Effect of polyglycerol esters additive on palm oil crystallization using focused beam reflectance measurement and differential scanning calorimetry

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A B S T R A C T
The effect of 0.1–0.7% (w/w) of polyglycerol esters (PGEmix-8) on palm oil crystallization was studied using focused beam reflectance measurement (FBRM) to analyze the in-line changes of crystal size distribution during the crystallization. FBRM results show that 0.1–0.5% (w/w) of PGEmix-8 did not significantly affect nucleation but slightly retarded crystal growth. The use of 0.7% (w/w) additive showed greater heterogeneous nucleation compared to those with lower dosages of additive. Crystal growth was also greatly reduced when using 0.7% (w/w) dosage. The morphological study indicated that the palm oil crystals were smaller and more even in size than when more additive was added. Isothermal crystallization studies using differential scanning calorimetry (DSC) showed increased inhibitory effects on palm oil crystal growth with increasing concentration of PGEmix-8. These results imply that PGEmix-8 is a nucleation enhancing and crystal growth retarding additive in palm oil crystallization at 0.7% (w/w) dosage.

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1. Introduction

Palm oil is an edible oil derived from the fruits of the oil palm Elaeis guineensis. The physical nature of palm oil which exhibits a semi-solid state in tropical climate, allows its separation as a low melting fraction (olein) and a high melting fraction (stearin) (Defesse, 1985). The quality of the olein fraction depends on the crystallization step, whereas the quality of the stearin fraction depends on both the crystallization and separation steps (Timms, 2005). Therefore, an understanding of crystallization is very important in modifying the fractionation process to ensure good yield and quality of the products. In recent years, fractionation technology has undergone some important improvements (Saw, Chong, & Yeoh, 2015). The developments in palm oil fractionation are mainly focused on areas related to crystallization and solid-liquid separation, i.e. the development of more efficient crystallizers and high-pressure membrane filter presses (Kellens & Hendrix, 2000). These modifications served to reduce utilities consumption, increasing yield and production of higher purity fractions, thereby reducing processing cost.

The use of crystallization enhancers is another interesting area of development in palm oil fractionation. Crystallization enhancers may vary the crystal size distribution of the palm oil slurry, thus affecting the yield and quality of the products. There are numerous publications on the influence of minor components or additives on the physical properties of oils and fats during crystallization (Basso et al., 2010; De Oliveira, Grimaldi, & Goncalves, 2014; Fredrick, Foubert, De Sype, & Dewettinck, 2008; Garbolino, Bartocci, & Flöter, 2005; Kurijama, Miyaji, Tamura, Zaliha, & Chong, 2011; Saberi, Lal, & Toro-Vázquez, 2011; Sakamoto et al., 2003; Shimamura, Ueno, Miyamoto, & Sato, 2013; Verstringe, Danthine, Blecker, Depypere, & Dewettinck, 2013). The additives can be categorized into two types: indigenous components and added components (Smith, Bhaguan, Talbot, & van Malssen, 2011). These minor components include free fatty acids (FFA), monoacylglycerols (MAG), diacylglycerols (DAG), and phospholipids, triglycerol monostearate and polyglycerol esters (Smith et al., 2011). These additives may affect crystallization of oils and fats by influencing the nucleation, crystal growth, morphology, heat capacity, rheology and polymorphic stability (Smith et al., 2011).

Jacobsberg and Ho (1976) discussed several factors influencing the crystallization of palm oil whereby palm oil fractionation is adversely affected by the increases in the FFA, DAG content and degree of oxidation. De Oliveira et al. (2014) reported that 6.0–8.5% of DAG increased the initial crystallization rate of palm oil. In contrast to this, Saberi et al. (2011) reported a reduction in the rates of nucleation and crystal growth of palm oil with the
addition of 5% palm-based DAG. Nonetheless, high concentration (30 and 50%) of DAG have shown a significant reduction in the induction time and an elevated Avrami constant (k), which suggested promoting effects on nucleation and crystallization rates of palm oil (Saberi et al., 2011). These differences could also be influenced by the type and dosage of DAG added, as well as the crystallization conditions. Basso et al. (2010) reported that tripalmitin increases crystallization rate of palm oil and causes the formation of larger crystals. This is because of the crystallization of the tripalmitin itself due to its high concentration in palm oil (Basso et al., 2010). The research paper also pointed out that the addition of MAG led to the formation of a large number of nuclei without changing the final solid content, accelerating the process of crystal formation, leading to the formation of smaller crystals than those found in the refined palm oil (Basso et al., 2010). Verstringe, Dewettinck, Ueno, and Sato (2014) studied the templating effects on crystallization of palm oil with 8% of monopalmitin using synchrotron radiation microbeam. The study found that monopalmitin promoted palm oil crystallization and crystal formation was oriented by the previously crystallized monopalmitin (Verstringe et al., 2014). Most of the research activities involved the use of high concentration of additives of above 5% to achieve a significant effect on crystallization, except Sakamoto et al. (2003), who reported that 1% of polyglycerol behenic acid esters promoted nucleation and inhibited crystal growth of palm oil.

The initial study investigated the effect of low concentrations of polyglycerol esters (PGEmix-8) as the additive for palm oil isothermal crystallization at 24 °C (Kuriyama et al., 2011). The additive was specially designed by Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan) for enhancing palm oil fractionation process. It is made of a mixture of fatty acids of palmitic acid, stearic acid and oleic acid, with a melting point of 42.8 °C (Kuriyama et al., 2011). Preliminary results as reported by Kuriyama et al. (2011) indicated that olein yield was increased with the use of 0.5% of the additive. The study reported that the increase of olein yield was due to better filtration efficiency, caused by more homogeneous crystals formed (Kuriyama et al., 2011). The objectives of this study were to evaluate the role of this additive in palm oil crystallization using FBRM, DSC and optical microscopy, and a possible mechanism of crystallization was predicted based on the data obtained from these techniques. The use of FBRM ensures real-time and in-situ monitoring of particle characteristics within different physical and chemical processes such as granulation, flocculation, dissolution as well as in agitated crystallization system (Hishamuddin & Omar, 2016), which is very much comparable to the actual crystallization process in fractionation. Moreover, the device is able to detect the onset of nucleation, analyzing the in-line changes in particle dimension, concentration and population (Hishamuddin, Stapley, & Nagy, 2011). The changes in total particle count and mean particle size can be used to describe nucleation and crystal growth, respectively (Yu, Chow, & Tan, 2008).

2. Materials and methods

2.1. Materials

Refined, bleached and deodorized palm oil (RBDPO) was purchased from Moi Foods Malaysia Sdn. Bhd (Selangor, Malaysia). The GRAS graded polyglycerol esters – PGEmix-8 additive was provided by Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan). It was made of a mixture of fatty acids of palmitic acid, stearic acid and oleic acid, with a melting point of 42.8 °C (Kuriyama et al., 2011).

2.2. Crystal size distribution by FBRM

The changes in chord length distribution of crystals during isothermal crystallization of palm oil and its blends with polyglycerol esters (PGEmix-8) was monitored in a 1 L stirred, jacketed glass Mettler Toledo Labmax reactor equipped with a Lasentec D600L probe (Schwerzenbach, Switzerland). The probe was used to monitor the particle counts and size distribution within the crystallizer.

Low concentrations of PGEmix-8 additive of 0.1, 0.3, 0.5 and 0.7% (w/w) were used in this study. About 700 g of the pre-melted RBDPO and the additive were first loaded into the reactor that was equipped with a glass anchor agitator and stirred at the rate of 30 rpm. The mixture was then heated to 70 °C and held at that temperature for one hour to destroy the entire crystal structures. The melt was then cooled down to 30 °C in one hour and the temperature was further reduced to 24 °C in 20 min. The isothermal crystallization was carried out at 24 °C for 120 min. During the isothermal run, data were collected using a 90 log-channel over the size range of 1–1000 µm. The chord Length distribution of crystals was recorded at every 30 s during the run. Crystal counts were categorized into five classes: 1–5 µm, 10–23 µm, 29–86 µm, 100–251 µm and 293–1000 µm. Each experiment was done in duplicate. The same procedure was conducted for RBDPO crystallization at all additive dosages. The control run was carried out without the addition of the additive.

2.3. Crystal morphology by polarized light microscope

Crystal morphology study of RBDPO and its blends with additives during the isothermal crystallization was conducted using a Leica DMLP polarized light microscope (Wetzlar, Germany). Images were captured and recorded using Leica Qwin V3 imaging system (Cambridge, UK). Samples of the slurries were collected at 20 min intervals during the 120 min isothermal crystallization and images were microscopically captured. A total of 7 samples were collected for each run. A drop of the slurry was placed onto a glass slide and covered with a cover slip. Microscope images were captured at a magnification of 100×.

2.4. Isothermal crystallization by DSC

Isothermal crystallization of RBDPO and its blends with different dosages of PGEmix-8 were performed with a Perkin-Elmer DSC (DSC 8000) equipped with an autosampler. The instrument was calibrated using indium and a temperature programme of 120 °C–180 °C at a rate of 5 °C/min. About 5–10 mg of samples was prepared in a volatile aluminium sample pans. The sample was first heated to 80 °C to erase the previous crystal history. The sample was then cooled at a fast cooling rate of 100 °C/min to the isothermal temperature (24 °C). The sample was held at the isothermal temperature for 90 min and the heat flow during the crystallization was recorded. Peak time was determined using exotherm from zero time until the exotherm reached to a maximum heat flow.

2.5. Statistical analysis

The FBRM data were analyzed using the analysis of variance (one-way ANOVA) to determine the significance of the additive dosages on overall crystal growth rate, total particle count and mean particle size at 5% (w/w) confidence level. Comparisons were made using Dunnett Method, with 0.0% (w/w) as the control. The software used was Minitab 16.2.
3. Results and discussion

3.1. Effect of polyglycerol esters (PGE) additive on nucleation and early crystallization

Crystallization of oils and fats consists of a few stages; supercooling of the melt, nucleation, and crystal growth (Kellens, Gibon, Hendrix, & Greyt, 2007). Nucleation occurs when the melt becomes supercooled, whereby the temperature of the melt is much lower than the thermodynamic equilibrium temperature (Kellens et al., 2007; Lawler & Dimick, 2002). The effects of additives with respect to nucleation are alterations of nucleation time, shift in nucleation temperature, and changes in the number and nature of the nuclei formed (Smith et al., 2011). Many techniques for nucleation measurements do not detect nucleation directly, as those techniques require nuclei to grow into crystals to be detectable by these devices or methods (Smith et al., 2011). This limitation also applies to FBRM. However, the device is able to detect particles or crystals as fine as 1 μm. This early detection of crystal formation is very useful for predicting nucleation mechanisms. Therefore, information such as total particle count at the beginning of crystallization can be directly related to nucleation.

Fig. 1 shows the total particle count of the palm oil slurries during isothermal crystallization at 24 °C, with and without the addition of PGEmix-8. Initially, particle counts increased drastically at the first 20 min of the crystallization due to nucleation. The gradient of the curves indicates the rate of increase of total particle count which can be related to nucleation. From the zoomed image in Fig. 1, the rate was increased with higher dosages of PGEmix-8 added. In comparison, 0.1% (w/w) to 0.3% (w/w) showed slightly lower rates than the control, indicating minor retardation of nucleation. As for 0.5% (w/w) and 0.7% (w/w) PGEmix-8, the slope was steeper than that of the control. This indicates that these dosages promote nucleation, the effect being most significant with 0.7% (w/w) concentration.

The early crystallization was also observed microscopically, as illustrated in Fig. 2A–C. The crystals for the control (0% (w/w)) were uneven in size with some relatively larger crystals present. There were more uniform crystals when 0.1% (w/w) of the additive was used, whereby no large crystals were observed. Similar observation was found for the 0.3 and 0.5% (w/w) addition. For the 0.7% (w/w) additive dosage, a very large number of very fine particles were detected. This observation is in-line with the FBRM results in Fig. 1, which indicates a drastic increase in total particle count at the early stage of crystallization. In comparison, the crystal sizes of palm oil slurry with 0.7% (w/w) additive were significantly smaller as compared to the control and that at lower dosages. Similar findings were found in Fig. 3, which also indicates that the initial crystal sizes were smaller when the dosage was increased, in which 0.7% (w/w) was the most significant dosage that impacts the mean particle size at the beginning of crystallization.

3.2. Effects of PGEmix-8 additive on crystal growth

Monitoring of crystal growth was performed as the crystallization process progressed and it was found that the total particle count continued to increase with longer isothermal holding time. Fig. 1 shows that 0.1 and 0.3% (w/w) of PGEmix-8 decreased the total particle count as compared to the control palm oil, while 0.5% (w/w) slightly increased the total particle count. However, data analysis using Dunnnett’s comparison method shows that total particle count at the end of the isothermal crystallization (120 min holding time) were insignificantly affected by 0.1% (w/w) to 0.5% (w/w) of PGEmix-8, but 0.7% (w/w) had significantly increased the total counts from about 2500 count/s to 6000 count/s. Fig. 3 shows that the mean particle size reduced with the increase in the PGEmix-8 additive. The crystallization achieved equilibrium crystal size at around 20 min of the isothermal crystallization except for 0.7% (w/w) when the equilibrium crystal size was only achieved 25 min after the isothermal crystallization. On top of this, slight mean particle size reduction was observed for 0.7% (w/w) at 5 min holding time. This is probably due to a drastic increase in the total particle count at the initial stage of crystallization, as shown in Fig. 1. The mean particle size then steadily increased to around

![Fig. 1. Total particle counts of palm oil isothermal crystallization (24 °C) for the control (0% (w/w)) and with addition of 0.1, 0.3, 0.5, and 0.7% (w/w) of PGEmix-8 additives.](image-url)
According to Hishamuddin et al. (2011), a slight reduction of mean chord length in their study was due to the secondary nucleation that caused a decrease in average crystal sizes. This study is consistent with their study, whereby this slight reduction of mean chord length was also due to secondary nucleation, possibly caused by slight breaking of large crystals or formation of new nuclei in the process to achieve crystallization equilibrium.

Towards the end of the crystallization, the mean particle size at 0.1% (w/w) and 0.3% (w/w) were about 140 µm which were about 20–30 µm lower than the control. The mean particle size further reduced to below 140 µm with 0.5% (w/w) additive. The most obvious effect was observed when 0.7% (w/w) of PGEmix-8 was added, whereby mean particle size reduced from about 165 µm to 65 µm. Statistically, only 0.7% (w/w) dosage reduced the mean particle size significantly when compared to the control, whereas the effects of lower dosages were all insignificant. Overall crystal growth rate was calculated from the gradient of the mean particle size graph versus time. Data analysis shows that the reduction of overall crystal growth rate with 0.1% (w/w) to 0.7% (w/w) of PGEmix-8 was all significant. Low amount of PGEmix-8 (0.1% (w/w) to 0.5% (w/w)) slightly reduced the overall crystal
growth rate. The effect was highly significant when 0.7% (w/w) of PGEmix-8 was added, during which the overall crystal growth rate was reduced from 4.6 µm/min to 2.1 µm/min. This indicated that the addition of 0.1–0.5% (w/w) of PGEmix-8 slightly retards crystal growth. The retardation effect was more obvious when 0.7% (w/w) of PGEmix-8 was added.

3.3. Effect of PGEMix-8 additive on crystal size distribution

The effect of PGEmix-8 additive on crystal size distribution of palm oil is shown in Fig. 4. The evolution of particle counts were categorized into five classes: extra-small crystals (XSc, 1–5 µm), small crystals (Sc, 10–23 µm), medium crystals (Mc, 29–86 µm), large crystals (Lc, 100–251 µm) and extra-large crystals (XLc, 293–1000 µm). It was found that originally the control has almost equal amount of Mc and Lc, with minimal amounts of Sc and XLc. Overall, 0.1% (w/w) to 0.5% (w/w) shared similar patterns of crystal size distribution. When 0.1% (w/w) of PGEmix-8 was added (Fig. 4B), the crystal size distribution changed. The number of Lc reduced from about 1200 count/s to about 800 count/s. At the same time, the number of Mc increased, and no XLc was detected. Interestingly, when 0.7% (w/w) PGEmix-8 was added (Fig. 4C), Lc almost disappeared, and a large number of XSc with a size range of 1–5 µm was detected.

This observation indicates that low dosages of PGEmix-8 (0.1% (w/w) to 0.5% (w/w)) prevent the formation of XLc and reduced the number of Lc. In other words, the size range of the crystals in the palm oil slurries were steeper compared to that of the control. It was also found that the impact of 0.7% (w/w) PGEmix-8 on palm oil crystallization was substantial. These results were in-line with the prediction of crystal growth rate, where the retardation effects on crystal growth increased with increasing amounts of PGEmix-8.

The evolution of chord length distribution during the first 25 min of isothermal crystallization at 24 °C is shown in Fig. 5. For the control palm oil, the number of crystals with a peak chord length of 92 µm gradually increased to 130 counts in the first 25 min of the holding time. When 0.3% (w/w) of PGEmix-8 was added, the number of crystals increased at a higher rate, indicating accelerated nucleation. The crystal size distribution also shifted slightly to smaller chord length region, causing the peak chord length to shrink to 73 µm. The rate of increase of crystals number had gradually slowed down 15 min after the isothermal crystallization. For 0.7% (w/w) PGEmix-8, the rate of increase of crystal number was significantly higher than the control. The crystal size distribution peak was found to be much sharper, with crystal sizes ranging from 5 to 140 µm compared to 10–340 µm and 10–290 µm for the control palm oil and the 0.3% (w/w) PGEmix-8, respectively. The rapid increase in the number of crystals with 0.7% (w/w) PGEmix-8 suggests more effective nucleation promotion than with 0.3% (w/w) of the additive.

Fig. 6 shows the DSC thermograms for palm oil crystallization with addition of different dosages of PGEmix-8 additive. The thermogram shows the amount of heat released upon isothermal crystallization for 40 min. The DSC curves show two exothermal bands between 5 and 25 min of isothermal time. The bands can possibly indicate a two-step crystallization, which was similar to the findings of Fredrick et al. (2008) who also observed a possible two-step crystallization in palm oil at the isothermal temperature of 25 °C. The multiple-step crystallizations could be either due to formation of crystals with different polymorphic forms, crystallization of triacylglycerols fraction with different thermal properties or the combination of both (Fredrick et al., 2008). As illustrated in Fig. 6, the addition of 0.1% (w/w) of PGEmix-8 did not show obvious inhibitory effects on crystal growth of palm oil molecules. Higher amounts of the additive (0.3% (w/w) to 0.5% (w/w)) slightly
retarded the crystal growth, whereby the bands shifted from 17.1 min to 19.3 min and 21.3 min, respectively. The retardation effect increased with the addition of 0.7% (w/w) PGEmix-8, during which the band shifted further to longer crystallization time and significantly lower peak intensity was observed. The trends observed in the DSC profiles corresponded to the results from FBRM which also showed an explicit increase in the inhibitory effect on crystal growth with the addition of higher dosages of PGEmix-8 additive.

The effect of the additive on the final crystal size distribution was observed microscopically, as shown in Fig. 2a–c. From the crystal morphological images, it was found that the size of the crystals was inversely proportional to the amount of PGEmix-8 added. The palm oil crystals were also more even in size when higher amounts of the additive were added.
3.4. Prediction of crystallization mechanism

These data obviously show that the mechanism of nucleation and crystal growth of palm oil with 0.7% (w/w) PGEmix-8 was different from the others. For pure palm oil and those with lower dosages of PGEmix-8, the heterogeneous nucleation occurs without significant interferences from the additive molecules. When more additive is used (0.7% (w/w)), significant enhancement of heterogeneous nucleation is observed, in which the PGEmix-8 molecules act as foreign materials for the formation of more nuclei (Sato, Ueno, & Yano, 1999). The possible mechanism involves in this crystallization is where PGE molecules act as the material for cluster formation, and therefore accelerate nuclei formation/nucleation when 0.7% (w/w) of PGEmix-8 is used. At a later stage, low dosages of the additives play a role in crystal growth by blocking the molecule packing, thus retarding crystal growth. When increasing amounts of additive is added (0.7% (w/w)), more of the crystal surface is covered and the growth is further hindered (Smith et al., 2011). This explains the detection of huge amounts of XSc found in 0.7% (w/w) crystallization, which were not present in the other crystallization systems.

From a molecular point of view, PGEmix-8 was found to have a great effect on palm oil crystallization because the additive is made of a mixture of palmitic acid, stearic acid and oleic acid, which are similar to majority of fatty acids that make up palm oil. The additive molecules are able to join the crystal matrix at the growth sites because the fatty acids attached to the PGEmix-8 molecules are similar to the crystallizing species in palm oil in terms of chain length, saturation, and type and position of unsaturation (Smith et al., 2011). Therefore, a very small amount of PGEmix-8, as low as 0.1% (w/w), is sufficient to give a significant impact on crystal growth because the additive acts on the growth sites specifically (Smith et al., 2011).

4. Conclusions

In conclusion, it was found that PGEmix-8 additive significantly affected palm oil crystallization and the effects varied with different dosage levels used. Low dosages of PGEmix-8 (0.1% (w/w) to 0.5% (w/w)) did not significantly affect nucleation of palm oil crystallization as indicated by total particle count results. However, overall crystal growth rate implied that their impact on crystal growth was significant. The growth rate was significantly reduced as compared to the control, suggesting retardation effect on crystal growth. When 0.7% (w/w) PGEmix-8 was used, the high concentration of the additive creates additional heterogeneous nuclei, which give rise to a remarkable nucleation promotion effect. However, a fast nucleation does not imply faster crystal growth. Crystal growth was inversely affected by 0.7% (w/w) PGEmix-8 as shown by FBRM results, in which smaller crystal population was clearly observed. These findings corresponded well to the DSC results. The exothermic bands shifted to longer crystallization time with significantly lower intensity, indicating marked inhibitory effects on palm oil crystal growth. Crystal morphology study also indicated that palm oil crystals were smaller and more even in size than when higher amounts of the additive were added. These results imply that PGEmix-8 is a nucleation enhancing and a crystal growth retarding additive in palm oil crystallization when 0.7% (w/w) is used.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.07.084.

References

Basso, R. C., Ribeiro, A. P. B., Masuchi, M. H., Gioielli, L. A., Goncalves, L. A. G., Santos, A. O. D., ... Grimaldi, R. (2010). Tripalmitin and monoacylglycerols as modifiers in the crystallization of palm oil. Food Chemistry, 122, 1185–1192.

De Oliveira, I. F., Grimaldi, R., & Goncalves, L. A. G. (2014). Effect of diacylglycerols on crystallization of palm oil (Elaeis guineensis). European Journal of Lipid Science and Technology, 116, 904–909.

Deforse, E. (1985). Fractionation of palm oil. Journal of American Oil Chemist Society, 62, 376–385.

Fredrick, E., Foubert, I., De Sype, J. V., & Dewettinck, K. (2008). Influence of monoglycerides on the crystallization behaviour of palm oil. Crystal Growth and Design, 8, 1833–1839.

Garbolino, C., Bartoccini, M., & Flöter, E. (2005). The influence of emulsifiers on the crystallization behavior of a palm oil-based blend. European Journal of Lipid Science and Technology, 107, 616–626.

Hishamuddin, E., & Omar, Z. (2016). In situ characterisation of palm olein crystallisation behaviour by focused beam reflectance measurement (FBRM). Journal of OIl Palm Research, 28, 44–51.

Hishamuddin, E., Stapley, A. G. F., & Nagy, Z. K. (2011). Application of laser backscattering for monitoring of palm oil crystallization from melt. Journal of Crystal Growth, 335, 172–180.

Jacobsberg, B., & Ho, O. C. (1976). Studies in palm oil crystallization. Journal of American Oil Chemist Society, 53, 609–617.

Kellens, M., Gibon, V., Hendrix, M., & Greyt, W. D. (2007). Palm oil fractionation. European Journal of Lipid Science and Technology, 109, 336–348.

Kellens, M., & Hendrix, M. (2000). Fractionation. In D. O. Richard, E. F. Walter, & J. W. Peter (Eds.), Introduction to fats and oils technology (second ed.). Champaign: AOCS Press.

Kuriyama, J., Miyaji, Y., Tamura, K., Zaliba, O., & Chong, C. L. (2011). Improved sustainable fractionation of palm oil using polyglycerol fatty acid esters. Journal of Oil Palm Research, 23, 1141–1145.

Lawler, P. J., & Dimnick, P. S. (2002). Crystallization and polymorphism of fats. In C. A. Casimir & B. M. David (Eds.), Food lipids chemistry, nutrition, and biotechnology (second ed., revised and expanded. New York: Marcel Dekker Inc.

Saberi, A. H., Lai, D., & Toro-Vázquez, J. F. (2011). Crystallization kinetics of palm oil blends with palm-based diacylglycerol. Food Research International, 44, 425–435.

Sakamoto, M., Maruo, K., Kuriyama, J., Kouno, M., Ueno, S., & Sato, K. (2003). Effects of adding polyglycerol behenic acid esters on the crystallization of palm oil. Journal of Oleo Science, 52, 639–645.

Sato, K., Ueno, S., & Yano, J. (1999). Molecular interactions and kinetic properties of fats. Progress in Lipid Research, 38, 91–116.

Saw, M. H., Chong, C. L., & Yeoh, C. B. (2015). New developments in palm oil fractionation. Palm Oil Development, 62, 4–9.

Shimamura, K., Ueno, S., Miyamoto, Y., & Sato, K. (2013). Effects of polyglycerine fatty acid esters having different fatty acid moieties on crystallization of palm stearin. Crystal Growth & Design, 13, 4746–4754.

Smith, K. W., Bhaggan, K., Talbot, G., & van Malssen, K. F. (2011). Crystallization of fats: Influence of minor components and additives. Journal of American Oil Chemist Society, 88, 1085–1101.

Timms, R. E. (2005). Fractional crystallization – the fat modification process for the 21st century. European Journal of Lipid Science and Technology, 107, 48–57.

Verstrine, S., Danthine, S., Blecker, C., Depypere, F., & Dewettinck, K. (2013). Influence of monopalmitin on the isothermal crystallization mechanism of palm oil. Food Research International, 51, 344–353.

Verstrine, S., Dewettinck, K., Ueno, S., & Sato, K. (2014). Triacylglycerol crystal growth: Templating effects of partial glycerol studied with synchrotron radiation microbeam X-ray diffraction. Crystal Growth & Design, 14, 5219–5226.

Yu, Z. Q., Chow, P. S., & Tan, R. B. H. (2008). Interpretation of focused beam reflectance measurement (FBRM) data via stimulated crystallization. Organic Process Research & Development, 12, 646–654.