

EFFECT OF STORAGE TEMPERATURE AND DURATION ON RHEOLOGICAL AND THERMAL CHARACTERISTICS OF SUPEROLEIN OLEOGELS

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ABSTRACT

The study was conducted to investigate the effects of storage temperature and duration on the rheological and thermal characteristics of superolein oleogels derived from 3% w/w of polyglycerol behenic acid ester (PBA), 3% w/w of sunflower wax (SFW) and 8% w/w of fully hydrogenated palm-based monoacylglycerols (MGHO). The results indicated that the storage modulus (G'), loss modulus (G'') and critical stress values were much higher for all the oleogels when stored at 5°C. At 15°C, the rheological parameters for SFW and MGHO oleogels were gradually increased during storage. From the thermal analysis, the peak intensity at approximately 20°C also gradually increased during storage, demonstrating the marked increase in the rheological parameters were due to the crystallisation of the triacylglycerol (TAG) in the superolein during the three-day storage. This effect was not observed for PBA oleogels, showing that the PBA inhibited or delayed crystallisation of the superolein molecules at 15°C. However, an extended storage study revealed that the PBA actually delayed and did not inhibit the crystallisation of the superolein. At 25°C, all the oleogels were highly unstable with poor thermal and rheological properties. The results suggested that 15°C was a more suitable temperature for the storage of superolein oleogels.

Keywords: monoacylglycerol, oleogels, polyglycerol behenic acid ester, palm superolein, sunflower wax.

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INTRODUCTION

Oils and fats consist of molecules known as triacylglycerols (TAG), which are made up of three fatty acids attached to a glycerol backbone. Their physical properties are mainly dependent on the chemical structure and polymorphic behaviour of the TAGs (Birker and Padley, 1987), as well as the constituent fatty acids attached to the glycerol backbone. Oils and fats are important for various

edible purposes and the applications rely on their physical, rheological and polymorphism properties. For edible purposes, solid fat is desirable. Over the decades, lipid scientists attempted to modify fatty acid and TAG composition to make it more marketable as it possessed the desired properties for formulating various food applications (Gunstone, 2011). One of these popular modification processes is hydrogenation. This process is mainly used to prepare shortenings and margarine from soft vegetable oils such as sunflower oil and rapeseed oil. It causes the production of fat products with high levels of saturated content and monounsaturated fatty acids with *trans* configuration. Numerous clinical researches have suggested that intake of *trans* fatty acid decreases the serum high density lipoprotein (HDL or 'good' cholesterol) in combination with an increase in serum low density lipoprotein (LDL or 'bad' cholesterol) (Marangoni

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and Garti, 2011), whereas saturated fats induce an increase in serum LDL levels that have a negative effect on cardiovascular health (Flöter *et al.*, 2021; Zetzl and Marangoni, 2011). Therefore, a new strategy for structuring edible oils is required to reduce the use of high saturated fatty acids as well as to eliminate the use of *trans* fats in fat products.

In the food industry, there have been many attempts to find alternative components that can provide the desired features of texture, structuring, stability, and taste that are normally found in animal and vegetable fats or hydrogenated oils (Marangoni and Garti, 2011). One of the alternatives –oleogel, have been recognised for their potential for use to reduce oil migration in multi component foods and to act as an alternative to butter or margarine (Marangoni and Garti, 2011). A study conducted by Hwang *et al.* (2013) investigated the making of margarine from oleogels of plant wax and soybean oil. The literature shows that making of margarine is possible using oleogels from rice bran wax and sunflower wax (SFW), whereby SFW showed the greatest firmness of margarine and higher melting points compared to the commercial margarine and spreads (Hwang *et al.*, 2013).

This non-traditional structuring technique – organogelation has become the current trend of producing solid fat products to reduce the amounts of saturated components and increase the unsaturated components used in the solid products. Most of the research on oleogel preparations involved the use of soft vegetable oils such as sunflower oil, soybean oil, safflower oil, olive oil, canola oil and rice bran oil (Doan *et al.*, 2015; Jang *et al.*, 2015; Ögütçü and Yılmaz, 2014; Toro-Vazquez *et al.*, 2007). There are limited literatures that evaluated the use of palm-based products such as palm olein, superolein or top olein for the preparation of oleogels. According to Co and Marangoni (2012), organogel formation is highly dependent on the type of solvent/ liquid oil that is gelled. Unlike many other vegetable oils, palm superolein contains more saturated components such as POP, this high melting component may also involve the oleogelation and strengthen the oleogels. Therefore, it would be interesting to study the use of palm liquid oils in the formation of oleogels.

The objective of this research work is to investigate the possibility of using palm superolein for the preparation of oleogels using different types of organogelators and the effect of superolein on oleogel formation. In this study, a food-grade polyglycerol ester comprises a mixture of long chain acid esters such as stearic and behenic acid; a food-grade SFW and a palm-based fully hydrogenated monoacylglycerol were chosen for the preparation of superolein oleogels. The stability, physical and rheological characteristics of the oleogels were

studied at three temperatures of 5°C, 15°C and 25°C for three days. The effect of temperatures and preparation duration on the oleogel characteristics were discussed.

MATERIALS AND METHODS

Materials

Refined, bleached and deodorised superolein of IV 64 and soybean oil were obtained from PGEO Sdn. Bhd. (Johor, Malaysia). The gelator – polyglycerol behenic acid ester (PBA) was obtained from Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan), food grade SFW was obtained from Shri Balaji Driers (Karnataka, India), with a melting point of 77°C. Fully hydrogenated palm-based monoacylglycerol (MGHO), was obtained from a local manufacturer in Klang Valley, Malaysia.

Acylglycerol Composition

Acylglycerol composition analysis of palm superolein was performed using high-performance liquid chromatography (U-HPLC) (ACQUITY UPLC H-Class System, Waters Cop., Milford, Massachusetts, USA) according to the AOCS Official Methods Ce 5c-89 and Ce 5c-93 (AOCS, 2017a; AOCS, 2017b). The instrument was equipped with a refractive index detector (Waters Cop., Milford, Massachusetts, USA) set at 35°C, and an ACQUITY UPLC® BEH C18 column (Waters Cop., Milford, Massachusetts, Column specifications: particle size of 1.7 µm, id. 2.1 mm x 150 mm length). The oil samples were solubilised in acetone to form a 5% w/v solution. About 1 µL of the solution was injected through the column which was maintained at 30°C. The mobile phase consisted of a mixture of acetone (TEDIA Company, Inc., Fairfield, Ohio, USA) and acetonitrile (Merck KGaA, Darmstadt, Germany) in a volume-to-volume ratio of 63.5:36.5 and at a fixed flow rate of 0.25 mL/min. TAG peaks were identified based on the retention times of TAG standards and from the earlier published literature (Ghazali *et al.*, 1995; Haryati *et al.*, 1998; Sulaiman *et al.*, 1997). The TAGs were quantified using the peak area normalisation method. All TAGs concentrations were normalised based on the total TAG present in the sample. Isomers of TAGs are unable to separate using this method. Analyses were carried out in duplicate.

Fatty Acid Composition

Preparations of fatty acid methyl ester (FAME) for the liquid oil and the gelators were conducted using the boron trifluoride method according to ISO 12966-2:2011 (ISO, 2011). FAME was investigated

by using 430-GC gas chromatography (Bruker, Germany). One μL of the sample was injected into the SGE BPX70 column with a dimension of $60\text{ m} \times 0.25\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$. The instrument was fitted with a flame ionisation detector (FID). The carrier gases used were hydrogen with a ratio of 1:100 with air and a flow rate of 0.8 mL/min . Detector and injector temperature were both set at 240°C . The separation of FAME was performed under the isothermal condition with a temperature of 185°C . The standard material used for the fatty acid identification was RM6 FAME mix purchased from Supelco.

Preparation of Oleogels

Oleogel sample was prepared by adding 3% w/w of PBA gelator into 200 g of palm superolein of IV 64. The mixture was heated in an oven for an hour at 90°C for the melting of the gelator materials. The mixture was then homogenised by manually stirring using a glass rod until fully dissolved and after which the heating was extended for an additional 15 min. The oleogel mixtures were transferred to three plastic containers, each container being filled with 40 g of the oil mixture. The samples were transferred and incubated at three different temperatures (5°C , 15°C and 25°C) for three days (day 0 denoted as the day of sample preparation) to obtain the oleogels. The same preparation method was conducted using 3% w/w SFW and 8% w/w MGHO gelators. The selection of gelator dosages was based on the indication from the previous study (Saw *et al.*, 2020). The preparation was conducted in duplicate for each oleogel. The oleogels were analysed for their melting properties and rheology properties.

Rheology

The rheological analysis of the oleogel was conducted using Haake Rheostress 600 equipped with a compressor, a water circulator and a universal temperature controller, and a 35 mm parallel-plate geometry. The mixture of the appropriate gelator with palm superolein was melted and homogenised in a 90°C oven. Approximately 100 g of the mixture was placed into a polypropylene plastic container. The samples were left at room temperature for an hour before transferring into incubators set at temperatures of 5°C , 15°C and 25°C . The measurements were conducted from day 1 to day 3. The plate was pre-conditioned to the storage temperature before performing the test. All samples were handled gently to avoid structural damage during the transfer from the incubators. The sample was removed from the incubator and immediately loaded on the temperature-controlled plate geometry at the storage temperature using a stainless-steel spatula. Oscillatory stress sweep was performed at 0 to 1000 Pa with 1 mm gap and 1 Hz

frequency to determine the storage modulus (G') and loss modulus (G'') [method modified from Doan *et al.* (2017) and Patel *et al.* (2015)]. For each type of gelator dosage and palm superolein combination, two experimental replicates were performed, while measurement was done in duplicate. The G'_{LVR} and G''_{LVR} values were determined from the G'_{LVR} and G''_{LVR} curves in the linear viscoelastic region (LVR). It is the constant value obtained from the curves at the LVR. The critical stress value was determined from the G'_{LVR} . It is the point at which the G' curve starts to deviate. After running the oscillatory sweep experiments at the storage temperature, the most suitable strain amplitude was selected and used for the frequency sweep experiments. The frequency sweep experiments were measured between 1 to 100 Hz and the G' and G'' were obtained. The data for the analysis was collected using RheoWin software. The jobs required for analysis were selected using Job Manager.

Thermal Properties by Differential Scanning Calorimetry (DSC)

The thermal properties of the gelators in the bulk stage were measured using a Perkin-Elmer DSC (DSC 8000) equipped with an autosampler. The instrument was calibrated using indium by a temperature ramp of 120°C to 180°C at a rate of 5°C/min . Volatile sample pans made of aluminium were used. The sample weights used were from 5-10 mg with an empty sample pan as the reference. The sample was heated from 15°C to 120°C at a heating rate of 10°C/min to determine the melting properties of the gelator. The sample was held at 120°C for 5 min to destroy the entire crystal structure. The sample was then cooled to 0°C at a cooling rate of 10°C/min for the recording of the cooling thermogram. For determination of the melting properties of the oleogels, 5-10 mg of molten oleogels samples were weighed in volatile aluminium sample pans. The sample was then kept in incubators with storage temperatures (T_s) set at 5°C , 15°C and 25°C and stored for 1-3 days for analysis. Each sample was held at T_s for 2 min. The sample was then heated from T_s to 120°C at a rate of $10^\circ\text{C min}^{-1}$. Each analysis was conducted in duplicate.

A storage extension study was conducted for PBA oleogels for verification of the inhibitory effects on the crystallisation of the superolein when stored at 15°C for 14 days. The 3% w/w PBA oleogels were prepared in the DSC sample pans and kept in a 15°C incubator. The melting properties of the oleogels during the storage (day 1 to day 14) were determined by melting the samples from 15°C to 120°C at a heating rate of 10°C/min . The enthalpy of melting for the samples was calculated using Pyris software (Perkin Elmer).

Statistical Analysis

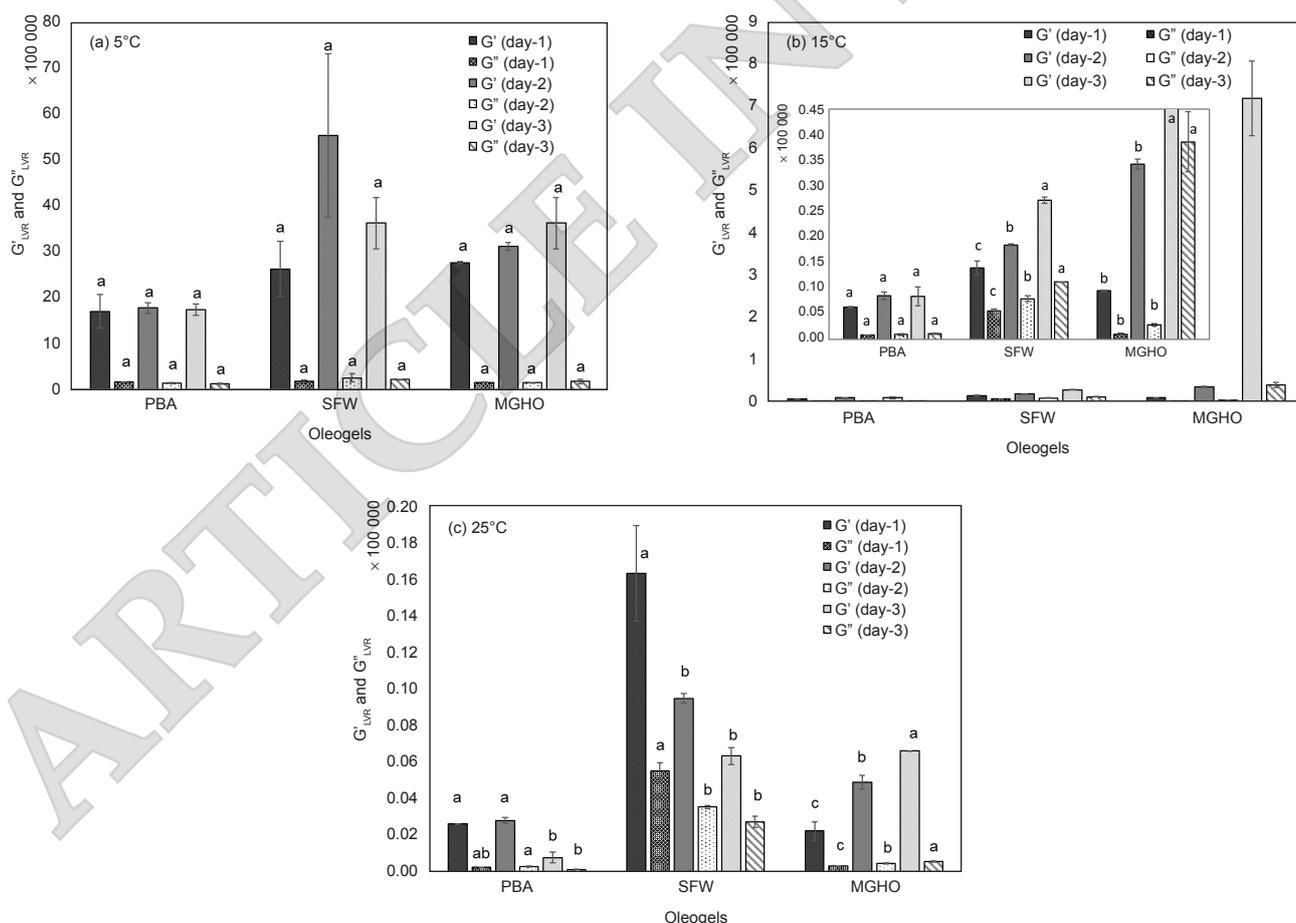
The data were analysed using the one-way analysis of variance (ANOVA) to determine the significance of the day of preparation on the enthalpy of melting and the rheological properties of the palm superolein oleogels. The software used was Minitab 16.2.

RESULTS AND DISCUSSION

Effect of Storage Conditions on Rheology of Superolein Oleogels

The effect of preparation conditions on the oscillatory rheological behaviour of the superolein oleogels was obtained via the stress sweep test at a frequency of 1.0 Hz at 5°C, 15°C and 25°C. The LVR of 3% w/w PBA, 3% w/w SFW and 8% w/w MGHO on day 1 to day 3 is shown in Figure 1.

The G' indicates solid-like behaviour, whereas G'' indicates the liquid-like behaviour of the oleogel system (Doan *et al.*, 2015). The G' values were higher than G'' for all samples, indicating that all the samples exhibited a gel-like property (Doan *et al.*, 2015; Wang *et al.*, 2019). The G'_{LVR} and G''_{LVR} values of superolein oleogels increased with lower storage temperature. This is because the superolein oil in the gel structure easily crystallised at 5°C. The high values for the rheological properties were the result of both the superolein crystallisation and the gel structure. Although a slight increase in G' was observed in the SFW and MGHO oleogels, the changes were insignificant ($p>0.05$). The oscillatory rheological behaviour of all the oleogels was not significantly different in the first three days after preparation ($p<0.05$) (Figure 1a). This is because, at 5°C, the major factor that gave rise to the high values of G'_{LVR} and G''_{LVR} was the crystallisation of the superolein. In contrast, the effect of organogelation was less significant at this temperature. Only a



Note: Significance testing was conducted to assess the oleogels over time. Different letter indicate significant differences at $p < 0.05$ according to the Tukey test.

Figure 1. G'_{LVR} and G''_{LVR} on day 1 and day 3 of superolein oleogels prepared with 3% w/w PBA, 3% w/w SFW and 8% w/w MGHO at (a) 5°C, (b) 15°C and (c) 25°C.

mild effect of organogelation on the rheological properties was observed, causing the PBA oleogels to have lower G'_{LVR} and G''_{LVR} values than other oleogels. This was probably due to the inhibitory effect of the PBA gelator that prevents the crystallisation of superolein molecules.

Solid fat content results from Saw *et al.* (2014) showed that palm superolein was fully melted at 20°C and a minimal solid fat was observed at 15°C, indicating that superolein could be slowly crystallised during storage at 15°C. Therefore, it was believed that superolein began to crystallise slowly into a semi-solid fat at 15°C. At this temperature, two events might have taken place simultaneously, *i.e.*, organogelation and superolein crystallisation. *Figure 1b* shows a significant increase of the G'_{LVR} and G''_{LVR} values during the three days of storage for the SFW and MGHO oleogels. This could be due to the increase of gel strength with increasing time after the preparation. The G'_{LVR} and G''_{LVR} values increased linearly in the SFW gels, from 14 000 Pa to 27 000 Pa, from day 1 to day 3.

The most obvious change observed was the dramatic increase of G' and G'' in the MGHO oleogels, in which G' was increased from 9500 Pa to 35 000 Pa on day 2 and further increased to 700 000 Pa on day 3 after preparation. Doan *et al.* (2015) reported that a higher G' indicated a stronger gel. In this case, the increase of G' and G'' was probably due to the slow crystallisation behaviour of the superolein liquid oil at 15°C. On day 1, the G' and G'' were relatively low, indicating PBA oleogels had the lowest G' (6000 Pa), followed by MGHO (9500 Pa) and SFW (14 000). These rheological properties were believed to be contributed by organogelation, as the superolein remained as a liquid on day 1. The organogelation is generally affected by both the type of gelator and the liquid oils, therefore each oleogels showed different trends in its rheological properties. The G' and G'' values of the PBA oleogels in the LVR did not vary significantly during the first three days after preparation ($p > 0.05$), which was similar to the observations for the 5°C storage. This again shows that the PBA gelator may inhibit the crystallisation of superolein within the gel network structure.

At 25°C, superolein appeared as a liquid, indicating the rheological property of the gels was contributed only by the microstructural development of the gelator. The G'_{LVR} of PBA oleogel was significantly reduced on day 3, indicating the occurrence of the reduction in gel strength due to the rupture of the gel structure. Therefore, the PBA oleogel was not stable at 25°C. Similar to PBA oleogels, significant reductions of G'_{LVR} and G''_{LVR} were observed for the SFW oleogels due to the decrease in gel strength. Interestingly, a significant increase of G'_{LVR} and G''_{LVR} was observed for the MGHO oleogel during the third day of storage,

which indicates a possible increase of gel strength or the formation of more crystals. The increase in G'_{LVR} and G''_{LVR} could be due to the agglomeration of the MGHO crystals and the high saturation component in the superolein during prolonged storage at room temperature. Saw *et al.* (2017) and Smith *et al.* (2011) mentioned that compounds with identical acyl groups to the crystallising species can join the crystal matrix by acting at the growth site and altering the morphology of the crystals. Similar to our system, the major component in MGHO is monoacylglycerol with a fatty acid chain lengths of C16 and C18, which are very similar to the fatty acid of the superolein. Therefore, these acylglycerols could agglomerate into larger crystals during storage, thus, increasing the G'_{LVR} and G''_{LVR} .

The critical value stress was determined from the oscillatory stress sweep from LVR. It is the point at which the G' curve starts to deviate. At stresses below critical stress value, G' and G'' curves displayed a plateau trend due to zero-permanent deformation (Doan *et al.*, 2015). Above this critical point, the oleogels underwent irreversible or permanent deformation, causing a decrease in G' and G'' (Doan *et al.*, 2015). According to Bot and Agterof (2006), the critical stress value tells the stability of gels during stress sweeps and the range of stress for oleogels to have linear viscoelastic behaviour during processing. The critical stress value for all oleogels is summarised in *Figure 2*.

Similar to the previous G'_{LVR} and G''_{LVR} results shown in *Figure 1*, the critical stress value was also dependent on the type of gelator, storage temperature and duration of storage. For oleogels stored at 5°C, the oleogels showed similar patterns according to the type of gelator, except for the SFW oleogel, where a slight increase in the critical stress value was observed with longer storage time. The slight increase could be caused by an increase in the gel strength during the third day of storage.

At 15°C, the critical stress values increased over the storage time for the SFW and MGHO oleogels, shown in *Figure 2b*. This finding revealed that the critical stress values were proportional to their G'_{LVR} and G''_{LVR} values. This was not the case for SFW stored at 25°C, as the reduced G'_{LVR} and G''_{LVR} values during storage did not result in the decrease in critical stress values but remained constant throughout the storage. In other words, the reduction of the G'_{LVR} and G''_{LVR} values in the SFW oleogels did not affect the stability of the gels, as deformation can only occur when stress beyond the critical stress value is applied (Bot and Agterof, 2006).

Frequency sweeps were conducted to evaluate the time-dependent deformation behaviour of the oleogels at a stress value within their LVR (Doan *et al.*, 2015). Based on the previous results, the oleogels formed at 15°C showed interesting

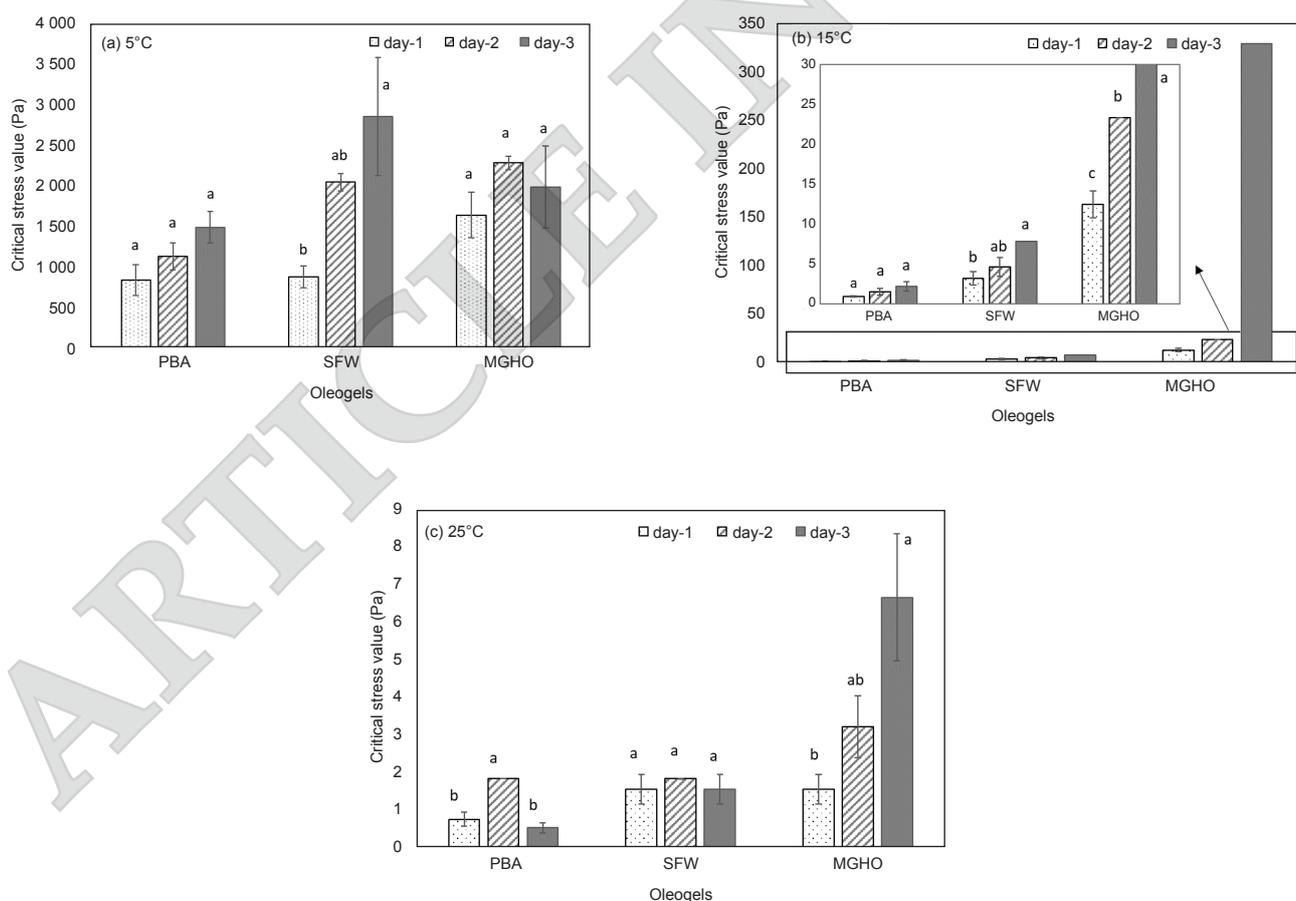
rheological behaviours in which the G'_{LVR} , G''_{LVR} and the critical stress values increased drastically with longer times after preparation; the frequency sweep curves for the oleogels are discussed below and shown in Figure 3.

As expected, the trend of moduli values of the G' and G'' curves in the frequency sweeps were consistent with their G'_{LVR} , G''_{LVR} and critical stress values shown in Figures 1 and 2. An increase in the G' and G'' moduli values was observed for the SFW and MGHO oleogels, and this was probably due to the slow crystallisation of superolein at 15°C. For all oleogels, the G' and G'' curves were almost linear, with G' being higher than G'' . This indicated that the oleogels were in good tolerance with the rate of deformation within the tested time frame (Doan *et al.*, 2015). As the angular frequency increases, the PBA and SFW oleogels showed a slight upward trend in the G' and G'' curves, indicating weak gel characteristics (Bin Sintang *et al.*, 2017; Doan *et al.*, 2015; Trappe and Weitz, 2000).

Towards the end of the test at a high angular frequency of nearly 100 Hz, an increase of G' was observed for the SFW oleogel on day 3; this was thought to be due to the deformation in the gel structure. On the other hand, the MGHO oleogels analysed on day 1 and day 2 showed the least frequency dependence, as constant moduli values were observed during the frequency sweep, implying that MGHO formed a stronger gel compared to the others (Patel *et al.*, 2015). However, a slight increase in the gradient of elastic moduli for MGHO oleogel was observed on day 3, which indicates an increase of frequency dependency or a reduced gel strength with longer storage times.

Effect of Preparation Conditions on Melting Behaviour of Superolein Oleogels

The thermal behaviour of superolein oleogels was conducted to study the effect of storage temperature and duration on the melting



Note: Significance testing was conducted to assess the gels over time. Different letters indicate significant differences at p < 0.05 according to the Tukey test.

Figure 2. Critical stress value on day 1 to day 3 of superolein oleogels prepared with 3% w/w PBA, 3% w/w SFW and 8% w/w MGHO at (a) 5°C, (b) 15°C and (c) 25°C.

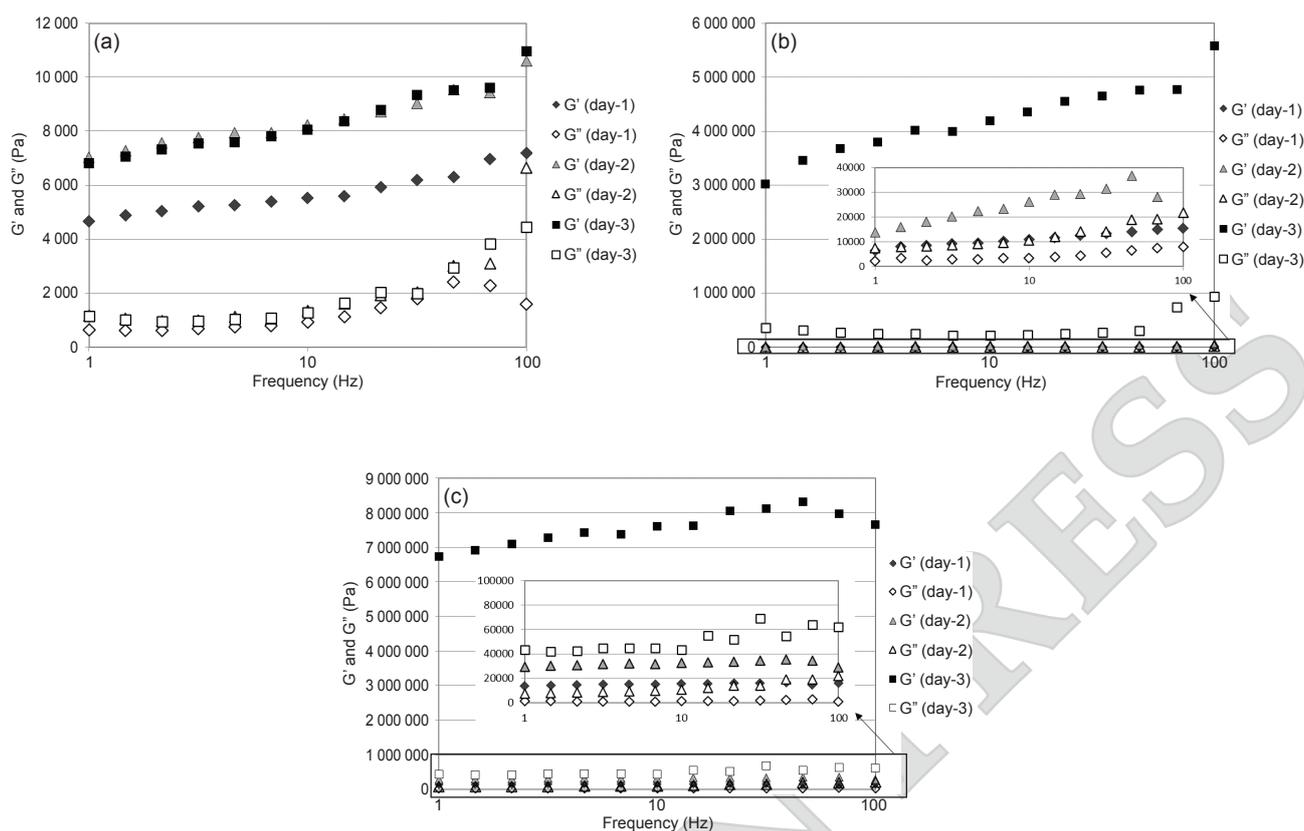


Figure 3. Frequency sweep on day 1 to day 3 of superolein oleogels prepared with (a) 3% w/w PBA, (b) 3% w/w SFW and (c) 8% w/w MGHO at 15 °C.

behaviour of superolein oleogels produced with a different type of gelators. The chemical nature and molecular composition of gelators are very important to understand thermodynamic results in the oleogel systems (Blake *et al.*, 2014). Figure 4 shows the melting profiles of superolein oleogels from PBA, SFW and MGHO melted from their respective T_s from day 1 to day 3. The results show that the short storage duration did not affect the melting properties of PBA oleogels when storing at 15°C and 25°C. Besides, an almost identical melting peak profile was observed consistently at 44°C for all PBA oleogels stored at different temperatures, representing the melting of the gel structure or the deformation of the gel structure upon application of heat Figure 4a. This indicates that all the gel networks present in the PBA oleogels were identical even when they were stored at different temperatures.

At 5°C storage, a sharp peak was observed at 16°C for PBA oleogels analysed on day 2 and day 3. This can be associated with the melting of palm superolein TAG that crystallised during prolonged storage at low temperatures. This sharp peak was absent on day 1, which indicates that the liquid component was not crystallised on day 1.

Interestingly, the melting of liquid oil did not affect the gel structure as the sample continued to melt at the same melting profile as other PBA oleogels stored at higher temperatures.

Similar to the PBA oleogels, an endotherm with a peak at approximately 57°C was observed for all SFW oleogels. This indicates that T_s did not affect the melting of the gel structure. However, unlike the PBA oleogels, the storage duration seemed to affect the melting profiles of the SFW oleogels when stored at 5°C and 15°C. The peak intensity at 24°C increased when the gel was stored at 15°C because more crystals were formed with longer storage duration, and therefore more heat was required to melt the liquid oil crystals. This result is consistent with the rheological behaviour of the SFW oleogels, as shown in Figures 1 and 2. The DSC thermogram proved that a drastic increase in G'_{LVR} , G''_{LVR} and critical stress values was due to the slow crystallisation of some TAG components in the superolein within the gel structure. The impact of the crystallisation of superolein was more pronounced in SFW and MGHO oleogels as both of the gel structures were formed by crystalline networking. Table 1 shows the acylglycerol composition of the superolein used in the preparation of the oleogels

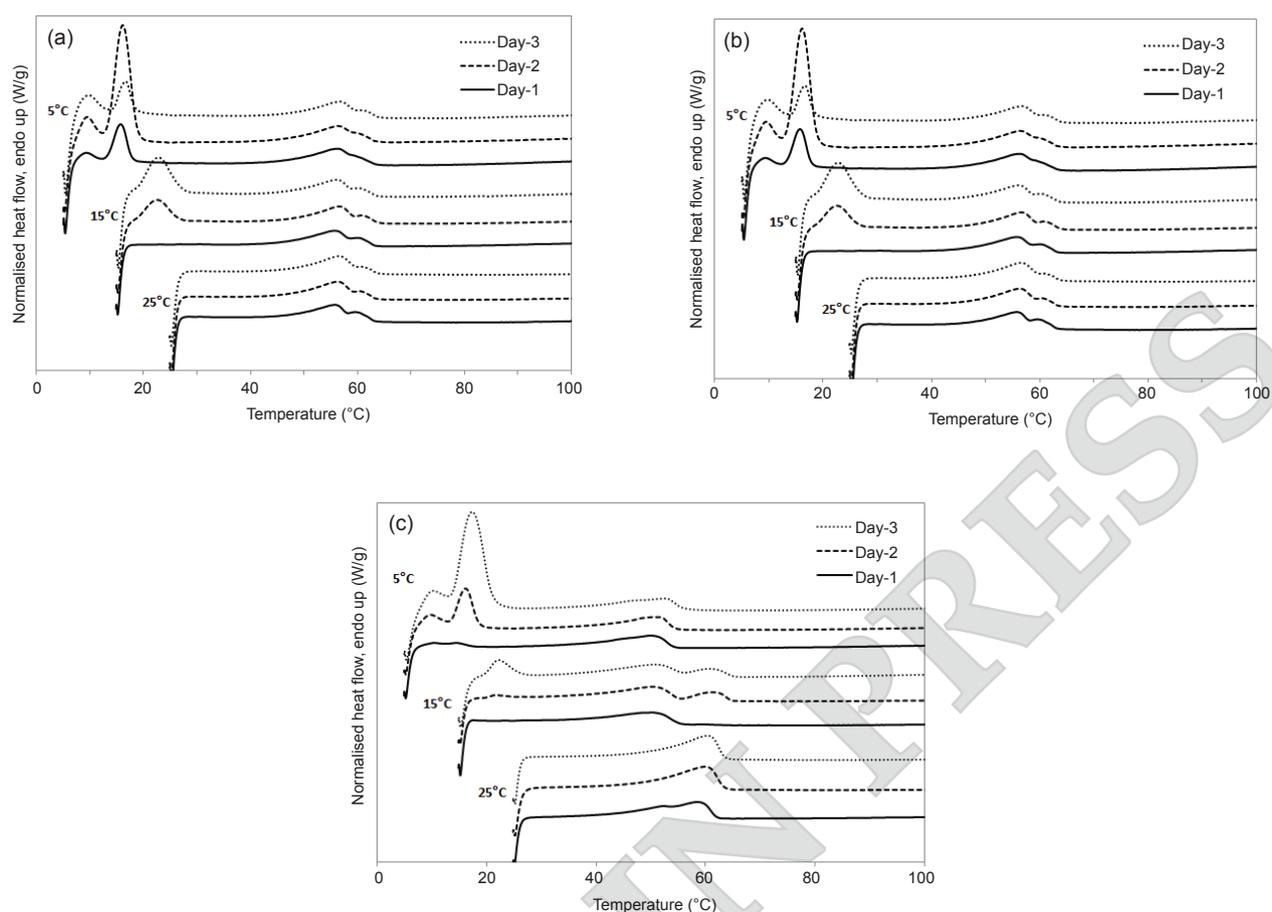


Figure 4. Melting thermograms on day 1 to day 3 of superolein oleogels prepared with (a) 3% w/w PBA (b) 3% w/w SFW and (c) 8% w/w MGHO at 5°C, 15°C and 25°C.

for this study. Superolein, which contained 19.11% of POP and 36.60% of POO, were easily crystallised at 5°C. A sharp peak at 17°C for SFW oleogels stored at 5°C was also detected due to the crystallisation of these superolein TAGs.

TABLE 1. NORMALISED TAG COMPOSITION (AREA %) OF PALM SUPEROLEIN IV 64 (POoIV64)

| Triacylglycerol | Palm superolein (area %) |
|-----------------|--------------------------|
| OLL | 0.67 ± 0.01 |
| PLL | 2.97 ± 0.05 |
| MLP | 0.57 ± 0.05 |
| OLO | 2.32 ± 0.03 |
| PLO | 12.81 ± 0.10 |
| PLP | 11.73 ± 0.01 |
| OOO | 6.38 ± 0.04 |
| POO | 36.59 ± 0.02 |
| POP | 19.11 ± 0.12 |
| SOO | 3.81 ± 0.06 |
| POS | 2.73 ± 0.06 |
| SOS | 0.31 ± 0.03 |

Note: O - oleic acid; L - linoleic acid; P - palmitic acid; S - stearic acid.

The peak intensity did not show an upward trend like those samples stored at 15°C because the crystals formed were highly unstable and easily melted during transferring from the incubator to perform the analysis. Unlike the other oleogels, MGHO oleogels were shown to have very different melting profiles when they are kept at different temperatures. At 25°C, only a broad endotherm with a peak of 59°C was detected on day 1. The peak intensity slightly increased and shifted to a higher temperature when stored for an additional 1 or 2 days. This could be due to the rearrangement of crystals during storage strengthening the gel network, which required additional energy to melt the oleogel. This observation was also consistent with the rheological behaviour, where a small increase in the G'_{LVR} and critical stress values was observed.

Interestingly, the melting profiles of the MGHO oleogels were very different over the third day of storage at 15°C. On day 1, only a single endothermic peak was observed at approximately 51°C. An additional peak at 62°C started to appear from day 2 onwards while another peak in the low-temperature region of 23°C was observed on day 3. These findings

indicate that rearrangement of the crystal structure could have occurred during the third day storage period. Alternatively, this change could also be due to the polymorphic transition of the MGHO crystals from β' -polymorph to a more stable β polymorph. These two possibilities were also reported by Bin Sintang *et al.* (2017), in which the sunflower oil oleogels formed with hybrid gelators of phytosterol-monoglycerides showed a significant increase in the melting temperature during isothermal storage at 5°C. Interestingly, their study showed that the single component monoglyceride oleogel produced with sunflower oil showed insignificant change in the melting point upon storage, which was different from our finding. This indicated that the change observed in our study could be due to the use of superolein. On day 1, the MGHO gelator formed an entanglement of large crystal network structures that entrapped the superolein. According to Table 2, the MGHO and liquid oils contained fatty acids with a similar fatty acid chain length of C16 and C18, in which the palmitic acid (C16:0) for POoIV64 and MGHO were detected at 36.7% and 40.9%, respectively. This similarity has resulted in the high solubility of the gelator in superolein affecting its gelling ability (Doan *et al.*, 2015).

TABLE 2. FATTY ACID COMPOSITION (area %) OF THE PALM SUPEROLEIN AND THE GELATORS

| Acylglycerol | POoIV64 | MGHO | PBA |
|--------------|------------|------------|------------|
| 12:0 | 0.4 ± 0.0 | 0.2 ± 0.0 | 0.7 ± 0.0 |
| 14:0 | 0.9 ± 0.0 | 0.9 ± 0.0 | 0.1 ± 0.0 |
| 16:0 | 36.7 ± 0.1 | 40.9 ± 0.1 | 1.6 ± 0.0 |
| 16:1 | 0.3 ± 0.0 | - | - |
| 18:0 | 3.5 ± 0.0 | 56.8 ± 0.1 | 32.6 ± 0.1 |
| 18:1 | 45.2 ± 0.1 | 0.2 ± 0.0 | 22.8 ± 0.1 |
| 18:2 | 12.4 ± 0.0 | 0.2 ± 0.0 | 3.5 ± 0.1 |
| 18:3 | 0.3 ± 0.0 | - | - |
| 20:0 | 0.2 ± 0.0 | 0.6 ± 0.0 | 9.8 ± 0.0 |
| 20:1 | - | - | 0.1 ± 0.0 |
| 22:0 | - | 0.1 ± 0.0 | 26.8 ± 0.0 |
| 24:0 | - | - | 1.8 ± 0.0 |

Note: POoIV64 - palm superolein; MGHO - fully hydrogenated palm monoacylglycerols; PBA - polyglycerol behenic acid ester.

Storage at 15°C has caused some of the saturated components in the superolein such as POP and some diacylglycerols to have tendency to interact with the MGHO crystals, which mostly consist of C16:0 and C18:0 fatty acids. The original crystal structure was then rearranged and aggregated into larger crystals that melted at higher temperatures. This explains why the additional peak appeared in the melting curves on day 2 and day 3. On day 3, the lower melting TAGs in the superolein started to crystallise within the large crystal network. The formation of

these crystals did not affect the crystalline structure that entrapped the liquid oil, as these crystals were first melted at 23°C. The gel crystalline structure was then melted from 45°C to 68°C. Such behaviour is the same as those oleogels kept for two days. This explanation can be correlated with the rheological behaviour data, in which the G'_{LVR} , G''_{LVR} and critical stress values drastically increased from day 1 to day 3 of storage, as shown in Figure 1b and Figure 2b.

Overall, the MGHO oleogels melted at the highest temperature, followed by SFW and PBA oleogels at the T_s . This could be due to the presence of the high amount of MGHO gelator used (8% w/w) in the oleogel formulation, which led to a high saturation content in the gel that rendered it the most thermally stable among the tested oleogels. Nevertheless, the melting peak for the SFW oleogels was approximately 57°C, which was much higher than that of the PBA oleogels, which melted at approximately 45°C. Therefore, these findings show that SFW oleogels have better thermal stability than PBA oleogels.

Verification of the Crystallisation Inhibitory Effect of PBA Oleogels

The DSC analysis again showed that PBA may have an inhibitory effect on the crystallisation of superolein, especially when stored at 15°C (Figure 4a). A storage extension for 14 days was conducted to verify this hypothesis. The DSC melting curves of PBA oleogels are shown in Figure 5. The melting profiles remained the same until day 8 and a very obscure broad endothermic peak was observed from day 1 to day 8. There were small but noticeable differences between the melting curves. One-way ANOVA revealed that the increase in enthalpy on day 8 was significant. However, the melting curves returned to their initial profiles between day 9 and day 12, showing that the enthalpy of melting (ΔH_m) was not significantly different from the oleogel on day 1. This indicates that the increase of ΔH_m on day 8 could be an outlier due to experimental error. As mentioned earlier, the melting curves remained stable until day 13, enabling the detection of a broad peak from 22°C to 35°C, followed by a steady melting of the sample at a peak of 44°C, as in those samples analysed from day 1 to day 12.

The curves were analysed and ΔH_m was determined and plotted in a bar chart (Figure 6). This analysis was able to quantify the total heat required to melt the oleogels during the 14-days storage period. The intensity of this broad peak has further increased on day 14, causing the melting profile to skew slightly to 42°C suggesting a change in the gel structure occurred on day 13. The appearance of the broad peak from 22°C to 35°C could be caused by the crystallisation of superolein, causing breakage of the gel structure.

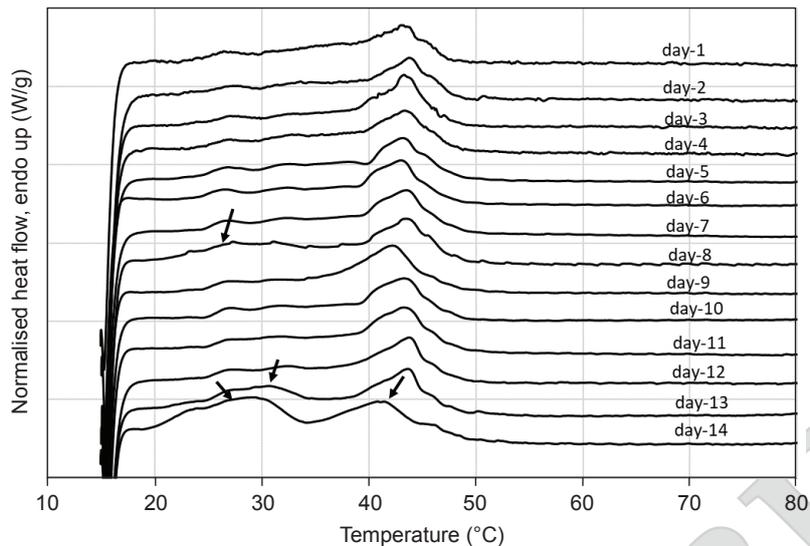


Figure 5. DSC melting curves for 3% w/w PBA superolein oleogels stored at 15°C for 14 days.

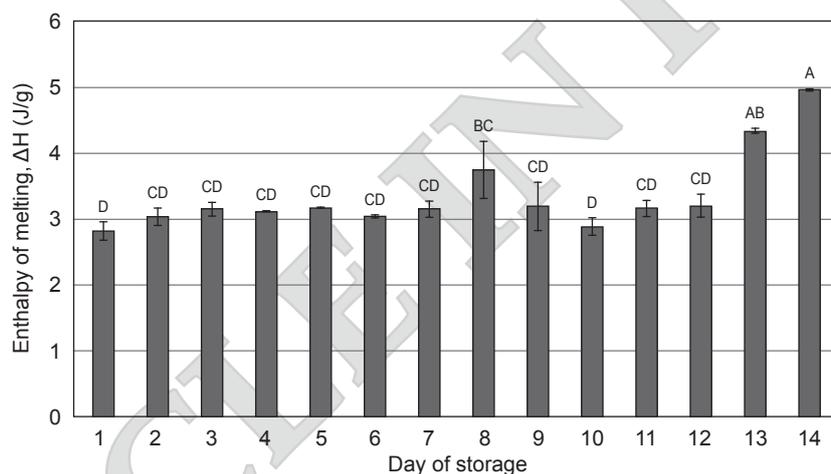


Figure 6. Enthalpy of melting for 3% w/w PBA superolein oleogels stored at 15°C for 14 days.

This observation was different from SFW and MGHO oleogels as the formation of more crystals increased the rheological properties of the SFW and MGHO oleogels. This is because the type of oleogelation in PBA oleogels was different from that of SFW and MGHO oleogels. The PBA oleogels is a self-assembly type of oleogels. Thus, the formation of more crystals did not further strengthen the gel structure but break the self-assembly structure formed by the PBA gelator. The rupture of the gel structure resulted in lower gel strength, as the peak of melting was shifted to a slightly lower temperature on day 14. This proves that PBA did not completely inhibit the crystallisation of superolein, but only caused a delay in the crystallisation process.

CONCLUSION

The investigation of the effect of storage temperature and duration revealed that both factors affect the rheological and melting properties of oleogels. In conclusion, the oleogelation of superolein oleogels happened when enough supercooling was provided. The temperature of 25°C was insufficient to supercool the oleogelators to form stable oleogels. Therefore, the produced oleogels demonstrated poor rheological and melting properties. During storage at 15°C, some high melting components in superolein showed the tendency to slowly crystallise, leading to gradually elevated rheology parameters and enthalpy of melting in SFW and MGHO oleogels. This effect

was not observed for PBA oleogels, which indicates that the PBA prevented or delayed crystallisation of the superolein molecules at 15°C. An extended storage study revealed that PBA delays rather than inhibit the crystallisation of superolein. At 5°C, high-melting components in superolein tended to crystallise and resulted in much higher G'_{LVR} , G''_{LVR} and critical stress values. As expected, the use of palm superolein in oleogels formation showed different characteristics compared to the oleogels produced from other soft vegetable oils. This is because the high melting components in the superolein may take part in the oleogelation via crystallisation at low storage temperature, which resulted in a unique characteristic of oleogels.

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