

Comparison of the Pomegranate Seed Oil Organogels of Carnauba Wax and Monoglyceride

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ABSTRACT: The aims of this study were to prepare organogels from pomegranate seed oil (PO) with carnauba wax (CW) and monoglyceride (MG), compare the organogels with a commercial margarine (CM) and evaluate 3 months storage stability. At 3% organogelator addition, no gels were formed, while at 7 and 10% additions, the oil binding capacities increased and were always higher in CW organogels, with crystal formation times of 8.0 to 14.0 min. Solid fat content (SFC) of the CW organogels varied between 2.96 and 8.71% at 20°C, while MG gels had 2.89–9.43%, and CM had 29.73% SFC. The peak melting temperatures of the CW organogels ranged from 74.73 to 75.74°C and MG organogels ranged from 11.09 to 50.63°C, whereas CM product exhibited 45.92°C peak melting temperature. The hardness of CW organogels was higher than that of MG organogels. The organogels showed potential as spreadable products. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41343.

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INTRODUCTION

Edible fats and oils can be utilized in liquid form or in stock solid form in which the level of plasticity can be as diverse as from flowing viscous liquid to hard solids. These products play a significant role in the formulations of a variety of food products like, margarines, baked products, salad dressings, pastries, confectionary products, spreads, frying shortenings and many other formulated, and processed foods. Fats and oils provide structure, flavor, stability, eating characters, eye appeal, flavor, and nutritional quality to food products. The suitability of any fat or oil product is dependent upon several important elements like, plasticity, spreadability, creaming, emulsification, consistency, crystal habits, flavor, stability, and nutritional concerns. It has long been a practice to structure edible liquid oils into plastic form by crystallization, hydrogenation, interesterification, fractionation, and blending technologies.¹ Another technique called organogelation, has begun to be searched extensively, as an alternative to structure edible liquid oils. Basically, organogelation has been defined as development of self-standing, thermoreversible, anhydrous, three-dimensional gel networks via noncovalent interactions of self-assembled small molecules or organogelators added into oil at very low concentrations. Through organogelation, liquid edible oil can be changed into plastic fats without any change in fatty acid composition or isomers. Hence, it is a very promising technique to produce healthy fat alternatives.^{2–5}

Pomegranate (*Punica granatum* L.) seed oil (PO) is a nonconventional, but nutritionally outstanding edible liquid oil. It is usually produced as cold press oil after juice processing of the fruit yielding the seed by-product. PO contains considerable amounts of polyunsaturated fatty acids (PUFA), including conjugated linolenic acid (CLA) isomers like punicic acid (18:3-9 *cis*, 11 *trans*, 13 *cis* isomer). It has been indicated that this fatty acid inhibits prostaglandin biosynthesis and other lipooxygenase and cyclooxygenase pathways.⁶ Hence, pomegranate seed oil has important beneficial roles in inflammation, atheromatous, plaque formation, platelet aggregation, and asthma in children. It was also linked to chemoprevention of skin and colon cancer.^{7,8} Also, in another study consumption of PO has shown to reduce weight gain and type 2 diabetes risks in mice.⁹ On the other hand, the use of PO as edible oil is limited.⁷ Preparation of PO in structured forms like organogels may provide more easiness and technical possibilities for its incorporation in various food products or directly as breakfast spreads or cooking margarine alternatives.

Many different organogelators have been studied. But for edible applications, it must be at least food-grade and safe, effective in lower levels, available in the market and economical, able to provide the expected properties and suitable.⁵ Among others, plant waxes and saturated monoglycerides have been suggested as very suitable organogelators for food lipid applications.^{5,10–13}

The objectives of this study were to produce edible grade organogels from pomegranate seed oil with the organogelators, carnauba wax (CW) and monoglyceride (MG), to characterize the products and to compare their storage stabilities for 3 months at both room and refrigerator temperatures storage. This study is unique in comparing two chemically different organogelators in structural, thermal, and textural organogel properties and their storage stability in terms of texture and oxidation. Furthermore, comparison of the produced organogel products with a commercial margarine was provided in this study.

MATERIALS AND METHODS

Materials

Commercial grade pomegranate seed oil was purchased from Çiftçizade Agriculture Co. (Antalya, Turkey). The fatty acid composition of the oil as provided by the producer is; 2.40% palmitic, 1.87% stearic, 4.68% oleic, 5.25% linoleic, 74.97% puniolic, 6.03% α -eleostearic, 3.34% catalpic, 0.30% arachidic, 0.42% gadoleic, and 0.23% behenic acid. Carnauba wax 5023 was purchased from KahlWax (Kahl GmbH). The specifications about carnauba wax provided by the producer are; yellow to brown solid powder/flakes with faint odor, density of 0.99–1.00 g/cm³ at 20°C, melting range of 78–88°C, acid value of 5–15 mg KOH/g, saponification value of 80–95 mg KOH/g, no dangerous material and no special precautions needed. Monomuls[®] 90–35 Saturated Monoglyceride was purchased from BASF. It is a white, tasteless, scentless microgranular solid with min 90% monoglyceride, max acid value of 3 mg KOH/g, saponification value of 155–165 mg KOH/g, max iodine value of 2 g/100 g, and melting range of 64–68°C. It is classified as GRAS with no known hazard. Commercial margarine was purchased from a local store. All other chemicals were of analytical grade and purchased from Merck and Sigma-Aldrich.

Preparation of the Organogels

The addition levels of carnauba wax (CW) and monoglyceride (MG) as the organogelators into the pomegranate seed oil (PO) were selected to be 3, 7, and 10% (w/w). First, calculated amounts of the organogelators and the oils were put in separate glasses and heated in a water bath set to 90°C. When the CW and MG were completely melted, each one was added into the PO at the same temperature and mixed thoroughly. When the mixture was still liquid, calculated portions of the mixture were placed into sterile plastic cups (150 mL) and glass tubes with caps for subsequent analyses. After 24 h setting at room temperature, the organogels were completely formed. For each analysis and storage study, separate plastic cups were filled and the storage study was performed by storing the samples at room temperature (20°C) and refrigerator (4°C) for 3 months and the samples were analyzed periodically. Organogel productions for each type organogelators were replicated twice, and all analyses within each production replicate were at least twice. In Figure 1, the picture of the produced CW and MG organogels is shown. In this study, for the easiness of data presentation, the samples were coded as: PO—pomegranate oil; CW—carnauba wax; MG—monoglyceride; CM—commercial margarine; PC3, PC7, and PC10—organogels of pomegranate seed oil and CW at 3, 7, and 10% addition level; PM3, PM7, and PM10—

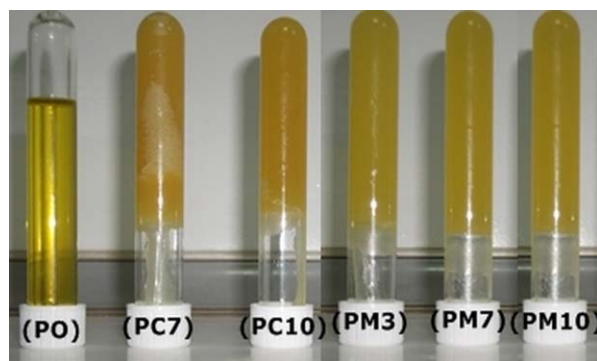


Figure 1. Pomegranate seed oil organogels of CW and MG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

organogels of pomegranate seed oil and MG at 3, 7, and 10% addition level.

Oil Binding Capacity

The organogel samples were first melted in water bath (90°C) and 1 mL of the melted gel was put into previously weighed (a) Eppendorf tube and kept in refrigerator for 1 h. After gelation, the tube was weighed (b) again. Then the Eppendorf tubes were centrifuged at 10,000 rpm for 15 min at room temperature. Finally, the tubes were turned over on to a paper cloth to drain the liquid oil. After drainage, the tubes were weighed (c) again. Finally, the oil binding capacity (OBC) values were calculated by eq. (1) written below.¹²

$$\% \text{ Released Oil} = [(b-a) - (c-a)] / (b-a) \times 100\% \quad (1)$$

$$\text{OBC} = 100 - \% \text{ Released Oil}$$

Crystal Formation Time

Glass tubes previously filled with the organogel samples were completely melted in water bath and kept for 2 h at 90°C for isothermal temperature setting. Then, the tubes were taken out from the water bath into room temperature, and meantime chronometer was started. When the stable gel formed, the time was recorded. The gelation time was decided by turning the tube 90° and observing no flow.¹⁰

Solid Fat Content

The organogel samples were first completely melted in water-bath at 90°C. Then, 3.5 mL sample was put into NMR tubes and conditioned in another waterbath at 0°C for 1 h. The tubes were conditioned for 1 h at 20 and 30°C for the measurement of solid fat content (% SFC) at the two temperatures, respectively. The calibration of the NMR (Bruker NMR Analyzer mq20 The Minispec, Bruker Optics) was done with standard solutions including 0, 31, and 73.5% solid fat. The measurements were accomplished according to ISO 8292 method.¹⁴

Color Measurement

The color of the organogel samples was measured with a Minolta CR-400 colorimeter (Konica Minolta Sensing) according to the manual of the instrument.

Thermal Analysis

The thermal properties of the organogel samples were measured with a Perkin-Elmer 4000 Series Differential Scanning

Table I. Some Physical Properties for the Organogels of PO with CW and MG

Sample	OBC (%)	CFT (min)	%SFC		<i>L</i>	<i>a</i> *	<i>b</i> *
			20°C	35°C			
PC3	39.17 ± 5.47	-	2.96 ± 0.17	2.98 ± 0.02	32.34 ± 0.13	-2.23 ± 0.11	7.50 ± 0.54
PC7	73.28 ± 3.59	14.00 ± 1.00	6.33 ± 0.04	6.25 ± 0.00	39.16 ± 0.49	-3.46 ± 0.03	13.73 ± 0.46
PC10	97.29 ± 2.68	9.50 ± 0.50	8.71 ± 0.04	8.58 ± 0.10	42.81 ± 0.06	-3.76 ± 0.01	16.94 ± 0.42
PM3	36.95 ± 0.64	-	2.89 ± 0.04	1.25 ± 0.04	26.63 ± 0.35	-0.50 ± 0.02	4.10 ± 0.22
PM7	54.00 ± 1.79	10.00 ± 1.00	7.00 ± 0.05	3.57 ± 0.40	31.14 ± 0.87	-1.13 ± 0.18	6.49 ± 0.62
PM10	72.25 ± 0.06	8.00 ± 0.00	9.43 ± 0.21	4.88 ± 0.05	33.00 ± 0.12	-1.59 ± 0.03	8.48 ± 0.07
CM	-	-	29.73 ± 0.39	-	90.81 ± 0.74	-2.66 ± 0.17	10.48 ± 0.19

Calorimetry (DSC). The instrument was calibrated with indium and zinc, and 5–7 mg of organogel samples were weighed into aluminum pans and sealed hermetically. The following temperature program was applied; heating from room temperature to 140°C by 10°C/min; cooling the samples to -20°C by 10°C/min rate and keeping 3 min at that temperature and finally; heating the samples again to 100°C by 5°C/min heating rate. The parameters of crystallization and melting temperatures and enthalpies were calculated by Pyris 1 Manager Software of the instrument.¹⁰

Texture Analysis

The textural parameters of the organogels were measured with a Texture Analyzer TA-XT2i (Stable Microsystems) by placing 150 g of sample gelled in plastic cups into a custom-built block and using a 45° conic acrylic probe. The samples stored at room temperature (20°C) or refrigerator (4°C) were taken out and analyzed immediately at that temperature. The measure force in compression technique was used as 3.0 mm/s penetration speed into 23 mm depth, and then pulling the probe out from the sample at 10 mm/s speed. The values of hardness and adhesiveness were calculated by using the Texture Exponent v.6.1.1.0 software (Stable Microsystems). The texture measurements were completed at the two storage temperatures through 90 days storage period each month.^{11,15}

Crystal Morphology

The polarized light microphotographs (PLM) of the organogel samples were taken with an Olympus BX51 polarized light microscope (Olympus Optical) equipped with a CCD color video camera (Canon). One drop melted sample was placed on a lam and sealed with a lamel and left at room temperature for full gelation. Finally, the pictures were obtained with the microscope.^{10,16}

X-ray Diffraction Analysis

The X-ray diffraction (XRD) patterns of the samples were measured with a Rigaku D-Max Rint 2200 model X-Ray Diffractometer (Rigaku Int.) at room temperature. Angular scans from 2.0° to 50° (2θ) were performed by 2°/min scan rate with a Cu source X-ray tube (λ = 1.54056 Å) at 40 kV and 40 mA. The data were analyzed with MDI Jade 7 Materials Data software.

FT-IR Spectroscopy

The infrared spectra of the samples were measured by Perkin Elmer FT-IR Spectrum One (Perkin Elmer) instrument. The

FT-IR spectra of the compounds were recorded using universal ATR sampling accessory (4000–550/cm).

Oxidative Stability

The peroxide values of the organogels were measured monthly according to Cd 8–53 method during 3 months storage at both room and refrigerator temperatures.¹⁷

RESULTS AND DISCUSSION

The physical properties of the samples measured in this study are presented in Table I. The oil binding capacity (OBC) enhanced as the concentration of organogelators increased in the organogel formulations. At all three concentration levels, the OBC was higher in carnauba wax (CW) organogels than that of monoglyceride (MG) organogels. OBC is a measure showing the degree of liquid oil entrapment in the gel network. It was indicated that gelation at relatively higher temperatures resulted in gels with lower OBC. Also, if the shear is lower during crystallization, the resulting gels have higher OBC. Similarly, organogelators with high degree of branching have yielded stronger oil entrapment.^{5,12} In this study, the crystallization was at room temperature with no shear applied. Hence, the difference can only be attributed to the differences of the organogelators used. Crystal formation time (CFT) shown in Table I indicates that at 3% concentrations of both organogelators, no stable gel was formed. Beyond this, MG organogels have shown relatively lower crystallization time than that of the CW organogels. For both types, it was observed that as organogelator concentration increased, CFT decreased, respectively. Similar findings with different concentrations of rice bran wax were shown.¹⁰ The solid fat content (SFC) measured at two different temperatures indicated that the organogels contained solid fat lower than that of the amounts of the added organogelators. The SFC was lower at 35°C than that at 20°C, expectedly. Commercial margarine (CM) had significantly higher levels of solid fats (29.73%). This finding indicated once again that the most important property of the organogels is that they are completely formed from liquid oils and there is no change either in the fatty acid saturation level or *trans* isomer level. The same results were shown in many other studies.^{2–5} The luminosity (*L*) of the CW organogels was a little higher than that of the MG organogels, but both were significantly lower than that of CM sample. On the other hand, there was no distinct difference among the samples for the color parameters of *a** and *b** values. Clearly, the color of

Table II. Thermal Properties for the Organogels of PO with CW and MG

Sample	Crystallization			Melting		
	Onset _c (°C)	Peak (<i>T_c</i> , °C)	ΔH_c (J/g)	Onset _m (°C)	Peak (<i>T_m</i> , °C)	ΔH_m (J/g)
PO	-11.09 ± 0.00	-16.26 ± 0.00	-1.93 ± 0.00	-25.00 ± 0.08	-23.54 ± 0.00	0.56 ± 0.03
CW	77.87 ± 0.12	75.04 ± 0.70	-183.81 ± 5.64	67.89 ± 0.60	81.04 ± 0.09	182.15 ± 7.09
MG(fr1)	11.16 ± 0.89	10.14 ± 0.12	-23.27 ± 3.08	10.62 ± 0.10	13.20 ± 0.02	24.20 ± 1.04
GM(fr2)	63.83 ± 0.03	61.17 ± 0.02	-105.71 ± 9.47	61.72 ± 0.15	65.83 ± 0.19	103.97 ± 6.42
CM	25.01 ± 0.00	22.85 ± 0.00	-7.17 ± 1.20	43.70 ± 0.00	45.92 ± 0.00	205.06 ± 0.01
PC3	48.54 ± 0.40	45.98 ± 0.42	-4.48 ± 0.22	8.95 ± 0.84	74.73 ± 0.52	4.68 ± 0.14
PC7	55.68 ± 0.50	49.79 ± 1.72	-11.31 ± 1.06	30.68 ± 0.05	75.48 ± 0.53	11.48 ± 0.88
PC10	56.16 ± 1.70	52.96 ± 0.12	-15.45 ± 1.08	10.07 ± 0.00	75.74 ± 0.29	13.84 ± 0.62
PM3(fr1)	11.33 ± 0.40	9.49 ± 0.50	-0.34 ± 0.04	36.65 ± 0.69	11.09 ± 0.58	0.37 ± 0.10
PM3(fr2)	32.29 ± 0.22	29.53 ± 0.54	-1.74 ± 0.20	11.29 ± 0.12	36.59 ± 0.84	0.74 ± 0.08
PM7(fr1)	12.14 ± 0.20	10.49 ± 0.09	-1.14 ± 0.09	37.37 ± 1.21	12.02 ± 0.06	1.18 ± 0.14
PM7(fr2)	43.80 ± 1.34	41.15 ± 1.74	-5.03 ± 0.31	60.71 ± 0.60	46.75 ± 0.21	3.84 ± 0.19
PM10(fr1)	12.84 ± 0.32	11.22 ± 0.39	-2.26 ± 0.42	59.65 ± 3.66	12.63 ± 0.21	1.94 ± 0.21
PM10(fr2)	48.48 ± 1.11	44.37 ± 0.79	-7.85 ± 0.04	62.98 ± 0.93	50.63 ± 0.29	7.81 ± 0.17

(fr1): fraction 1; (fr2): fraction 2.

organogels is mainly dependent on the color of the stock oil and to a limited extent on the color of the added organogelator. While, in margarines because of emulsion formation, the color of the final product is totally different from the stock oil. But surely, color of any organogel can be modified by adding suitable fat soluble coloring additives.

The thermal properties of the samples measured via DSC are given in Table II. Pomegranate seed oil (PO), as an unsaturated oil, starts to crystallize at -16.26°C , but its crystals start melting at much lower temperature, at -23.54°C . It is well known that fats and oils exhibit a range for crystallization or melting rather than a definite point.⁵ On the other hand, CW and MG have shown relatively closer melting and crystallization temperatures and enthalpies. In this study, MG was found to include two distinct fractions with very different melting and crystallization temperatures and enthalpies. Most probably, the sample used in this study is a mixture of two separate monoglycerides, although the producer specified a melting range of $64\text{--}68^\circ\text{C}$. The two fractions, low and high melting fractions, are also present in all organogel samples prepared with MG as the gelator. The organogels prepared with either CW or MG exhibited significantly different thermal properties than those of the pure organogelators. In general, MG organogels having melting peak temperatures ranging from 11.09 to 50.63°C are more similar to the peak melting temperature of the CM (45.92°C). On the other hand, CW organogels had much higher melting temperatures ($45.92\text{--}75.74^\circ\text{C}$). The enthalpy of CM was very high compared to the organogel samples indicating higher concentrations of SFC as shown in Table I. Organogels prepared with cod liver oil and MG had 12.9 J/g transition enthalpy and 53.2°C melting temperature at 7% organogelator addition level.¹³ Higher melting fractions (fr2) of MG organogel in this study have shown 3.84 J/g enthalpy and 46.75°C peak melting temperature. The values are comparatively similar. On the other hand, the melting

enthalpies ($4.68\text{--}13.84$ J/g) of the CW organogels were more similar to that of the CM sample. Thermal properties are essential components of plastic fats for applications and uses, but not the only characteristics. Textural properties must also be compared for broader understanding of the product specifications.

The hardness and adhesiveness values of the organogel samples are presented in Figures 2 and 3. The hardness of CW organogels was higher than that of MG organogels both at room and refrigerator storage. During storage, the hardness of MG organogels decreased gradually, while for CW organogels, there was no definite change. Also, the hardness values were higher in the samples stored at 4°C than at 20°C for both types of the organogels (Figure 2). Almost the same trends of changes were also evident for the adhesiveness values (Figure 3). The hardness and adhesiveness values of the CM ranged from 557.33 to 1334.95 g and from 303.53 to 816.26 g. Both values were higher

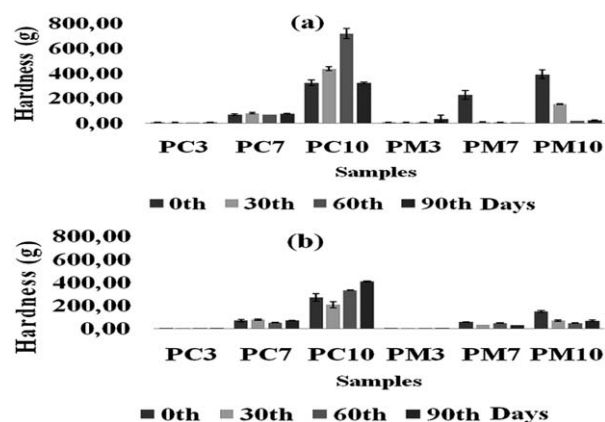


Figure 2. Hardness values of the organogel samples: (a) 4°C and (b) 20°C .

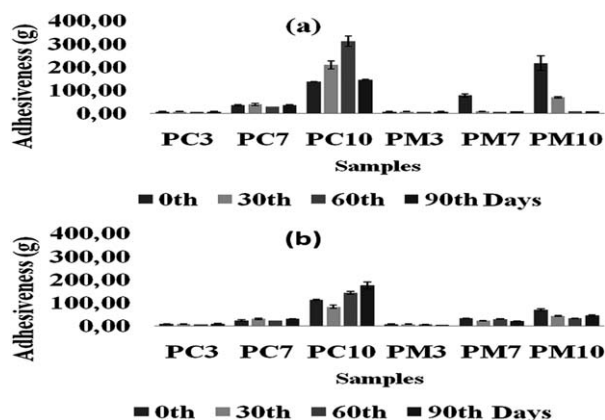


Figure 3. Adhesiveness values of the organogel samples: (a) 4°C and (b) 20°C.

than those measured in the organogel samples. But at 10% addition levels of the organogelators, the maximum hardness and adhesiveness values measured can fall into the range of those values measured in the CM. In a previous study, the hardness of salad oil and different wax organogels at 6% addition level was measured and rice bran wax was found to form the hardest gel followed by candelilla and carnauba wax organogels.¹⁰ The texture of MG and olive oil organogels were investigated rheometrically.¹⁸ It was shown that as MG concentration increases, the value of storage modulus (G') increased, just similar to the hardness value measured in our study. Also, it was observed that application of shear caused the oiling out problem. In our study, the organogels were formed at room temperature without any shear effect, and the samples were very stable

during 90 days of storage. Soybean oil and sunflower wax organogel yielded around 340 g of firmness at 5% addition level. Similar hardness (firmness) values at 10% CW or MG organogels were measured in this study (Figure 2). Taking into consideration the hardness and adhesiveness results, it can be concluded that CW can yield organogels more similar to CM than that of MG organogels.

The polarized light microphotographs of the organogel samples are shown in Figure 4. Since there was no true gel formed at 3% CW gel, its picture was not taken. Needle-like crystals in the organogels of CW with PO at 7 and 10% addition levels have been observed. Needle-like crystals were also determined in other wax (rice bran, sunflower, and candelilla) organogels.⁵ Although the crystal structures of MG organogels at 3, 7, and 10% addition levels in this study (Figure 4) were rosette-like or spherulitic. They seem very different from those of the CW crystals. Similar spherulitic crystal structure was reported for corn oil–MG organogels.¹⁹ Although cod liver oil–MG crystals were reported as needle like.¹² Clearly, the crystal structure of MG organogel is dependent on the oil type and perhaps some other factors. In order to gain more knowledge about the crystal structures of the organogel samples, the X-ray diffraction patterns were also measured. The pattern graphics for CM and two organogel samples are given in Figure 5, and the whole XRD data for all organogel samples were presented in Table III with $2-\theta$ and d (Å) values.

Obviously, 10% CW or MG containing organogels and CM had very similar d values with different intensities (Figure 5). No XRD measurements were performed for 3% organogelator containing samples because they had some fluidity. Generally, the

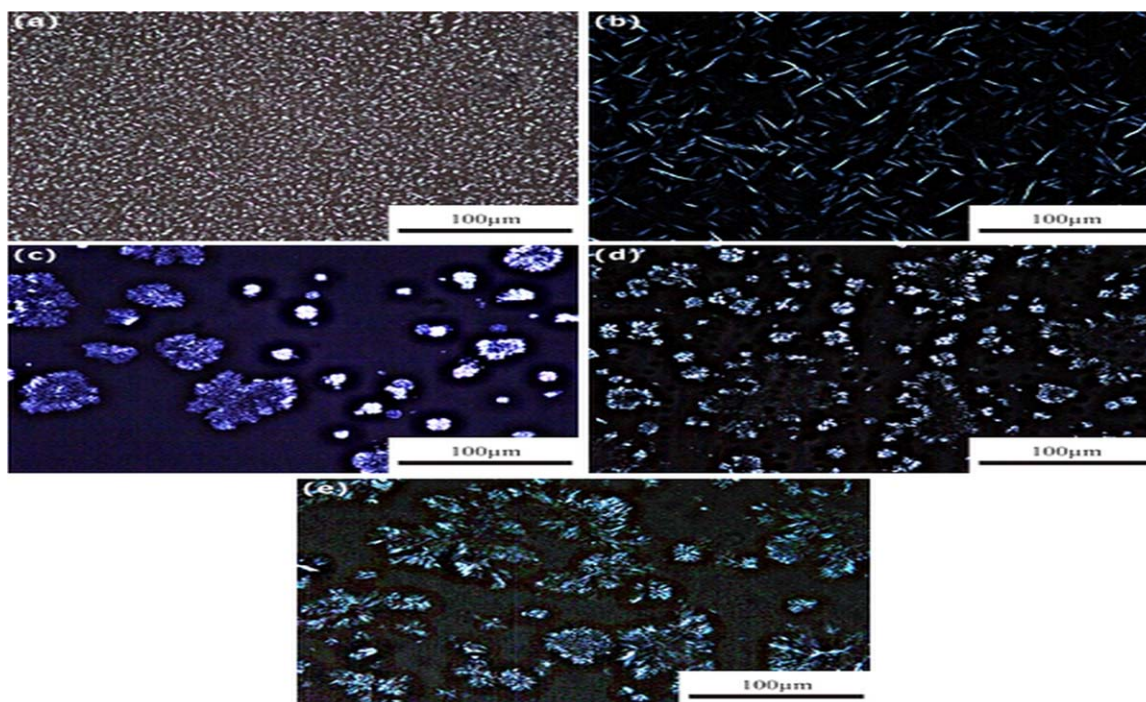


Figure 4. Polarized light microphotographs (PLM) of the organogel samples. (a) PC7, (b) PC10, (c) PM3, (d) PM7, and (e) PM10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

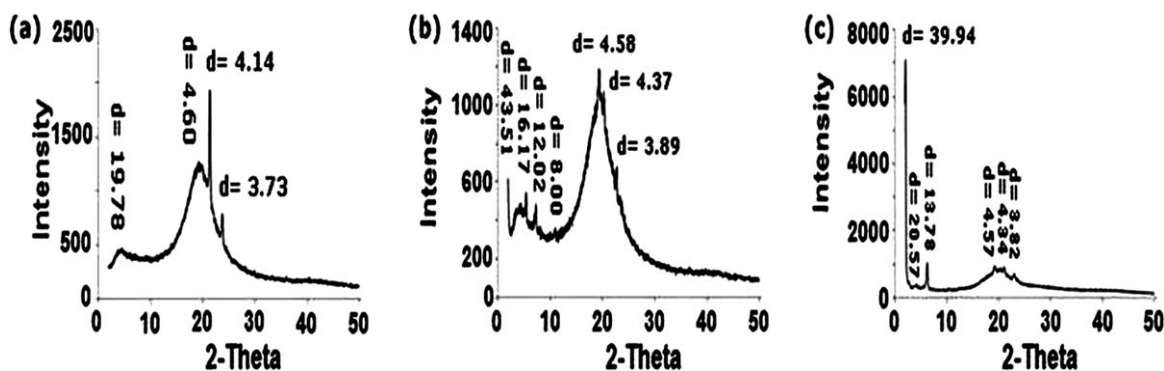


Figure 5. X-ray diffraction patterns of the samples: (a) PC10, (b) PM10, and (c) CM.

XRD patterns of MG organogels were more similar to the patterns of commercial margarine (CM) sample than that of CW organogel samples. CW organogels usually had wide angle region peaks at around 4.14–4.62 Å (18–22° 2 θ region), whereas MG organogels had wide angle region peaks at around 2.43–4.58 Å (18°–28° 2 θ region) (Table III). On the other hand, single diffraction peak in the small angle region for MG organogels shows an interplanar distance of monoglyceride bilayers consisting of a lamellae with 43.51 Å widths. The same distance for CW crystals was with a width of 19.87 Å, indicating the structural difference between the two organogelator structures shown in PLM pictures (Figure 4) as well. In the wide angle region of 10% MG organogel, the main peak at a distance of 4.58 Å (Figure 5) indicates other peaks along the band. The same findings were also observed in cod liver oil–MG organogels in two studies.^{12,13} On the other hand, studies with rice bran wax organogels have revealed that it crystallized in orthorhombic form with crystals having peaks of 0.41 and 0.37 nm which are similar to β' crystals form of triacylglycerols.¹⁰ The CW peak distances in this study seem similar to that of rice bran wax. In another study, probably lamellar arrangements for candelilla wax organogels was reported.²⁰ Szydłowska-Czerniak et al. indicated that wax organogels with smooth texture should be similar to the β' crystal form of the triacylglycerols.²¹ In this study, both CW and MG organogels were very smooth and homogenous in texture and structure, as shown by the hardness and adhesiveness measurements (Table II). With this structure, both types of the organogels quite resemble edible kitchen margarines and spreads.

The Fourier transform-infrared (FT-IR) spectra of the PO, CW, MG, and 10% CW and MG organogelators containing pomegranate seed oil organogel samples are given in Figure 6. Clearly organogel sample containing 10% MG had a band in the 3400–3200/cm wave number range. The same band also appeared in the MG samples, whereas that band did not appear in PO, CW, or organogel containing CW samples. According to den Adel et al., medium-intensity bands in the 3550–3450/cm wave number range indicate intermolecular hydrogen bonds.²² Also, medium intensity bands at 3570–3540/cm wave number range have been used as the indicator of intramolecular hydrogen bonds. The FT-IR spectra shown in Figure 6 indicate that there were some intermolecular hydrogen bonds in the MG organogels. This can be the case since there are –OH groups in MG molecule which can form hydrogen bonds within the molecule. The presence of the hydrogen bonds was also shown in β -sitosterol + γ -oryzanol-based organogel samples.²²

The oxidative stability of the organogel samples and CM sample were monitored during the 3 months storage both at room and refrigerator temperatures and the results are presented in Figure 7. At both storage temperatures, the peroxide values (PV) were lower in the CW organogels than that of MG organogels. Similarly, the samples stored at 4°C had always lower PV than that of the samples stored at 20°C. For all organogel samples and CM, the PV has increased through the storage period. But none of the samples have exceeded the limit PV of 10 meq O₂/kg oil, set by the codex standard for vegetable oils in Turkey, except the 10% MG containing organogel sample stored at room temperature for 90 days (11.88 meq O₂/kg oil).²³ Generally, it can

Table III. XRD Measurement Results for the Organogels of PO with CW and MG

Sample	2- θ	d (Å)
PC3	–	–
PC7	4.42, 19.17, 21.32, 23.68	19.96, 4.62, 4.16, 3.75
PC10	4.46, 19.25, 19.96, 21.40, 23.78	19.78, 4.60, 4.44, 4.14, 3.73
PM3	–	–
PM7	2.02, 3.65, 5.33, 7.32, 19.42, 20.32, 22.76, 36.84	43.69, 24.14, 16.54, 12.06, 4.56, 4.36, 3.90, 2.43
PM10	2.02, 5.45, 7.34, 11.09, 19.34, 20.30, 22.80, 36.65	43.51, 16.17, 12.02, 8.00, 4.58, 4.37, 3.89, 2.44
CM	2.21, 4.29, 6.40, 17.71, 19.37, 20.44, 21.23, 23.22	39.94, 20.57, 13.78, 5.00, 4.57, 4.34, 4.18, 3.82

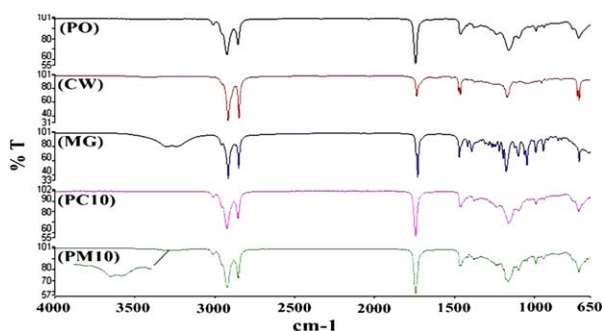


Figure 6. FT-IR spectrum of the organogel samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be claimed that MG organogels are less stable for oxidation than that of the CW organogels.

CONCLUSIONS

In this study, some important properties of the CW and MG organogels made with pomegranate seed oil in comparison with a commercial margarine were determined. CW organogels were found to bind more liquid oil and were more firm. MG organogels exhibited two melting and crystallizing temperatures. Higher point melting fraction was more similar to CM. In general, the enthalpies of CW organogels were closer to the enthalpies of the CM. The hardness of the MG organogels decreased during storage, whereas CW organogels did not change in large extent. For both types, hardness and adhesiveness values measured at 10% gelator including samples were higher than the others and also were more similar to the values of CM samples. Needle-like crystals were evident in CW organogels, while MG organogel crystals were spherulic in nature. The XRD patterns also indicated some differences, while MG organogels were found to be more similar to CM. Also, in MG organogels intermolecular hydrogen bonds were deducted by FT-IR spectra. As a conclusion, this study has revealed that both CW and MG organogels of pomegranate seed oil are very smooth, plastic texture products quite similar to CM in texture and thermal properties. During 3 months storage, the texture and oxidative stabilities of CW organogel samples were better than those of MG organogels. Both types of the organogels, but especially CW organogels at addition concentration levels of 7% or even

lower (but, certainly higher than 3%) can be used to produce products similar to commercial margarine. These organogels can be used as kitchen margarine or even breakfast spreadable products without any textural or thermal problem. They exhibited high stability at room temperature storage as well. Hence, the advantages of the beneficial health effects of the oil remain since no chemical change in fatty acids occur and the cost of temperature controlling during manufacture and delivery of products might be lowered significantly by organogelation technology. It has to be pointed out that carnauba wax as a food additive (E 903) was re-evaluated by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), and an Acceptable Daily Intake (ADI) of 7 mg/kg body weight was allocated for long term food uses since the committee indicated that although available toxicity data consistently reports no adverse findings with carnauba wax intake, the long-term toxicity data were still lacking.²⁴ The same document also indicated that carnauba wax is classified as GRAS in USA, and permitted in Canada, Japan, Australia, and New Zealand. Hence, any potential commercial application of CW for organogel production must consider its current safety instructions.

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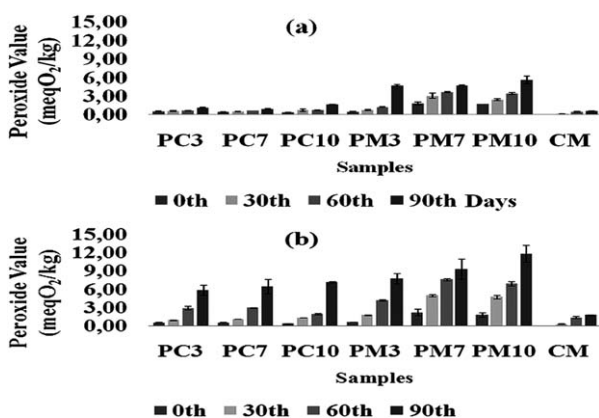


Figure 7. Peroxide values of the organogel samples: (a) 4°C and (b) 20°C.

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