste before tasting each type of chocolate. Each sensory attribute was evaluated using a continuous linear quantification scale ranging from 1 (not perceived) to 9 (high intensity).

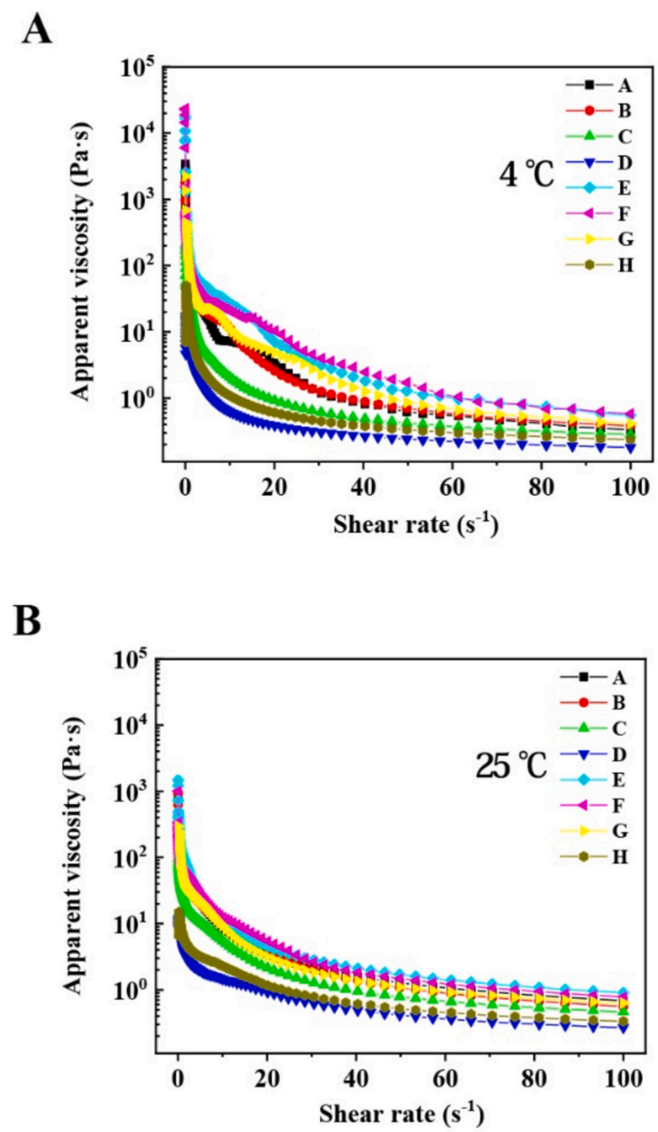

Fig. 4. Effect of gelator concentration (*c*), storage temperature (*t*) and FA/MG ratio (*r*) on the on apparent viscosity of oleogels (A: *r* = 0:100, *c* = 4 %; *B*: *r* = 25:75, *c* = 4 %; C: *r* = 50:50, *c* = 4 %; D: *r* = 75:25, *c* = 4 %; E: *r* = 0:100, *c* = 5 %; F: *r* = 25:75, *c* = 5 %; G: *r* = 50:50, *c* = 5 % ; H: *r* = 75:25, *c* = 5 %).

2.13. Statistical analysis

The experimental data were presented as mean ± standard deviation ($n = 3$). Data analysis was performed using IBM SPSS 22.0 software (Armonk, NY, USA), and Duncan's test was selected with a significance level of 0.05. The graphs were generated using Origin 8.0 software (Origin lab, Northampton, MA, USA).

3. Results and discussion

3.1. Formation of oleogel

Fig. 1 presents the appearance of the samples prepared under different conditions. When the gelator concentration ≥ 4 %, all samples except for the sample with the FA/MG ratio of 100:0 could form oleogels. The FA/MG ratio significantly influenced the oleogel formation when the gelator concentration were 2 % and 3 %. Additionally, the samples with the same ratio exhibited different gelation behaviors at 4 °C and 25 °C. In samples with FA/MG ratios of 50:50 and 75:25, the stability of the oleogel formed at 4 °C was higher than that formed at 25 °C. This may be attributed to the differences in sample cooling rates caused by varying storage temperatures. It was reported that different cooling rates had significant effects on the formation of oleogels (Trujillo-Ramírez, Lobato-Calleros, Vernon-Carter, & Alvarez-Ramirez, 2019). In terms of color and light transmittance, the oleogel samples appeared as a milky white color and exhibited an opaque state. According to the results of gelation experiment, the oleogel samples prepared at the FA/MG ratio of 0:100, 25:75, 50:50 and 75:25, gelator concentration of 4 % and 5 %, and storage temperature of 4 °C and 25 °C were selected for the following test.

3.2. Microstructure of oleogel

The gelation behavior of oleogel is closely related to its microstructure. In the polarizing microscopic analysis (Fig. 2), MG exhibited needle-like crystal structure in oleogel, while FA exhibited rectangular structure. As the primary assembly grows, the dissolved gelator molecules, whether in monomer or aggregate form, diffuse and attach to the surface of the formed primary assembly. Depending on the relative rate at which dissolved molecules adhere to the surfaces of different primary assemblies, the assemblies may grow in one -, two -, or three-dimensional directions. When the growth rate perpendicular to the direction of the layered crystal plane is greater than the growth rate parallel to the direction of the layered crystal plane during the aggregation process, fibrous or lamellar structures will be formed (Bai et al., 2023). In the case of lower gelator concentrations, the crystals of FA and MG were smaller, making it difficult to establish a complete three-dimensional network structure for structuring sunflower oil. Yang et al. found a similar phenomenon in the production of the oleogels developed by phytosterol and monoglyceride (Yang, Chen, & Yang, 2018). As the gelator concentration increased, the crystal size in the oleogel gradually grew, resulting in a more tightly overlapped crystal network within the system. This trapped a large amount of liquid oil in the dense crystal network, making the gel structure more stable, especially in the sample with a gelator concentration of 5 % and a FA/MG ratio of 25:75.

3.3. Gel strength of oleogel

The mechanical properties of oleogel are closely related to their structure and processing applications. Therefore, the effects of gelator concentration, storage temperature and FA/MG ratio on the gel strength of oleogel were investigated (Fig. 3). The increasing gelator concentration could improve the network structure of the oleogel and enhance the gel strength of the sample at the same storage temperature. At the same gelator concentration, the gel strength of the sample was higher when stored at 4 °C. This may be due to the fact that at lower temperatures, intermolecular interactions are enhanced, which helps to form a more stable gel structure (Bertasa et al., 2020). In addition, the gel strength of the sample with an FA/MG ratio of 25:75 was slightly higher than that of the other samples, which was consistent with the microscopic observation results (Fig. 2).

3.4. Texture properties of oleogel

The effect of gelator concentration, storage temperature and FA/MG ratio on the texture properties of oleogel was analyzed based on the TPA method in this study. As shown in Table 1, there were significant differences in hardness, adhesiveness, gumminess, and chewiness of the samples. At the same storage temperature, the hardness, adhesiveness, and chewiness of the oleogel samples all ascended rapidly with the increasing gelator concentration, and the absolute value of viscosity demonstrated the same trend. The MG-type oleogel exhibited a higher textural performance at 4 °C. However, at 25 °C, these textural parameters deteriorated rapidly, possibly due to hydrogen bonding being the

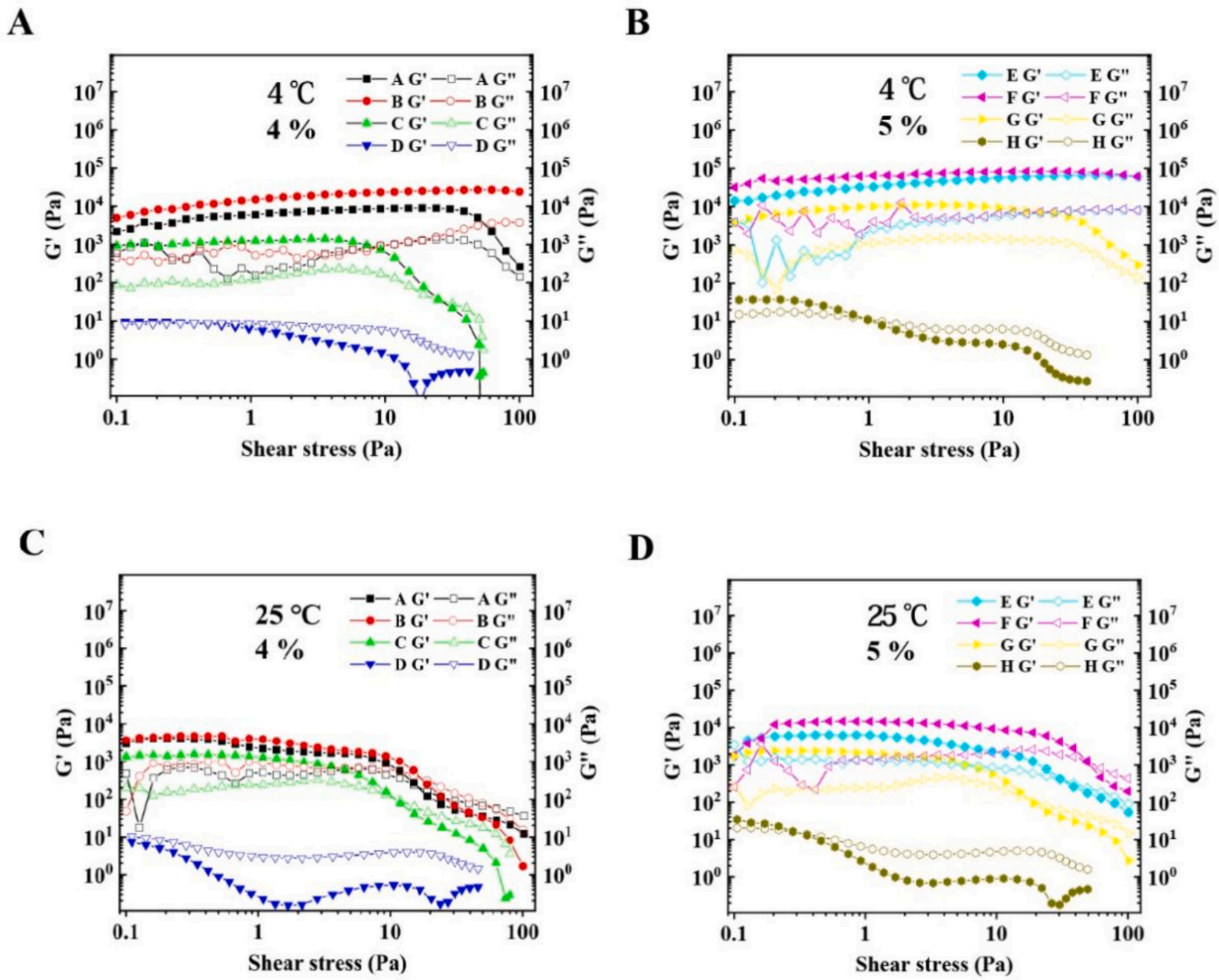

Fig. 5. Effect of gelator concentration (c), storage temperature (t) and FA/MG ratio (r) on the LVR of the oleogels (A: r = 0:100, c = 4 %; B: r = 25:75, c = 4 %; C: r = 50:50, c = 4 %; D: r = 75:25, c = 4 %; E: r = 0:100, c = 5 %; F: r = 25:75, c = 5 %; G: r = 50:50, c = 5 % ; H: r = 75:25, c = 5 %).

dominant factor in the formation of the MG network structure. As the temperature increased, intermolecular Brownian motion intensified, leading to a decrease in the binding effect of hydrogen bonds and a much weaker three-dimensional network structure compared to that at 4 °C. Consequently, this resulted in a decline in the relevant parameters. There were also studies indicating that the instability of the MG network caused by temperature was a consequence of weakened hydrogen bonding forces under high temperature conditions (Davidovich-Pinhas et al., 2015). In addition, for FA/MG type oleogels, the overall variation of textural properties followed a similar trend, with an increase in gelator concentration leading to enhanced textural properties, while an increase in temperature resulted in a decrease in textural properties. Moreover, the higher the proportion of MG, the more molecules could be used to form gel network. Although FA alone did not exhibit gelling properties, it possessed hydroxyl groups, ester bonds, and methoxy groups. When synergistically interacting with MG to form a gel network, it could enhance intermolecular interactions. At a gelator concentration of 5 %, the sample with a FA/MG ratio of 25:75 achieved an optimal balance between the number of gelator molecules and the intermolecular forces. The resultant samples possessed superior mechanical properties, with higher hardness, adhesiveness, and chewiness compared to other samples, and the absolute value of viscosity was also at a relatively high level.

3.5. Rheological properties of oleogel

This study systematically investigated the effects of gelator concentration, FA/MG ratio and storage temperature on the storage modulus (G'), loss modulus (G"), and apparent viscosity (η) of sunflower seed oil-based oleogels, aiming to further analyze their processing characteristics. Fig. 4 display the effect of shear rate (γ) on the apparent viscosity of the oleogels prepared at 4 °C and 25 °C, respectively, which can be fitted using the following Ostwald equation.

$$\eta = K\gamma^{n-1}$$

where, K is the consistency coefficient, and n is the power-law index.

As shown in **Table S2**, the fitting results indicated that the obtained oleogels were all pseudoplastic fluids ($n < 1$), and the samples with higher gelator concentration had smaller n values compared to those with lower gelator concentration. This is because the samples with higher gelator concentration had higher initial viscosity, but as the shear rate increased, the viscosity decreased rapidly, with a decrease rate much greater than that of the samples with lower gelator concentration.

Fig. 5 illustrate the variation trends of G' and G" of the different samples with shear stress. All samples maintain relatively stable G' and G" values within a certain range, known as the linear viscoelastic region (LVR). Within the LVR, the samples exhibited G' > G, confirming the solid-like behavior of the samples (Martins, Cerqueira, Cunha, &

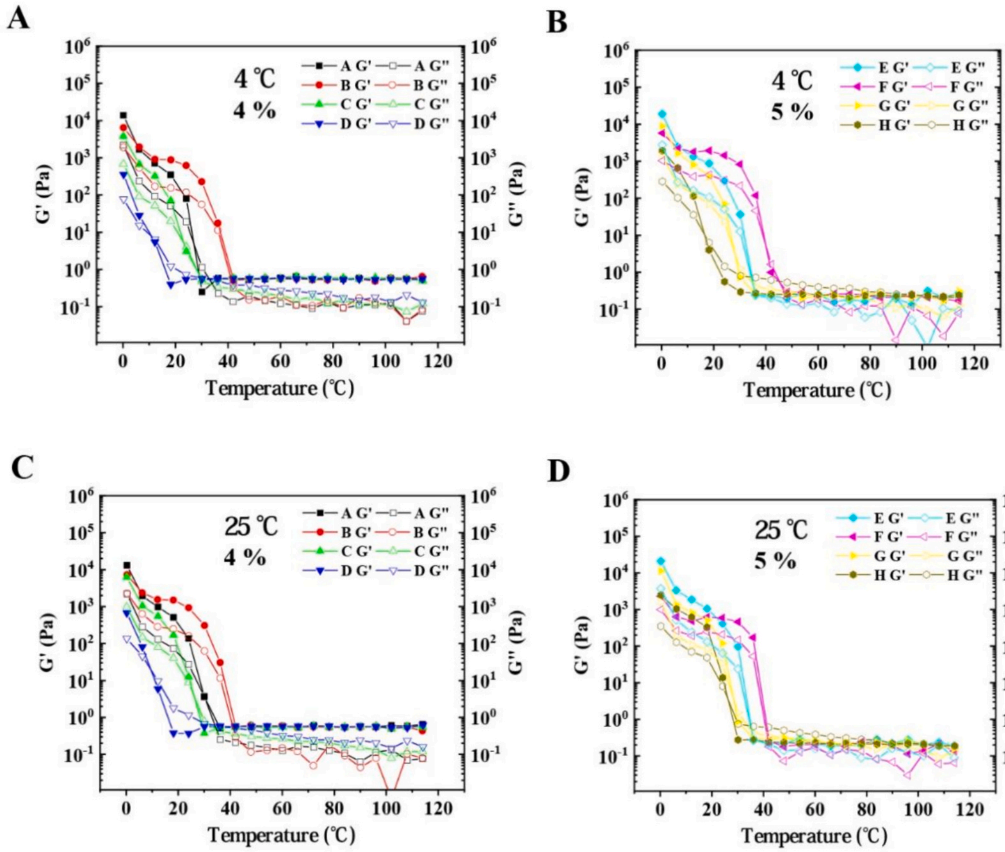

Fig. 6. Temperature sweep results of the oleogels (A: r = 0:100, c = 4 %; B: r = 25:75, c = 4 %; C: r = 50:50, c = 4 %; D: r = 75:25, c = 4 %; E: r = 0:100, c = 5 %; F: r = 25:75, c = 5 %; G: r = 50:50, c = 5 % ; H: r = 75:25, c = 5 %).

Vicente, 2017). Under the same storage temperature and FA/MG ratio, the yield stress of oleogels increased with increasing gelator concentration. However, at a constant gelator concentration and FA/MG ratio, the yield stress of oleogels declined with increasing storage temperature. Similar trends were also observed in the texture analysis, which may be attributed to different cooling rates caused by different storage temperatures. This leads to the growth and arrangement of crystalline fibers in sunflower oil in different ways, resulting in macroscopic rheological differences. This phenomenon was also observed in the experiment of structuring canola oil with 12-hydroxystearic acid (Rogers, Wright, & Marangoni, 2009). The results further suggested that the rheological properties of FA/MG-type oleogels were similar to those of MG-type oleogels, but the oleogel prepared at 4 °C with a gelator concentration of 5 % and a FA/MG ratio of 25:75 possessed higher yield stress and G'_{LVR} value. This was due to the greater number of cross-linking regions between its crystals, leading to strong interactions and high network strength. It confirmed that the internal network of the FA/MG-type oleogel was formed by non-covalent physical cross-linking interactions, which coincided with the report of Han et al. (Han et al., 2013).

The changing trend of gelation temperature of oleogel can be obtained by rising and falling temperature program. The gelation temperature is defined as the intersection of G' and G" curves, or the temperature when tan δ =1. In the gel system, the gelation temperature indicates that at the current temperature, the crystals have been formed and cross-linked with each other (Lupi et al., 2013). As shown in Fig. 6, the oleogel first melted at high temperature. G 'and G" were close to 0 Pa, when the oleogel sample melted into a liquid (Lupi et al., 2013). With the decrease of temperature, especially near the gelation temperature, there was a period of rapid increase in G' and G" of all samples. The results showed that the three-dimensional network structure of the samples had been cross-linked with each other and formed a viscoelastic oleogel. Moreover, with the increase of gelator concentration, the gelation temperature gradually increased. This is due to the fact that an increase in gelator concentration allowed for the formation of more crystals in the oleogel, resulting in a more complete gel network structure. Therefore, more energy was required to disrupt the three-dimensional network structure during the melting process. When the gelator concentration and composition were fixed, variations in storage temperature did not significantly affect the gelation temperature of the oleogel, indicating that the storage temperature had no impact on the gelation temperature of the oleogel. It was also observed that the oleogels prepared at the gelator concentration of 5 % and the FA/MG ratio of 25:75 had a higher gelation temperature.

3.6. *β-Carotene protective capacity of oleogel*

β-Carotene is a common vitamin A supplement, which can improve human visual function, but its application is limited because of its unstable exposure to oxygen, heat and light. This study compared the ability of oleogels prepared at gelator concentration of 5 % to protect β-carotene against ultraviolet radiation (**Fig. S1**). Compared to the control, the oleogels exhibited a significant protective effect on the loaded β-carotene. On the second day of ultraviolet irradiation, the retention rate of β-carotene in the control group was close to zero. However, the retention rate of β-carotene in MG type oleogel was 33.16 ± 0.68 %, while the retention rate of β-carotene in FA-MG type oleogel was higher than 50 %. On the sixth day, β-carotene in the MG-type oil gel completely decomposed, while the retention rates of β-carotene in the oleogels prepared with the FA/MG ratios of 25:75, 50:50, and 75:25 were 23.05 ± 1.63 %, 27.87 ± 0.90 %, and 35.07 ± 1.69 % respectively, showing a linear correlation with their FA concentration (r^2 = 0.987).

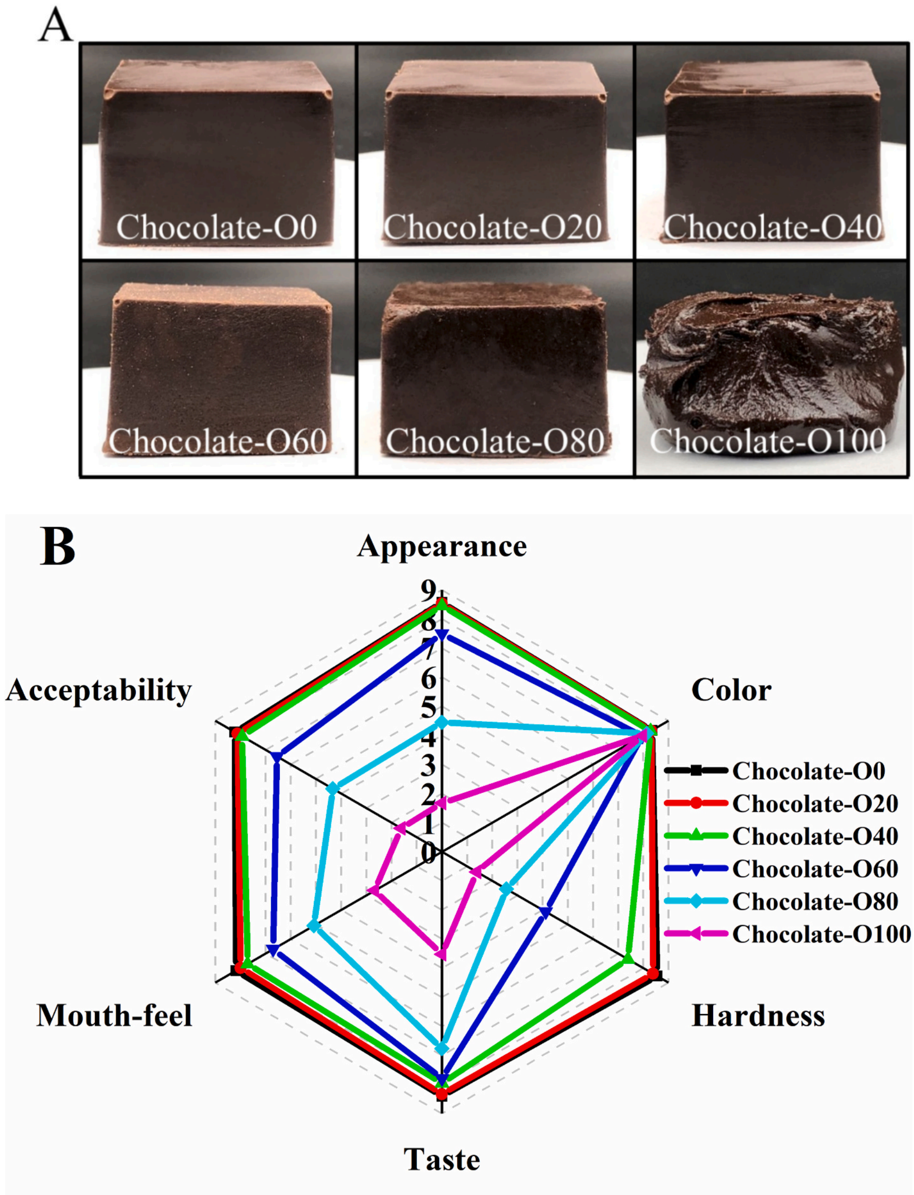

Fig. 7. Appearance (A) and sensory analysis (B) of the chocolate samples.

The result indicated that the protective effect of oleogel on β-carotene was mainly from the ultraviolet absorption and antioxidant properties of FA.

3.7. Appearance of chocolate

Fig. 7A illustrates the appearance of chocolates under different formulations. Chocolate-O0, Chocolate-O20, and Chocolate-O40 exhibited a firm, cuttable, and uniformly shaped exterior with a smooth and glossy texture. Chocolate-O60 had a relatively rough exterior and lacked shine. Chocolate-O80 showed a tendency to melt on the surface, while Chocolate-O100 collapsed and lacked support.

Color is one of the fundamental indicators for evaluating chocolate. L* reflects brightness, with higher values indicating greater brightness. a* represents the red-green axis, with larger values indicating a stronger presence of red. b* represents the yellow-blue axis, with higher values indicating more yellow color. From **Table S3**, it could be observed that with an increase of W_{CBS}, both L* and b* values showed a decreasing trend, indicating a decrease in brightness and yellowness, which was attributed to the inherent yellow color of cocoa butter itself.

3.8. Texture properties of chocolate

The texture properties of chocolate can not only reflect its structure, but also closely related to its quality. The effect of W_{CBS} on the textural properties of chocolate is exhibited in **Table S4**. Chocolate-O0 showed the highest hardness (11,494.09 ± 971.52 g), while Chocolate-O20 and Chocolate-O40 decreased. The change trend of gumminess, chewiness, resilience and hardness of the sample was similar, while that of adhesiveness, springiness, cohesiveness was the opposite. Li and Liu also observed that chocolate containing oleogel had a softening effect, which may be due to the differences in content and types of glycerides in cocoa butter and oleogel (Li & Liu, 2019). This phenomenon is called eutectic softening effect, which means that when the chemical composition of cocoa butter substitute differs from that of cocoa butter, the obtained chocolate will have lower hardness than pure cocoa butter chocolate.

3.9. Thermodynamic properties of chocolate

The lipid phase in chocolate, namely cocoa butter, is a solid at room temperature (20–25 °C), but it forms a smooth and dense suspension at oral temperature (37 °C), which affects the perception of taste and texture (Afoakwa, Paterson, Fowler, & Vieira, 2008). Therefore, the thermodynamic properties of chocolate will provide insights into the impact of oleogel incorporation on the chocolate melting behavior, which is related to sensory characteristics in the oral cavity. **Fig. S2** demonstrated the thermodynamic analysis of the chocolate samples. Regarding peak temperature (T_{max}), there was not much difference between Chocolate-O0, Chocolate-O20, Chocolate-O40, and Chocolate-O60, but they were significantly higher than Chocolate-O80 and Chocolate-O100. The enthalpy change (ΔH_m) of Chocolate-O0 was slightly higher than that of Chocolate-O20 and Chocolate-O40, and significantly higher than that of Chocolate-O60, Chocolate-O80 and Chocolate-O100. Afoakwa et al. confirmed that the enthalpy of chocolate products with lower fat content decreased (Afoakwa et al., 2008). Furlán et al. found that the addition of hydrogenated oil led to changes in crystal and melting properties, resulting in a decrease in enthalpy (Furlán, Baracco, Lecot, Zaritzky, & Campderrós, 2017). The reason for the lower enthalpy value was attributed to the lower cocoa butter content in the chocolate formulated with sunflower oil-based oleogel, which directly affected the quantity and shape of the formed crystals, thus affecting the melting performance. The obtained thermodynamic results were consistent with the texture results, as chocolate with lower melting enthalpy had a softer texture. Kadivar et al. also observed that the T_{max} of chocolate prepared from sunflower oil-based cocoa butter substitute decreased (Kadivar, De Clercq, Mokbul, & Dewettinck, 2016), which was consistent with our results that the decrease was due to the high content of unsaturated triglycerides in the substitute.

3.10. Sensory characteristics of chocolate

As shown in Fig. 7B and **Table S5**, W_{CBS} had different effects on the appearance, color, hardness, taste, mouth-feel and acceptability of chocolate. With the increase of W_{CBS}, all the indexes decreased, in which the color parameter was consistent with the trend of L* value in section 3.7, the change of hardness was similar to that of section 3.8. The taste value was lower after Chocolate-O80, which was due to the low content of cocoa butter. When W_{CBS} was too high, the acceptability decreased, while the acceptability scores of Chocolate-O0, Chocolate-O20 and Chocolate-O40 were similar. At this time, the replacement of cocoa butter with oleogel did not reduce the acceptability of chocolate, confirming that this oleogel could be used in the production of chocolate.

4. Conclusions

The results show that the FA/MG ratio had a significant effect on the minimum gelling concentration of the gelator. When the gelator concentration ≥ 4 %, all the samples could form oleogel except the sample with the FA/MG ratio of 100:0. FA exhibited rectangular structures in the oleogel, while MG appeared as needle-shaped crystals. They interlocked with each other to form a three-dimensional network, structuring the oil. The obtained oleogels were pseudoplastic fluids with similar rheological properties. The mechanical parameters of samples stored at 4 °C were higher. Their gelation temperature was determined by the gelator concentration and composition, and was independent of the storage temperature. Their protective ability of β-carotene against ultraviolet irradiation was proportional to the FA concentration. The oleogel prepared at a FA/MG ratio of 25:75, gelator concentration of 5 %, and storage temperature of 4 °C could be used as a cocoa butter substitute for chocolate production. As W_{CBS} ascended, the appearance of the resulting chocolate became rough, color intensity declined, and texture properties as well as enthalpy change gradually decreased. But when $W_{CBS} \leq 40$ %, the oleogel had no significant effect on the sensory characteristics of chocolate. Our results can provide reference for the development of new oleogel and promote the application of oleogel in food industry.

CRediT authorship contribution statement

Sheng Zhang: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Sheng Geng:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Hanjun Ma:** Writing – review & editing, Writing – original draft, Resources, Funding acquisition. **Benguo Liu:** Writing – review & editing, Writing – original draft, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 32472288), the Major Science and Technology Project in Henan Province of China (No. 221100110500), and the Program for Innovative Research Team (in Science and Technology) in University of Henan Province of China (No. 25IRTSTHN026).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.102067.

Data availability

Data will be made available on request.

References

Afoakwa, E. O., Paterson, A., Fowler, M., & Vieira, J. (2008). Characterization of melting properties in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry. *Food Research International, 41*, 751–757. https://doi.org/10.1016/j.foodres.2008.05.009

Bai, S., Wang, H., Gu, G., Gou, Y., Zhou, X., Yu, S., Wang, Q., Guo, X., & Wang, Y. (2023). Transient and directional growth of supramolecular hydrogels through reaction-diffusion-mediated self-assembly for dynamic wet gluing. *Chemical Engineering Journal, 475*, Article 146125. https://doi.org/10.1016/j.cej.2023.146125

Bascuas, S., Espert, M., Llorca, E., Quiles, A., Salvador, A., & Hernando, I. (2021). Structural and sensory studies on chocolate spreads with hydrocolloid-based oleogels as a fat alternative. *LWT- Food Science and Technology, 135*, Article 110228. https://doi.org/10.1016/j.lwt.2020.110228

Bertasa, M., Dodero, A., Alloisio, M., Vicini, S., Riedo, C., Sansonetti, A., Scalarone, D., & Castellano, M. (2020). Agar gel strength: A correlation study between chemical composition and rheological properties. *European Polymer Journal, 123*, Article 109442. https://doi.org/10.1016/j.eurpolymj.2019.109442

Bin Sintang, M. D., Danthine, S., Patel, A. R., Rimaux, T., Van De Walle, D., & Dewettinck, K. (2017). Mixed surfactant systems of sucrose esters and lecithin as a synergistic approach for oil structuring. *Journal of Colloid and Interface Science, 504*, 387–396. https://doi.org/10.1016/j.jcis.2017.05.114

Chen, C. H., Van Damme, I., & Terentjev, E. M. (2009). Phase behavior of C18 monoglyceride in hydrophobic solutions. *Soft Matter, 5*, 432–439. https://doi.org/10.1039/b813216

Davidovich-Pinhas, M., Gravelle, A. J., Barbut, S., & Marangoni, A. G. (2015). Temperature effects on the gelation of ethylcellulose oleogels. *Food Hydrocolloids, 46*, 76–83. https://doi.org/10.1016/j.foodhyd.2014.12.030

Espert, M., Hernández, M. J., Sanz, T., & Salvador, A. (2021). Reduction of saturated fat in chocolate by using sunflower oil-hydroxypropyl methylcellulose based oleogels. *Food Hydrocolloids, 120*, Article 106917. https://doi.org/10.1016/j.foodhyd.2021.106917

Furlán, L. T. R., Baracco, Y., Lecot, J., Zaritzky, N., & Campderrós, M. E. (2017). Influence of hydrogenated oil as cocoa butter replacers in the development of sugar-free compound chocolates: Use of inulin as stabilizing agent. *Food Chemistry, 217*, 637–647. https://doi.org/10.1016/j.foodchem.2016.09.054

Gravelle, A. J., Barbut, S., & Marangoni, A. G. (2012). Ethylcellulose oleogels: Manufacturing considerations and effects of oil oxidation. *Food Research International, 48*, 578–583. https://doi.org/10.1016/j.foodres.2012.05.020

Gravelle, A. J., Blach, C., Weiss, J., Barbut, S., & Marangoni, A. G. (2017). Structure and properties of an ethylcellulose and stearyl alcohol/stearic acid (EC/SO:SA) hybrid oleogelator system. *European Journal of Lipid Science and Technology, 119*, Article 1700069. https://doi.org/10.1002/ejlt.201700069

Han, L. J., Li, L., Zhao, L., Li, B., Liu, G. Q., Liu, X. Q., & Wang, X. D. (2013). Rheological properties of organogels developed by sitosterol and lecithin. *Food Research International, 53*, 42–48. https://doi.org/10.1016/j.foodres.2013.03.039

Jang, A., Bae, W., Hwang, H. S., Lee, H. G., & Lee, S. (2015). Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry, 187*, 525–529. https://doi.org/10.1016/j.foodchem.2015.04.110

Kadivar, S., De Clercq, N., Mokbul, M., & Dewettinck, K. (2016). Influence of enzymatically produced sunflower oil based cocoa butter equivalents on the phase behavior of cocoa butter and quality of dark chocolate. *LWT- Food Science and Technology, 66*, 48–55. https://doi.org/10.1016/j.lwt.2015.10.006

Li, J. Q., Geng, S., Zhen, S. Y., Lv, X. F., & Liu, B. G. (2022). Fabrication and characterization of oil-in-water emulsions stabilized by whey protein isolate/phloridzin/sodium alginate ternary complex. *Food Hydrocolloids, 129*, Article 107625. https://doi.org/10.1016/j.foodhyd.2022.107625

Li, L. L., & Liu, G. Q. (2019). Corn oil-based oleogels with different gelation mechanisms as novel cocoa butter alternatives in dark chocolate. *Journal of Food Engineering, 263*, 114–122. https://doi.org/10.1016/j.jfoodeng.2019.06.001

Li, L. L., Liu, G. Q., & Lin, Y. W. (2021). Physical and bloom stability of low-saturation chocolates with oleogels based on different gelation mechanisms. *LWT- Food Science and Technology, 140*, Article 110807. https://doi.org/10.1016/j.lwt.2020.110807

Li, L. L., Wan, W. B., Cheng, W. W., Liu, G. Q., & Han, L. P. (2019). Oxidatively stable curcumin-loaded oleogels structured by β-sitosterol and lecithin: Physical characteristics and release behaviour in vitro. *International Journal of Food Science and Technology, 54*, 2502–2510. https://doi.org/10.1111/ijfs.14208

Liu, W., Gao, H. X., McClements, D. J., Zhou, L., Wu, J., & Zou, L. Q. (2019). Stability, rheology, and β-carotene bioaccessibility of high internal phase emulsion gels. *Food Hydrocolloids, 88*, 210–217. https://doi.org/10.1016/j.foodhyd.2018.10.012

Lupi, F. R., Gabriele, D., Greco, V., Baldino, N., Seta, L., & Cindio, B. D. (2013). A rheological characterisation of an olive oil/fatty alcohols organogel. *Food Research International, 51*, 510–517. https://doi.org/10.1016/j.foodres.2013.01.013

Martins, A. J., Cerqueira, M. A., Cunha, R. L., & Vicente, A. A. (2017). Fortified beeswax oleogels: Effect of β-carotene on the gel structure and oxidative stability. *Food & Function, 8*, 4241–4250. https://doi.org/10.1039/c7fo00953d

Moriano, M. E., & Alamprese, C. (2017). Organogels as novel ingredients for low saturated fat ice creams. *LWT- Food Science and Technology, 86*, 371–376. https://doi.org/10.1016/j.lwt.2017.07.034

Oh, I., Lee, J., Lee, H. G., & Lee, S. (2019). Feasibility of hydroxypropyl methylcellulose oleogel as an animal fat replacer for meat patties. *Food Research International, 122*, 566–572. https://doi.org/10.1016/j.foodres.2019.01.012

Okuro, P. K., Malfatti-Gasperini, A. A., Vicente, A. A., & Cunha, R. L. (2018). Lecithin and phytosterols-based mixtures as hybrid structuring agents in different organic phases. *Food Research International, 111*, 168–177. https://doi.org/10.1016/j.foodres.2018.05.022

Pakseresht, S., & Tehrani, M. M. (2022). Advances in multi-component supramolecular Oleogels- a review. *Food Reviews International, 38*, 760–782. https://doi.org/10.1080/87559129.2020.1742153

Palla, C., Giacomozzi, A., Genovese, D. B., & Carrín, M. E. (2017). Multi-objective optimization of high oleic sunflower oil and monoglycerides oleogels: Searching for rheological and textural properties similar to margarine. *Food Structure-Netherlands, 12*, 1–14. https://doi.org/10.1016/j.foostr.2017.02.005

Pehlivanoglu, H., Demirci, M., Toker, O. S., Konar, N., Karasu, S., & Sagdic, O. (2018). Oleogels, a promising structured oil for decreasing saturated fatty acid concentrations: Production and food-based applications. *Critical Reviews in Food Science and Nutrition, 58*, 1330–1341. https://doi.org/10.1080/10408398.2016.1256866

Pehlivanoglu, H., Ozulku, G., Yildirim, R. M., Demirci, M., Toker, O. S., & Sagdic, O. (2018). Investigating the usage of unsaturated fatty acid-rich and low-calorie oleogels as a shortening mimetics in cake. *Journal of Food Processing and Preservation, 42*, Article e13621. https://doi.org/10.1111/jfpp.13621

Pinto, T. C., Martins, A. J., Pastrana, L., Pereira, M. C., & Cerqueira, M. A. (2021). Oleogel-based Systems for the Delivery of bioactive compounds in foods. *Gels, 7*, 86. https://doi.org/10.3390/gels7030086

Puscas, A., Muresan, V., & Muste, S. (2021). Application of analytical methods for the comprehensive analysis of Oleogels-a review. *Polymers, 13*, 1934. https://doi.org/10.3390/polym13121934

Rogers, M. A., Wright, A. J., & Marangoni, A. G. (2009). Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid / canola oil organogels. *Current Opinion in Colloid & Interface Science, 14*, 33–42. https://doi.org/10.1016/j.cocis.2008.02.004

Sim, S. Y., Ng, J. W., Ng, W. K., Forde, C. G., & Henry, C. J. (2016). Plant polyphenols to enhance the nutritional and sensory properties of chocolates. *Food Chemistry, 200*, 46–54. https://doi.org/10.1016/j.foodchem.2015.12.092

Trujillo-Ramírez, D., Lobato-Calleros, C., Vernon-Carter, E. J., & Alvarez-Ramirez, J. (2019). Cooling rate, sorbitan and glyceryl monostearate gelators elicit different microstructural, viscoelastic and textural properties in chia seed oleogels. *Food Research International, 119*, 829–838. https://doi.org/10.1016/j.foodres.2018.10.066

Wang, X. C., Ma, D., Liu, Y. W., Wang, Y., Qiu, C. Y., & Wang, Y. (2022). Physical properties of oleogels fabricated by the combination of diacylglycerols and monoacylglycerols. *Journal of the American Oil Chemists Society, 99*, 1007–1018. https://doi.org/10.1002/aocs.12622

Wolfer, T. L., Acevedo, N. C., Prusa, K. J., Sebranek, J. G., & Tarté, R. (2018). Replacement of pork fat in frankfurter-type sausages by soybean oil oleogels structured with rice bran wax. *Meat Science, 145*, 352–362. https://doi.org/10.1016/j.meatsci.2018.07.012

Yang, D. X., Chen, X. W., & Yang, X. Q. (2018). Phytosterol-based oleogels self-assembled with monoglyceride for controlled volatile release. *Journal of the Science of Food and Agriculture, 98*, 582–589. https://doi.org/10.1002/jsfa.8500

Zhai, Y., Wang, T., Fu, Y., Yu, T., Ding, Y., & Nie, H. (2023). Ferulic acid: A review of pharmacology, toxicology, and therapeutic effects on pulmonary diseases. *International Journal of Molecular Sciences, 24*, 8011. https://doi.org/10.3390/ijms24098011

Zhang, L. L., & Qin, B. T. (2016). Rheological characteristics of foamed gel for mine fire control. *Fire and Materials, 40*, 246–260. https://doi.org/10.1002/fam.2283

Zhou, F. F., Pan, M. K., Liu, Y., Guo, N., Zhang, Q., & Wang, J. H. (2020). Effects of Na^{+} on the cold gelation between a low-methoxyl pectin extracted from Premna microphylla turcz and soy protein isolate. *Food Hydrocolloids, 104*. https://doi.org/10.1016/j.foodhyd.2020.105762