Characteristics of Red Palm Oil Oleogel Based on Beeswax and Cocoa Butter and Its Application in Red Chocolate Spread

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ABSTRACT

Red palm oil (RPO) is a product obtained from crude palm oil with a high carotenoid content. Despite the potential, the susceptibility of the constituent β-carotene to degradation and liquid state at room temperature poses a significant challenge to its use by affecting the texture of the final chocolate spread. Several studies have proposed using the oleo gelation technique to overcome this challenge, which regulates the structure of oil and fats mixture using an oleo gelator. Therefore, this study aims to evaluate the physicochemical characteristics of RPO oleogel produced using an oleo gelator from a beeswax and cocoa butter blend. The best product obtained was then applied to produce a red chocolate spread. The results showed that RPO oleogel obtained at a high beeswax-cocoa butter ratio had higher hardness values, β-carotene content, and melting points. In addition, the crystal microstructure of the product was needle-form with larger crystal sizes, leading to a significant increase in the oil binding capacity. Combining 9% beeswax and 1% cocoa butter (BW9-LK1) was the best formula for producing a chocolate spread. The characteristics of the red chocolate spread obtained from the best oleogel were 61.47 brightness level (L*), 5.81 red intensity (a*), and 57.81 yellowish (b*), with an oil binding capacity of 99.95%. The melting temperature was 31.89-41.67 ºC, indicating that it could melt at body temperature and was stable at room temperature. During 5 weeks of storage, the hardness and β-carotene content were 6.01-6.21 N and 469.07-302.67 ppm, respectively. Based on these results, the oleo gelator from beeswax and cocoa butter blend improved the hardness, melting points, and β-carotene content of RPO oleogel. This indicated that it potentially could be used as an alternative to produce a carotenoid-rich chocolate spread.

Keywords: Beeswax; cocoa butter; double oleo gelator; red chocolate spread; red palm oil oleogel

INTRODUCTION

Red palm oil (RPO) is a product derived from crude palm oil without a deodorization process. Consequently, most components, such as tocopherols, tocopherols, and unsaturated fatty acids, still remain. Several studies have also shown that RPO has a high concentration of carotenoids, primarily β-carotene, which produces a distinctive red color (Hasibuan and Ijah, 2018). β-carotene concentration in RPO is typically 15–30 times greater (600–1000 ppm) compared to other vegetable oils, such as olive, maize, and soybean oil. (Purnama et al., 2020; Sumarna, 2014). RPO is more suitable for consumption because it contains high levels of phytochemicals and β-carotene as provitamin A. A previous study found that it could be used as a

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functional ingredient in oil or fat-based products, including margarine, shortening, and spreads. In this context, chocolate spread is generally used as a filling for bakery and confectionery commodities in semi-solid (paste) form. This filling often consists of refined sugar, skim milk, and other components dispersed into a fat phase, such as margarine, butter, and vegetable oil. The semi-solid chocolate spread comprises 55 parts solids and 45 parts slurry until the dissolved solid content has a paste-like thickness (Wibisono et al., 2015).

According to previous studies, RPO cannot be directly applied to chocolate spread because it is liquid at room temperature, thus affecting the texture's stability. The liquid nature is primarily due to the presence of unsaturated fatty acids in the form of oleic acid, linoleic acid, and linolenic acid (Ayustaningwarno, 2012). Several studies on the use of RPO oleogel have proposed to overcome the limitations associated with its application. The oleo gelation technique organizes the structure of oil and fats to improve their functional characteristics, such as color, texture, and nutritional content, when applied to food products (Risanti et al., 2018). Oleogel is a semi-solid material with a mixture of liquid oil and oleo gelator, which can trap liquid oil by forming a matrix (Huang et al., 2018). In addition, the benefits of the material are its simplicity, ease of use, inability to chemically alter the fatty acid components, quick preparation time, and ability to effectively lower the amounts of saturated fatty acid in chocolate spread (Chaves et al., 2018).

In line with these findings, oleogel is typically formed through the oleo gelation process using an oleo gelator. RPO tends to be liquid, necessitating its combination with an oleo gelator to achieve more stability (Samuditha et al., 2012). In this context, cocoa butter (CB) and beeswax (BW) can also be used in oleogel and are safe to apply to chocolate spread (food grade). The advantage of using CB is that it can provide a dense structure and improve the color (Ramlah et al., 2019).

According to Doan et al. (2016), BW is a low-calorie wax with superior adhesion and compactness properties to carnauba and candelilla wax. Fayaz et al. (2017) also reported that BW has the advantage of high oil binding capacity compared to propolis wax and monoglycerides in pomegranate seed oil oleogel. Despite the potential, it has been shown to have several limitations, such as providing a hard texture when applied to chocolate spread. The use of CB as an oleo gelator in the oleo gelation process can be an alternative to maintaining elasticity (Ramlah et al., 2019). Based on the physical properties of BW and CB, their combination is expected to complement each other in strengthening the formation of the RPO oleogel network structure. The chocolate spread product is also expected to have paste-like characteristics in stable conditions. Therefore, this study aims to evaluate the characteristics of RPO oleogel produced by a combination of BW and CB as well as its application in red chocolate spread. The characteristics examined include crystalline microstructure, melting point, hardness, oil binding capacity, and β-carotene content. The color and oil binding capacity of fresh red chocolate spread were analyzed, followed by an assessment of its hardness and β-carotene levels during storage.

METHODS

Materials

Refined sugar and skimmed milk powder of the "Point" brand was obtained from Pondasi Inti Sejahtera Limited Company, Bantul, Yogyakarta. "Dolphin" fine salt was produced by Susanti Megah Limited Company, Surabaya, and food-grade CB (cocoa butter) was produced by Darjeeling Sembrani Limited Company, Bandung, Indonesia. Food-grade "Anugerah Kebun Ku" red palm oil was obtained from the Palm Oil Farmers Group from Metro City, Lampung, Indonesia, and food-grade BW (beeswax) was obtained from CV. Asli Madu Dokter Lebah, Makassar. Additionally, hexane and β-carotene were obtained from Merck KGaA (Darmstadt, Germany).

Red Palm Oil Oleogel

Oil oleogels were prepared according to Loppies et al. (2019) with modifications. BW and CB were weighed and mixed in a ratio of 5:5, 6:4, 7:3, 8:2, 9:1, and 10:0. The Oleo gelator mixture was heated at 90 °C until melted and stirred for 15 minutes using a magnetic stirrer at a speed of 500 rpm. The next stage of the process was adding 90% RPO to each formula. The mixture was stirred using a magnetic stirrer at a speed of 500 rpm and maintained at a temperature of 60 °C for 30 minutes, and temperature conditions were controlled with a thermometer. Moreover, the mixture was poured into a 175 mL glass jar and left for 15 minutes. The final stage was cooling and storage at 11 °C for 24 hours in a showcase until RPO oleogel was formed.

Preparation and Storage of Red Chocolate Spread

Red chocolate spread was performed according to Fayaz et al. (2017) with modifications. A total of 30 g of refined sugar, 29.8 g of skimmed milk powder, 20 mL of water, and 0.2 g of salt in a beaker were weighed and heated at 90 °C until melted for 15 minutes using a magnetic stirrer at a speed of 500 rpm. The next was the addition of 20 g of RPO oleogel to each formula. The mixture was stirred using a magnetic stirrer at 700 rpm and maintained at 60 °C for 30 minutes until homogeneous or evenly distributed like a paste. Moreover, the mixture was transferred into a 175 mL glass jar and left for 15 minutes. The sample was stored at room temperature for 24 hours to produce a red chocolate spread product, and this was stored and analyzed at weeks 0, 1, 2, 3, 4, and 5.

Observation Parameters

The parameters observed in this study included crystal microstructure (Biswas et al., 2017) analyzed using the polarized light microscope (PLM) method, melting point using the slip melting point (SMP) method (Kumar et al., 2016), hardness using the universal testing machine (UTM) method (Godoi et al., 2020), oil binding capacity using the centrifugation method (Meng et al., 2018), β-carotene using the spectrophotometric method (Ulumi et al., 2021), color using the chromameter method (Oh et al., 2017) and texture using a texture analyzer (Kumar et al., 2016).

Statistic Analysis

Statistical analysis used the SPSS version 19 software program with experiments carried out in 3

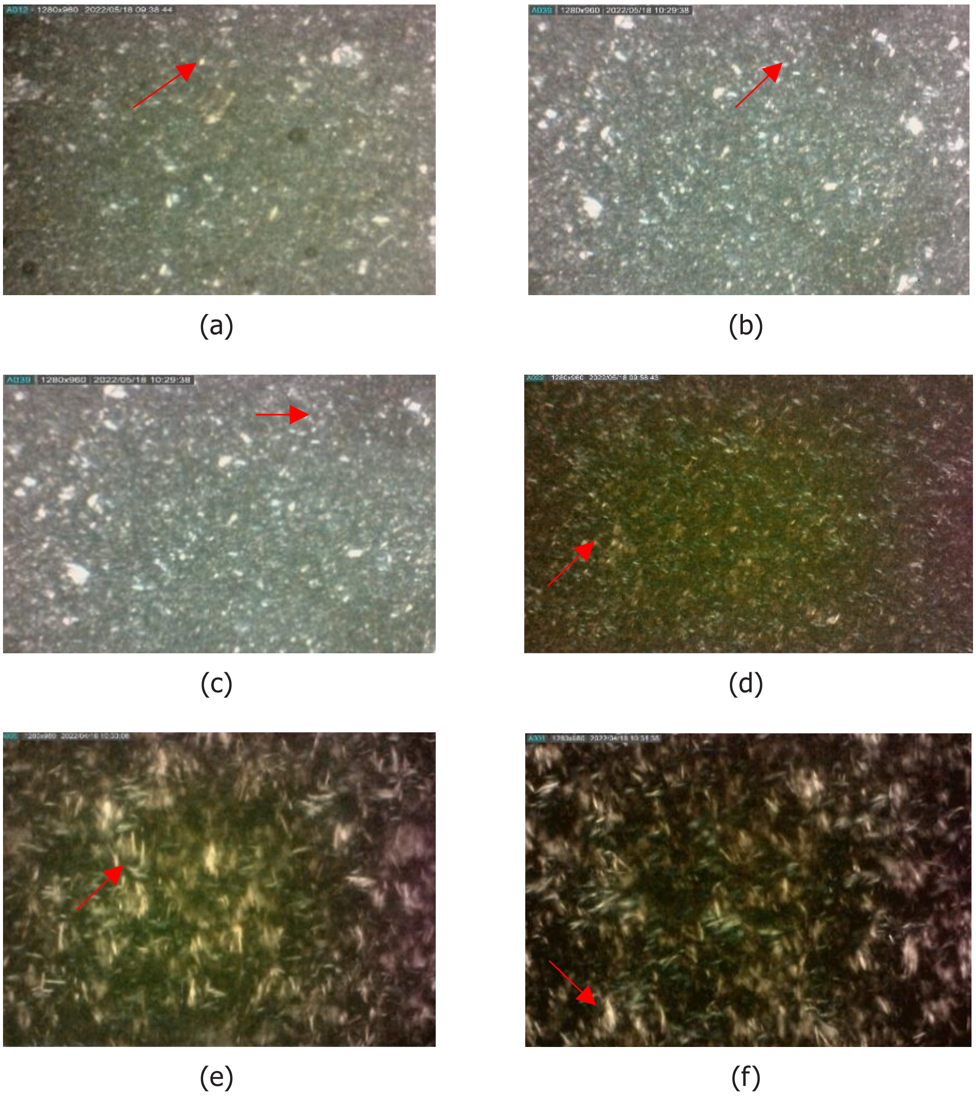

Figure 1. Crystal microstructure of RPO oleogel with varying concentrations of BW and cocoa butter. BW: beeswax, CB: cocoa butter, 90% RPO, (a) RPO oleogel with oleo gelator BW 5% and CB 5%, (b) RPO oleogel with oleo gelator BW 6% and CB 4%, (c) RPO oleogel with oleo gelator BW 7% and 3% CB, (d) RPO oleogel with oleo gelator BW 8% and CB 2%, (e) RPO oleogel with oleo gelator BW 9% and CB 1%, and (f) RPO oleogel with oleo gelator BW 10% without CB.

replications, and then the data were statistically analyzed using Analysis of Variance (ANOVA). When a significant difference was found ($p<0.05$), it then proceeded with Duncan's Multiple Range Test (DMRT).

RESULTS AND DISCUSSION

Physicochemical Characteristics of Red Palm Oil Oleogel

Effect of the beeswax and cocoa butter ratio on the crystalline microstructure of red palm oil oleogel

Red palm oil (RPO) oleogel BW5- CB5 (Figure 1.a), BW6-CB4 (Figure 1.b), and BW7-CB3 (Figure 1.c) samples showed the appearance of shorter crystals in small amounts in the form of needles. Sample BW8-CB2 (Figure 1.d) had a needle-shaped crystal microstructure with a greater number of crystals than BW5-CB5 (Figure 1.a), BW6-CB4 (Figure 1.b), and BW7-CB3 (Figure 1.d). BW9-CB1 (Figure 1.e) and BW10-CB0 (Figure 1.f) had needle-shaped crystals with a longer size and greater number than other oleogels. The results showed that increasing the BW concentration in the oleo gelator mixture resulted in denser needle crystals, longer crystal sizes, and even distribution (Giacomozzi et al., 2019). Similar results were obtained by Winkler-Moser et al. (2019) in soybean oil oleogel at a lower BW concentration, the number of crystals was found to be fewer and shorter.

An increase in BW caused an increase in needle crystals with a tighter arrangement, and a more solid gel was produced because the crystals formed had a spherulite pattern with strong cross-links (Huang et al., 2018). Loppies et al. (2019) reported that the addition of more than 3% CB mixed into the wax reduced the intensity of the crystals formed in soybean oil oleogel. Increasing the concentration of CB caused the matrix space to swell. Hence, the formed crystal network decreased, and therefore, it became less dense and less stable (Domingues et al., 2018). As a result, fat migrated and came out on the oleogel surface. Therefore, it reduced the basic crystalline structure that had formed (Lombardo et al., 2017).

Effect of the beeswax and cocoa butter ratio on the melting point of red palm oil oleogel

The combination of BW and CB concentrations influenced the slip melting point and melting point of RPO oleogel ($p<0.05$) (Table 1). Slip melting point and melting point increased with increasing BW concentration with CB mixing at low concentrations, and these results were similar to those of Loppies et al. (2019). The melting point of palm oil and soybean oil oleogel using BW 9% and CB 1% had the highest melting point compared to BW 7% and CB 3%, and this was because BW had a high melting point. Increasing the CB concentration caused the melting point of the oleo gelator mixture to decrease; therefore, the interaction between crystal particles decreased and allowed more oil to be released. Additionally, fat migration and a decrease in the slip melting point and melting point could reduce the solidity of the oleogel (Domingues et al., 2018; Martins et al., 2017).

When the BW concentration increased, the melting point increased, and BW had dendritic crystals with strong gel structure formation ability. However, interactions in the form of cross-links in the gel and nucleation were formed in the form of a crystallization process, which formed a matrix to trap liquid oil into the gel properly. BW had a high melting point and formed a strong gel structure. Hence, the ability to trap oil in the oleogel network was more than 90% (Doan, 2016; Rochmah, 2019).

Description. Values followed by different letters in the same column indicated a significant difference at the 0.05 significance level namely BW: Beeswax, CB: Cocoa Butter, 90% RPO, BW5-CB5: RPO oleogel with oleo gelator BW 5% and CB 5%, BW6-CB4: RPO oleogel with oleo gelator BW 6% and CB 4%, BW7-CB3: RPO

Table 1. Melting point of red palm oil oleogel with varying concentrations of beeswax and cocoa butter

Sample code	Slip melting point (°C)	Melting point (°C)
BW5-CB5	28,67±1,32[a]	30,89±0,78[a]
BW6-CB4	30,22±0,67[b]	31,78±0,83[b]
BW7-CB3	33,11±0,93[c]	35,67±0,87[c]
BW8-CB2	34,44±0,88[d]	39,56±0,88[d]
BW9-CB1	36,67±0,70[e]	41,67±0,50[e]
BW10-CB0	40,56±0,73[f]	43,33±0,50[f]

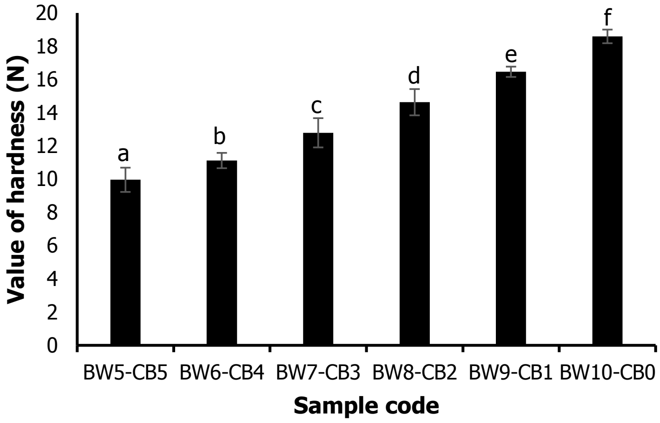

Figure 2. Hardness of RPO oleogel with varying concentrations of beeswax and cocoa butter. Values followed by different letters in the same column indicated a difference at the 0.05 significance level namely BW: BW, CB: Cocoa Butter, 90% RPO, BW5-CB5: RPO oleogel with oleo gelator BW 5% and CB 5%, BW6-CB4: RPO oleogel with oleo gelator BW 6% and CB 4%, BW7-CB3: RPO oleogel with oleo gelator BW 7% and CB 3%, BW8-CB2: RPO oleogel with oleo gelator BW 8% and CB 2%, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, and BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB.

oleogel with oleo gelator BW 7% and CB 3%, BW8-CB2: RPO oleogel with oleo gelator BW 8% and CB 2%, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, and BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB.

Effect of the beeswax and cocoa butter ratio on the hardness of red palm oil oleogel

The combination of BW and CB concentrations influenced the hardness level of RPO oleogel ($p<0.05$). Figure 2 presents the increase in hardness values in RPO oleogel. A high BW ratio in the oleo gelator mixture could increase hardness. Ristanti et al. (2018) showed a similar thing where increasing the concentration of BW combined with CB at a low concentration resulted in an increase in hardness in "Tropical" cooking oil oleogel. Increasing BW produced larger crystal sizes, which could induce crystal nucleation. As a result of the low CB concentration, there was no increase in volume. Therefore, the BW crystal spherulites (needles) could interact with hydrogen bonds and van der Walls interactions between oil and BW, which could encourage the formation of a stronger gel and increase hardness (Winkler-Moser et al., 2019; Lupi et al., 2016).

Increasing the concentration of CB in the mixture reduced the hardness of the RPO oleogel. This occurred due to incompatibility between CB and other fats in RPO when mixed, namely lauric acid, which caused eutectic symptoms. This caused the formed fat crystal structure in the mixture to become unstable and could not be distributed evenly, resulting in fat migration and separation. This separation made the texture less solid and could reduce the hardness of the RPO oleogel (Limbardo et al., 2017; Ristanti et al., 2018).

Effect of the beeswax and cocoa butter ratio on the oil binding capacity of red palm oil oleogel

The combination of BW and CB concentrations as oleo gelator did not affect the oil binding capacity of RPO oleogel ($p>0.05$), and similar results were also obtained by Fayaz et al. (2017). The use of BW and propolis wax at different concentrations did not affect the binding capacity of pomegranate seed oil oleogel. Pomegranate seed oil oleogel had an oil binding capacity ranging from 98.22% - 99.96%. Meng et al. (2018) reported that increasing BW caused an increase in oil binding capacity, which made the oleogel stable because the oil loss value was low. The oil binding capacity was not significantly different because BW had strong adhesion (Ogutchu et al., 2014).

The binding capacity of oil was related to the number of crystals contained. According to Fayaz et al. (2017), this was because BW had a crystal structure resembling a needle, where the higher the concentration, the more and longer the crystals that were formed; therefore, it could

Table 2. Oil binding capacity of red palm oil oleogel with varying concentrations of beeswax and cocoa butter

Sample code	Oil binding capacity (%)
BW5-CB5	99,78±0,17[a]
BW6-CB4	99,79±0,33[a]
BW7-CB3	99,89±0,02[a]
BW8-CB2	99,92±0,05[a]
BW9-CB1	99,98±0,01[a]
BW10-CB0	99,98±0,01[a]

Description. Values followed by different letters in the same column indicated a significant difference at the 0.05 significance level including BW: Beeswax, CB: Cocoa Butter, 90% RPO, BW5-CB5: RPO oleogel with oleo gelator BW 5% and CB 5%, BW6-CB4: RPO oleogel with oleo gelator BW 6% and CB 4%, BW7-CB3: RPO oleogel with oleo gelator BW 7% and CB 3%, BW8-CB2: RPO oleogel with oleo gelator BW 8% and CB 2%, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, and BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB.

trap more than 90% of the oil into the oleogel network. A high BW concentration could induce crystal nucleation in the form of an increased number of crystals formed. Therefore, it could encourage the formation of a stronger gel and hold or bind oil well, consequently reducing the percentage of oil loss (Tavernier et al., 2017; Wijaya et al., 2019).

Effect of the beeswax and cocoa butter ratio on the β-carotene content of red palm oil oleogel

The combination of BW and CB concentrations influenced β-carotene levels in RPO oleogel (p<0.05), and Figure 3 shows the increase in β-carotene levels. Chen et al. (2016) found similar results where increasing the wax concentration in zein-based oil oleogels could inhibit the degradation of β-carotene. High BW concentrations with CB mixing at low concentrations could maintain β-carotene. The content obtained was related to the crystal microstructural characteristics of the oleogel system. Additionally, increasing the BW concentration caused the number of crystals to increase. Mixing CB in low concentrations did not cause an increase in volume. Therefore, the interaction between crystal particles became stronger in a limited space and increased protective mobility in trapping oil in the gel matrix. This could prevent singlet oxygen and reactive radical species in the surrounding environment. Therefore, it inhibits the degradation of β-carotene (Chen et al., 2016).

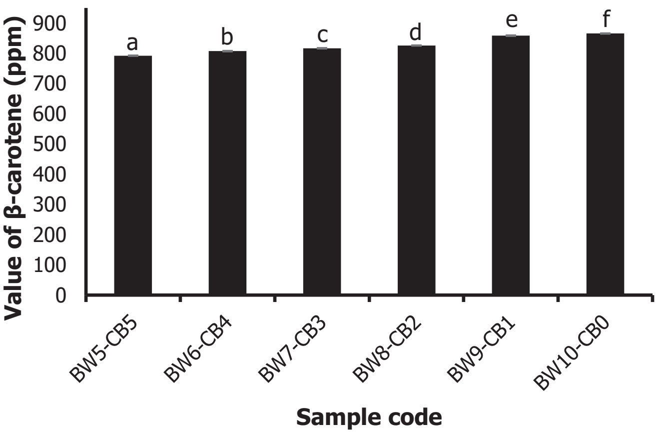

Figure 3. β-carotene content of RPO oleogel with varying concentrations of beeswax and cocoa butter. Values followed by different letters in the same column indicated a significant difference at the 0.05 significance level namely BW: Beeswax, CB: Cocoa Butter, 90% RPO, BW5-CB5: RPO oleogel with oleo gelator BW 5% and CB 5%, BW6-CB4: RPO oleogel with oleo gelator BW 6% and CB 4%, BW7-CB3: RPO oleogel with oleo gelator BW 7% and CB 3%, BW8-CB2: RPO oleogel with oleo gelator BW 8% and CB 2%, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, and BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB.

The initial level of β-carotene in RPO was 905.27 ppm, which decreased in oleogel. This was due to heating at 90 °C for 45 minutes when making the oleogel. Azarine (2019) reported that heating RPO for 120 minutes at 50 °C caused a decrease in β-carotene of 3% and continued to increase with increasing temperature and heating time. According to Mursalin (2018), the decrease in β-carotene content was caused by oxidation of carotene during heating. Hydroperoxide compounds (the main product of fat oxidation) triggered the oxidation of carotene in RPO oleogel. Sugiyono et al. (2012) reported that other factors that caused a decrease in β-carotene were exposure to oxygen, light, and heat, which could catalyze the oxidation of carotene in RPO oleogel.

Physicochemical Characteristics of Red Chocolate Spread

As a control, the red chocolate spread was made using RPO oleogel from the best treatment, namely BW9-CB1 and BW10-CB0. This was based on BW9-CB1 having a characteristic crystal microstructure with a larger number of crystals, long and homogeneous, having a high melting point (36.67–41.67 °C) with a denser and denser texture (hardness) and the highest oil binding capacity. The product was expected to have the lowest oil loss with the highest β-carotene. The parameters for assessing the quality of red chocolate spread fresh products were color and oil binding capacity. At the same time, during 5 weeks of storage, the level of hardness and β-carotene content were evaluated.

Effect of the beeswax and cocoa butter ratio in oleogel on the color of red chocolate spread

The combination of BW and CB concentrations in RPO oleogel influenced the brightness level (L*) of the red chocolate spread (p<0.05). Table 3 showed that red chocolate spread with the addition of BW-based oleogel combined with CB (BW9-CB1) had a higher brightness level than red chocolate spread with only BW (BW10-CB0). Commercial chocolate spread without adding oleogel (SC-K) had the lowest brightness level compared to oleogel (BW9-CB1 and BW10-CB0). Similar results were found in Sampebarra et al. (2019), that chocolate spread with the addition of soybean oil oleogel with a combination of CB and BW produced a higher level of brightness and shine. Ramlah and Alfrida (2019) stated that CB underwent a deodorization process, resulting in a bright CB color

Table 3. Color analysis of red chocolate spread based on red palm oil oleogel

Sample Code	Color			
	Brightness (L*)	Redness (a*)	Yellowish (b*)	Color difference (ΔE)
BW9-CB1	61,47±0,30[c]	5,81±0,20[b]	57,81±0,60[b]	2,42
BW10-CB0	59,31±0,27[b]	5,81±0,31[b]	57,80±0,41[b]	1,78
SC-K	34,80±0,51[a]	3,18±0,09[a]	0,67±0,07[a]	-

Description. Values followed by different letters in the same column indicated a significant difference at the 0.05 significance level, including BW: Beeswax, CB: Cocoa Butter, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, BW10-CB0: RPO oleogel with 10% BW oleo gelator without CB, and SC-K: Commercial Chocolate Spread.

and increasing the brightness of the resulting chocolate spread product.

The addition of oleo gelator-based RPO oleogel from a combination of BW and CB applied to the red chocolate spread resulted in red (a*) and yellow (b*) color intensities that were significantly different from the commercial chocolate spread (SC-K). The total color difference (ΔE) in the oleogel-based chocolate jam sample (BW9-CB1) compared to commercial chocolate spread (SC-K) was very high. This was because the ΔE value ranged from 1.5 to 3 (Oh et al., 2017). The color difference was due to the presence of pigment in the material, namely RPO oleogel. The addition of RPO oleogel produced a higher yellowish-red color intensity compared to chocolate jam without the addition. This was because RPO had natural pigments in the form of carotenoids, which produce red to yellowish colors (Sumarna, 2014).

The effect of the beeswax and cocoa butter ratio in oleogel on the oil binding capacity of red chocolate spread

The combination of BW and CB concentrations as an oleo gelator had no significant effect on the oil binding capacity of red chocolate spread (P>0.05). According to Fayaz et al. (2017), BW had a spherulite crystal pattern structure with high binding strength. Therefore, it could trap oil in the chocolate spread network of more than 90%. Similar results were obtained by Fayaz et al. (2017), and the use of BW in pomegranate seed oil oleogel had an oil binding capacity that was not significantly different, with a value reaching 99.96%. The use of oleogel could induce crystal nucleation. The increased number of crystals helped form a stronger gel structure. It trapped the oil well because its capacity in the chocolate spread increased (Wijaya et al., 2019).

Chocolate spreads based on RPO oleogel (BW9-CB1 and BW10-CB0) had oil binding capacity values that were significantly different (p<0.05) from commercial chocolate spread without the addition of oleogel (SC-K). Commercial chocolate spread (SC-K) had the lowest oil binding capacity compared to BW9-CB1 and BW10-CB0 (Table 4). Similar results were also obtained by Doan et al. (2016), where hazelnut filling with the addition of BW-based oleogel had the most effective oil binding capacity compared to the addition of oleogel. The results showed that the addition of oleogel was proven to help network restructuring and increase the oil-binding capacity of the resulting chocolate spread.

Effect of the beeswax and cocoa butter ratio in oleogel on the hardness of red chocolate spread during storage

The combination of BW and CB concentrations as an oleo gelator had a significant effect on the hardness of red chocolate spread (p<0.05). Based on the results, it was known that chocolate spread with BW-based RPO oleogel combined with CB (BW9-CB1) had a lower hardness than without the addition of CB (BW10-CB0)). Sutrisno (2018) reported that chocolate spread with cashew filling and the addition of CB emulsion could reduce its hardness. This was because the hardness was influenced by the constituent fatty acids and the characteristics of the fat crystals. A decrease in the

Table 4. The oil binding capacity of red chocolate spread based on red palm oil oleogel

Sample	Oil binding capacity (%)
BW9-CB1	99,95±0,05[a]
BW10-CB0	99,93±0,05[a]
SC-K	99,14±0,08[b]

Description. Values followed by different letters in the same column indicated a significant difference at the 0.05 significance level, namely BW: Beeswax, CB: Cocoa Butter, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB, and SC-K: Commercial Chocolate Spread.

hardness of chocolate products due to fat incompatibility occurred through the formation of imperfect crystal lattices, which could increase the mobility of molecular movements, change the polymorphic structure, and change the crystallization rate.

Samples BW9-CB1 and BW10-CB0 did not experience changes in hardness during storage. Marzelly et al. (2017) stated that the stable hardness value during storage was caused by cross-linking in the gel, hence forming a 3-dimensional structure bound to each other. Furthermore, the tissue captured water in the gel and then formed a stable structure. This caused the hardness of the chocolate spread to become stable like paste, and adding sugar could also affect the hardness of the chocolate spread. According to Marsigit et al. (2018), this could be influenced by the fact that sugar could bind water during the heating process in the chocolate spread, producing a texture with stable hardness.

Effect of the beeswax and cocoa butter ratio in oleogel on the β-carotene content of red chocolate spread during storage

Red chocolate spread BW9-CB1 and BW10-CB0 showed a significantly different decrease in β-carotene concentrations every week during 5 weeks of storage. This was because making red chocolate spread involved 2 stages of the heating process. The first heating process was when the RPO and oleo gelator were heated at 90 °C for 45 minutes, and the second heating was when making the chocolate spread at a temperature of 60 °C for 45 minutes, which allowed damage to β-carotene. According to Mursalin (2018), the decrease in β-carotene was caused by heating, which initiated carotene oxidation. This caused hydroperoxide compounds, the main product of fat oxidation, and triggered carotene oxidation. Another factor causing the decrease in β-carotene was exposure to oxygen, light, and heat, which could catalyze the oxidation of carotene in red chocolate spread (Sugiyono et al., 2012).

The combination of BW and CB concentrations in RPO oleogel had a significant effect ($p<0.05$) on the β-carotene content of red chocolate spread. The oleo gelation technique using a double oleo gelator (a mixture of BW and CB) obtained better carotene stability than a single oleo gelator when applied to chocolate spread for 5 weeks of storage. This was because the combination of BW and CB as oleo gelators easily interacted and restructured to strengthen the formation of the chocolate spread network structure to trap oil and prevent oil migration, thereby preventing damage to β-carotene. According to Chen et al. (2016), carotene degradation could be slowed and stabilized by emulgel. The network in emulgel could protect β-carotene by trapping and isolating it in a gel matrix that could protect against singlet oxygen compounds. The results of β-carotene levels indicated that the combination of BW and CB in RPO oleogel, when applied to chocolate spread, could contribute to vitamin A intake in the body.

Table 5. Physicochemistry of red chocolate spread based on red palm oil oleogel during 5 weeks of storage

Sample Code	Hardness (N)	β-carotene content (ppm)
BW9-CB1M0	6.01±0.22^{aA}	469.07±0.30^{aF}
BW9-CB1M1	6.02±0.14^{aA}	444.50±0.91^{aE}
BW9-CB1M2	6.07±0.21^{aA}	356.56±0.53^{aD}
BW9-CB1M3	6.12±0.23^{aA}	330.05±0.80^{aC}
BW9-CB1M4	6.17±0.90^{aA}	306.35±0.61^{aB}
BW9-CB1M5	6.21±0.62^{aA}	302.67±0.30^{aA}
BW10-CB0M0	7.04±0.02^{bA}	457.31±0.30^{bF}
BW10-CB0M1	7.06±0.48^{bA}	396.93±0.80^{bE}
BW10-CB0M2	7.14±0.40^{bA}	349.36±0.61^{bD}
BW10-CB0M3	7.35±0.06^{bA}	330.23±0.53^{bC}
BW10-CB0M4	7.38±0.54^{bA}	281.60±0.30^{bB}
BW10-CB0M5	7.40±0.16^{bA}	258.08±0.91^{bA}

Description. Values followed by the same lowercase letter in the same column and the same uppercase letter in the same column were not significantly different at the 0.05 significance level, namely M0: week 0, M1: week 1, M2: week 2, M3: week 3, M4: week 4, and M5: week 5. Others included BW: Beeswax, CB: Cocoa Butter, BW9-CB1: RPO oleogel with oleo gelator BW 9% and CB 1%, and BW10-CB0: RPO oleogel with oleo gelator BW 10% without CB.

CONCLUSION

In conclusion, the combination of BW and CB as oleo gelator affected its crystal shape. Increasing the concentration of BW causes more needle-shaped crystals, denser crystals with a longer size, evenly distributed, and the obtained RPO oleogel is more stable. Hardness, β-carotene content, and melting point of RPO oleogel increased with increasing BW concentration in the oleo gelator. The best RPO oleogel was obtained from a combination of 9% BW and 1% CB (BW9-CB1), where the hardness, β-carotene content, and melting point were high, and the crystal morphology was compact. The best RPO oleogel-based red chocolate spread had a better color (brightness) and oil binding capacity compared to oleogel-based red chocolate spread without

CB (BW10-CB0) or commercial chocolate spread (SC-K). The red chocolate spread had a brightness (L*) of 61.47, red color intensity (a*) of 5.81, and yellowness (b*) of 57.81, with an oil binding capacity of 99.95%. The melting point of the red chocolate spread was 31.89-41.67 °C, which indicated that the product melts at body temperature and is stable at room temperature. The hardness of the Red chocolate spread was 6.01-6.21 N, and the carotene content was 469.07-302.67 ppm during 5 weeks of storage. Therefore, the use of RPO oleogel with a combination of BW and CB could improve physicochemical properties, including color, hardness level, and β-carotene content, and could be an alternative for making chocolate spreads rich in β-carotene.

CONFLICT OF INTEREST

The author declared that there was no conflict of interest in this publication manuscript and only published in this journal.

REFERENCES

Ayustaningwarno, F. (2012). Proses pengolahan dan aplikasi minyak sawit merah pada industri pangan. *Jurnal Manajemen Kualitas Hidup* (*Vitasphere)*, *1*(12), 1–11.

Azarine, I. P. (2019). Fortifikasi Minyak Sawit Merah sebagai Sumber Provitamin A pada Susu Rekombinasi: Kajian Pengaruh Nilai HLB, Konsentrasi *Emulsifier*, dan Jenis Homogenisasi terhadap Stabilitas Emulsi. *Skripsi*. Fakultas Teknologi Pertanian. Universitas Gadjah Mada. Yogyakarta.

Biswas, N., Cheow, Y. L., Tan, C. P., & Siow, L. F. (2017). The physical, rheological, and sensorial properties and bloom formation of dark chocolate made with cocoa butter substitute (CBS). *Journal Food Science and Technology*, *82,* 420–428. https://doi.org/10.1016/j.lwt.2017.04.039

Chaves, K. F., Barrera-Arellano, D., & Ribeiro, A. P. B. (2018). Potential application of lipid organogels for the food industry. *Food Research International*, *10*(5), 863–872. https://doi.org/10.1016/j.foodres.2017.12.020

Chen, X. W., Fu, S. Y., Hou, J. J., Guo, J., Wang, J. M., & Yang, X. Q. (2016). Zein based oil-in-glycerol emulgels enriched with β-carotene as margarine alternatives. *Journal Food Chemistry*, *211,* 836–844. https://doi.org/10.1016/j.foodchem.2016.05.133

Doan, C. D., Patel, A. R., Tavernier, I., Clercq, N. D., Raemdonck, K. V., de Walle, D. V., Delbaere, C., & Dewettinck, K. (2016). The feasibility of wax-based *oleogel* as a potential co-structured with palm oil in low-saturated fat confectionery fillings. *Eur. J. Lipid Sci. Technol*, *118(12)*, 1903–1914. https://doi.org/10.1002/ejlt.201500172

Domingues, M. A. F., Da Silva, T. L. T., Ribeiro, A. P. B., Chiu, M. C., & Gonçalves, L. A. G. (2018). Structural characteristics of crystals formed in palm oil using sorbitan tristearate and sucrose stearate. *International Journal of Food and Properties*, *21*(1), 618–632. https://doi.org/10.1080/10942912.2018.1440237

Fayaz, G., Goli, S. A. H., Kadivar, M., Valoppi, F., Barba, L., Calligaris, S., & Nicoli, M. C. (2017). Potential application of pomegranate seed oil *oleogel*s based on monoglycerides, beeswax, and propolis wax as partial substitutes for palm oil in functional chocolate spread. *LWT – Food Science and Technology*, *86*, 523–529. https://doi.org/10.1016/j.lwt.2017.08.036

Giacomozzi, A. S., Palla, C. A., Carrin, M. E., & Martini, S. (2019). Physical properties of monoglycerides *oleogel*s modified by concentration, cooling rate, and high-intensity ultrasound. *Journal of Food Science*, *84*(9), 1–13. https://doi.org/10.1111/1750-3841.14762

Godoi, K. R. R. de, Basso, R. C., Ming, C. C., da Silva, A. Á., Cardoso, L. P., & Ribeiro, A. P. B. (2020). Crystallization, microstructure, and polymorphic properties of soybean oil organogels in a hybrid structuring system. *Food Research International*, *13*(7), 109–460. https://doi.org/10.1016/j.foodres.2020.109460

Huang, H., Hallinan, R., & Maleky, F. (2018). Comparison of different *oleogel*s in processed cheese product formulation. *International Journal of Food Science and Technology*, *53*(11), 2525–2534. https://doi.org/10.1111/ijfs.13846

Kumar, P. K. P., Jeyarani, T., & Gopala K. A. G. (2016). Physicochemical characteristics of phytonutrient retained red palm olein and butter-fat blends and its utilization for formulating chocolate spread. *Journal of Food Science and Technology*, *53*(7), 3060–3072. http://doi.org/10.1007/s13197-016-2279-8

Limbardo, R. P., Herry, S., & Judy, R. W. (2017). The effect of coconut oil and palm oil as substituted oils to cocoa butter on chocolate bar texture and melting point. *International Proceedings and Application of Chemical Engineering*, *1840*, 1–12. https://doi.org/10.1063/1.4982281

Loppies, J. E., Risanti. E. Y., Ramlah, S., Lullung, A., & Amalia, A. N. (2019). Karakteristik oleogel dari minyak nabati menggunakan lilin lebah dan lemak kakao sebagai oleogelator. *Jurnal Industri Hasil Perkebunan*, *14*(2), 33–43. https://doi.org/10.33104/jihp.v14i2.5552

Lupi, F. R., Gabriele, D., Facciolo, D., Baldino, N., Seta, L., & de Cindio, B. (2016). Effect of organooleogelator and fat source on rheological properties of olive oil-based organogels. *Food Research International*, *46*(1), 177–184. https://doi.org/10.1016/j.foodres.2011.11.029

Marsigit, W., Tutuarima, T., & Hutapea, R. (2018). Pengaruh penambahan gula dan karagenan terhadap karakteristik fisik, kimia dan organoletik *soft candy* jeruk kalamansi

(*Citrofortunella microcarpa*). *Jurnal Agroindustri, 8*(2), 113–123. https://doi.org/10.31186/j.agroind.8.2.113-123

Martins, A. J., Silva, P., Maciel, F., Pastrana, L. M., Cunha, R. L., Cerqueira, M. A., & Vicente, A. A. (2019). Hybrid gels: influence of oleogel/hydrogel ratio on rheological and textural properties. *Journal of Food Research International*, *116*, 1298–1305. https://doi.org/10.1016/j.foodres.2018.10.019

Marzelly, A. D., Yuwanti, S., & Lindriati, T. (2017). Karakteristik fisik, kimia, dan sensoris *fruit leather* pisang ambon (*Musa paradisiaca* S.) dengan penambahan gula dan karagenan. *Jurnal Agroteknologi, 11*(2), 173–185. https://doi.org/10.19184/j-agt.v11i02.6526

Meng, Z., Qi, K., Guo, Y., Wang, Y., & Liu, Y. (2018). Macro-micro structure characterization and molecular properties of emulsion-templated polysaccharide oleogels. *Food Hydrocolloids*, *77*, 17–29. https://doi.org/10.1016/j.foodhyd.2017.09.006

Mursalin, M. (2018). Engineering process of deodorization to improve product quality of red palm oil with rich carotene. *Indonesian Food Science and Technology Journal*, *1*(1), 20–26. https://doi.org/10.22437/ifstj.v1i1.5014

Ogutchu, M. & Yilmaz, E. (2014). Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas Aceites*, *65*(3), e040. https://doi.org/10.3989/gya.0349141

Oh, I. K., Amoah, C., Lim, J., Jeong, S., & Lee, S. (2017). Assessing the effectiveness of wax-based sunflower oil oleogels in cakes as a shortening replacer. *Journal of LWT Oleo Technology*, *86*, 430–437. https://doi.org/10.1016/j.lwt.2017.08.021

Purnama, K. O., Setyaningsih, D., Hambali, E., & Taniwiryono, D. (2020). Processing, characteristics, and potential application of red palm oil - a review. *International Journal of Oil Palm*, *3*(2), 40–55. https://doi.org/10.35876/ijop.v3i2.47

Ramlah, S., Asriati, D. W., Wahyuni, A. N., & Eky, R. (2019). Characteristic of fat content and fatty acid composition of chocolate compound made from vegetable oil oleogel and cocoa butter substitute with cocoa butter oleogator. *Journal of Plantation Based Industry*, *15*(1), 74–82. https://doi.org/10.33104/jihp.v15i1.5978

Ristanti, E. Y., Yunus, M. R., Ramlah, S., Justus E. L., Sampebarra, A. L., Rejeki, E. S., Winaldi, A., Asriati, D. W., & Amalia, A. N. (2018). *Aplikasi Oleogel dengan Oleogator Lemak Kakao pada Produk Pangan Olahan Kakao*. Balai Besar Industri Hasil Perkebunan. BPPI. Kementerian Perindustrian. https://doi.org/10.33104/jihp.v14i2.5479

Rochmah, M. M., Ferdyansyah, M. K., Nurdyansyah, F., & Ujianti R. M. D. (2019). Pengaruh penambahan hidrokoloid dan konsentrasi sukrosa terhadap karakteristik fisik dan organoleptik selai lembaran pepaya (*Carica papaya L.*). *Jurnal Pangan dan Agroindustri*, *7*(4), 42–52. https://doi.org/10.21776/ub.jpa.2019.007.04.5

Sampebarra, A. L., Khaerunnisa, Ristanti, E. Y., & Asriati, D. W. (2019). Karakteristik cokelat spread dengan penambahan oleogel dari oleogator lemak kakao. *Jurnal Industri Hasil Perkebunan*, *14*(2), 24–32. https://doi.org/10.33104/jihp.v14i2.5387

Samuditha, L., Dassanayake, K., Kodali, D. R., & Ueno, S. (2012). Current opinion in colloid & interface science formation of oleogels based on edible lipid materials. *Current Opinion in Colloid & Interface Science*, *16*(5), 432–439. https://doi.org/10.1016/j.cocis.2011.05.005

Sugiyono, Wibowo, M., Soekopitojo, S., & Wulandari, N. (2012). Pembuatan bahan baku spreads kaya karoten dari minyak sawit merah melalui interesterifikasi enzimatik menggunakan reaktor batch. *Jurnal Teknologi dan Industri Pangan*, *23*(2), 117–125. https://doi.org/10.6066/jtip.2012.23.2.117

Sumarna, D. (2014). Study on red palm oil characteristics produced from CPO (crude palm oil). *Agritech*, *12*(2), 35–38.

Sutrisno, A. D., Yusep, I., & Nurul, P. (2018). Karakteristik cokelat filling kacang mete yang dipengaruhi jenis dan jumlah lemak nabati. *Journal of Food Technology*, *5*(2), 91–101. https://doi.org/10.23969/pftj.v5i2.1040

Tavernier, I., Doan, C. D., Van der Meeren, P., Heyman, B., & Dewettinck, K. (2018). The potential of waxes to alter the microstructural properties of emulsion-templated oleogels. *European Journal of Lipid Science and Technology*, *120*(3), 1–13. https://doi.org/10.1002/ejlt.201700393

Ulumi, M. L., Dwi, S. W., Reza, F., Cathrine, O., & Desiana, N. (2021). Mikroenkapsulasi pigmen beta-karoten dengan metode foam mat drying menggunakan gelatin tulang ikan kakap merah sebagai bahan penyalut. *Jurnal Agrointek*, *15*(4), 1183–1195. https://doi.org/10.21107/agrointek.v15i4.11689

Wibisono, A., Lestari, N., & Isyanti, M. (2015). Pengaruh variasi komposisi lemak cokelat, olein sawit, dan minyak ikan patin terhadap kandungan nutrisi cokelat oles. *Warta IHP, 32*(2), 51–61. https://doi.org/10.32765/warta ihp.v32i02.2637

Wijaya, W., Sun, Q. Q., Vermeir, L., Dewettinck, K., Patel, A. R., & Van der Meeren, P. (2019). pH and protein to polysaccharide ratio control the structural properties and viscoelastic network of HIPE-templated biopolymeric oleogels. *Journal of Food Structure*, *21*(4), 100–112. https://doi.org/10.1016/j.foostr.2019.100112

Winkler-Moser, J. K., Julie, A., Frederick, C. F., & Hong-Sik, H. (2019). Physical properties of beeswax, sunflower wax, and candelilla wax mixtures, and oleogels. *Journal Am Oil Chemical Soc.*, *96*, 1125–1142. https://doi.org/10.1002/aocs.12280