

# PALM OIL CRYSTALLISATION: A REVIEW

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## ABSTRACT

*Palm oil is one of the most traded oils in the world oils and fats market for food applications. This has led to many studies on aspects such as nutritional, food design and formulation, and its crystallisation behaviour. Palm oil crystallisation behaviour has important implications in the manufacture of food products such as margarines and shortenings where physical properties depend largely on the fat crystals. This article reviews the effects of chemical composition (fatty acid and mono-, di- and tri-acylglycerol composition), crystallisation conditions and the presence of additives on the crystallisation of palm oil. In addition, the crystallisation kinetics, thermal properties, polymorphism and recrystallisation of palm oil will also be discussed.*

**Keywords:** crystallisation, palm oil, fat crystals, polymorphism, thermal properties.

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## INTRODUCTION

Palm oil is derived from the outer pulp (mesocarp) of the fruits of oil palm, *Elaeis guineensis*. The mesocarp contains almost 49% palm oil, and the kernel consists of about 50% palm kernel oil (Pantzaris, 2000). They have many applications with new potential uses currently being explored. Palm oil is 50% unsaturated and contains mainly oleic (C18:1) and palmitic (C16:0) acids with an iodine value of about 52 (Wahid *et al.*, 2011).

In 2013, the world production of palm oil reached 58.4 million tonnes from 30 million tonnes in 2004 (USDA, 2014). This accounted for more than 34% of the world production of major vegetable oils in 2013. The remarkable increase in palm oil production in the last decade signifies its importance as one of the world's main commodity crops. Various modification processes such as blending, hydrogenation, fractional crystallisation and interesterification allow palm oil to be applied

in many diverse areas with both edible and non-edible usages.

Fractionation process is necessary to meet specific uses, which separates the palm oil into fractions with different melting properties. For edible purposes, palm oil and its fractions are used in the manufacturing of margarines, vanaspati, shortening, spreads, ice creams, whipped topping, mayonnaise and salad dressing, filled milk, coffee creamer, cheese and coconut milk substitutes (Miskandar *et al.*, 2011). The oil is also very suitable for commercial deep frying because of its good non-foaming property and oxidative stability (Pantzaris, 2000; Ismail, 2005; Ahmad Tarmizi and Siew, 2008; Ahmad Tarmizi and Ismail, 2008; 2014). For non-edible purposes, palm oil is mainly used in the soap industry and fatty acids manufacturing.

## FACTORS AFFECTING THE PALM OIL CRYSTALLISATION

### Fatty Acid and Triacylglycerol Composition of Palm Oil

Fatty acids are the starting points in lipid structure. They are the main components that form triacylglycerols (TAG), monoacylglycerols (MAG)

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and diacylglycerols (DAG) in oils and fats. There are nine major fatty acids present in palm oil. Palmitic acid and oleic acid account for about 44% and 40% of the total fatty acid content of palm oil, respectively (Wahid *et al.*, 2011). Other fatty acid constituents of palm oil include myristic, stearic and linoleic acids with trace amounts of lauric, palmitoleic, linolenic and arachidic acids as tabulated in *Table 1*.

TABLE 1. FATTY ACID COMPOSITION OF PALM OIL

Fatty acid	Carbon number	Amount (wt%)
Lauric	12:0	0.0 - 0.4
Myristic	14:0	0.5 - 2.0
Palmitic	16:0	40.1 - 47.5
Palmitoleic	16:1	0.0
Stearic	18:0	3.5 - 6.0
Oleic	18:1	36.0 - 44.0
Linoleic	18:2	6.5 - 12.0
Linolenic	18:3	0.0 - 0.5
Arachidic	20:0	0.0 - 1.0

Source: Wahid *et al.* (2011).

Fats and oils are mainly mixtures of TAG and palm oil consists of about 93% - 95% TAG. Palm oil also contains appreciable amounts of DAG (5% - 8%) and free fatty acids, which can have a substantial effect on its physical properties. The two dominant TAG are POP (28%) and POO (24%) with significant amounts of PLO, PLP, PPP (5%), POS and OOO. The remaining TAG are present at less than 3% (Hishamuddin, 2009). *Table 2* tabulates the TAG composition of palm oil (positional isomers are not separated).

Crystallisation of palm oil has been extensively investigated due to its importance in controlling product quality. Crystallisation can be generally classified into two steps: nucleation, followed by crystal growth. Before nucleation occurs, the solution must be under supercooling or supersaturation conditions. The driving force for a supercooled melt to undergo crystallisation is determined by the degree of supercooling (the difference between the process value and the slip melting point (SMP) (Ghostra *et al.*, 2002). Palm oil crystallisation is known to be a rather complex process (Jacobsberg and Oh, 1976; Kawamura, 1979; 1980; van Putte and Bakker, 1987; Berger, 1989) due to the slow crystallisation behaviour that leads to post-hardening (Timms, 1984; Duns, 1985; Ward, 1998; Zaliha *et al.*, 2004; 2005; Hishamuddin *et al.*, 2011).

Chemical composition such as TAG, DAG, free fatty acid (FFA) and additives has been shown to influence palm oil crystallisation. Braipson-Danthine and Gibon (2007) reported that there was a clear

TABLE 2. TRIACYLGLYCEROL COMPOSITION OF PALM OIL

Triacylglycerol	Weight (%)
OLL	0.6
PLL	1.9
MLP	0.9
OLO	2.0
PLO	10.8
PLP	8.9
MPP	0.7
OOO	3.9
POO	24.3
POP	27.7
PPP	5.1
SOO	2.1
POS	4.6
PPS	0.8
SOS	0.3

\*Note: M = myristic; P = palmitic; S = stearic; O = oleic; L = linoleic.

Source: Adapted from Hishamuddin (2009).

relationship between TAG composition, melting properties and polymorphic behaviour of palm oil and fractions after analysing a series of palm oil, solid and liquid fractions (stearins, mid fractions, oleins and superoleins). Three major endotherms namely low-melting, high-melting and very high-melting peaks (LMP, HMP and VHMP) were detected in the differential scanning calorimetry (DSC) melting profiles ( $5^{\circ}\text{C min}^{-1}$ ). The VHMP was only recorded for palm stearin which contains more trisaturated (SSS) components. The HMP contribution was weak for palm olein and was not observed for palm super oleins. The LMP is usually made up of triunsaturated (UUU), diunsaturated-saturated (SUU) and disaturated-unsaturated (SUS) components. The SUS components were reported to be present in both LMP and HMP. The HMP is also made up of some SSS, except for palm oleins and super oleins.

DAG have also been shown to inhibit the nucleation process and retard crystal growth rates of palm oil TAG, particularly of the saturated dipamitoylglycerol species. This behaviour was more effective at concentrations higher than 5% and at lower degrees of supercooling (Siew and Ng, 1999). Saberi *et al.* (2011) studied the effects of different concentrations (2%, 5%, 10%, 30% and 50% w/w) of palm-based diacylglycerols (PB-DAG) on the crystallisation kinetics of palm oil. The isothermal crystallisation properties of palm oil were dependent on the concentration of PB-DAG. Addition of 5% PB-DAG decreased significantly ( $p < 0.05$ ) nucleation

rate, crystallisation rate and crystal growth mode of palm oil (PO). On the other hand, the addition of 30% and 50% of PB-DAG increased significantly ( $p < 0.05$ ) nucleation rate, crystallisation rate and crystal growth mode of PO. A recent study by de Oliveira *et al.* (2014) also indicated that naturally occurring DAG in PO (6% - 8.5%) interfere with the nucleation times and crystallisation rate of PO.

Siew and Ng (1996) investigated the effect of different types of DAG on palm olein crystallisation and concluded that DAG have different effects on the crystallisation behaviour. The enhancing or retarding role of crystallisation depends on the type of DAG as well as on the oil composition. The crystallisation time of palm olein was reduced rapidly with the addition of palm diacylglycerols. Of the palm DAG, dipalmitoylglycerol in particular, the 1, 3-isomer, was more effective in causing rapid crystallisation of palm olein. On the other hand, the palmitoyloleoylglycerol appeared to have a retardation effect on the crystallisation time.

Basso *et al.* (2010) characterised the changes induced in the crystallisation of PO by the addition of two different levels of tripalmitin and two different types of MAG. The addition of MAG led to the formation of a large number of crystallisation nuclei without changing the final solids content, accelerating the process of crystal formation, leading to the formation of smaller crystals than those in the refined palm oil. Higher levels of tripalmitin produced larger crystals, reducing the induction period and resulted in a higher level of solids at the end of the crystallisation period. A recent study by Verstringe *et al.* (2013; 2014) reported that the addition of saturated MAG caused an earlier onset on both isothermal and non-isothermal crystallisation of PO.

A study on palm oil and palm stearin blend systems by Saadi *et al.* (2012) indicated that high melting TAG namely, PPO/POP was the dominant component responsible for primary crystal formations and aggregation. While Miura and Konishi (2001) reported that POP was one the major TAG existed in granular crystals of margarine produced by an excess of palm oil. POP and POO were found to be immiscible with each other, resulting in POP crystals surrounded by POO.

Additives also have been shown to play some inhibitory effects in palm oil crystallisation. Kawamura (1980) investigated the retardation effect of sorbitan esters on the crystal polymorphic transformation in palm oil and found that sorbitan tristearate was the most effective in retarding the transformation from the unstable  $\alpha$  and  $\beta'$  crystal forms to the stable  $\beta$  at concentrations and heating rates greater than 1.5% and 5 K min<sup>-1</sup>, respectively.

The effects of sorbitan tristearate (STS) and soya lecithin on PO and on palm olein blends with low SMP for fluidised palm oil formulation by

temperature cycling were studied by Miskandar *et al.* (2006). This study showed that the emulsifiers could be useful agents for controlling crystallisation in fluidised palm oil formulations. In 2007, Miskandar *et al.* determined the effect of STS and soya lecithin on blends of PO and palm olein by slow crystallisation (0.7°C min<sup>-1</sup> for 32 min). Results indicated that STS acted as a crystal inhibitor (0.06% - 0.09%), while at 0.03%, it was a crystal promoter. Slow crystallisation process of the blends with 0.03% lecithin produced homogeneous crystals with low solid fat content (SFC) and viscosity for fluidised products.

## Polymorphism

Polymorphism and phase behaviour have by far the greatest influence on PO crystallisation. These two phenomena are closely linked together and a description of one of them is usually incomplete without the other. Polymorphism is the ability of compounds to crystallise in different crystalline structures. They result from the stereochemical configuration of the molecules of the crystal which exhibits different orientations of the zigzag arrangement of the glyceridic chains (Jacobsberg and Oh, 1976). The phase behaviour of the different TAG in the solid state usually affects the efficiency of the crystallisation process (Timms, 1984). Palm oil also forms mixed crystals or solid solutions (Timms, 1984; Berger, 1989). This tendency is ascribed partly to the relatively high amount of symmetric monooleic disaturated TAG such as POP (Jacobsberg and Oh, 1976). It is also strongly enhanced by the presence of asymmetric TAG such as partial glycerides as these act in increasing the  $\alpha$ -lifetime and decreasing the SFC (Knoester *et al.*, 1972; Persmark *et al.*, 1976; Berger, 2001; De Clercq *et al.*, 2012). Intersolubility is known as the mutual solubility of a TAG in another leading to the formation of solid solutions (Timms, 1994). The formation of a solid solution is highly dependent on the chemical composition and the crystal structure of different TAG within a certain mixture.

The polymorphism and phase behaviour of PO and its fractions have been reviewed to a certain extent (Persmark *et al.*, 1976; Timms, 1984; Berger, 1989; Braipson-Danthine and Gibon, 2007). The four polymorphic forms which have been well-established for palm oil are the sub- $\alpha$ ,  $\alpha$ ,  $\beta'$  and  $\beta$ . It is well-known that PO is  $\beta'$  stable and of this type, the stable sub-polymorph being  $\beta_1'$ . Persmark *et al.* (1976) conducted an X-ray diffraction study on the phase behaviour of PO and found the existence of three polymorphs, namely  $\alpha$ ,  $\beta_1'$  and  $\beta_2'$ . Utilising the diffraction-pattern-temperature (DPT) camera, they observed X-ray diffraction patterns of the lower melting  $\beta'$ ,  $\beta_2'$  prevailing at subzero temperatures below -10°C upon rapid cooling. They further

discovered a mixture of  $\alpha$  and  $\beta_1'$  polymorphs existing between  $-10^\circ\text{C}$  and  $-5^\circ\text{C}$  when the oil was further heated slowly. At  $7^\circ\text{C}$ , the  $\beta_1'$  form was found to dominate.

In another study, Jacobsberg and Oh (1976) revealed that fast cooling of PO produces a crystals, which are unstable, and when provided with sufficient energy they are transformed into  $\beta'$  and  $\beta$  polymorphic forms. The easiest way to obtain these transitions is to keep the crystals at temperature slightly below the melting point of the required polymorphic form. Oh (1989) in his study indicated that PO when crystallised from melt showed a polymorphic form of a single short spacing band at ca. 0.415 nm;  $\beta'$  of two short spacing at ca. 0.43 nm and 0.38 nm, also sometimes at 0.40 nm medium or weak short spacing; and  $\beta$  form of a strong short spacing at ca. 0.45 nm or 0.46 nm with two or three strong or medium bands at 0.39, 0.38 and 0.37.

In a separate study carried out by Deffense and Tirtiaux (1989),  $\beta$  type crystals were observed when PO was maintained or cooled slowly around temperatures between  $40^\circ\text{C}$  and  $45^\circ\text{C}$ . These types of crystals were thought to originate from handling and storage, thus necessitating melting the oil at high temperatures to destroy all crystal memory upon proceeding with crystallisation.

Mazzanti *et al.* (2005) studied the influence of shear rates on phase transitions during PO crystallisation at  $17^\circ\text{C}$  and  $22^\circ\text{C}$ . Applying different shear rates from 0 to  $2880\text{ s}^{-1}$ , they discovered that the acceleration of the phase transition from  $\alpha$  to  $\beta'$  increased with increasing shear at both temperatures of study. A simple model was developed in which they describe that initially, the  $\alpha$  phase nucleates from the melt followed by nucleation of the  $\beta'$  phase on the  $\alpha$  crystallites. They concluded that under shear, small crystallites are formed from the  $\alpha$  nuclei which easily transform to the  $\beta'$  form. A lower shear retards the nucleation of the  $\beta'$  crystals since this causes the  $\alpha$  nuclei to aggregate and provide fewer nucleation sites per unit volume for the  $\beta'$  form to nucleate.

In a study conducted by Chong *et al.* (2007) using coupled time-resolved synchrotron X-ray diffraction (XRDT) with high sensitivity DSC found that PO in its crude form crystallises into two different  $\beta$  polymorphs of double and triple chain length stacking when a cooling rate of  $0.1^\circ\text{C min}^{-1}$  was applied. This was evident at temperatures below  $27^\circ\text{C}$  and was revealed through the XRD peaks which displayed two  $\beta$  subcells developing successfully. They also suggested that PO is composed of a three-phase system involving a  $\beta'$ , a  $\beta$  and a liquid phase (two solids and one liquid) rather than a single solid and single liquid system due to the coexistence of stable  $\beta'$  plus  $\beta$  forms at high temperatures.

The most comprehensive comparative study on the polymorphic behaviour of PO and its fractions was carried out by Braipson-Danthine and Gibon (2007). They examined the polymorphic behaviour of 24 samples of PO and its solid and liquid fractions, which included oleins, superoleins, stearins and mid fractions using DSC and powder XRD spectroscopy. They observed that for PO, palm stearin, and mid fractions, low melting peak components comprising mainly UUU, SUU and SUS TAG exhibited sub- $\alpha_2$ , sub- $\alpha_1$  and  $\alpha$  polymorphs in the DSC melting curves. The high melting peaks which contained SUS and SSS components were found to crystallise in  $\beta'_2$ ,  $\beta'_1$  and partially in  $\beta$ . Polymorphism for palm oleins and super oleins were found to be in the sub- $\alpha_2$ , sub- $\alpha_1$ ,  $\alpha$  and  $\beta'_2$  for lower melting peaks (UUU, SUU and SUS) while  $\beta'_1$  was observed for high melting peaks only in palm oleins due to the higher content of SUS TAG.

Zaliha and Norizzah (2012) investigated the physico-chemical properties of binary blends of PO products with deodorised cocoa butter (DCB) at levels ranging from 10% - 90% (w/w). The addition of DCB at all concentration with cocoa butter equivalent (CBE) resulted in the formation of a strong  $\beta$  in a mixture of  $\beta+\beta'$  polymorphic forms. On the other hand, when 10% - 20% palm mid fraction (PMF) and CBE were mixed, a strong  $\beta'$  in a mixture of  $\beta+\beta'$  polymorphic forms was obtained.

### Crystallisation Kinetics

The kinetics of fat crystallisation is important in controlling operations in the food industry in order to produce products of desired quality (Metin and Hartel, 1998; Himawan *et al.*, 2006; Walstra, 1998). Crystallisation kinetics on PO has been studied to improve its processing and storage condition (Ng, 1990; Ng and Oh, 1994; van Putte and Bakker, 1987; Chen *et al.*, 2002). Van Putte and Bakker (1987) investigated the kinetics of PO crystallisation and showed that PO crystallised in the  $\beta'$ -modification when cooled to between  $21^\circ\text{C}$  and  $29^\circ\text{C}$  and into the  $\beta$ -modification when crystallised between  $34^\circ\text{C}$  and  $46^\circ\text{C}$  under non-stirring conditions. The amount of SSS components present in the washed filtrate was more than 55% for the former temperature conditions and exceeded 75% for the latter. When stirring condition was applied, PO crystals formed agglomerates of the  $\beta'$  type consisting of spherulites with numerous needles growing from the centre.

Yap *et al.* (1989) used DSC and pNMR to estimate crystallisation kinetics of PO and modified palm oils. DSC was found to be more sensitive and could differentiate between crystallisation during cooling and isothermal conditions. They reported that hydrogenated palm oils crystallised quickly

and completely when cooled from 60°C to 20°C while PO and fractionated palm stearin continued to crystallise when held isothermally at 20°C.

Zhang *et al.* (2013) compared the thermal behaviour of palm stearin (PS) and palm olein (POo) by using DSC, the isothermal crystallisation kinetics by pNMR and isothermal microstructure by polarised light microscopy (PLM). Both PS and POo had quite similar exotherms but PS had sharper exotherms with respect to isothermal crystallisation. The Avrami exponent ( $n$ ) value in Avrami equation increased when the crystallisation temperature rose and the  $n$  values for both PS and POo were almost the same at the same crystallisation temperature. This could be due to the same kind of fatty acids present in both PS and POo. Hence, both the PS and POo had the same mechanism of nucleation and crystal growth. However, PS showed different crystal morphology compared to POo at the same crystallisation temperature.

Abd Rashid *et al.* (2012) investigated the isothermal crystallisation of PS, palm kernel olein and their blends at 10°C, 15°C and 20°C using DSC. Based on the  $n$  obtained (Avrami, 1939; 1940; 1941) PS and palm kernel olein have different nucleation and crystallisation mechanisms. The suggested mechanism for palm kernel olein was high nucleation rate at the beginning of crystallisation, which decreased with time, and plate-like growth ( $n = 2$ ). On the other hand, the mechanism for PS was instantaneous heterogeneous nucleation followed by spherulitic growth ( $n = 3$ ). For blends of PS and palm kernel olein, the mechanisms of crystallisation were 2 and 3 depending on the composition of the blends and crystallisation temperatures.

### Thermal Properties

DSC is a useful tool for studying crystallisation of oils and fats (as well as their melting). Oh and Berger (1983) proposed a routine procedure to characterise the crystallisation and melting behaviours of PO using DSC. The procedure requires PO sample to be melted at 80°C for 10 min, cooled to -50°C at 10°C min<sup>-1</sup>, held at -50°C for 10 min and finally heated to 80°C at 10°C min<sup>-1</sup> for cooling thermogram. For melting thermogram, the sample was held at -40°C for 10 min before heating up to 80°C at a heating rate of 5°C min<sup>-1</sup>.

The crystallisation of PO was characterised by two easily distinguishable peak areas in the exotherms as depicted in Figure 1 (Kawamura, 1979; 1980; Ng and Oh, 1994; Ng, 1990; Zaliha *et al.*, 2004; Braipson-Danthine and Gibon, 2007). These two peaks correspond to two different groups of TAG crystallising at different temperatures. One group is designated as the higher melting TAG

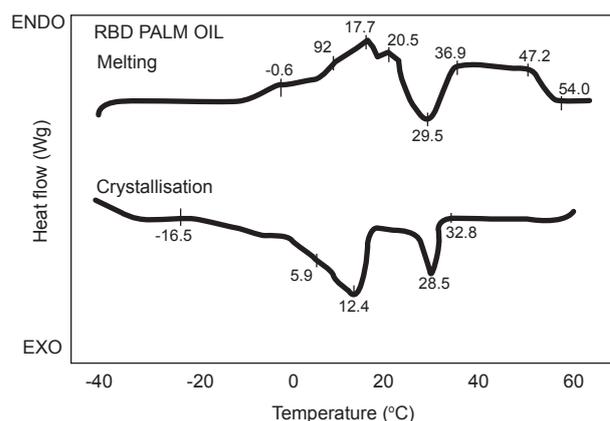


Figure 1. Differential scanning calorimetry crystallisation and melting thermogram of palm oil (adapted from Zaliha *et al.*, 2004).

which comprises mainly of trisaturated TAG such as PPP, PPS and MPP. These higher melting TAG start to crystallise at around 28.5°C. The other group crystallising at lower temperatures mainly consists of lower melting TAG which start crystallising at around 12.4°C. The melting thermogram also shows two broad peaks in the endotherm. These depict the same two groups of TAG which have different melting temperatures. The first endothermic peak represents the lower melting TAG completely melted at 29.5°C while the second broader peak signifies the higher melting TAG melting between 36.9°C to 54.0°C. The presence of these two types of TAG groups is apparent when the oil forms a semi-solid solution when left at room temperature.

Busfield and Proschogo (1990) investigated the thermal properties of PS and observed several thermal transitions within their DSC profiles. The stearin melted as almost two independent components in separate temperature ranges. The high-melting component, consisting mainly of POP (33%), PPP (≈15%), POS (4%) and PPS (2%), crystallised initially in an  $\alpha$  crystal form which rearranged on tempering successively to  $\beta'$  and  $\beta$  crystal forms. The lower-melting component was mainly POO (14% overall), PLP (13% overall) and SOO (1% overall). It crystallised initially in a sub  $\alpha$  form which rearranged to  $\beta'$  when tempered at 0°C, and to the  $\beta$  crystal form when tempered at 10°C. The liquid phase contained mainly PLO (8% overall), OOO (6% overall), PLL (4% overall) and LOO (1% overall).

Mihara *et al.* (2007) examined how PPP affected the crystallisation of POP and POO by DSC and XRD on PPP/POP and PPP/POO mixtures. High and low temperature peaks were noted to appear on the DSC crystallisation curve for both mixtures. The high temperature peak was possibly due to PPP, and the low temperature peak corresponded to POP or POO. DSC isothermal analysis revealed that the rate

of crystal growth of either mixture exceeded that of pure POP or POO, crystal mixture structure also was complicated compared to the pure form.

## FRACTIONATION

PO has a characteristic that makes it a versatile ingredient in food products. By simple fractionation process, PO can be resolved into a liquid, a solid and intermediate fractionated palm olein (also known as palm mid fraction) and various grades of palm stearin (Zaliha *et al.*, 2004). Both olein and stearin have applications in certain margarine formulations. For example, olein is a useful source of liquid oils, which is required in certain soft margarine formulations while stearin is frequently used as a hard stock for palm-based margarine and vegetable shortenings.

The fractionation process has been extensively reviewed by several authors in the last decade (Gibon and Tirtiaux, 2002; Timms, 2005, Kellens *et al.*, 2007). The principle of fractionation is the partial crystallisation of the oil followed by separation of the crystallised phase from the remaining liquor by various filtration techniques. This process is largely based on the differences in the melting points of the constituent TAG in an oil or fat. The resulting products are a liquid phase and a solid phase which are termed as olein and stearin, respectively.

PO is the most fractionated oil worldwide, and the majority is fractionated via the dry fractionation process. This process has been reviewed as the cheapest and most natural modification process compared to hydrogenation and interesterification (Kellens, 1996; Deffense, 1998). This fractionation technique has the advantage of being a pure modification process without the use of any chemicals or additives compared to the detergent and solvent routes. Hence, it is preferable over other fractionation processes due to the low processing costs involved and the higher yield of liquid olein obtained, which is comparable to the solvent process.

Zaliha *et al.* (2004) studied the crystallisation behaviour of PO in relation to the dry fractionation process and revealed that the physico-chemical properties of the fractions were affected by the crystallisation temperatures. In another study, using polarised microscopy (PLM) and XRD, Chen *et al.* (2002) observed spherical crystals formed from the first fraction were  $\alpha$  form, while needle-like crystals nucleated later from the second fraction were  $\beta$  and  $\beta'$  during a two-stage dry fractionation process of PO below 295K.

Kuriyama *et al.* (2011) improved the dry fractionation of PO using a series of Generally Regarded as Safe (GRAS) Polyglycerol Fatty Acid Esters (PGE). This study revealed that the hydrophobic PGE reduced the fractionation time and

hence the energy consumed during fractionation. The fractionated oleins exhibited better cloud point (between 7°C - 8°C). The crystal size was observed to be homogeneous with majority at 100-300  $\mu\text{m}$  without posing any filtration difficulty.

## RECRYSTALLISATION OR POST-CRYSTALLISATION

The post-crystallisation in PO-based products has been ascribed to its slow crystallisation behaviour hence leads to processing difficulties. Post-crystallisation of PO increases the hardness of finished products several weeks after manufacturing. According to Timms (1984) and Duns (1985), the post-crystallisation might be due either to the transformation of  $\beta'$  to  $\beta$  form or crystal networking after crystallisation. The transformation of  $\beta'$  to  $\beta$  polymorph leads to coarse crystals, causing product graininess and unacceptable to the consumers. Ward (1998) reported that there is always a tendency for the fat to be transformed to the most stable crystal form during storage if the stable crystal form has not been achieved in the processing.

Timms (1990) reported that post-hardening was caused by an increased interlocking of the crystals in addition to an increase in the solid phase. He also reported that recrystallisation or post-hardening process was due to the smallness of the crystals. When PO fractions are used in products, a slow crystallisation or recrystallisation can take place after manufacture. During production, cooling conditions may be applied that do not lead to the thermodynamic equilibrium between the composition of the solid and the liquid phases. Recrystallisation can occur to form a new solid phase as thermodynamic equilibrium is approached (Smith *et al.*, 1994).

Fat crystals can sinter, or in other words, link together through bridges formed, apparently by TAG with melting points between those of the existing solid and liquid phases (Johansson *et al.*, 1995). Thus  $\beta'$  crystals are bridged by  $\beta'$  solid and  $\beta$  crystals by  $\beta$  solid. deMan and deMan (2001) have reported that temperature treatment of fats can have a profound influence on the  $\beta'$  polymorph stability in fats. The stable  $\beta'$  polymorph in fats may transform wholly or partially to the  $\beta$  form when subjected to temperature fluctuations during storage. It is customary to temper shortenings for several days, usually at a temperature above which they are processed, but not higher than 28°C. They suggested that ideal tempering should not lead to the formation of  $\beta$  crystals.

The crystal networking can be quantified by fractal dimension via rheological and image analysis as suggested by Marangoni and Narine (2002) and Marangoni (2005). The quantification of the spatial

distribution of microstructural elements within the microstructures in fat-crystal networks has been studied using the relationship of the shear elastic modulus ( $G'$ ) to the volume fraction of solid fat (F) via the mass fractal dimension (D) of the network.

A study on the effects of storage temperatures and time on the physico-chemical properties of refined bleached deodorised palm oil by Zaliha *et al.* (2004; 2005; 2006) showed that post-hardening had occurred upon storage without transformation of polymorphic form from  $\beta'$  to  $\beta$ . Hence, the post-hardening phenomenon could be due to crystal networking after crystallisation process. The fractal dimension by both the rheological method and image analysis can be a good indicator for the hardness and mass distribution of the fat crystal networks for palm-based products during storage.

### CONCLUSION

The polymorphism, phase behaviour and chemical composition of PO have been shown to have a profound influence on the crystallisation of PO. The addition of additives such as sorbitan esters and polyglycerol fatty acid esters at various levels affect the nucleation rate, crystallisation rate and crystal growth of PO. Various techniques have been used to monitor the crystallisation process such as DSC, PLM, pNMR, XRD, combined DSC and time resolved XRD. The recrystallisation of PO was postulated to be due to polymorphic transformation, but recent study shows that it could be due to crystal networking. Further studies should be carried out in this research area.

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