

# PHASE BEHAVIOUR OF HIGH, MEDIUM AND LOW MELTING FRACTIONS IN LAURIC FAT BLENDS FORMULATED BASED ON MELTING TRIACYLGLYCEROL GROUP

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## ABSTRACT

Lauric fat blends aimed for bakery shortening were prepared as a ternary mixture characterised by three distinct melting peaks on their differential scanning calorimeter (DSC) melting thermograms. Those melting peaks closely correlated to the high, medium, and low melting fractions (HMF, MMF, and LMF) in the blends. In the simpler binary mixture, hard fats, (i.e. palm stearin and fully hydrogenated rapeseed oil) formed an ideal solubility in different liquid oils [i.e. medium chain triacylglycerol oil (MCT-oil) and high oleic sunflower oil (HOSO)]. However, slight deviations from ideality were observed when liquid oils were replaced by lauric oils (i.e. palm kernel oil and coconut oil). In the more complex ternary mixture, the HMF formed an ideal solubility in both the MMF and LMF within the range of given formulas. In addition, the interaction of solid crystals in lauric fat blends was of monotectic behaviour as shown in the isosolid diagram. Nevertheless, the influence of solubility seemed to override that of solid interaction. Both the solubility curves and isosolid lines can provide valuable information about the interaction of HMF, MMF, and LMF in lauric fat blends. Therefore, they are useful for improving the formulation of plastic fats.

**Keywords:** lauric, fat blend, tag group, solubility, isosolid, phase behaviour.

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## INTRODUCTION

Lauric fat blends in this research are a ternary mixture of a lauric oil [i.e. palm kernel oil (PKO) or coconut oil (CO)] with two other vegetable oils and fats prepared for the production of plastic fats (e.g. shortening, margarine, and fat spread). Lauric fat blends can be formulated based on melting

triacylglycerol (TAG) group (Nusantoro *et al.*, 2017), enabling some adjustments on the solid fat content (SFC) at temperature intervals particularly from 0°C-20°C and above 20°C (Nusantoro *et al.*, 2013), to have the required SFC profiles for bakery shortening production. Lauric oils are mainly composed of fully saturated medium-chain fatty acids. The TAG derived from this type of fatty acids serve as the main source of medium melting TAG. These medium melting components play an important role in developing the key functionalities of plastic fats such as structure, mechanical performance and oral properties (Chai *et al.*, 2018; Liu *et al.*, 2018).

In order to get good plasticity, both solid and liquid phases should be present in a proper proportion in the fat blends (Nusantoro *et al.*, 2016; Yanty *et al.*, 2017). Liquid oils comprise entirely of low melting components and contribute to the

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major part of the blends as the liquid phase. In addition, some amount of hard fats is added as they are required in the blends to provide high melting components that give desired appearance, texture, and mouthfeel properties (O'Brien, 2009). Medium chain triacylglycerol oil (MCT-oil) and high oleic sunflower oil (HOSO) are examples of the liquid oils while palm stearin (PS) and fully hydrogenated rapeseed oil (FHRO) are those of the hard fats. Fat and oil sources for the fat blends can thus come naturally or from fat modification.

The study of the phase behaviour of fat blends can lead to a better understanding of the interactions, occurring among the blend constituents and the various phase changes of their physical state. The knowledge of phase behaviour is of particular importance in the prediction of fat and fat blend properties, control of physical attributes, process optimisations, and eventually product quality maintenance (Timms, 1984; Saberi *et al.*, 2011). The formulated lauric fat blends have three distinct fractions differentiated by the melting point of their TAG compositions. The mixing behaviour of higher melting fractions in lower melting fractions directly relates to crystallisation behaviour of the fat blends. Moreover, there is a softening effect of LMF due to the dissolution of high-melting TAG (solute) into low-melting TAG (solvent). A solubility curve of fat blends can then be constructed to show equilibrium relationships between the temperature and the composition of solid fat in liquid oil (Zhou and Hartel, 2006).

When lower melting components do not involve in crystallisation, fat blends form an ideal solution and the solubility of high-melting TAG in low melting TAG, which follows the Hildebrand equation (Equation 1).

$$\ln x_s = -\frac{\Delta H_f}{R} \left( \frac{1}{T_m} - \frac{1}{T} \right) \quad \text{Equation (1)}$$

where  $x_s$  is the solubility of high-melting component (mole mole<sup>-1</sup>),  $\Delta H_f$  is the heat of fusion of high-melting component (J mol<sup>-1</sup>),  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T_m$  and  $T$  are melting temperatures of the high-melting component and the mixture (K), respectively. Although there are various methods to determine the melting temperature, the most preferred and widely used method is by using the differential scanning calorimeter (DSC). In the occurrence of some interactions among fat constituents, deviations from the ideal solution behaviour can be seen in a solubility curve (Walstra, 2003).

Lauric fat blends are a multicomponent system of TAG mixtures. In simpler binary TAG mixtures, phase behaviour of the blends can be either monotectic, eutectic, or peritectic depending on their molecular interaction. Moreover, physical

classification of TAG can be utilised as a method to reduce the complexity of TAG mixtures. TAG species are sorted into TAG categories that are supposed to form distinct separate solid fractions in the crystallised fat blend. In lauric fat blends, classification of TAG is based on the melting point of which four categories are formed namely heated (H), body (B), room (R), and cool (C) melting TAG groups. These groups represent the high, medium, and low melting components in the fat blends (Wesdorp *et al.*, 2005; O'Brien, 2009). Eventually, an isosolid diagram can then be constructed to investigate the type of solid solution behaviour of lauric fat blends. This pseudo-phase diagram shows lines of constant SFC at different temperatures (vertical axis) and composition (horizontal axis). For example, the isosolid line is commonly found to be a straight line parallel to the horizontal axis or to one of the lateral axes in the monotectic mixture. A eutectic mixture, on the other hand, exhibits a compression of the isosolid line which shows a constant SFC and a melting temperature below that of the individual fat. In the eutectic system, a considerable decrease of the SFC followed by softening of the fat blend is commonly observed (Timms, 1984; Zhou *et al.*, 2010).

In this study, the complex interaction of high, medium, and low melting fractions (HMF, MMF, and LMF) in lauric fat blends was investigated. The solubility of hard fats in either lauric or liquid oils was firstly observed by solubility diagram in a simpler system as binary mixtures. Then, the application of Hildebrand equation was extended to evaluate the solubility of both HMF in lower melting components and HMF/MMF in LMF as a ternary mixture of lauric fat blends. Accordingly, the isosolid diagram was constructed for lauric fat blend at different formulations. The melting group TAG formulation was employed to give different ratios of HMF to MMF as isosolid lines which can evaluate such interaction of both fractions. Any changes and deviations from ideality of both the solubility curves and isosolid lines were indicated in order to provide useful guidance for developing plastic fat products.

## MATERIALS AND METHOD

### Materials

All vegetable oils and fats are commercial products as follows: Neobee M5 as the MCT-oil (Stepan, USA), high oleic sunflower oil (Oleon, Belgium), palm stearin and palm kernel oil (Loders Crocklaan, The Netherland), coconut oil (Palko Sari Eka, Indonesia), and fully hydrogenated rapeseed oil (Palsgaard, Denmark). All other chemicals and solvents for analysis are those of the high purity grade.

## The Binary Mixtures and Lauric Fat Blends

In the first part of the investigation, six binary blends were prepared from two types of hard fats (PS and FHRO) and three types of either lauric or liquid oils (PKO, HOSO and MCT-oil) at different molar ratios of the high melting fraction from 1 to 0 with an interval of 0.1 mole mole<sup>-1</sup>. This simpler binary model of fat blends was used to study the ideal solubility of hard fats in lower melting components. The outcomes were then utilised to study the pseudo-phase behaviour of more complex ternary mixture of lauric fat blends.

Lauric fat blends were formulated based on the grouping of various TAG species according to their melting points (mp). The TAG were grouped into four namely chilled (C) (mp ≤ 5°C), room (R) (5°C < mp < 25°C), body (B) (25°C < mp < 45°C) and heated (H) (45°C ≤ mp) melting TAG groups. For example, a formulation of BH50H15 indicated that the sample consisted of 50% TAG from a combination of B and H groups and 15% TAG from H group (thus, B group had 35% TAG). The other 50% of TAG in the formulation then came from a combination of C and R groups (Nusantoro *et al.*, 2017).

In the second part of the study, two formulations of lauric fat blends were chosen. First, lauric fat blends were prepared from mixtures of FHRO, CO, and HOSO. The blends were formulated at constant BH50 and varied H from 2.5%-17.5% (seven blends, BH50 - H: 2.5/5/7.5/10/12.5/15/17.5). Second, lauric fat blends were prepared from FHRO, CO, and HOSO. The blends were formulated at constant H15 and varied BH from 50%-70% (five blends, H15 - BH: 50/55/60/65/70). Hildebrand plots and isosolid diagrams were then constructed from these formulated blends.

## Fatty Acid Composition

The fatty acid composition of the samples was determined by gas chromatography (GC) after conversion to fatty acid methyl esters (FAME) using 2 N KOH in methanol solution. The FAME were analysed by a Thermo Focus GC (Interscience, Belgium) equipped with an RTX-2330 column (cyanopropyl polysiloxane, 60 m length, 0.25 mm internal diameter, 0.2 μm layer thickness) and a flame ionisation detector (FID). FAME were identified by comparing their retention time to authentic standards. Fatty acid levels were reported as relative proportions of the total composition.

## TAG Distribution

The TAG distribution based on the equal carbon number was determined by non-aqueous reversed-phase high-performance liquid chromatography (NARP-HPLC). The chromatographic system

consisted of a Shimadzu HPLC system (Shimadzu, Japan) fitted with a 150 x 3.0 mm Alltima HP C18-HL column (Grace Alltech, Belgium), and the detection was done by an Alltech 3300 ELSD (Grace Alltech). An optimised method as previously described (Rombaut *et al.*, 2009) was used for the measurement. Elution was carried out using an acetonitrile/dichloromethane gradient at 0.72 ml min<sup>-1</sup>. The result was processed by LC solution software (Shimadzu).

## Melting Behaviour by DSC

Thermal analyses of the samples were performed on a TA Q1000 DSC (TA Instruments, USA) equipped with a refrigerated cooling system. Nitrogen was used to purge the system. The samples (5-15 mg) were hermetically sealed in aluminium pans. An empty pan was used as a reference during the measurements. The time-temperature program of the measurements was as follows: holding at 90°C for 10 min, cooling at a rate of 5°C min<sup>-1</sup> to a temperature of -70°C, holding for 10 min at that temperature to allow complete crystallisation, and then heating at a rate of 5°C min<sup>-1</sup> to 90°C. The obtained data were processed by the TA Universal Analysis 2000 software (TA Instruments).

## SFC by pNMR

SFC was measured according to the official IUPAC method by a Maran Ultra NMR (Oxford Instruments, United Kingdom) equipped with R4 cryostat cooler (Grant Instruments, United Kingdom). NMR tubes (Bruker, Germany) were used for the direct SFC measurement. The samples were prepared by the stabilising fat procedure where a tempering stage was included at 26°C for 40 hr and subsequently at 0°C for 90 min. The SFC values were then recorded at 5°C intervals from 0°C-60°C. Before each reading, the samples were conditioned for 60 min at that chosen measurement temperature.

## Determination of Solubility and Isosolid Diagrams

The solubility of the fat blends was depicted by solubility curves showing the equilibrium relationship between temperature and composition of higher melting components in lower melting components. The Hildebrand equation (Equation 1) was used in the calculation to construct the solubility diagram of which the melting point of samples was measured by DSC. Meanwhile, the SFC data (by p-NMR measurement) was used to construct the isosolid diagram following a procedure as previously reported (Timms, 1979). The solid interaction of the fat blends is then described by isosolid lines that connect points with a common SFC value.

## Texture Analysis

Texture analysis was carried out using a universal testing machine Instron 5942 (Instron, USA). A constant speed penetration was used to measure the samples as previously described (Braipson-Danthine and Deroanne, 2004). Prior to analysis, approx. 50 g lauric fat blends were completely melted at 90°C for 10 min and then stored in a thermostatic cabinet at 15±1°C for 24 hr. Four penetration tests were run on each fat blend and the data were processed by the Bluehill 3 software (Instron).

## RESULTS AND DISCUSSION

### Chemical Composition of Starting Oils and Fats

The fatty acid composition of starting oils and fats is presented in *Table 1*. Lauric oils, such as coconut oil and palm kernel oil, characterised by a high content of medium-chain saturated fatty acids namely lauric (48.90%-50.49%) and myristic (15.46%-17.70%) acids. High oleic sunflower oil is composed mainly of long-chain monounsaturated fatty acid, namely oleic acid (85.13%). Meanwhile, palm stearin and fully hydrogenated rapeseed oil consisted of long-chain saturated fatty acids with palmitic (82.19%) and stearic (89.77%) acids as their major constituents, respectively. The TAG distribution of starting oils and fats was also found to be close to the expected proportions of the relevant fatty acids as indicated in *Table 2*. When TAG were sorted based on their melting points, a handful of variables with easier physical interpretation can be obtained. It was shown that high, medium, and low melting fractions were closely related to the categorisation of TAG in the fat blends without neglecting the nature of starting oils and fats. The LMF was associated with both C and R groups while the MMF and HMF were associated with B and H groups, respectively.

### Solubility of the Simpler Binary System

Melting properties of hard fats in the binary mixtures. A pure hard-melting fat which is composed of only a few TAG species usually melts within a very narrow temperature range. Moreover, the hard fat with longer fatty acid chain-length has a higher melting point and molar enthalpy of fusion compared to the one with shorter fatty acid chain length (Zhou and Hartel, 2006). *Figures 1* and *2* showed the DSC melting thermograms of binary mixtures of hard fats (PS or FHRO) in medium melting fat (PKO) or low melting oils (HOSO or MCT-oil) at different molar ratios of the high melting fraction. Palm stearin melted completely at a lower temperature compared to FHRO in different types of solvents (PKO, HOSO, or MCT-oil) at all molar ratios. The softening effect of the solvents was also observed on which the melting point of the hard fats was depressed followed their molar ratios in the binary mixtures. For example, the peak maximum of PS and FHRO in HOSO was decreased from 61.08°C and 68.26°C to 48.93°C and 57.42°C, at 0.7 and 0.1 molar of high melting fraction, respectively. This depressed melting point of hard fats plays an important role in the formulation of plastic fats as their high melting components can result in unwanted pasty and waxy mouthfeel. The HMF is known to have a tendency to adhere to palate, teeth, and tongue (Drewnowski and Almiron-Roig, 2010; Podchong *et al.*, 2020). Higher SFC of fat blends is commonly achieved by the addition of hard fats but higher molar ratios of the high melting fraction can significantly increase the melting point of the products. Therefore, the amount of hard fat should be carefully calculated to avoid undesired textural and sensorial properties, yet still giving appropriate functional attributes to the system such as structure, stabiliser, and moisture barrier (O'Brien, 2009; Danthine, 2012; Nusantoro *et al.*, 2016).

TABLE 1. FATTY ACID COMPOSITION OF STARTING OILS AND FATS

| Fatty acid        | Samples* |        |         |        |          |
|-------------------|----------|--------|---------|--------|----------|
|                   | HOSO (%) | CO (%) | PKO (%) | PS (%) | FHRO (%) |
| Caprylic (C8:0)   | -        | 8.59   | 4.07    | -      | -        |
| Capric (C10:0)    | -        | 6.62   | 4.06    | -      | -        |
| Lauric (C12:0)    | -        | 48.90  | 50.49   | -      | -        |
| Myristic (C14:0)  | -        | 17.70  | 15.46   | 1.31   | -        |
| Palmitic (C16:0)  | 3.95     | 8.26   | 7.81    | 82.19  | 6.97     |
| Stearic (C18:0)   | 3.17     | 2.44   | 2.13    | 4.73   | 89.77    |
| Oleic (C18:1)     | 85.13    | 5.51   | 13.75   | 9.57   | 0.40     |
| Linoleic (C18:2)  | 7.75     | 1.27   | 2.23    | 1.92   | -        |
| Arachidic (C20:0) | -        | -      | -       | 0.28   | 1.96     |
| Behenic (C22:0)   | -        | -      | -       | -      | 0.90     |

Note: \*HOSO - high oleic sunflower oil, CO - coconut oil; PKO - palm kernel oil; PS - palm stearin and FHRO - fully hydrogenated rapeseed oil. Each value in the table represents the means of triplicate.

TABLE 2. TRIACYLGLYCEROL DISTRIBUTION OF STARTING OILS AND FATS

| Group     | TAG**   | Samples' |        |         |        |          |
|-----------|---------|----------|--------|---------|--------|----------|
|           |         | HOSO (%) | CO (%) | PKO (%) | PS (%) | FHRO (%) |
| Chilled   | OLL     | 0.54     | -      | -       | -      | -        |
| Chilled   | OOL     | 2.55     | -      | -       | -      | -        |
| Chilled   | OOO     | 87.99    | -      | -       | 1.15   | -        |
| Chilled   | PLO     | -        | -      | -       | 0.27   | -        |
| Room      | CaCC    | -        | 0.24   | -       | -      | -        |
| Room      | CaCLa   | -        | 2.22   | -       | -      | -        |
| Room      | LaOO    | -        | 0.43   | 1.37    | -      | -        |
| Room      | POO     | 5.24     | -      | -       | 1.50   | -        |
| Room      | LaLaO   | -        | 0.71   | 3.12    | -      | -        |
| Room      | SOO     | 3.00     | -      | -       | 0.43   | -        |
| Room      | LaMO    | -        | 0.60   | 2.78    | -      | -        |
| Room      | MLP     | 0.68     | -      | -       | -      | -        |
| Room      | PPL     | -        | -      | -       | 0.50   | -        |
| Body      | CCLa    | -        | 17.20  | 7.70    | -      | -        |
| Body      | MPO     | -        | -      | 0.44    | -      | -        |
| Body      | LaPO    | -        | -      | 2.25    | -      | -        |
| Body      | CLaLa   | -        | 22.41  | 9.78    | -      | -        |
| Body      | POP     | -        | -      | -       | 9.38   | -        |
| Body      | LaLaLa  | -        | 25.18  | 37.34   | -      | -        |
| Body      | LaLaM   | -        | 17.44  | 21.91   | -      | -        |
| Body      | POS     | -        | -      | -       | 6.37   | -        |
| Body      | LaMM    | -        | 8.98   | 8.91    | -      | -        |
| Heated    | LaMP    | -        | 3.67   | 2.68    | -      | -        |
| Heated    | LaPP    | -        | 0.93   | 0.93    | -      | -        |
| Heated    | PPP     | -        | -      | -       | 80.41  | -        |
| Heated    | SSP     | -        | -      | -       | -      | 18.12    |
| Heated    | SSS     | -        | -      | -       | -      | 81.87    |
| [chilled] |         | 91.08    | -      | -       | 1.42   | -        |
| [room]    | (Total) | 8.92     | 4.20   | 7.27    | 2.42   | -        |
| [body]    |         | -        | 91.21  | 88.63   | 15.75  | -        |
| [heated]  |         | -        | 4.59   | 3.61    | 80.41  | 99.99    |

Note: \*HOSO - high oleic sunflower oil; CO - coconut oil; PKO - palm kernel oil; PS - palm stearin and FHRO - fully hydrogenated rapeseed oil. Each value in the table represents the means of triplicate.

\*\*Arranged fatty acid Ca - caprylic; C - capric; M - myristic; La - lauric; P - palmitic; S - stearic; O - oleic and L - linoleic.

In an ideal solubility mixture, the type of solvents (*i.e.* medium melting fat and liquid oils) does not give any different influence as long as those solvents do not interact with the high melting fraction during solidification. In this investigation, however, the melting thermogram showed some deviations on the onset of both binary mixtures at melting peaks of the high melting fraction. When the interval of melting peaks between the solute and the solvent was getting narrow such as in PKO mixtures (*Figures 1c* and *2c*), the deviations of the onset on the baseline were getting apparent. Some exothermic peaks, albeit few and small, were also observed on those deviated baselines. The presence of exothermic peak on the melting thermogram might indicate recrystallisation or polymorphic changes of the fat crystals. When molecular volume, shape, and polymorph of the

components in the mixture differ considerably yet those components have a comparable melting point, the eutectic system tends to take place (Timms, 1984).

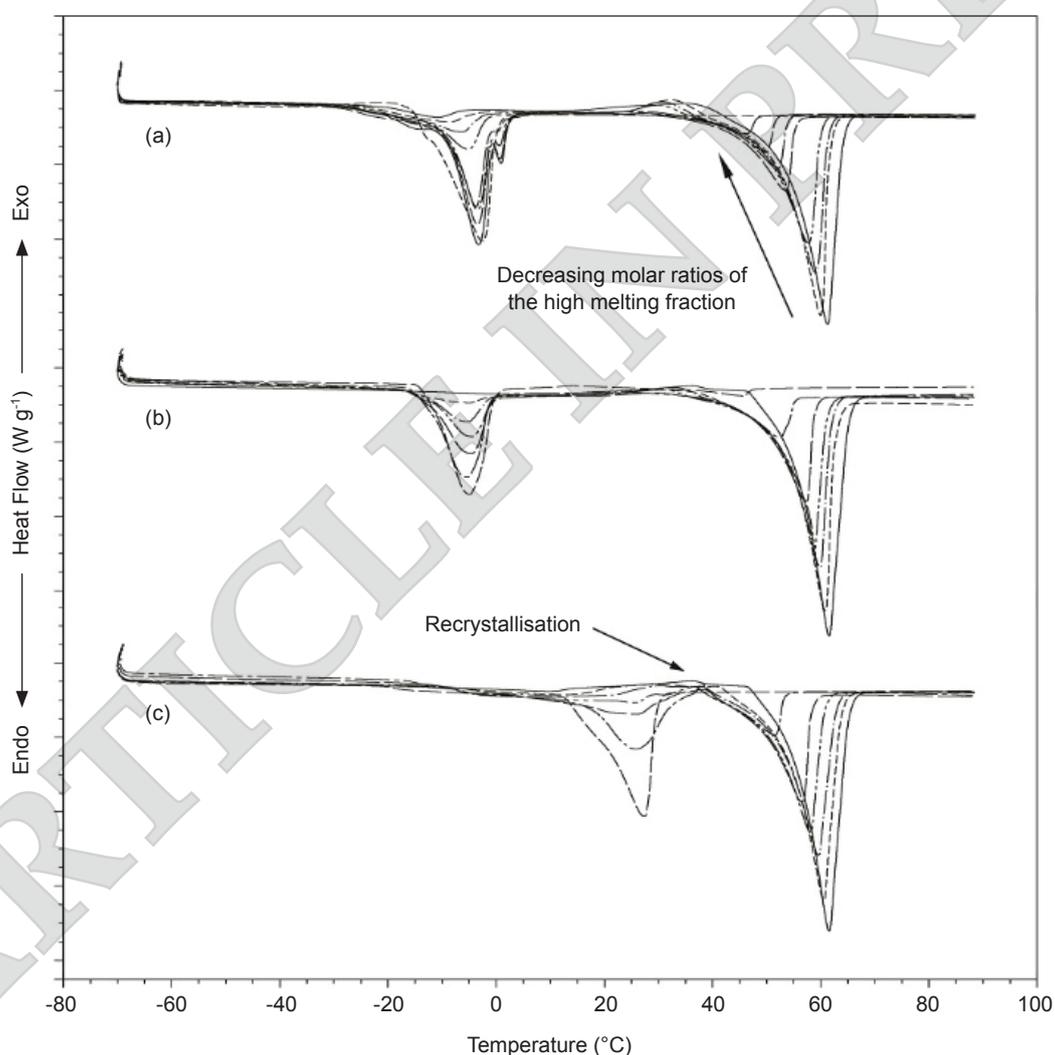
Meanwhile, the shape of melting peaks of the high melting fractions at different molar ratios was generally comparable for both PS and FHRO binary mixtures. Lower molar ratios of hard fats gave smaller peaks with shifts of peak maximum to the lower temperatures. *Table 3* showed that the type of solvents weakly influenced the experimental melting point ( $T_m$ ) of the hard fats. Palm stearin had lower experimental  $T_m$  than FHRO at the interval temperature range from 63.12°C-63.68°C and from 70.12°C-70.30°C respectively, as influenced by the different type of solvents. Those values were comparable and in agreement with the melting point of pure systems.

**TABLE 3. THE EXPERIMENTAL MELTING TEMPERATURE ( $T_m$ ) AND HEAT OF FUSION ( $\Delta H_f$ ) OF HARD FATS IN DIFFERENT LOWER MELTING OILS**

| Fat blend <sup>*</sup> | Melting properties <sup>**</sup> |  |
|------------------------|----------------------------------|--|
|                        | Melting temperature (°C)         | Heat of fusion (kJ mol <sup>-1</sup> ) |
| PS in MCT-oil          | 63.12 ± 0.07                     | 155.80 ± 1.87                          |
| PS in HOSO             | 63.30 ± 0.00                     | 145.41 ± 0.03                          |
| PS in PKO              | 63.68 ± 0.13                     | 115.44 ± 2.81                          |
| FHRO in MCT-oil        | 70.13 ± 0.03                     | 187.91 ± 1.26                          |
| FHRO in HOSO           | 70.12 ± 0.05                     | 174.51 ± 1.49                          |
| FHRO in PKO            | 70.30 ± 0.02                     | 146.09 ± 0.71                          |

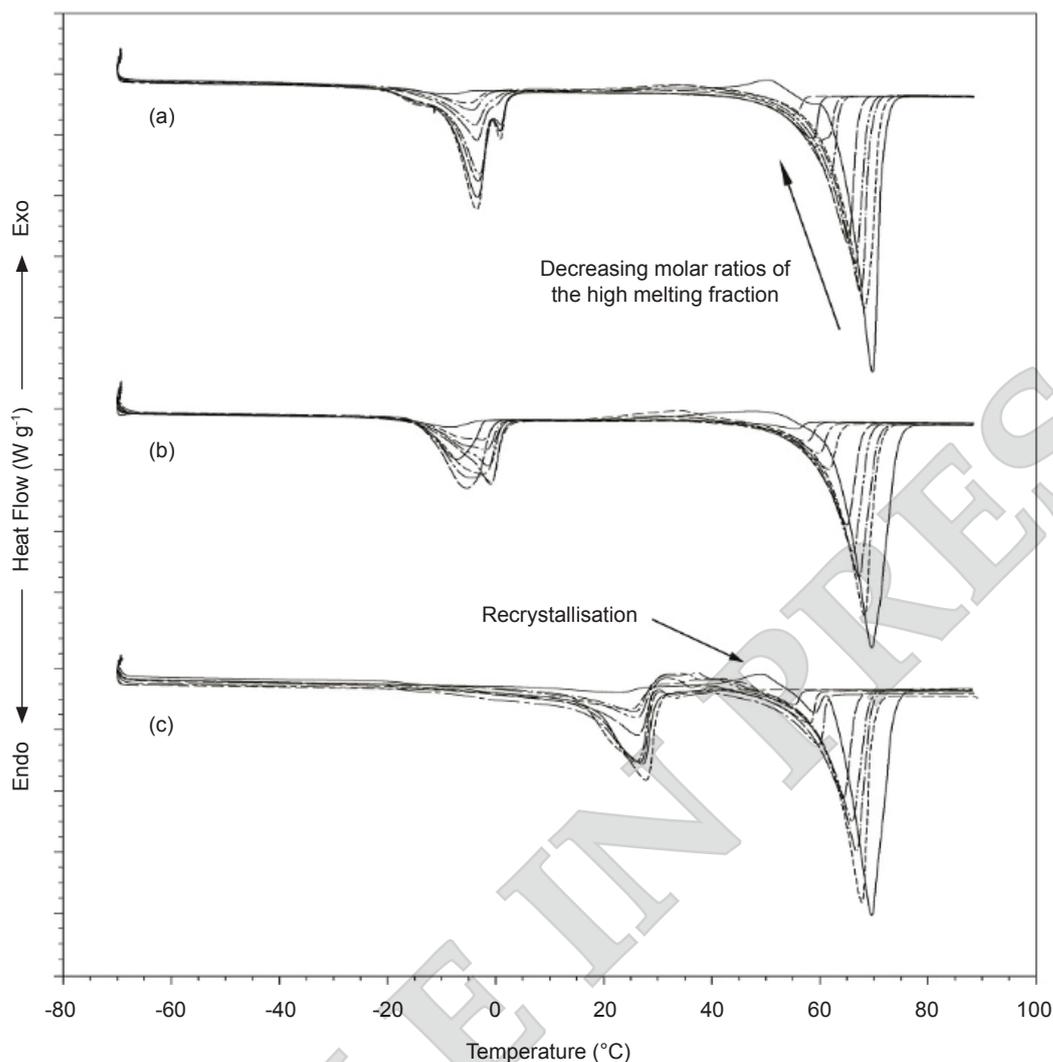
Note: \*MCT-oil - medium chain triglycerides oil; HOSO - high oleic sunflower oil; PKO - palm kernel oil; PS - palm stearin and FHRO - fully hydrogenated rapeseed oil.

\*\*Hildebrand equation is used in the calculation using data from differential scanning calorimeter (DSC) measurements. Each value in the table represents the means of triplicate.



Note: DSC - differential scanning calorimeter; PS - palm stearin; MCT-oil - medium chain triacylglycerol oil; HOSO - high oleic sunflower oil and PKO - palm kernel oil.

Figure 1. DSC-melting behaviour of binary mixtures of PS in (a) MCT-oil, (b) HOSO, and (c) PKO.



Note: DSC - differential scanning calorimeter; FHRO - fully hydrogenated rapeseed oil; MCT-oil - medium chain triacylglycerol oil; HOSO - high oleic sunflower oil and PKO - palm kernel oil.

Figure 2. DSC-melting behaviour of binary mixtures of FHRO in (a) MCT-oil, (b) HOSO, and (c) PKO.

On the other hand, the experimental heat of fusion ( $\Delta H_f$ ) of the hard fats was altered considerably depending on the type of solvents used in the binary mixtures. The liquid oils composed only of low melting TAG (*i.e.* MCT-oil and HOSO) slightly affected and resulted in comparable values of the experimental heat of fusion. The experimental  $\Delta H_f$  of PS in MCT-oil and HOSO were 155.80 and 145.41 kJ mol<sup>-1</sup>, respectively while those of FHRO were 187.91 and 174.51 kJ mol<sup>-1</sup>, respectively. Nevertheless, PKO as the solvent in the binary mixtures caused considerably lower values of the experimental heat of fusions. The experimental  $\Delta H_f$  of PS and FHRO with PKO as the solvent were 155.80 and 145.41 kJ mol<sup>-1</sup>, respectively. These lower values of experimental  $\Delta H_f$  also coincided with stronger deviations on the onset of melting peaks of the hard fats. It should be taken into account that PKO contains some amount of high melting TAG such as 1-lauroyl-2-myristoyl-3-palmitoyl-*sn*-glycerol (LaMP) and 1-lauroyl-2,3-

dipalmitoyl-*sn*-glycerol LaPP (Table 2). These TAG could solidify together with the HMF of PS or FHRO thus modified its HMF composition, especially at lower molar ratios of the hard fats (meaning higher ratios of PKO, thus more LaMP and LaPP in the blends). As a result, different crystallisation behaviour and compensation of smaller  $\Delta H_f$  of LaMP/LaPP brought the experimental  $\Delta H_f$  of PS and FHRO lower.

In general, even though there were some indications of deviations from ideal solubility, the experimental  $T_m$  values were still comparable and in agreement with the values of pure systems. Meanwhile, the values of experimental  $\Delta H_f$  were also found to be comparable to those of pure systems when the solvents composed only of low melting TAG (*e.g.* MCT-oil and HOSO). As a comparison, the melting point and heat of fusion of tripalmitin (purity > 85%) are 63.4°C and 150.5 kJ mol<sup>-1</sup>, respectively (Zhou and Hartel, 2006).

**Solubility of hard fats in the binary mixtures.** The texture, mouthfeel, and melting point of plastic fats are influenced by the solubility of high-melting components in LMF of the fat blends. The melting and dissolution processes are characterised by melting enthalpy and enthalpy of dissolution of the mixtures. Hildebrand solubility equation (Equation 1) is theoretically valid when there is no enthalpy of dissolution during the process. However, it is acknowledged that fats and fat blends are a multicomponent TAG system of which some deviation from ideal solubility is commonly observed at some degrees (Humphrey and Narine, 2005).

In this investigation, the temperature of peak maximum on melting thermogram was chosen as the melting temperature ( $T$ ) of the blends for Hildebrand equation calculation. Meanwhile, the molecular weight of the samples was estimated from the average molecular weight of their fatty acid composition and it was used to convert the unit from gram to mole. The Hildebrand plot for the binary mixtures of two hard fats in three lower melting oils was then depicted in *Figure 3*. It was shown that the log value of the solubility [ $\ln(1/x_s)$ ] generally had a linear relationship with the temperature ( $1/T$ ), with a high coefficient of determination ( $R^2$ ) values. These linear relationships indicated that hard fats (PS or FHRO) might form an ideal solution with each of the lower melting oils. However, it was again noticed that hard fats diluted in PKO had solubility lines with stronger deviation from ideality compared to those of diluted in MCT-oil and HOSO, especially on the lower molar ratios. These deviations could be attributed to the changing in HMF composition of the hard fat and, thus, their crystallisation behaviours. In general, the explanations were similar to the DSC melting behaviour as already discussed above.

### Solubility of High, Medium and Low Melting Fractions in Lauric Fat Blends

Lauric fat blends were formulated as a ternary mixture composed of HMF, MMF and LMF. It was demonstrated in the simpler binary mixtures that hard fats were dissolved in either lauric or liquid oils. At the same time, the lauric oil was also shown to be dissolved in the liquid oils. Therefore, three distinct endothermic peaks were then observed on the DSC melting thermogram of lauric fat blends referring to those three fractions. Using the parameter of melting peaks of both HMF (H-group) and MMF (B-group), Hildebrand plot of FHRO lauric fat blends was constructed where the relationship between the solubility of both groups and temperature was illustrated by solubility curves as shown in *Figure 4*. We did not further elaborate the solubility of lauric fat blends with PS

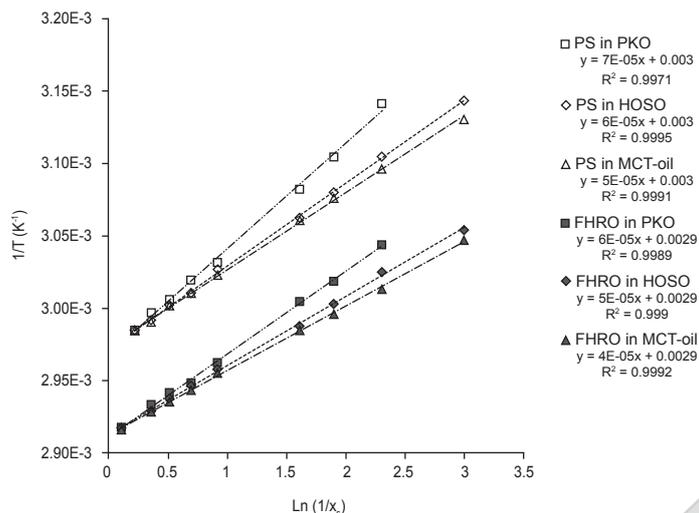
as the hard fat in this study as they had a similar pattern with that of FHRO lauric fat blends.

Lauric fat blends with FHRO as the hard fat formulated at constant BH50 with varied H from 2.5%-17.5% had two solubility curves representing the H and B groups. When the amount of H-group was increased, the amount of B-group was decreasing in order to compensate for the final sum of both groups at 50% in the blends. The changing of their ratios can be considered as the solubility of H and B groups in the LMF (C and R groups, fixed at 50%). In the case of H-group, this HMF was dissolved both in MMF (B-group) and LMF (CR-group). As a result, the solubility of H-group was similar to that of the simpler binary mixture between HMF and lower melting components. It was found from the solubility curve that H group had a good linear relationship with  $R^2$  value of 0.9782 thus showed an ideal solubility. For B-group, this MMF dissolved in the LMF at the presence of H-group fat crystals. The lower amount of B-group resulted in more solid fat of H-group in the blends. The presence of solid fat might alter the crystallisation behaviour of B-group especially when the amount of both H and B groups was always changed following different formulation of the blends. The solidification of fats in the presence of other fat crystals could change the crystallisation behaviour of fat blends from homogenous to heterogeneous nucleation. It was eventually shown that stronger deviation from ideality was indicated on the solubility curve of MMF (B-group) at which the linear relationship between the composition [ $\ln(1/x_s)$ ] and temperature ( $1/T$ ) had a lower  $R^2$  value of 0.9401.

On the other hand, FHRO lauric fat blends formulated at constant H15 with varied BH from 50%-70% had only one solubility curve in terms of H-group solubility in both MMF and LMF. Because the HMF was kept at 15% for all formulation, the solubility curve of H-group could not be drawn instead there was an average value of the correlation between the composition [ $\ln(1/x_s)$ ] and temperature ( $1/T$ ). Meanwhile, the solubility of B-group in the LMF was influenced by the presence of H-group fat crystals, now at a similar amount (15% H-group) for all blends. Since the amount of fat crystal was set constant, they affected in the same way and gave comparable influences on the solubility of B-group in all blends. As a consequence, the solubility of B-group in lauric fat blends formulated at H15 was closer to ideality than that of blends formulated at BH50. Better linearity on the solubility curve of lauric fat blends formulated at H15 was shown by a higher  $R^2$  value of 0.9954.

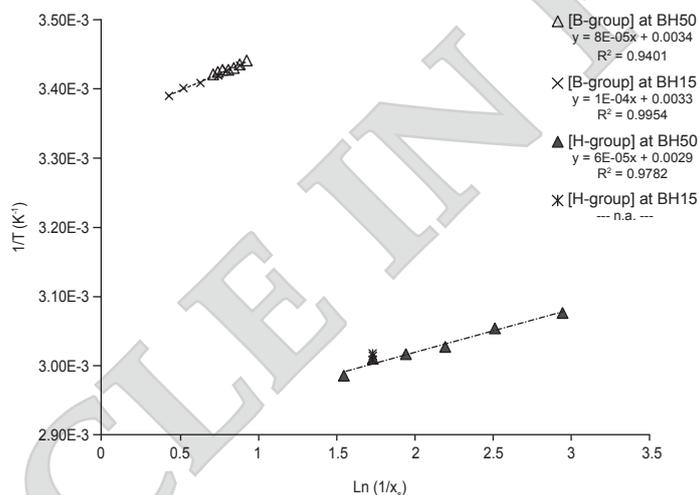
### Solid Interaction in Lauric Fat Blends

The interaction of solid fractions in the fat blends can be described by an isosolid diagram.



Note: PS - palm stearin, FHRO - fully hydrogenated rapeseed oil, PKO - palm kernel oil, HOSO - high oleic sunflower oil and MCT-oil - medium chain triacylglycerol oil.

Figure 3. Hildebrand plot of binary mixtures of high melting fractions in lower melting oils.



Note: B-group and H-group indicate the amount of medium melting fractions and high melting fractions in lauric fat blends, respectively. A formulation at BH50 or H15 refers to the fat blend composed of 50% TAG from a combination of B and H groups or the fat blend composed of 15% TAG from H groups, respectively. Fully hydrogenated rapeseed oil (FHRO) was the hard fat added to lauric fat blends.

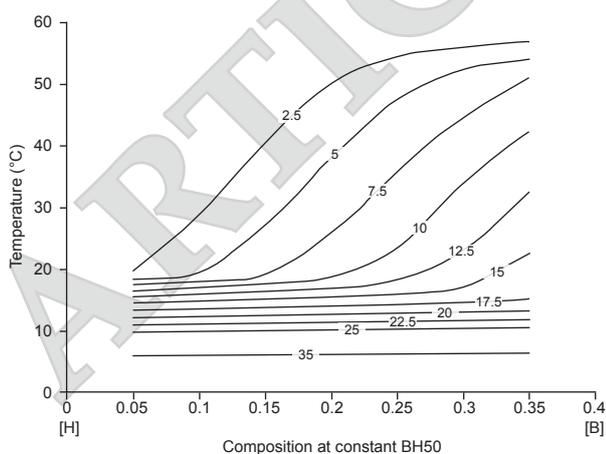
Figure 4. Hildebrand plot of FHRO lauric fat blends at different formulations.

This diagram contains isosolid lines representing the correlation between temperature and composition at constant SFC values. An isosolid line showed monotectic interaction as a straight horizontal line connecting two starting fats in fat blends. Meanwhile, eutectic interaction is indicated by compressed isosolid lines with melting temperatures below than those of the starting fats. Eutectic blends are usually undesirable as they had lower SFC than those of starting fats, showing that starting fats are not compatible (Timms, 1984; Lida *et al.*, 2002). For solid interaction, we also discussed only FHRO lauric fat blends in this study as lauric fat blends with PS as the hard fat showed a comparable result.

The isosolid diagram of FHRO lauric fat blends formulated at constant BH50 was shown in Figure 5. In this formulation, all blends had a similar amount of LMF (C and R groups) at 50%. Therefore, different H values indicated different ratios of both H-group and B-group in the constant amount of LMF (CR50). No depression was observed on the isosolid lines of lauric fat blends at this range of formulation (BH50 with varied H from 2.5%-17.5%) although a monotectic interaction was evident. Taking into account the previous binary mixture at which the solubility of hard fats in medium melting components had a slight deviation from ideality, this monotectic interaction seemed to coincide with its solubility curve. Thus, the effect

of solid interaction was considered to be less pronounced than that of solubility. Moreover, the MMF formulated at BH50 was completely melted at approximately 20°C as indicated in the isosolid diagram. At any temperature higher than 20°C, the SFC of the blends was apparently the function of H-group ratios. It was shown that the higher ratios of H-group yielded higher SFC for isosolid lines, yet, with constant SFC less than 17.5%.

Figure 6 showed the isosolid diagram of FHRO lauric fat blends formulated at constant H15. In this formulation, the amount of HMF in the blends was set constant at 15%. Meanwhile, the amount of MMF (B-group) was varied against that of LMF (CR-group) in order to fix the amount of both fractions at 85% in the blends. As the amount of HMF was fixed at 15%, the isosolid lines at constant SFC up to 10% displayed straight horizontal lines. These lines indicated the amount of fat crystal from H-group present in the blends at the temperature above the melting temperatures of both B-group and CR-group. Further, the isosolid lines at constant SFC values higher than 15% showed a monotectic interaction. The presence of solid fat (H-group) during B-group solidification seemed only imparting small influence as no depressions were noticed on those isosolid lines. The more closely spaced isosolid lines were also observed with the increment of B-group ratios indicating the dilution effect of B-group in CR-group (Ribeiro *et al.*, 2009). The effect of solid interaction between HMF and MMF was thus considered to be less pronounced than the solubility effect of HMF/MMF in LMF similar to the previously formulated blends (BH50).



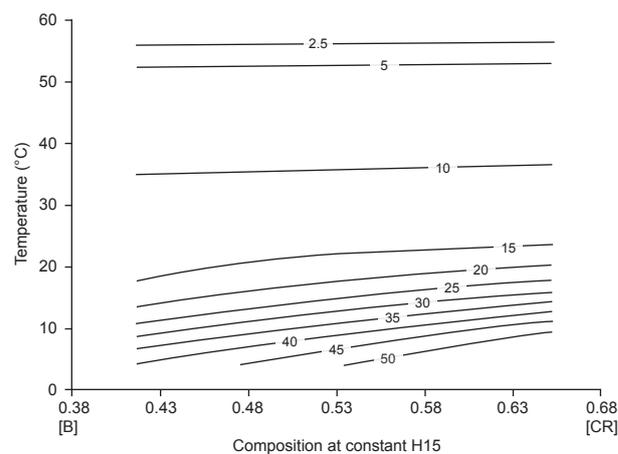
Note: A formulation at BH50 refers to the fat blend composed of 50% triacylglycerol (TAG) from a combination of B and H groups. Fully hydrogenated rapeseed oil (FHRO) was the hard fat added to lauric fat blends.

Figure 5. Isosolid diagram of FHRO lauric fat blends formulated at constant BH50.

### Hardness of Lauric Fat Blends

The viscoelastic behaviour of plastic fats is mainly dictated by the structure of fat crystal network where the amount of solid fat, polymorphism, and microstructure are known as the main influencing factors (Braipson-Danthine and Deroanne, 2004; Narine and Humphrey, 2004; Yanty *et al.*, 2017). Hardness is commonly used to correlate that behaviour to the perceived texture of a plastic fat. It was shown that hardness of lauric fat blends was influenced by the amount of solid fat from both H and BH group. When the amount of TAG from BH-group was fixed at 50% (BH50) but that of H-group was varied (differ on the HMF ratio, H2.5-H17.5), hardness was generally found to be similar in the range 141-239 g and 164-308 g for PS and FHRO lauric fat blends, respectively (Figure 7). The different type of hard fats (PS, FHRO) also gave approximately comparable hardness. Nevertheless, an obvious pattern was observed at which hardness of FHRO lauric fat blends had higher values than that of PS lauric fat blends. The effect of both different ratios of HMF and hard fat types on hardness seemed to be small as the measurement was done at 15°C at which the amount of solidified fractions, both HMF and MMF, was thought to be similar (BH50).

Higher hardness values were found when the amount of TAG from BH-group was increased from BH50 to BH70 in lauric fat blends (Figure 8). At those blends, the HMF was set constant at 15% (H15). Hardness corresponded well with the total amount of both HMF and MMF although the correlation was not linear. The variability in hardness could still arise from different crystal polymorph and network

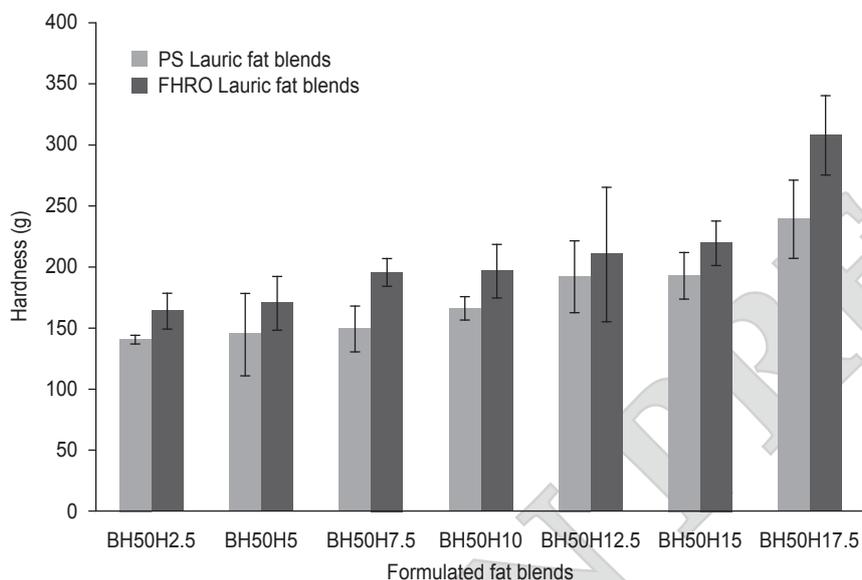


Note: A formulation at H15 refers to the fat blend composed of 15% triacylglycerol (TAG) from H group. Fully hydrogenated rapeseed oil (FHRO) was the hard fat added to lauric fat blends.

Figure 6. Isosolid diagram of FHRO lauric fat blends formulated at constant H15.

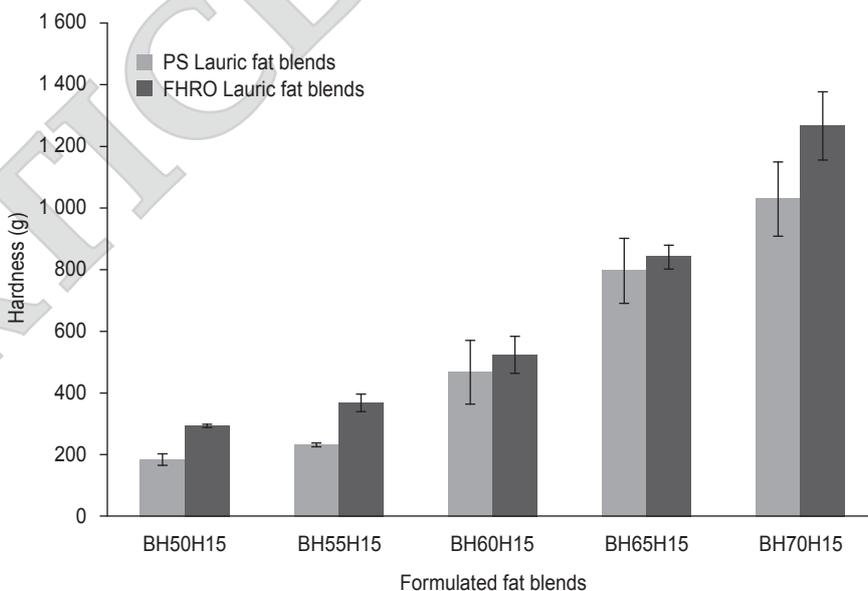
structures (Braipson-Danthine and Deroanne, 2004) even when the system was revealed to have a monotectic interaction. In addition, higher hardness was also evident for all FHRO lauric fat blends compared to that of PS blends even so the values

were mostly comparable. The higher concentration of the hard fats and longer carbon chain length of fatty acids on the TAG can result in fat blends with firmer texture (Zárubová *et al.*, 2010; Manaf *et al.*, 2019).



Note: Either palm stearin (PS) or fully hydrogenated rapeseed oil (FHRO) was the hard fat added to lauric fat blends. Meanwhile, a formulation at BH50 refers to the fat blend composed of 50% triacylglycerol (TAG) from a combination of B and H groups. Lauric fat blends were formulated at constant BH50 and varied H from 2.5%-17.5% (BH50H2.5, BH50H5, BH50H7.5, BH50H10, BH50H12.5, BH50H15 and BH50H17.5).

Figure 7. Hardness of lauric fat blends formulated at constant BH50.



Note: Either palm stearin (PS) or fully hydrogenated rapeseed oil (FHRO) was the hard fat added to lauric fat blends. Meanwhile, a formulation at H15 refers to the fat blend composed of 15% triacylglycerol (TAG) from H group. Lauric fat blends were formulated at constant H15 and varied BH from 50%-70% (BH50H15, BH55H15, BH60H15, BH65H15 and BH70H15).

Figure 8. Hardness of lauric fat blends formulated at constant H15.

## CONCLUSION

This study demonstrated that the simpler binary mixtures could provide some basic information in describing the phase behaviour of more complex ternary lauric fat blends. It was shown in the binary mixture that hard fats (PS or FHRO) formed an ideal solubility in different liquid oils (MCT-oil or HOSO). However, the solubility of hard fats in the lauric oil was indicated by some deviation from ideality as PKO contained some amount of high melting TAG. They might, therefore, affect the composition of high melting fraction and its crystallisation behaviour of the hard fats. The experimental melting point ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) of the hard fats were comparable to those of pure system as ideal solubility was evidence. In the ternary lauric fat blends, the HMF formed an ideal solubility in the both MMF and LMF within the range of given formulations (at constant BH50 and H15). Meanwhile, the MMF also had a linear relationship on their solubility curves but with stronger deviation from ideality as affected by the presence of fat crystals from HMF. Further, the isosolid diagram of lauric fat blends generally exhibited monotectic behaviour. The influence of solubility, nevertheless, seemed to override the influence of solid interaction. In addition, the hardness of lauric fat blends was influenced by the total amount of HMF and MMF. Different type of hard fats gave small variability, yet FHRO lauric fat blends gave higher hardness values than those of PS blends. The solubility curves and isosolid lines, in general, provided valuable information about the interaction of high, medium, and low melting fractions in the lauric fat blends. The pseudo-phase diagrams presented here could then be useful for improving the formulation of plastic fats, enriching the previous formulation based on the melting TAG group.

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