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Polymorphic Behaviour of Blends of Palm Oil and Palm Olein with Sunflower Oil and Palm Kernel Olein as Affected by Blending and Interesterification

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ABSTRACT

Palm oil (PO) and palm olein with an iodine value of 60 (POo-I.V.60), were blended with sunflower oil (SFO) and palm kernel olein (PKOo) according to the conventional three component mixture design. The effects of blending and chemical and enzymatic interesterification on the polymorphic behaviour of the ternary blends of PO/SFO/PKOo and POo-I.V. 60/SFO/PKOo were studied. The PO and PKOo crystallized exclusively in β' crystals, whilst POo-I.V.60 crystallized in mixed polymorphic forms with β crystals dominating. Blends containing PKOo crystallized exclusively in ß' crystals or with β' crystals dominating. PO, POo-I.V.60 and blends of PO/SFO and POo-I.V.60/SFO were dominated by ß crystals following chemical interesterification. Chemically interesterified PKOo stabilized exclusively in β' crystals. Blends containing PKOo also crystallized exclusively in β' crystals or with β' crystals dominating following chemical interesterification. Enzymatically interesterified PO, POo-I.V.60, binary blends of PO/SFO, POo-I.V.60/SFO, PKOo/SFO and ternary blends of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo crystallized in mixed polymorphic forms with β' crystals dominating or at least present in equal proportions with the β crystals. Enzymatically interesterified PKOo crystallized exclusively in the β' form. It was also observed that the proportion of β crystals increased with increasing percentage of SFO in the blends, either before or after interesterification.

ABSTRAK

Minyak sawit (PO) dan olein sawit bernilai iodin 60 (POo-I.V.60) diadun bersama minyak bunga matahari (SFO) dan olein isirung sawit (PKOo) berdasarkan reka bentuk campuran konvensional tiga komponen. Kesan peng-adunan serta pengesteran kimia dan berenzim ke atas sifat penghabluran campuran pertigaan PO/SFO/PKOo dan POo-I.V.60/SFO/PKOo dikaji. PO dan PKOo menghablur secara eksklusif dalam bentuk β'. POo-I.V.60 menghablur dalam bentuk campuran hablur β dan β' dengan β' mendominasi. Kesemua adunan yang mengandungi PKOo menghablur secara eksklusif dalam bentuk ß' atau dengan β' mendominasi. PO, POo-I.V.60 dan adunan PO/SFO dan POo-I.V.60/SFO didominasi oleh hablur β selepas pengesteran kimia. PKOo menghablur secara eksklusif dalam bentuk ß' selepas pengesteran kimia. Kesemua adunan yang mengandungi PKOo menghablur secara eksklusif dalam bentuk β' atau dengan β' mendominasi selepas pengesteran kimia. PO, POo-I.V.60, adunan perduaan PO/SFO, POo-I.V.60/SFO dan PKOo/SFO, serta adunan pertigaan PO/SFO/PKOo dan POo-I.V.60/SFO/PKOo menghablur dalam bentuk campuran polimof β dan β' dengan β' mendominasi atau sekurang-kurangnya hadir dalam nisbah yang sama dengan hablur β selepas pengesteran berenzim. PKOo menghablur secara eksklusif dalam bentuk β' selepas pengesteran berenzim. Diperhatikan juga bahawa nisbah hablur β meningkat dengan peningkatan peratusan SFO di dalam adunan, baik sebelum atau selepas pengesteran.

Keywords: palm-based blends, chemical interesterification, enzymatic interesterification, polymorphic behaviour.

INTRODUCTION

The physical properties of an oil or fat are of critical importance in determining their uses in

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food products (Timms, 1985). One of the physical properties that should be taken into serious consideration is the crystalline form of the oil or fat, as it will strongly influence the functionality of the finished products. For instance, in plastic fats such as margarines and shortenings, the crystal polymorphs are of primordial importance for final product consistency and acceptability (deMan, 1998).

Fat crystals can exist in three polymorphic forms, *i.e*., α, β' and β. The β' form is metastable, but it is the most desirable form. The β' crystals are relatively small and can incorporate a large amount of liquid oil in their crystal network. The β' crystals result in a good spreadability, smooth texture and glossy surface of margarines and fat spreads and good creaming properties of bakery fats (deMan, 1998). Although the most stable, the β form, is not desirable in large amounts since large crystals with sizes ranging from 5-25 µm, impart a coarse and grainy texture to margarines and fat spreads (Yap *et al*., 1989). The β crystals also result in poor aeration in cakes and loss of creaming power in icings. When β' crystals change into the β polymorphic form, the melting point will increase by about 2°C-3°C (deMan and deMan, 1994).

PO is an important edible oil source for the food industry due to its desirable properties such as high thermal and oxidative stability, plasticity at room temperature and tendency to crystallize in the β' form. Therefore, PO is an attractive option for production of plastic fats. However, the use of PO for plastic fats usually encounters some difficulties due to its crystallization properties, one of which is the formation of granular crystals upon storage or post hardening (Watanabe *et al*., 1992). Post hardening is particularly apparent when the product is stored after processing at refrigeration temperatures (deMan and deMan, 1994). The formation of granular crystals can be eliminated by reducing the content of symmetrical triacylglycerols, notably POP (P = palmitic and O = oleic acids) through interesterification with other oils and/or fats low in saturated long chain fatty acids (Watanabe *et al*., 1992). Hence, to improve its crystallization properties, PO may be blended and/or interesterified with a lauric fat that contains short and medium chain fatty acids such as PKOo and/or a liquid oil high in polyunsaturated long chain fatty acids such as SFO.

Interesterification is one of the three important processes currently utilized for modifying the physico-chemical characteristics of oils and fats. The other two processes are hydrogenation and fractionation. Interesterification causes randomization of fatty acid distribution within (intraesterification) and among (interesterification) triacylglycerol molecules in oils and fats until a thermodynamic equilibrium is reached (Sreenivasan, 1978). Thus, it leads to modifications in triacylglycerol composition and, consequently, in its physical characteristics. The reason fatty acid interchanges resulting from interesterification lead to changes in the physical characteristics of oils and fats is that, in nature, fatty acids are not randomly distributed between the triacylglycerols present. In most oils and fats, the 2-position of the triacylglycerol molecules are preferentially occupied by unsaturated fatty acids. Interesterification produces a truly random distribution of fatty acids that lead to an increased number of triacylglycerol species. This results in changes to the physical characteristics, such as melting and crystallization behaviour, of oils and fats (Rousseau *et al.*, 1996; Rozendaal, 1989). There is also a tendency for the wide range of triacylglycerol types present in interesterified fats to show more regular crystallization behaviour during the manufacturing of plastic fats such as margarines, spreads and shortenings. Moreover, the rate of recrystallization processes during storage of such products may be retarded; β'-modification is stabilized and the transformation into the most stable β-modification proceeds more slowly (Rozendaal, 1989).

Two types of interesterificaton are used commercially, *i.e.*, chemical and enzymatic interesterification. Chemical interesterification produces complete positional randomization of acyl groups in triacylglycerols, using chemicals such as sodium metal or sodium methoxide as catalyst. Enzymatic interesterification uses microbial lipases as catalyst. Each type of interesterification possesses advantages and disadvantages. Advantages of chemical interesterification over enzymatic interesterification primarily include cost recovery and initial investment. Chemical catalysts are much cheaper than lipases. Chemical interesterification is also a tried-and-true approach, as it has been around for a long time, and industrial procedures and equipment are available. On the other hand, enzymatic interesterification reactions are more specific, require less severe reactions and produce less waste than chemical interesterification and may represent the way of the future.

The aim of this work was to investigate the effects of blending and both chemical and enzymatic interesterification on the polymorphic behaviour of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo blends.

MATERIALS AND METHODS

Materials

The PO, POo-I.V.60, SFO and PKOo were obtained from Lam Soon Malaysia Sdn Bhd, Petaling Jaya, Selangor, Malaysia. Commercial immobilized *Rhizomucor miehei* lipase, Lipozyme IM 60 (with 2%-3% moisture content), was obtained from Novo Nordisk Ind. (Copenhagen, Denmark). This lipase has positional specificity at the 1,3-positions of triacylglycerol.

Blends Preparation

Ternary blends of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo were prepared in the following mass ratios: A(1:0:0), B(3:1:0), C(1:1:0), D(1:3:0), E(0:1:0), F(0:3:1), G(0:1:1), H(0:1:3), I(0:0:1), J(1:0:3), K(1:0:1), L(3:0:1), M(4:1:1), N(1:4:1), P(1:1:4) and Q(1:1:1).

Chemical Interesterification

Chemical interesterification was carried out according to the procedure described by Noor Lida *et al*. (2002).

Enzymatic Interesterification

Prior to use, molten fat blends were freed from moisture by adding anhydrous sodium sulphate (about 10% w/w) at 60°C-70°C, thoroughly mixed for about 30 min and vacuum filtered. Precisely 20.0 g of the moisture-free sample was placed in a screw-capped 50 ml flat bottom flask. The sample was pre-heated to 60°C in a model ROSI 1000 shaking incubator (Thermolyne, Dubuque, IA) and subjected to agitation at 250 rpm for the duration of the experiment. Once the desired temperature was reached, the reaction was initiated by addition of 2.0 g enzyme powder. The mixture was allowed to react for 3 hr. Reaction was stopped by removal of the enzyme by filtration. In this investigation, the reaction was conducted in the absence of additional water, as oils could act as the dispersing medium as well as substrate for the reaction (Elliot and Parkin, 1991). No further purification was done.

Polymorphism

The polymorphic form(s) of fat crystals in the blends was determined by X-ray diffraction using an Enraf Nonius Diffractic X-ray generator model FR592 (Delft, the Netherlands) and an Enraf Nonius Guinier camera model FR552 with a temperature controlled sample holder operated at 5°C. Samples were heated at 70°C for 30 min to destroy any *memory* of earlier crystals, followed by crystallization at 0°C for 90 min. The samples were then tempered at room temperature for three days and at 5°C for two days prior to measurement. Short spacing on the X-ray film were measured with an Enraf Nonier Guinier viewer. The short spacing of the β' form are at 4.2 and 3.8Å and that of the β form at 4.6 Å (D'Souza *et al*., 1990). Levels of the β' and β crystals were estimated by the relative intensity of the short spacing at 3.8, 4.2 and 4.6 Å.

RESULTS AND DISCUSSION

Polymorphic Behaviour of Initial Oils and Oil Blends

The polymorphic crystal behaviour of PO, POo-I.V.60, SFO, PKOo and blends of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo in various ratios are displayed in *Figures 1* and *2*. The PO and PKOo crystallized exclusively in the β' crystalline form. These results are consistent with those reported by Timms (1984; 1990). According to Timms, the stable polymorph of PO is normally β'-2, although there is a high proportion of symmetrical triacylglycerols, particularly POP, and significant amounts of PPO, PLinP and PPP (Lin = linoleic acid). The POP cannot achieve its stable β-3 form in the presence of PPO and PLinP. The PPP forms a solid solution with POP and also does not seem able to exhibit its stable β-2 form. PKOo, a lauric fat, tends to possess a stable β' polymorphic form because of its mixed chain length triacylglycerols, which are due, in turn, to the presence of various chain length fatty acids. A means of stabilizing the β' crystals is to have triacylglycerols with varying chain lengths. Variation in the chain length results in a more disordered packing near the methyl end regions, leading to less chances of a tightly knit crystal lattice being formed. As β crystals have the most ordered structure, a decrease in the chain length variety will increase their likelihood (Larsson, 1994). The PKOo comprises about 4.7% short chain fatty acids (C6-C8), 62% medium chain

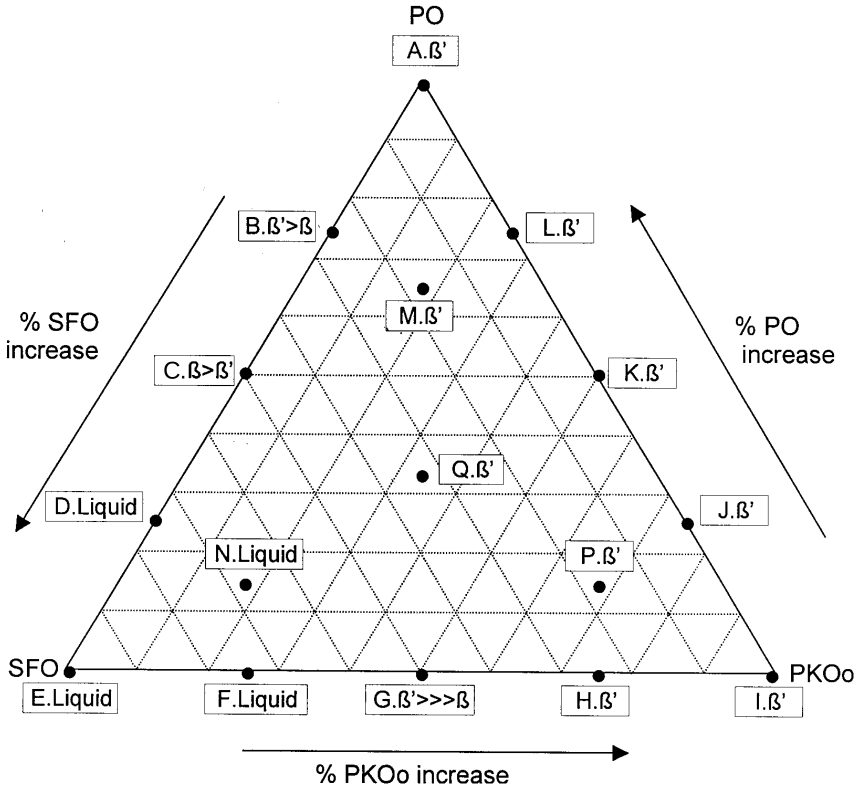

Figure 1. Polymorphic behaviour of the blends of palm oil (PO), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

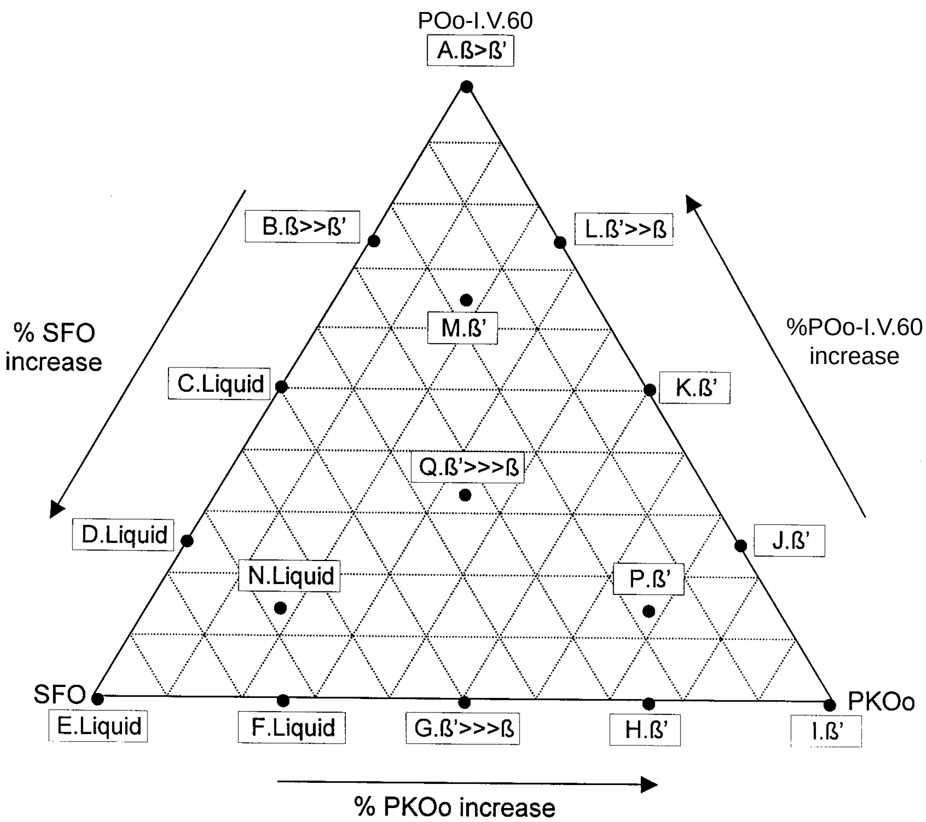

Figure 2. Polymorphic behaviour of the blends of palm olein with iodine value of 60 (POo-I.V.60), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

fatty acids (C10-C14) and 32.2% long chain fatty acids (C16-C20). In POo-I.V.60, a more β crystalline form was observed. This was probably because POo-I.V.60 do not have PPP, which has a tendency to inhibit the transformation of POP from the metastable (β') to the stable (β) form. SFO was fully liquid at the measuring temperature (5°C) as it contained a high proportion of unsaturated fatty acids. The fatty acid compositions of PO, POo-I.V.60, SFO and PKOo are shown in *Table 1*.

Incorporation of SFO to a certain proportion into PO, POo-I.V.60 and PKOo led to increases in β content in the PO/SFO, POo-I.V.60/SFO and PKOo/SFO blends. This result is in agreement with that of deMan (2000), who reported that when diluted with liquid oils, the β forming tendency of palm products increases. According to deMan *et al*. (1995), incorporation of large amounts of liquid oil increases the tendency of the desirable β' polymorphic form to convert to the β form. All blends containing PKOo tended to crystallize exclusively in β' crystals or with β' crystals dominating, as this oil was exclusively β' stable. Blends containing high proportions of SFO were liquid at the measurement temperature.

Polymorphic Behaviour of Chemically Interesterified Oils and Oil Blends

The polymorphic crystal behaviour of the chemically interesterified PO, POo-I.V.60, SFO, PKOo and the blends of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo in various ratios are illustrated in *Figures 3* and *4*. A more β crystalline form was observed in the chemically interesterified PO. The same trend was observed in the chemically interesterified POo-I.V.60 and chemically interesterified binary blends of PO/SFO and POo-I.V.60/SFO. This could be due to the fact that PO and POo-I.V.60 are rich in palmitic and oleic acids. According to Duns (1985), the molecular rearrangement that takes place in interesterification reduces the proportion of the native symmetrical triacylglycerol POP, and increases that of PPO. This phenomenon facilitates β-2 compound formation. This may be regarded as the transformation of a mixture of two triacylglycerols of different polymorphs into a single new polymorph, attributed to interaction between the POP (stable in β-3 polymorph) and PPO (stable in β'-3 polymorph), as described by Timms (1984). Furthermore, interesterification distributes the palmitic acid evenly over all positions in the triacylglycerol molecules and therefore reduces the β' stability of PO. According to deMan and deMan (1994), one of the important criteria for β' stability is the presence of palmitic acid in the 1- or 3-position of the glycerol moiety. Chemically interesterified PKOo and blends containing PKOo stabilized exclusively in the β' crystalline form or with β' crystalline dominating for the reasons discussed earlier. SFO and blends containing a high proportion of SFO were liquid at the measurement temperature following chemical interesterification.

Polymorphic Behaviour of Enzymatically Interesterified Oils and Oil Blends

The polymorphic crystal behaviour of the enzymatically interesterified PO, POo-I.V.60,

TABLE 1. FATTY ACID COMPOSITION OF PALM OIL, PALM OLEIN WITH IODINE VALUE OF 60, SUNFLOWER OIL AND PALM KERNEL OLEIN[a]

FAC (wt %)	Oil			
	PO	POo-I.V.60	SFO	PKOo
C8:0	-	-	-	4.7
C10:0	-	-	-	3.8
C12:0	0.2	0.3	-	44.5
C14:0	1.0	1.0	0.1	13.7
C16:0	42.9	35.8	6.3	8.4
C18:0	4.4	3.8	3.7	2.8
C18:1	40.8	46.0	24.3	18.1
C18:2	10.2	12.5	65.1	2.9
Others	0.5	0.6	0.5	1.1

Note: [a]FAC, fatty acid composition; PO, palm oil; POo-I.V.60, palm olein with iodine value of 60; SFO, sunflower oil; PKOo, palm kernel olein; C8:0, caprylic acid; C10:0, capric acid; C12:0, lauric acid; C14:0, myristic acid; C16:0, palmitic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid. Others include caproic (C6:0) and / or linolenic (C18:3) and/or aracidic (C20:0) acids.

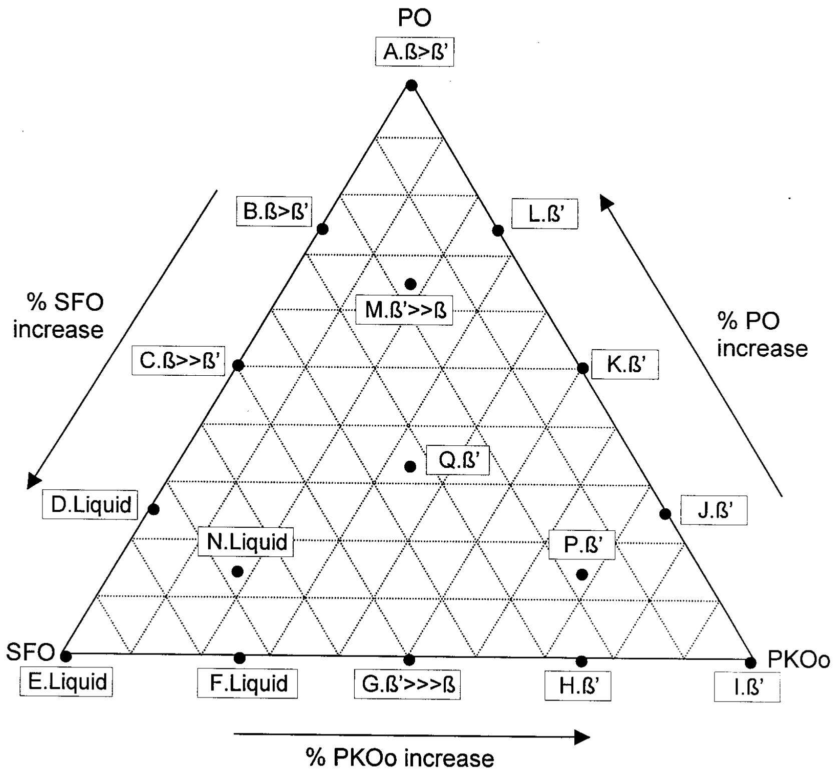

Figure 3. Polymorphic behaviour of chemically interesterified blends of palm oil (PO), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

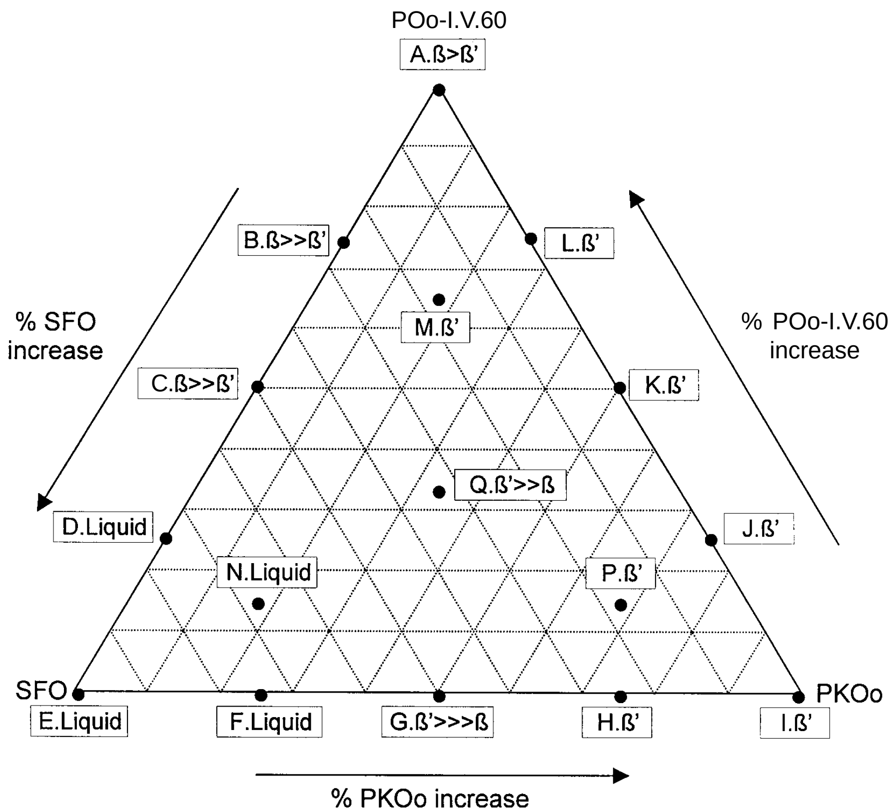

Figure 4. Polymorphic behaviour of chemically interesterified blends of palm olein with iodine value of 60 (POo-I.V.60), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

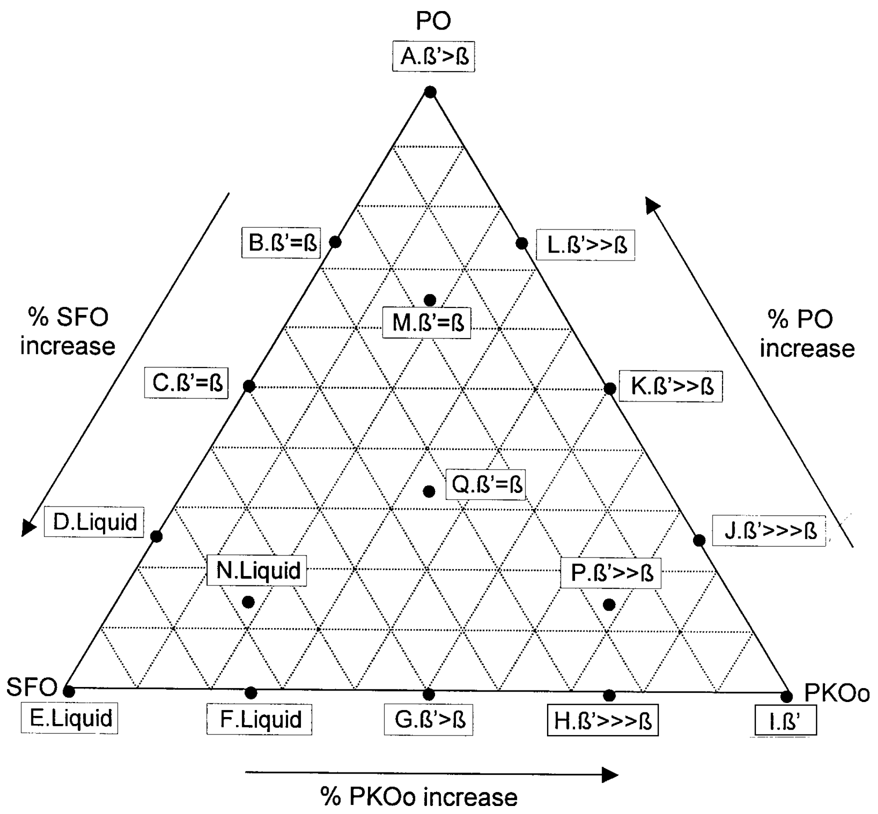

Figure 5. Polymorphic behaviour of enzymatically interesterified blends of palm oil (PO), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

SFO, PKOo and blends of PO/SFO/PKOo and POo-I.V.60/SFO/PKOo in various ratios are displayed in *Figures 5* and *6*. Enzymatically interesterified PO and blends of PO/SFO with high proportion of PO crystallized in mixed polymorphic forms. A more β' than β crystalline form was observed in the enzymatically interesterified PO. There were equal proportions of β and β' crystals in the PO/SFO blends. The POo-I.V.60 and blends of POo-I.V.60/SFO with a high proportion of POo-I.V.60 also stabilized in mixed polymorphic forms but with β' crystals dominating. Enzymatically interesterified PKOo and blends containing PKOo stabilized exclusively in the β' crystalline form or with β' crystals dominating. Blends containing high proportions of SFO were liquid at the measurement temperature following enzymatic interesterification.

Generally, in the absence of PKOo, the enzymatically interesterified blends were more β' stable compared to the non-interesterified blends (except the non-interesterified PO/SFO blends) and chemically interesterified blends. One plausible explanation could be that randomization of the fatty acids at the 1- and 3-positions by the 1,3 specific lipase led to diversification of the triacylglycerols in the resulting blends, thus promoting β' stability. Another plausible explanation could be that enzymatic interesterification of oils and fats resulted in the formation of diacylglycerols, the intermediates in the reaction. The presence of high levels of diacylglycerols in the enzymatically interesterified blends could have influenced the polymorphism of the fats. Diacylglycerols are known to retard the β' to β transition (Hernqvist *et al.*, 1981; Reddy and Prabhakar, 1986) and thereby stabilize the β' polymorph.

CONCLUSION

Blending and interesterification modified the polymorphic behaviour of palm-based blends. Increasing the concentration of SFO, a liquid oil rich in unsaturated fatty acids, in the palm-based oils increased the proportion of the β form in the mixture. PKOo, a lauric type fat rich in saturated medium chain triacylglycerols, helped in stabilizing the fat blends in the β' polymorph. In the absence of PKOo, enzymatic interesterification increased the β' stability of the palm-based oil blends. Stabilization of β' crystals in palm oil and palm olein following incorporation of PKOo and interesterification could be an advantage in the commercial production of margarines and shortenings.

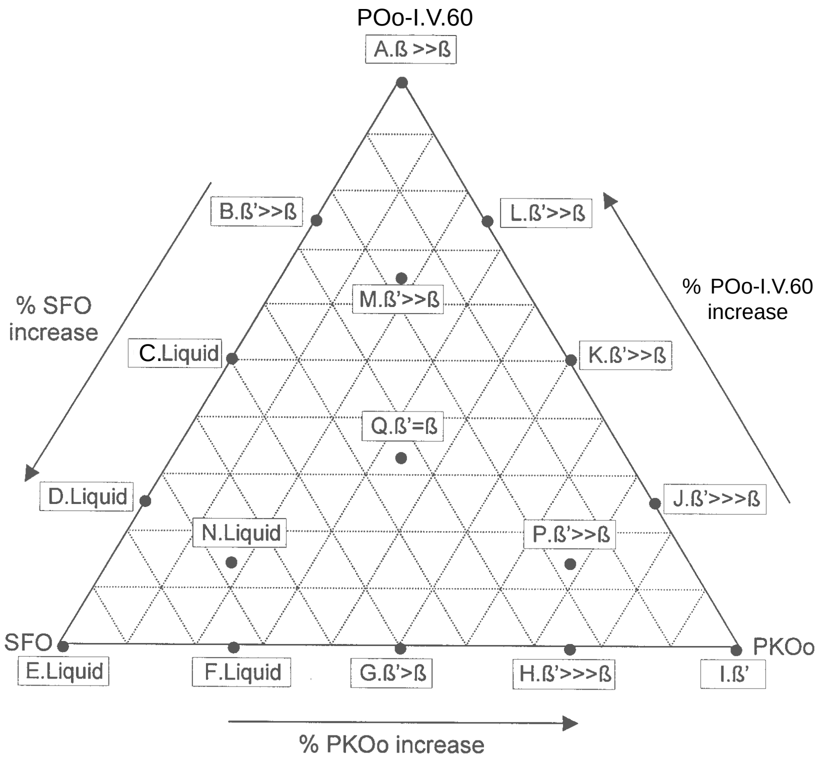

Figure 6. Polymorphic behaviour of the enzymatically interesterified blends of palm olein with iodine value of 60 (POo-I.V.60), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios.

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