Understanding the Interactions of Diacylglycerols with Oils for Better Product Performance**

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INTRODUCTION

Oils and fats consist of complex mixtures of triacylglycerols (TAGs), diacylglycerols (DAGs), free fatty acids and other minor components. The crystallization of TAG mixtures depends on the nature, chain length and saturation/unsaturation characteristics of the TAGs and the interaction of these TAGs with each other. The presence of DAGs further complicates the crystallization and melting behaviour. In most oils which are derived from oilseeds, the effects of DAGs are less conspicuous, being only present in small quantities. Other oils, *e.g.* sal fat, palm oil and olive oil, contain higher amounts of DAGs. These DAGs consist of fatty acid moieties that reflect those of the TAGs of the oils.

SIGNIFICANCE OF DIACYLGLYCEROLS IN QUALITY EVALUATION OF OILS

DAGs can represent a useful element of quality judgement for oils, particularly palm and olive oils. Catalano *et al*. (1994) established the remarkable differences in total DAGs, *i.e*. 1,2(2,3)- and 1,3-diacylglycerols as characteristic parameters of virgin olive oil quality. In extra virgin oils, the total DAG were less than 2.0%, 97.7% of the oils had less than 1.5% of 1,2 DAG, and less than 0.4 % of 1,3 DAG. Clear differences were observed for edible or lampant samples from those of virgin and extra virgin samples. Also, the neutralized oils still retained their DAG levels.

Several researchers have studied the DAG concentration of palm oil. Jacobsberg and Oh (1976) found that the total DAG concentrations in oils of unbruised and bruised fruits were 5.6% and 7.6%, respectively. The ratio of 1,3 DAG to 1,2 DAG in oils extracted from unbruised fruits was low (0.38), compared to 1.53 for oil from bruised fruits and values ranging from 1.47-1.63 for commercial oils. Studies by Goh and Timms (1985) supported the findings of Jacobsberg and Oh. No correlations were observed between the free fatty acid (FFA) level and DAG content. Similar findings were also observed by Siew and Ng (1995).

The quality of palm oil, like that of other oils, is defined by several parameters, such as FFA, peroxide value (PV), iodine value (IV), moisture and impurities, *etc*. The DAG content is normally not included unless specified. Usually, the FFA value is used to indicate the extent of hydrolysis of the oil. However, in refined oil where the FFA has been removed, it is no longer possible to evaluate the extent of degradation of the crude oil that had been refined. Should there be a need to know the quality of the oil of origin, it may be more appropriate to include the DAG content as a complementary parameter. Generally, freshly extracted oils have a low DAG content of 2.3% to 4%. However, the conditions prevailing in the industry such as harvesting conditions, transportation of fruits to factories, etc. result in commercial oils having DAG contents of 4.0% to 7.5% (*Table 1*). DAGs increase during storage under different conditions

TABLE 1. AVERAGE DIACYLGLYCEROL (DAG) CONTENTS IN REFINED PALM OIL PRODUCTS

Sample	Total DAG (wt.%)	1,2 DAG (wt. %)	1,3 DAG (wt. %)	X1,3/X1,2
Palm oil	6.0	1.8	4.2	2.33
Palm olein	6.1	1.8	4.3	2.33
Palm stearin	4.4	1.2	3.1	2.7

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(*Figure 1*). Also, in freshly extracted oils, the 1,2 isomers predominate over the 1,3 isomers, in distinct contrast to commercial oils. The high 1,2 DAG content of the oil in the fruits reflects the residual DAG of the biosynthetic pathway for TAG formation in the fruits. Fruits kept at different temperatures and in the field showed varying DAG contents. For example, *Figure 2* shows the changes in the mole ratio of X1,3/X1,2 for underripe, ripe and overripe fruits. The increase in this ratio is more rapid for ripe and underripe fruits. Similarly, when palm oil is stored at temperatures varying from 40½C to 100½C, the change in the ratio is significantly more rapid during the first few days at 100½C (*Figure 3*). Thus, oils from fresh fruits with a X1,3/X1,2 ratio of 0.2 gradually change to values of 1.8-3.3 as observed in commercial oils.

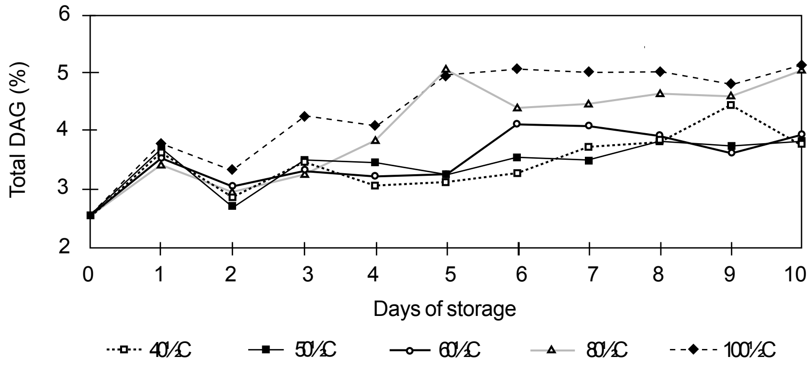

Figure 1. Changes in diacylglycerol content of palm oil upon storage at different temperatures.

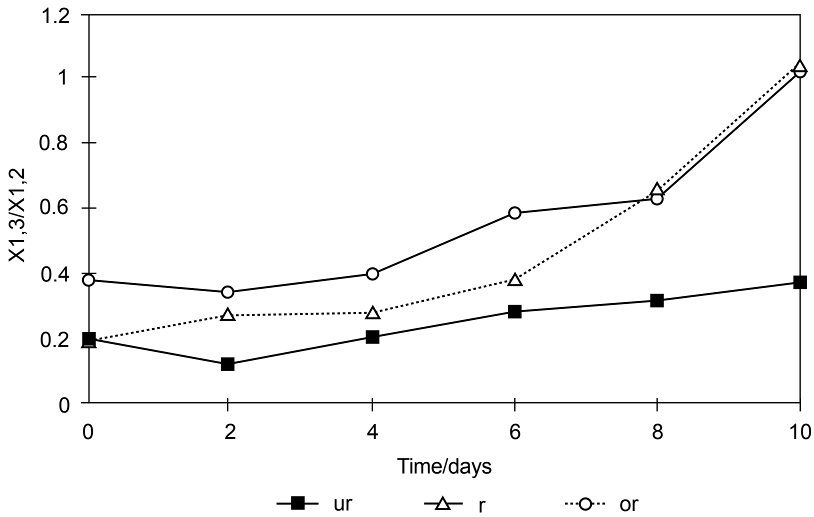

Figure 2. Changes in mole ratio (X1,3/X1,2) of diacylglycerol isomer in oils fruit of different degree of ripeness.

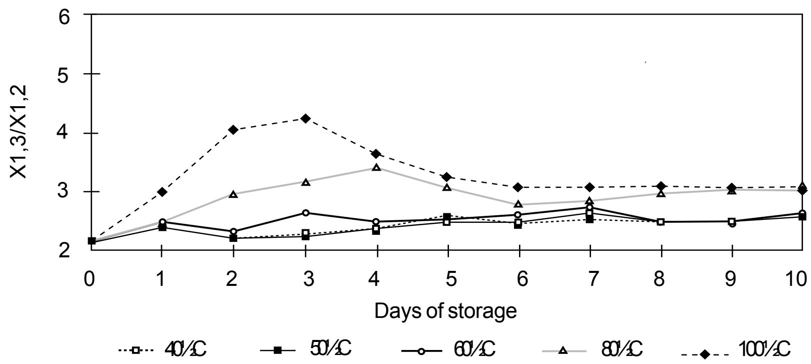

Figure 3. Effect of storage on X1,3/X1,2 of crude palm oil.

SIGNIFICANCE OF DIACYLGLYCEROLS IN OIL PRODUCT APPLICATIONS

Confectionery Fats

DAGs have been shown to have significant effects on the physical properties of oils and fats. These vary from melting point and polymorphism changes, rate of crystallization, crystal size and habits. Most of the work has been carried out on palm oil, sal fat, hydrogenated oils and coconut oil. Some of these studies will be discussed here.

Confectionery fats are made from both lauric and non-lauric oils. Cocoa butter is the ideal fat used in chocolate and related confectionery industries but, being expensive, it is partially replaced by cheaper fats in some products. The properties of cocoa butter are essentially affected by the main TAG component, SOS triacylglycerol. The DAG level in cocoa butter is around 2%, and, at this proportion, it does not affect the properties to a significant extent. The influence of DAGs on the rate of transformation of α to β' crystals was investigated by Wahnelt *et al.* (1991) who showed that 1,2-(2,3) DAGs cause more significant changes compared to 1,3 DAG.

Sal (*Shorea robusta*) fat comprises mainly the symmetrical monounsaturated, disaturated type of TAGs, mostly 2-oleodistearin. Its application in cocoa butter extenders and confectionery fat formulations has been increasing steadily. One major problem of this fat is the inconsistency in solidification properties which may vary from batch to batch. This presents problems in optimizing fractionation conditions, particularly obtaining a sal stearin with suitable properties for the confectionery industry. Yella Reddy and Prabhakar (1986) have shown that DAGs inhibit or delay the phase transition of all the crystal forms of TAGs from lower melting crystal forms to the next higher melting forms. This delay in transition was more pronounced with higher concentrations of DAGs. The DAGs also delayed the transition of form IV to V even after tempering. Thus, while the DAGs present may have a beneficial effect in producing a smooth consistency in margarines, they however, have somewhat deleterious effects in chocolate manufacture.

Other studies on high quality confectionery fats have shown that DAGs cause early crystallization, which may be due to the nucleating species being DAGs, further triggering the nucleation of saturated TAGs (Cebula and Smith, 1992).

Palm mid fraction (PMF), so called because it is the middle fraction of a second fractionation process, is used in confectionery fats. The main TAG is POP, which undergoes polymorphic changes similar to those of cocoa butter. The effects of DAGs from palm oil on POP crystallization behaviour of PMF have been evaluated by Okiwachi and Sagi (1985). DAGs at 5% to 6% levels disturb the transformation of crystals when the ageing process is not long. It also prolongs the solidification process. When DAGs at about 6% are present, the hardness of the product is much lower, meaning that demoulding may be affected during processing.

Palm Oil Products

Effects on polymorphism and crystal morphology. Early works on the effects of DAGs on palm oil were illustrated by Okiy (1978). The transition time of α crystals, obtained when palm oil is tempered for 90 min at 0½C, varied between 11 min to 23 min when DAG was increased from nil to 10% concentration. The tempering temperature is a factor in considering whether there are any significant effects of DAGs on the crystallization behaviour. At a higher temperature, for example, 20°C, there was no difference in the α lifetime at 10% of DAGs, with the exception of the 15% level. At this concentration, the effects of DAGs were observed throughout all the crystallization properties of the oil. The melting point was reduced from 40°C to 34°C. Differential scanning calorimetry (DSC) heating curves showed that the amount of higher melting components was reduced with increasing DAG level, thus accounting for the lower melting point. The presence of 2%, 10% and 15% DAGs led to a reduction in solids by 11%, 19% and 22%, respectively. In this study, the authors expected problems in using palm oil in applications such as in margarines, especially, as the palm oil investigated was from Africa, with high FFAs and probably, high DAGs as well.

Our own studies (Siew and Ng, 1996) showed that the DAG effect of lowering the melting point is not consistent for all types of oils. The extent of reduction or elevation in melting point also depends on the type of DAG and isomer. The 1,2 isomer was found to be more effective in causing a melting point depression. The 1,3 dipalmitoylglycerol (PP) did not seem to have this effect, in contrast; even when the concentration was exceedingly higher than those normally found in oils, for example at 5%, there was elevation of melting point observed (*Table 2*). The DSC melting thermograms showed additional

TABLE 2. EFFECT OF DIACYLGLYCEROL (DAG) ON MELTING POINT OF PALM OIL, OLEIN AND STEARIN

DAG	Palm oil	Olein	Stearin
No DAG	44.5	23.5	52.5
1,3PP			
1%	45.0	20.0	52.5
5%	54.5	20.0	58.0
1,2PP			
1%	40.0	20.0	47.0
5%	38.0	19.5	42.0
1,3OO			
2.5%	41.0	20.0	52.0
5%	40.0	20.0	52.0
10%	40.0	20.0	45.0
1,2OO			
2.5%	44.0	21.0	51.0
1,3PO			
2.5%	41.0	20.0	52.0
5%	40.0	20.0	52.0
10%	40.0	20.0	45.0
1,2PO			
2.5%	39.5	21.5	52.5
5%	39.0	22.0	52.0
10%	38.5	21.0	52.0
PDG			
2.5%	39.5	20.0	52.0
5%	39.0	19.0	52.0
10%	39.0	18.5	52.0

high melting point endotherm reflecting the high melting point observed.

Crystal habit and *morphology* are terms commonly used for describing the external shape of crystals. The equilibrium form of a crystal depends on the relative rates of growth of the different faces of the crystal. The study of habit modification is carried out at a higher temperature, at which the palm oil crystals are large and well defined. The temperature of 37°C is selected temperature of study as the rate of crystallization is slow enough to permit easy photographing of the crystals. For oil with no DAG (PTG oil) two types of spherulite crystals are clearly seen. One type of spherulite appears to start off as bow-tie shape, the other type has long needle-like growth. Except for the crystal size reduction, the crystal habit of palm oil is not affected by the presence of DAGs such as dioleoylglycerol (OO), palmitoyloleoyl glycerol (PO) or even palm DAGs. The 1,3 and 1,2 PP are habit modifiers, crystals formed in the presence of 1,2 PP appear as clusters. Both are significantly smaller than those observed in the case of palm oil containing palm DAGs. At high concentrations of PO, numerous tiny crystals are observed. The change in crystal habit and reduction of crystal size may be the factors affecting fractionation and filtration of samples of oil having higher contents of DAGs.

Effects on solid fat content.
Solid fat content (SFC) is generally suppressed by the presence of DAGs. The reduction of solids in palm oil is found for palm DAG mixtures and all individual DAGs such as OO and PO, with the exception of 1,3 PP, where the solids are found to be enhanced (*Figures 4* to *7*). This increase in solids is especially pronounced at higher temperatures. Among the DAGs, 1,2 PO has a stronger effect than others in reducing the SFC. That only certain DAGs can reduce the SFC is an indication of the

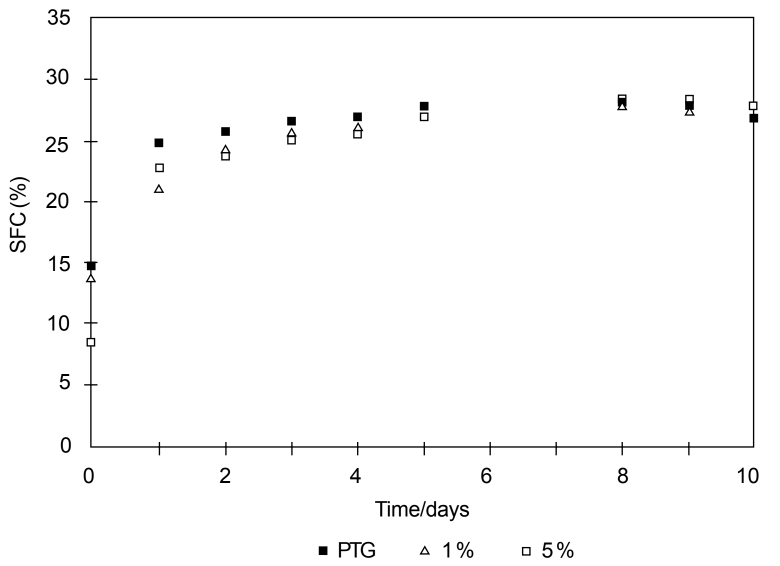

Figure 4. Effect of 1,2 dipalmitoylglycerol on solid fat content of palm oil at 20½C.

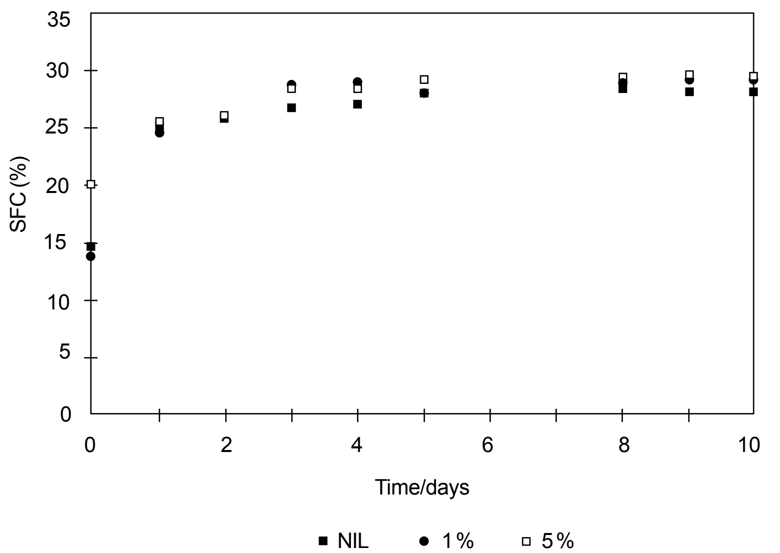

Figure 5. Effect of 1,3 dipalmitoylglycerol on solid fat content of palm oil at 20½C.

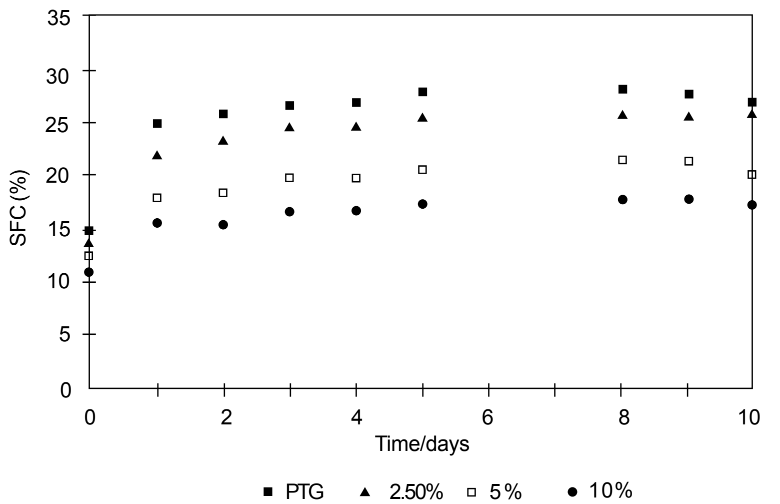

Figure 6. Effect of 1,2 palmitoyloleoyl glycerol on solid fat content of palm oil at 20½C.

co-crystallization, which occurs with these components and the TAGs of the oil. The wide variation generally observed in the SFC of palm oil samples, while generally believed to be attributed to differences in TAG, is more likely to be due to the differences in DAGs. These variations may affect product consistency and due consideration in correct product formulations may be required to adjust for the differences in solids.

Effects on kinetics of crystallization. The crystallization process is made up of nucleation and crystal growth. DAGs have been found to inhibit the nucleation process. This effect is found to be less pronounced at a higher degree of supercooling. The extent of inhibition depends also on the type of DAG and its concentration (*Figure 8*). For palm oil, OO DAG is not an effective inhibitor. The most effective inhibitor is saturated dipalmitoyl-glycerol. At 1% level and 28½C, both 1,2 and 1,3 PP can prolong the induction period of palm oil from 10 min to 25 and 30 min, respectively. However, at higher concentrations, *e.g.* 5%, only the 1,2 PP continues to exert an inhibitory effect (*Figure 9*). The 1,3 PP isomer tends to crystallize out and cause rapid crystallization of the bulk oil.

During crystallization, it is observed that in the presence of 1,3 PP at 1% level, the growth rate of palm oil is almost half its normal rate over the temperature range of 23½C-28½C. The inhibitory effect of 1,2 PP observed in the nucleation stage is highly significant at this stage (*Figure 9*). Mixtures of palm DAGs have an inhibition effect at the 5% level and are more pronounced at higher temperatures. Certainly, it is evident that the level of DAGs in palm oil would exert significant effects on unit processing as in fractionation programmes and filtration properties.

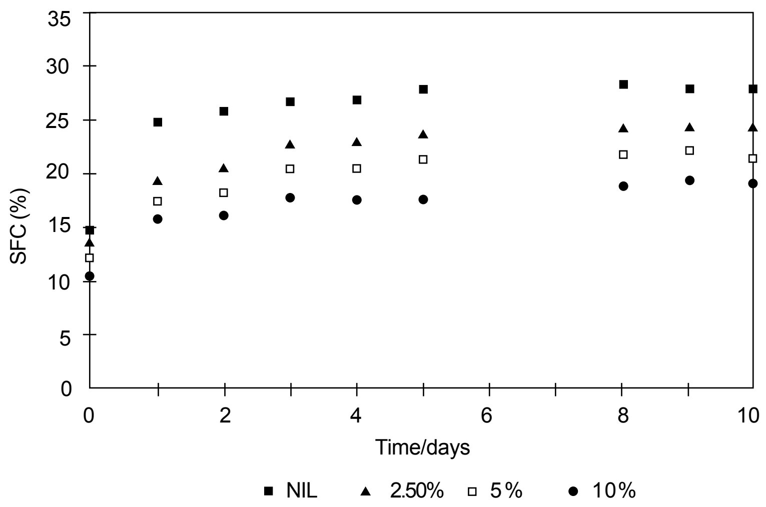

Figure 7. Effect of palm diacylglycerol mixtures on solid fat content of palm oil at 20½C.

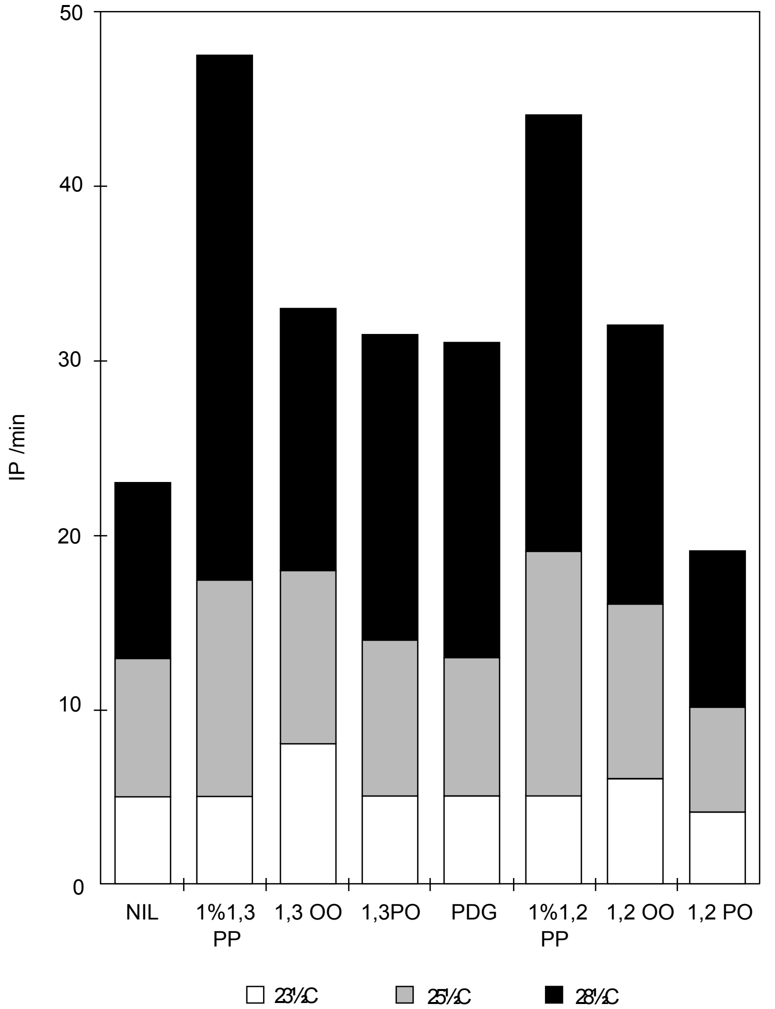

Figure 8. Effect of added diacylglycerol (1% and 2.5%) on induction period of crystallization of palm oil.

COLD STABILITY OF PALM OLEIN

Palm olein is the liquid fraction of palm oil, obtained through careful fractionation programmes. The first olein has an IV of minimum 56, whilst higher IV olein may be obtained through double or triple fractionation processes. The cold stability of palm olein depends on the IV. In general, palm olein does not meet the AOCS cold stability test and can remain clear only at temperatures of 22½C-25½C. At lower temperatures, palm olein may show cloudiness or sedimentation of white crystals which are found to be mainly DAGs and saturated TAGs. Our study on the crystallization behaviour of palm olein (IV of 61-65), stored under the accelerated cold test has revealed that the crystals obtained have a high concentration of DAGs (in particular 1,3 PP). The DSC heating and cooling thermograms of these crystals revealed two peaks (*Figure 10*). The heating thermogram shows a low melting component (3½C), which melts completely at 13½C and a high melting component (62½C) which melts completely at 65½C. Upon cooling, the crystals exhibit a large exotherm at 52.7½C and a small exotherm at -16½C. The high melting component is attributed to 1,3 PP. This is particularly significant as DAGs are preferentially distributed into the olein fraction during fractionation, thus causing oleins to have higher contents of DAGs. Thus, it is important to select palm oil with low DAG levels for further fractionation process, both from ease of processing as well as for obtaining palm olein with suitable cold stability properties.

As can be seen from all the above evaluations and discussions, DAGs structures, isomeric forms and concentrations all play different roles on the crystallization properties of the oil. The PO DAGs, being a component of the POP/PPO/OOP TAGs of palm oil product, can be expected to exert the most effects on the oil properties. This is because the PO can easily co-crystallize with the TAGs, forming mixed crystals. An understanding of the interactions between the minor components and the TAGs of oils is therefore intrinsic for better product properties and performance.

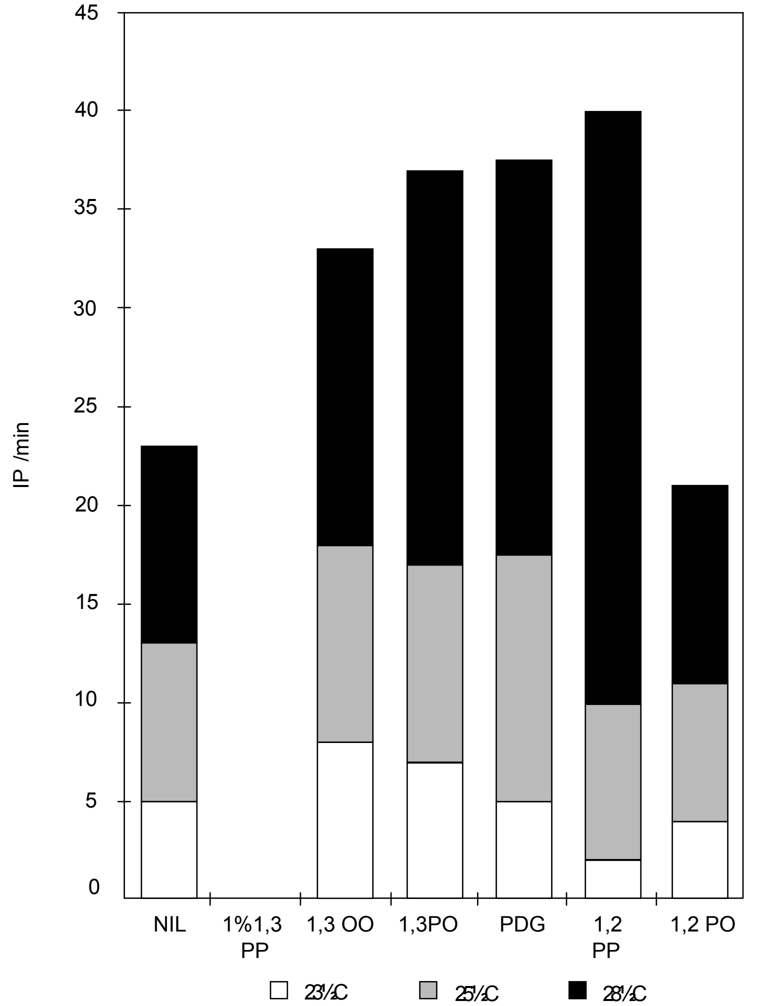

Figure 9. Effect of added diacylglycerol (5%) on induction period of crystallization of palm oil.

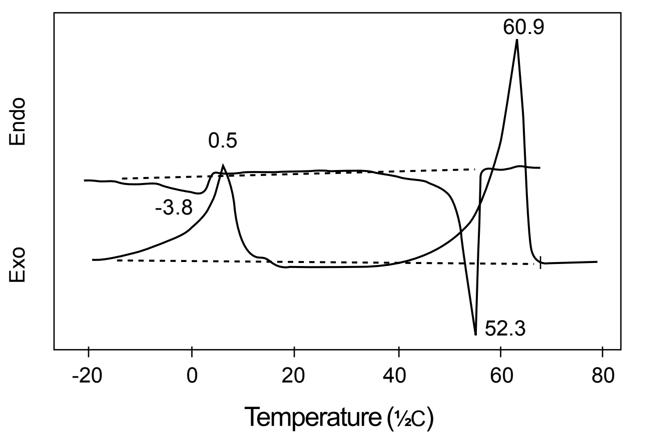

Figure 10. DSC thermograms of crystals of palm olein, stored under temperature cycle of 28½C/10½C.

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REFERENCES

CATALANO, M; De LEONADIS, T and COMES, S (1994). Diacylglycerols in the evaluation of virgin olive oil quality. *Grasas y Aceites, 45*:80-384.

CEBULA, D J and SMITH, K W (1992). Differential scanning calorimetry of confectionery fats. Part II- effects of blends and minor components. *J. Amer. Oil Chem. Soc., 69*:92-998.

GOH, E M and TIMMS, R E (1985). Determination of mono and diglycerides in palm oil, olein and stearin. *J. Amer. Oil Chem. Soc., 62*: 730.

JACOBSBERG, B and OH, C H (1976). Studies in palm oil crystallization. *J. Amer Oil Chem. Soc., 53*: 609.

OKIWACHI, T and SAGI, S (1985). Confectionery fats from palm oil. *J. Amer. Oil Chem. Soc., 62:* 421-425.

OKIY, D A (1978). Interaction of triglycerides and diglycerides of palm oil. *Oleagineux Vol. 33*: 625-628.

WAHNELT, V S; MEUSEL, D and TULSNER, M (1991). Influence of isomeric diglycerides on phase transition of cocoa butter- investigations by isothermal DSC. *Fat Sci Technol, 93*:174-178.

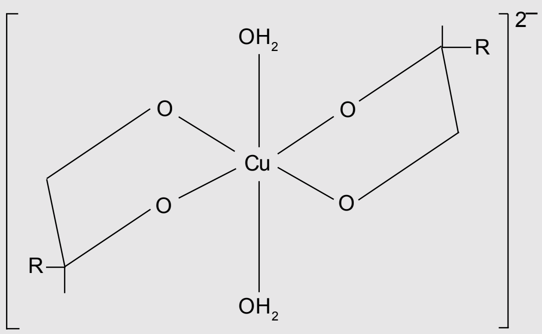
YELLA REDDY, S and PRABHAKAR, J V (1986). Study on the polymorphism of normal triglycerides of sal (Shorea robusta) fat by DSC. 1. Effect of diglycerides. *J. Amer Oil Chem. Soc., 63*: 672-676.

SIEW, W L and NG, W L (1995). Diglyceride content and composition as indicators of palm oil quality. *J. Sci. Food and Agric., 69*: 73-79.

SIEW, W L and NG, W L (1996). Characterisation of crystals in palm olein. *J. Sci. Food and Agric, 71*: 212-216.

ERRATUM

Please note the typographical error in Illustration V (structure of copper-glycerol complex) on page 9 of Palm Oil Developments No. 35. The correct label is:



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The error is regretted.