J Am Oil Chem Soc (2011) 88:1857–1865
DOI 10.1007/s11746-011-1860-6

ORIGINAL PAPER

Phase Behavior of Palm Oil in Blends with Palm-Based Diacylglycerol

Amir Hossein Saberi · Tan Chin-Ping · Lai Oi-Ming

Received: 10 November 2010 / Revised: 19 January 2011 / Accepted: 14 May 2011 / Published online: 24 June 2011

Abstract Phase behavior of palm oil (PO) in blends with different concentrations (10% intervals) of palm-based diacylglycerol oil (PO-DAG) was studied using the iso-solid diagram, solid fat content (SFC) with the hardness thermal protocol, DSC melting and crystallization curves, X-ray diffraction curves, and texture analysis (hardness). Minor eutectic effects were observed at around 20–50% PO-DAG in 20–50% SFC iso-lines. The phase behavior predicted by the iso-solid diagram as well as SFC with the hardness thermal protocol did not account for hardness variations observed between PO and PO blends with 10–40% PO-DAG. Nevertheless, the latter could be attributed to the corresponding DSC data as well as crystal polymorphism. However, as the concentration of PO-DAG increased from 40% to 100%, iso-line temperatures, SFC with the hardness thermal protocol, and also hardness were found to steadily increase. PO-DAG at 10% concentration was found to have a β'-stabilizing effect on the polymorphism of PO, while a β-tending effect was observed as the concentration of PO-DAG increased from 10% to 90%.

A. H. Saberi · L. Oi-Ming (✉)
Department of Bioprocess Technology,
Faculty of Biotechnology and Bimolecular Sciences,
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
e-mail: omlai@biotech.upm.edu.my

A. H. Saberi
e-mail: amir57515@gmail.com

T. Chin-Ping
Department of Food Technology, Faculty of Food Science and Technology, Universiti Putra Malaysia UPM,
43400 Serdang, Selangor, Malaysia

L. Oi-Ming
Institute of Bioscience, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia

Keywords Palm-based diacylglycerol · Phase behavior · Crystallization · Polymorphism · Hardness

Abbreviations

DAG	Diacylglycerol
PO	Palm oil
PO-DAG	Palm oil-based diacylglycerol
TAG	Triacylglycerol
SFC	Solid fat content
DSC	Differential scanning calorimetry
SPD	Short path distillation
FAC	Fatty acid composition
SAFA	Saturated fatty acid
USAFA	Unsaturated fatty acid

Introduction

Diacylglycerols (DAGs) are esters of glycerol where two of the hydroxyl groups are esterified with fatty acids. DAG is naturally found as a minor component of different fats and oils at levels up to 10% (w/w). DAG is also used in small quantities in foods as an emulsifier [1, 2]. Recent studies have indicated that DAG consumption in large amounts has metabolic characteristics different from those of triacylglycerol (TAG) and several advantageous effects on lipid metabolism. Intake of DAG oil as compared with TAG oil in animals and humans decreased postprandial TAG levels in serum [3, 4] and suppressed body fat accumulation as well as liver TAG levels [5], in spite of having comparable energy value and digestibility to TAG [4]. Furthermore, many animal and human studies have verified the safety of DAG oil for human consumption when used in a similar manner to other edible oils [6].

DAG oils have been produced experimentally from different sources of fat and oils, e.g., milk fat [7], palm oil (PO) deodorizer distillates [8], soy bean oil deodorizer distillates [9], palm olein [10], and lard [11]. Today, a functional DAG cooking oil containing approximately 80% DAG is commercially manufactured from soy bean and canola oils and is marketed in Japan and the USA [1]. PO is most important in terms of fat and oil production, contributing 25% to the global output of 154 million tonnes. It also accounts for 51% of trade (worldwide exports) in oils and fats [12]. As such, it is timely to develop functional palm-based fat products with beneficial health effects.

DAG oil is an expensive product due to the enzymatic reaction and purification process required for its production. Furthermore, it is noted that preferably more than 40% DAG oil is required in edible fat composition to achieve its beneficial health effects [13]. Consequently, utilization of palm-based DAG oil (PO-DAG) in blends with the same source of oil, PO, seems to be a good solution to minimize the purification step (skipping the separation of DAG from TAG) and thereby lower the price. Nevertheless, the complicated interactions occurring among TAGs and DAGs as a function of different ratios of PO and PO-DAG must first be understood to achieve specific functional properties through blending.

Natural fat is a system containing a mixture of domains (phases) in equilibrium. The occurrence of phase changes and phase interactions is considered as the phase behavior. Phase behavior can be characterized using iso-solid, liquid–solid phase, and polymorphism phase diagrams. Phase behavior characterized using the iso-solid diagram is of particular importance in production process optimization, product quality maintenance, and prediction of properties such as mouthfeel and hardness which are important in fat products. Furthermore, study of the phase behavior of fat blends which have relatively more complex phases can also lead to better understanding of the interactions occurring among the blend ingredient phases [14]. Although several studies have been conducted to investigate the effect of low concentrations of DAG on the physical properties of fats and oils [15, 16], very little information concerning the effect of high concentrations of DAG on the physical properties of fats and oils has been published so far [11, 17].

As mentioned, although the iso-solid diagram is able to explain some aspects of intersolubility, it may not illustrate polymorphism changes and/or predict hardness [18]. On the other hand, the liquid–solid phase diagram obtained through differential scanning calorimetry (DSC) can indicate polymorphism and intersolubility variations. Nevertheless, these changes are not ascribable to intersolubility and polymorphic effects if pure DSC data are used [14, 18]. Consequently, it is crucial to study the phase behavior using various methods such as SFC, DSC, crystal polymorphism, and texture analysis. Based on this framework, our objective is to study the phase behavior of PO in blends with PO-DAG (from low to high concentrations) using the various techniques mentioned above, and to investigate the correlation between the phase behavior and mechanical properties of this binary system.

Materials and Methods

Palm oil was provided by Sime Darby Sdn. Bhd. (Banting, Selangor, Malaysia). Commercial immobilized lipase from *Candida antarctica* (Novozyme 435) was purchased from Novozymes A/S (Bagsvaerd, Denmark). All chemicals and solvents used were of analytical and high-performance liquid chromatography (HPLC) grade, respectively.

Production of DAG

Palm oil-DAG synthesis was conducted in a 16-L packed-bed bioreactor consisting of a 10-L reaction vessel and a 6-L filtration vessel. The immobilized enzyme, Novozyme 435 (10% of oil mass), was packed in the filtration vessel. Glycerolysis reaction was conducted through stepwise addition of glycerol where the mole ratio of glycerol to oil was 1:1. PO (6 kg) and one-seventh of total mass of glycerol were added to the reactor vessel and heated up to 65 °C while stirring using the impeller stirrer. After temperature equilibration, the mixture of PO and glycerol was passed through the packed enzyme column using a centrifugal pump at flow rate of 850 mL/min. The rest of the glycerol was added at the following times: 0.5, 1, 1.5, 2, 2.5, and 3 h, and the reaction was continued for 7 h. The reaction mixture was then removed from the bottom of the packed-bed vessel and stored at −18 °C for purification.

Purification of DAG

The reaction mixture comprised glycerol, free fatty acid (FFA), monoacylglycerol (MAG), DAG, and TAG. Therefore, purification of DAG was carried out in two steps using short path distillation (SPD, KD6 system; UIC, Alzenau-Hoerstein, Germany). Separation of glycerol, FFA, and MAG from the reaction mixture was done in the first step. The mixture of DAG and TAG collected from the residue vessel was used for the second purification step, where the DAG was segregated from the TAG and collected from the distillate vessel. The following invariable conditions were used for both purification steps: evaporator vacuum, 0.001 mbar; feeding rate, 1.3 L/h; condenser temperature, 85 °C; feeding tank temperature, 75 °C; roller

speed, 280 rpm. The variable condition was evaporation temperature of 200 and 250 °C, applied in the first and second steps, respectively.

Blend Preparation

Palm oil-DAG was melted at 70 °C and added to PO at different concentrations of 0–100% (w/w) in 10% increments with final weight of 500 g. Each blend was prepared in duplicate.

Fatty Acid Composition (FAC) Analysis

FAC was determined as fatty acid methyl esters (FAME). The samples (0.05 g) were weighed and dissolved in 1 mL hexane. The mixtures were then added with sodium methoxide solution [0.2 mL $NaOCH_3$ (2 M) in anhydrous methanol] and then mixed for 1 min using a vortex mixer. After sedimentation of sodium glycerolate, 1 μL of the clear supernatant was injected (using a PerkinElmer Auto System XL autoinjector) into a Supelco sp^{TM} 2340 fused silica capillary column (60 m × 0.25 mm × 0.2 μ) and analyzed using a PerkinElmer auto system excel gas chromatograph (PerkinElmer Auto System XL, USA), equipped with a flame ionization detector (FID). Injection and detection temperatures were 250 °C. The oven temperature was programmed as follows: heat from 130 to 170 °C (20 °C/min), heat from 170 to 230 °C (10 °C/min), hold at 230 °C for 10 min, heat from 230 to 250 °C (30 °C/min), and hold for 1 min at 250 °C. The carrier gas (nitrogen) flow rate was 50 mL/min. Peaks were identified by comparing retention times with FAME standards and quantified using the peak area normalization method. Determination was carried out in duplicate.

Acylglycerol Composition Analysis

The DAG composition was determined using a Shimadzu HPLC (Shimadzu, Kyoto, Japan). The samples were dissolved in acetone at concentration of 5% (v/v). They were then filtered through a 0.2-μm nylon membrane filter to remove impurities. Samples (2 μL) were then injected into a Shimadzu LC column (Shim-Pack XR-ODS II, Shimadzu, Japan), a RP-C18 column with 2.2 μm particle size (150 mm × 2.0 mm) at oven temperature of 35 °C using a Shimadzu ultrafast liquid chromatography (UFLC) 2010 (Kyoto, Japan) equipped with a Shimadzu autoinjector (Kyoto, Japan) and Corona Plus detector (ESA, Chelmsford, MA, USA) at gas pressure of 35 psi within the 500 pA detection range. The following elution gradient was used for each analysis: 0 min—10%A + 90%B, 15 min—15%A + 85%B, 21 min—93%A + 7%B, 25 min—86%A + 14%B, 26 min—10%A + 90%B, 28 min—10%A + 90%B. Flow rate of 0.5 mL/min for mobile phase with total run time of 28 min was employed. Chromatographic peaks were identified by comparison of peak time with elution times of commercial and synthetic standards and quantified using the peak area normalization method.

Dynamic DSC Analysis

Dynamic calorimetric analysis was performed using a PerkinElmer Pyris 8000 DSC (PerkinElmer, Boston, MA). The instrument was calibrated using indium. Samples (6–10 mg) were sealed in the aluminum pan. The exotherm was obtained by holding the samples for 10 min at 80 °C followed by cooling to −50 °C at 5 °C/min. To obtain endotherms, the samples were held at −50 °C for 10 min and then heated to 80 °C at 5 °C/min. Crystallization onset was determined using PerkinElmer software as the first deviation from the baseline in exotherms. For each blend, analysis was conducted in duplicate.

Solid Fat Content (SFC) Analysis for Construction of Iso-solid Diagram

The SFC of the samples was measured by pulsed nuclear magnetic resonance (pNMR) using an NMS 120 Minispec NMR analyzer (Bruker Rheinstetten, Germany). The non-stabilized procedure was used according to PORIM test methods [19]. The samples (3–4 mg) were poured into the NMR tubes and were tempered in a water bath at 70 °C for 30 min. Afterwards, the NMR tubes were cooled and held at 0 °C for 90 min. SFC was determined at temperatures ranging from 5 to 45 °C (at 5 °C intervals) by equilibrating the NMR tubes at these temperatures for 30 min before measurement. Determinations were conducted in duplicate. To construct iso-solid diagram, SFC values obtained for the PO blends with 0–100% PO-DAG were plotted against temperature in the range 0–50 °C at 5 °C intervals. Equations describing curves of SFC value versus temperature were then obtained using Data fit software version 9.0 trial (Oakdale Engineering, Oakdale, PA 15071, USA) for all blends. Then, the temperatures at SFC values of 5–50% (in 5% intervals) were calculated using the equations obtained by the software for each of the blends, and these temperatures were used to plot the iso-solid diagram [14].

Analysis of SFC with the Hardness Thermal Protocol

The samples contained in the NMR tubes were melted and equilibrated at 80 °C for 5 min. They were then

immediately cooled to −18 °C and equilibrated for 1 h. Afterwards, NMR tubes were stored at 25 °C for 24 h. The isothermal SFC was then measured. Determinations were done in duplicate.

Crystal Polymorphism

The samples were melted and equilibrated at 80 °C for 5 min. They were then immediately cooled to −18 °C and equilibrated for 1 h. Afterwards, the samples were stored at 25 °C for 24 h. The fat crystal polymorphism of samples was determined by X-ray diffractometer (Rint Series, Rigaku, Japan). β'-Polymorph was characterized by two short spacings at 3.8 and 4.2 Å, while β-form was characterized by short spacing at 4.6 Å [20].

Hardness

The samples were melted and equilibrated at 80 °C for 5 min. They were then immediately cooled to −18 °C and equilibrated for 1 h. Afterwards, the samples were stored at 25 °C for 24 h. Hardness was measured using a TA-TX2 texture analyzer (Stable Micro Systems Ltd., Godalming, UK). A flat-ended cylindrical needle 5-mm plunger probe attached to a 5 kg compression load cell was used to penetrate the samples at 1.0 mm/s to depth of 12 mm from the sample surface, and withdrawn at the same speed. The maximum force (g) during the first compression was reported as the hardness. Analysis was conducted in duplicate.

Results and Discussion

Acylglycerol and Fatty Acid Compositions

Acylglycerol and fatty acid composition of PO and PO-DAG are shown in Table 1. PO was found to have originally 9.02% DAG, which was slightly different from the DAG concentration range of 4.5–7% reported previously [16]. Enzymatic glycerolysis followed by purification of the reaction mixture using SPD increased the concentration of PO-DAG from 9.02% to 90.02%. The isomer ratio of 1,3- to 1,2-DAG for PO-DAG was observed to be 7:4.29. In general, 1,3- and 1,2-DAG isomers undergo acyl migration to equilibrate at ratio of 6–7:3–4 [1]. Comparison of the FAC of PO and PO-DAG showed that the enzymatic glycerolysis and purification process of PO did not considerably alter the FAC, showing palmitic and oleic acids (as the main FAs), and total saturated (SAFA) and unsaturated fatty acids (USAFA) of 44.7%, 38.6%, 50.5%, and 49.5% for PO as compared with 45.6%, 38.4%, 51.8%, and 48.2% for PO-DAG, respectively.

Table 1 Acylglycerol and fatty acid composition (FAC) of palm oil (PO) and palm-based diacylglycerol oil (PO-DAG)

	PO	PO-DAG
Acylglycerol compositions (%)		
TAG[a]	90.98	5.60
MAG[b]	0.0	4.39
DAG	9.02	90.02
1,3-DAG/1,2-DAG	–	7/4.29
FAC (%)		
C12:0	0.2 ± 0.02	0.5 ± 0.02
C14:0	1.1 ± 0.01	1.2 ± 0.01
C16:0	44.7 ± 0.03	45.6 ± 0.03
C16:1	0.3 ± 0.02	0.2 ± 0.02
C18:0	4.1 ± 0.01	4.3 ± 0.01
C18:1	38.6 ± 0.04	38.4 ± 0.04
C18:2	10.3 ± 0.01	9.2 ± 0.01
C20:0	0.3 ± 0.01	0.3 ± 0.01
C18:3	0.4 ± 0.00	0.3 ± 0.00
SAFA[c]	50.5 ± 0.06	51.8 ± 0.06
USAFA[d]	49.5 ± 0.06	48.2 ± 0.06

All measurements conducted using peak area normalization

[a] Triacylglycerol

[b] Monoacylglycerol

[c] Saturated fatty acid

[d] Unsaturated fatty acid

Iso-solid Diagram

Phase behavior can be explained in terms of solution behavior using the iso-solid diagram. Figure 1 shows an iso-solid diagram constructed using SFC data. Each iso-solid line connects those points with the same SFC value. The topmost line is the 5% SFC line, and subsequent lines increase in 5% increments to 50%. A noticeable increment in temperature was found for all iso-solid lines with presence of 10% PO-DAG as compared with PO. A general increasing trend was observed in 5% and 10% iso-lines with increasing concentration of PO-DAG from 0% to 100%, while minor temperature decrements were found at around 20–50% PO-DAG for 20–50% iso-lines. The latter was more evident in 45% and 50% iso-lines at 20–30% PO-DAG. This indicated the occurrence of a minor eutectic effect at the SFC range of 20–50%, at the mentioned concentrations of PO-DAG. Since PO and PO-DAG were found to have similar FAC, the minor eutectic effect observed could be due to the different acylglycerol structures rather than different FAC. As the concentration of PO-DAG increased from 50% to 100%, it could be noticed

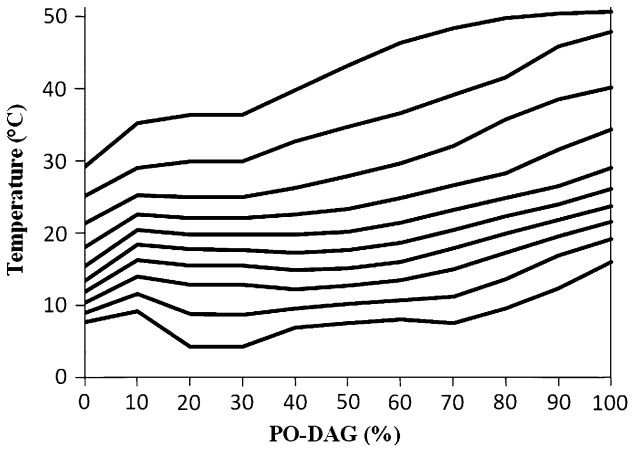

Fig. 1 Iso-solid lines spaced in 5% solid fat content (SFC) intervals from 5% SFC (*top curve*) to 50% SFC (*bottom curve*)

that the temperatures of 5–45% SFC iso-lines steadily increased (Fig. 1).

Hardness

The variations of hardness as a function of different concentrations of PO-DAG in blends with PO are shown in Fig. 2a. A general decreasing trend in hardness was observed as the concentration of PO-DAG increased from 0% to 40%, while addition of 50–100% of PO-DAG steadily increased the hardness. The latter is in agreement with the increasing trends observed in the temperature range of 5–45% iso-lines as the concentration of PO-DAG increased from 50% to 100% (Fig. 1). Also, the lower hardness observed for the PO blend with 40% as compared with 10–20% PO-DAG is due to the minor eutectic effect observed for the former in 25–45% SFC iso-lines. On the other hand, the PO blend containing 10–40% PO-DAG as compared with PO was observed to have lower hardness (especially with 30–40% of PO-DAG, Fig. 2a) despite having 5–40% SFC iso-lines with relatively higher temperature (Fig. 1). It has been reported that SFC data are not the only factor that determines hardness [18, 21, 22]. Firmness or solid-like behavior of fats, in particular, is influenced by the amount of SFC, type of crystals (size and polymorphic form), and interaction among the crystals leading to the formation of fat crystal network [23, 24]. Unlike TAG, which can have three typical crystal structures (α, β', and β), 1,2-DAG as an asymmetrical DAG exhibits only α- and β'-forms and 1,3-DAG as a symmetrical DAG exhibits only two types of β-form: $\beta 1$ and the more unstable $\beta 2$. Furthermore, for 1,3-DAG, as its polar group is present in the center of the molecule, the resulting bilayer forms a V-shaped conformation, while 1,2-DAG has a hairpin-shaped conformation [25]. Therefore, the presence of different concentrations of 1,3- and 1,2-DAG in blends with TAG might also lead to different interactions among DAG and TAG crystals. Consequently, this event results in different crystalline packing and thereby different hardness of the crystal networks. Furthermore, as suggested by Saberi et al. [17], different concentrations of PO-DAG have also pronounced effects on the nucleation and crystal growth rate of palm oil, leading to different growth behaviors of the fat crystal network.

Figure 2b shows the SFC data for the blends obtained following the hardness thermal protocol. Comparison of Fig. 2a and b also shows that the SFC trend for these specific conditions did not correlate with the respective hardness variations within the concentration range of 0–40% PO-DAG. Nevertheless, both parameters were observed to increase steadily as the concentration of PO-DAG increased from 40% to 100%. Also, PO-DAG was found to have extremely higher hardness as compared with PO. This could be due to the ease of fatty acid chain arrangement of the DAG molecules and the strength of the respective hydrogen bonds formed among the free hydroxyl groups [25], giving rise to higher crystalline packing in the PO-DAG crystal network as compared with the PO crystal network.

DSC Thermogram

Crystallization and melting thermograms of PO and its blends with different concentrations of PO-DAG (0–100% at 10% intervals) are shown in Fig. 3a and b, respectively. The DSC cooling thermogram of PO showed two peaks, representing high- and low-melting fractions. Addition of 10–40% PO-DAG increased the respective crystallization onsets as compared with PO (Fig. 4a). As the concentration of PO-DAG increased from 30% to 100%, it could be noticed that a new exotherm appeared in the higher melting regions. Appearance of new exothermic peaks in the higher temperature region is indicative of crystallizing out of PO-DAG at the higher temperature region, and also the simultaneous intensity reduction of high-melting fraction of PO suggested co-crystallization as well as intersolubility of PO-DAG (30% and above) with the high-melting TAGs of PO. Furthermore, crystallization onset was found to steadily increase as PO-DAG increased from 50% to 100% (Fig. 4a). This event indicated the promoting effect of 30% PO-DAG and above on crystallization properties of PO. Addition of 10–20% PO-DAG decreased the intensity of high-melting endotherm of PO (Fig. 3b). Although the latter decreased in the presence of 30–100% PO-DAG, new peaks appeared at higher melting regions. This new endotherm not only increased in intensity, but also shifted to the higher temperature regions as the concentration of PO-DAG increased from 30% to 100%.

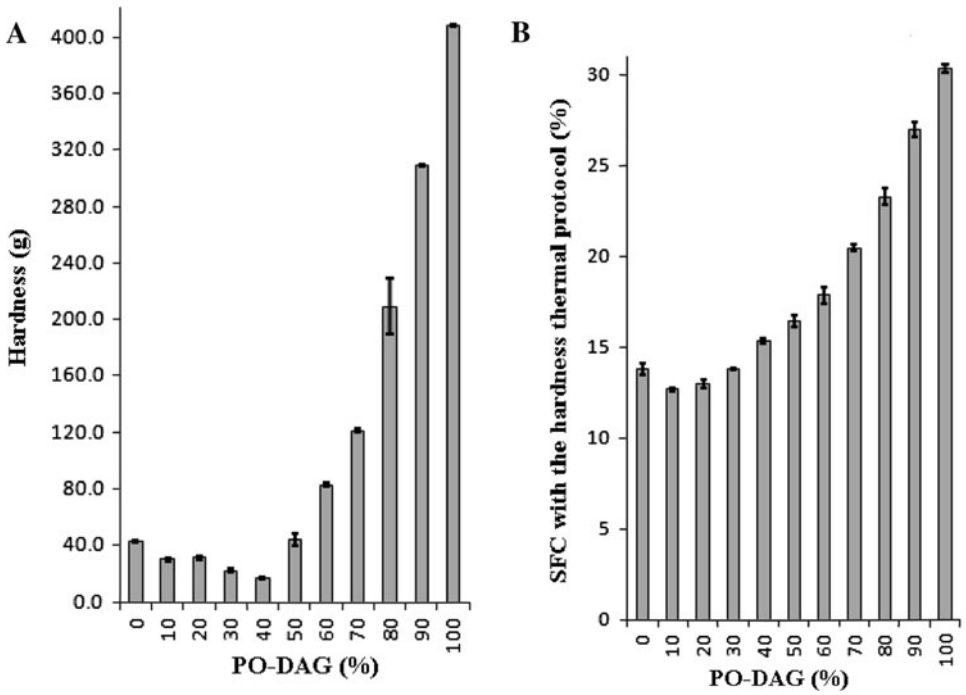

Fig. 2 Hardness (**a**) and isothermal SFC at 25 °C (**b**) versus concentration of palm-based diacylglycerol oil (PO-DAG)

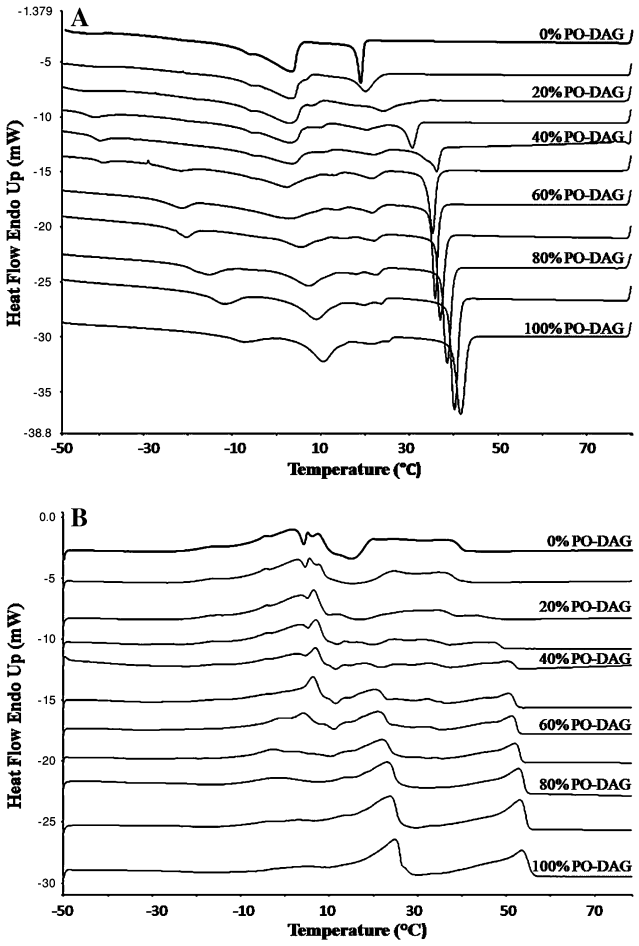

Fig. 3 Crystallization (**a**) and melting (**b**) thermograms of palm oil (PO) and PO with 10–100% of palm-based diacylglycerol oil (PO-DAG) at 10% intervals

Higher hardness values of PO blends with 10–40% DAG (despite having lower SFC with the hardness thermal protocol) as compared with PO could also be related to the different thermal transitions of the enthalpy curves. These results were further evidenced by the different heats of crystallization (Fig. 4b) and fusion (Fig. 4c) of the blends with 10–40% PO-DAG. Furthermore, the PO blend containing 40% PO-DAG as compared with the other blends was found to have the lowest heats of crystallization (Fig. 4b) and fusion (Fig. 4c), accounting for the lowest hardness observed for the PO blend with 40% PO-DAG (Fig. 2a).

Polymorphism

Phase variations caused by polymorphism changes among PO and PO blends with various concentrations of PO-DAG are shown as X-ray diffraction curves versus short spacings (*d*) in Fig. 5 and as short spacings with their visually estimated intensities in Table 2. β'-Polymorph is usually characterized by two strong spacings at 3.8 and 4.2 Å, while β-form has one strong spacing at 4.6 Å and usually a weaker spacing at 3.8 Å. Addition of 10% PO-DAG was observed to have a β'-stabilizing effect on PO. Similar results were reported by Okiy et al. [26] where 10% and 15% DAG (isolated from PO) stabilized β'-form of PO triglyceride. Also, minor amount of DAG (1,2- with a greater extent than 1,3-DAG) showed a strong inhibitory effect on $\beta' \rightarrow \beta$ transition in hydrogenated rapeseed oil with low content of erucic acid [27]. Furthermore, increase in the concentration of PO-DAG from 10% to 90% PO-DAG steadily increased β-polymorph in the corresponding blends, and blends

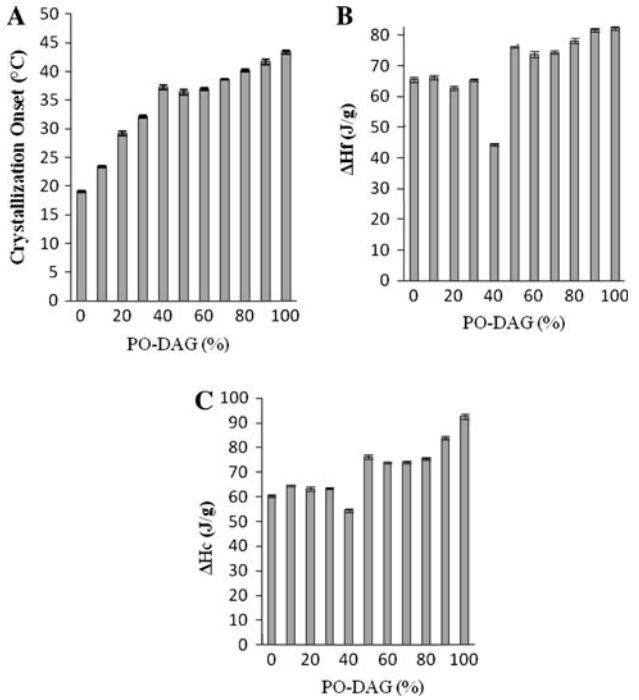

Fig. 4 Crystallization onset (**a**), and enthalpies of crystallization (ΔH_c) (**b**) and melting (ΔH_f) (**c**) versus concentration of palm-based diacylglycerol oil (PO-DAG)

containing 70–90% PO-DAG were observed to have only β-form. Nevertheless, PO-DAG was found to have β-form with relatively lower amount of β'-polymorph (Table 2). Based on the polymorphic forms of 1,3- and 1,2-DAG mentioned above, the relatively higher amount of β-polymorph compared with β'-form for PO-DAG could be attributed to the relatively higher concentration of 1,3-DAG compared with 1,2-DAG, where the ratio of 1,3-DAG to 1,2-DAG was found to be 7:4.29 (Table 1).

The polymorphic data (Table 2) along with the respective X-ray diffraction curves (Fig. 5) could also assist in illustrating the variations of hardness shown in Fig. 2a. X-ray diffraction curves were classified into the categories A, B, C, D, E, and F based on the position (Table 2) and shape (Fig. 5) of the peaks. The differences observed in X-ray diffraction classifications of PO blend including 10–40% PO-DAG (B, C, C, and D, respectively) as compared with PO (A, Table 2) could be attributed to the respective lower hardness, though the former showed SFC iso-lines in higher temperature regions. Also, as the con-

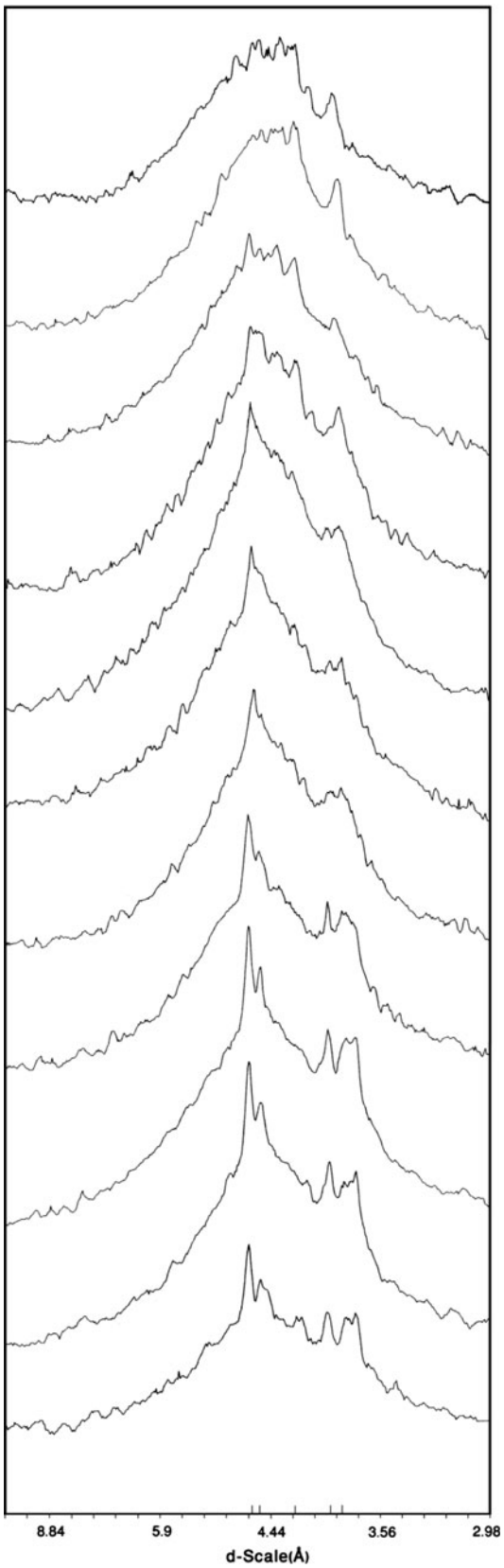

Fig. 5 X-ray diffraction curve versus *d* for palm oil (PO) and PO ▶ with 10–100% of palm-based diacylglycerol oil (PO-DAG) in 10% intervals. The *topmost curve* is for PO, and the *bottommost curve* is for PO-DAG

Table 2 Short spacings and polymorphism classification of palm oil (PO) in blends with palm-based diacylglycerol oil (PO-DAG)

PO-DAG (%)	Form	Short spacing[a,b]						Classification[c]
0	$\beta' + \beta$	–	3.88 (s)	–	4.2 (m)	4.53 (m)	4.6 (m)	A
10	β'	–	3.85 (s)	–	4.2 (s)	–	–	B
20	$\beta' + \beta$	–	3.87 (s)	–	4.2 (s)	–	4.64 (s)	C
30	$\beta' + \beta$	–	3.8 (s)	–	4.2 (s)	–	4.64 (s)	C
40	$\beta \gg \beta'$	–	3.84 (w)	3.94 (w)	4.2 (w)	–	4.64 (v.s.)	D
50	$\beta \gg \beta'$	–	3.82 (w)	3.91 (w)	4.2 (w)	–	4.63 (v.s.)	D
60	$\beta \ggg \beta'$	–	3.82 (w)	3.91 (w)	4.24 (v.w.)	–	4.61 (v.s.)	D
70	β	–	3.81 (m)	3.92 (s)	–	4.53 (m)	4.65 (v.s.)	E
80	β	3.72 (m)	3.78 (m)	3.92 (s)	–	4.52 (s)	4.65 (v.s.)	E
90	β	3.72 (m)	3.81 (w)	3.91 (s)	–	4.53 (m)	4.65 (v.s.)	E
100	$\beta > \beta'$	3.7 (m)	3.78 (m)	3.93 (s)	4.18 (m)	4.52 (s)	4.65 (v.s.)	F

[a] Peak intensities are indicated as *v.s.* very strong, *s* strong, *m* medium, *w* weak, *v.w.* very weak

[b] Predominant short spacings of β', 4.2 and 3.8 Å; β, 4.6 Å

[c] Classification of X-ray diffraction curves was conducted based on positions (as seen in this Table) and shapes (as seen in Fig. 5) of the peaks

centration of PO-DAG increased from 40% to 50%, their polymorphic characters changed from type C to D, which was reflected in the respective hardness (Fig. 2a).

Conclusions

Different concentrations of PO-DAG were observed to have different effects on dynamic SFC, SFC with the hardness thermal protocol, polymorphism, melting and crystallization properties, and hardness of PO. The β'-stabilizing effect of 10% PO-DAG can be considered to be of technical interest, and it might thus be used as a β'-stabilizing agent in palm-based products. PO-DAG was found to have a strong β-tending effect on the polymorphism of PO, especially for concentrations at which PO-DAG is able to contribute beneficial health effects (>40%). The isosolid diagram constructed using SFC data was found to be unable alone to entirely illustrate hardness variations observed for PO and PO blends with different concentrations of PO-DAG. However, the latter could be explained through the use of polymorphic as well as melting and crystallization behaviors.

Acknowledgments The authors appreciatively thank Mr. Razam, Mr. Ananthan, Mr. Radha Krishnan, Mr. Vijay Krishnan, and Ms. Sri Nesa from Sime Darby, Banting for their kind technical assistance. Financial support of this work by Sime Darby Sdn. Bhd. is also gratefully acknowledged.

References

1. Lo S-K, Tan C-P, Long K, Yusoff M, Lai O-M (2008) Diacylglycerol oil—properties, processes and products: a review. Food Bioprocess Technol 1:223–233
2. Yasukawa T, Katsuragi Y (2004) Diacylglycerols. In: Katsuragi Y, Yasukawa T, Matsuo N, Flickinger BD, Tokimitsu I, Matlock MG (eds) Diacylglycerol oil. AOCS Press, Champaign, pp 1–15
3. Murata M, Hara K, Ide T (1994) Alteration by diacylglycerols of the transport and fatty acid composition of lymph chylomicrons in rats. Biosci Biotechnol Biochem 58:1416–1419
4. Taguchi H, Watanabe H, Onizawa K, Nagao T, Gotoh N, Yasukawa T, Tsushima R, Shimasaki H, Itakura H (2000) Double-blind controlled study on the effects of dietary diacylglycerol on postprandial serum and chylomicron triacylglycerol responses in healthy humans. J Am Colloid Nutr 19:789–796
5. Maki KC, Davidson MH, Tsushima R, Matsuo N, Tokimitsu I, Umporowicz DM, Dicklin MR, Foster GS, Ingram KA, Anderson BD, Frost SD, Bell M (2002) Consumption of diacylglycerol oil as part of a reduced-energy diet enhances loss of body weight and fat in comparison with consumption of a triacylglycerol control oil. Am J Clin Nutr 76:1230–1236
6. Morita O, Soni MG (2009) Safety assessment of diacylglycerol oil as an edible oil: a review of the published literature. Food Chem Toxicol 47:9–21
7. Yang T, Zhang H, Mu H, Sinclair AJ, Xu X (2004) Diacylglycerols from butterfat: production by glycerolysis and short-path distillation and analysis of physical properties. J Am Oil Chem Soc 81:979–987
8. Lo SK, Baharin BS, Tan CP, Lai OM (2004) Dacylglycerols from palm oil deodoriser distillate. Part 2 - physical and chemical characterisation. Food Sci Technol Inter 10:157–161
9. Lo SK, Baharin BS, Tan CP, Lai OM (2004) Lipase-catalyzed production and chemical composition of diacylglycerols from soybean oil deodorizer distillate. Eur J Lipid Sci Technol 106:218–224
10. Cheong LZ, Tan CP, Long K, Affandi Yusoff MS, Arifin N, Lo SK, Lai OM (2007) Production of a diacylglycerol-enriched palm olein using lipase-catalyzed partial hydrolysis: optimization using response surface methodology. Food Chem 105:1614–1622
11. Cheong L-Z, Zhang H, Xu Y, Xu X (2009) Physical characterization of lard partial acylglycerols and their effects on melting and crystallization properties of blends with rapeseed oil. J Agric Food Chem 57:5020–5027
12. Anonymous (2008) Malaysian palm oil industry performance 2007. Global Oils Fats Business Mag 5:8
13. Masui K, Katsuragi Y, Toi T, and Yasukawa T (2002) Fat or oil composition, US Patent 6,495,536 B1

14. Humphrey KL, Narine SS (2005) Lipid phase behavior. In: Marangoni AG (ed) Fat crystal networks. Marcel Dekker, NY, pp 83–114
15. Siew WL, Ng WL (1996) Effect of diglycerides on the crystallisation of palm oleins. J Sci Food Agric 71:496–500
16. Siew WL, Ng WL (1999) Influence of diglycerides on crystallisation of palm oil. J Sci Food Agric 79:722–726
17. Saberi AH, Lai O-M, Toro-Vázquez JF (2011) Crystallization kinetics of palm oil in blends with palm-based diacylglycerol. Food Res Int 44:425–435
18. Humphrey K, Moquin P, Narine S (2003) Phase behavior of a binary lipid shortening system: from molecules to rheology. J Am Oil Chem Soc 80:1175–1182
19. Siew WL, Tang TS, Tan YA (eds) (1995) PORIM test methods. Palm Oil Research Institute of Malaysia, Ministry of Primary Industries, Kuala Lumpur
20. Yap P, de Man J, de Man L (1989) Polymorphism of palm oil and palm oil products. J Am Oil Chem Soc 66:693–697
21. Narine SS, Marangoni AG (1999) Relating structure of fat crystal networks to mechanical properties: a review. Food Res Int 32:227–248
22. Narine SS, Marangoni AG (1999) Factors influencing the texture of plastic fats. Inform 10:565–570
23. Deman JM, Beers AM (1987) Fat crystal networks: structure and rheological properties. J Text Stud 18:303–318
24. Marangoni A, Rousseau D (1999) Plastic fat rheology is governed by the fractal nature of the fat crystal network and by crystal habit. In: Widlak N (ed) Physical properties of fats, oils, and emulsifiers. AOCS Press, Champaign, pp 96–111
25. Nakajima Y, Fukasawa J, Shimada A (2004) Physicochemical properties of diacylglycerol. In: Katsuragi Y, Yasukawa T, Matsuo N, Flickinger BD, Tokimitsu I, Matlock MG (eds) Diacylglycerol oil. AOCS Press, Illinois, pp 182–196
26. Okiy DA, Wright WB, Berger KG, Morton ID (1978) The physical properties of modified palm oil. J Sci Food Agric 29:1061–1068
27. Hernqvist L, Larsson K, Herslöf B, Podlaha O (1981) Polymorphism of rapeseed oil with a low content of erucic acid and possibilities to stabilise the β'-crystal form in fats. J Sci Food Agric 32:1197–1202