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Effects of chemical interesterification on physicochemical properties of palm stearin and palm kernel olein blends

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Abstract

Fat and oil blends, formulated by mixing palm stearin (PS) and palm kernel olein (PKOo) in different ratios from 20:80 to 80:20 (wt%), were subjected to chemical interesterification with sodium methoxide as catalyst. The slip melting point (SMP), soild fat content (SFC), triglyceride (TG) profile, melting thermogram, polymorphic form and crystal morphology of the interesterified and non-interesterified mixtures were evaluated. Results indicated that all the interesterified blends had lower SMP than their non-interesterified blends. The melting thermogram confirmed a product of lower melting point being formed in interesterified blends with the disappearance of the high melting TGs. The TG profile of the interesterified blends of PS and PKOo also showed a decrease in the concentration of the high melting TGs. Chemical interesterification altered the PS and palm kernel blend fat-crystal morphology significantly. X-ray diffraction analysis revealed that all the interesterified blends were exclusively β' polymorph. Hence, interesterification of blends of PS and PKOo resulted in the formation of β' polymorphic oil, yielding mixtures with lower SMP and SFC. Such oil could be used for the production of margarine, shortening, non-temper-type confectionery fats, whip creams and other similar products.

Keywords: Chemical interesterification; Palm stearin; Palm kernel olein; Slip melting point; Solid fat content

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1. Introduction

Chemical interesterification has long been used to modify oils and fats into functional products. It modifies the physical properties of oils by rearranging the distribution of fatty acids on the glycerol backbone without changing their chemical composition. With the rising concerns over the nutritional impact of *trans* fatty acids on health, interesterification has become more popular for the preparation of low or zero *trans* functional plastic fats.

Palm stearin is the solid fraction obtained by fractionation of palm oil after crystallization at a controlled temperature. It is not used directly for edible purposes due to its high melting point ranging from 44 to 56 °C (Pantzaris, 2000). Palm kernel olein (PKOo) is the liquid phase from the fractionation of palm kernel oil. It contains a high proportion of saturated fatty acids and is characterized by its high lauric acid content which ranges from 40% to 50% (Sonntag, 1979). Palm kernel olein has limited application because of excessive foaming during heating due to the short-chain fatty acids present. The production of edible fats requires fat blends that are able to impart plasticity to products such as margarine and shortening. To achieve these properties, fat blends may be chemically modified.

The objective of this study was to modify the physical properties of PS and PKOo blends by chemical interesterification, in order to produce oils suitable for use in edible products. In this work, varying proportions of PS and palm kernel olein blends (20–80%) were interesterified and their physical properties, such as SMP, SFC, melting thermograms, crystal morphology and polymorphic forms, were examined.

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2. Materials and methods

2.1. Materials

Refined, bleached, and deodorized (RBD) palm stearin (PS) (SMP 53.4 °C, IV 40.3) and palm kernel olein (PKOo) were obtained from Golden Jomalina Sdn Bhd, Klang, Malaysia and Cargill Specialty Oils and Fats Sdn Bhd, Port Klang, Malaysia, respectively. The oils and fats were stored at 0 °C prior to use. All chemicals used were either of analytical or high-performance liquid chromatography (HPLC) grade.

2.2. Blend preparation

PS and PKOo were melted at 60 °C in an oven prior to use. The liquefied PS and PKOo were mixed in proportions ranging from 20% to 80% PS with 20% increments (w/w). Four blends were prepared: 20:80, 40:60, 60:40 and 80:20, identified by mass ratio of PS:PKOo.

2.3. Chemical interesterification

The fat blend was dried under nitrogen at 100 °C for 60 min. After lowering the temperature to 80 °C, 0.2% sodium methoxide powder (catalyst) was added. The mixture was heated to 110 °C under nitrogen for 60 min with vigorous stirring. It was then cooled to 70 °C and 5% citric acid solution was added to inactivate the catalyst. After the mixture was stirred mechanically at 70 °C for 15 min, the excess citric acid and sodium methoxide were removed with warm water washes. Then 1.5% bleaching earth was added and bleaching was continued under nitrogen for 25 min at 95 °C. Finally the interesterified oil was filtered through a Whatman # 4 filter paper. Non-interesterified oil is abbreviated to NIE and interesterified oil to IE.

2.4. Slip melting point (SMP)

SMP was determined according to AOCS Method Cc.3.25 (AOCS, 1990). Capillary tubes filled with a 1 cm high column of fat were chilled at 10 °C ± 1 °C for 16 h before being immersed in a beaker of cold distilled water. The water was stirred and heated and the temperature was recorded when the column of fat rose in the tube.

2.5. Solid fat content (SFC)

SFC was measured using a Bruker Minispec pulse Nuclear Magnetic Resonance (pNMR) spectrometer (Karlsruhe, Germany). The PORIM parallel method was used. The sample in the NMR tube was first melted at 70 °C for 30 min, followed by chilling at 0 °C for 90 min, and then held at each measuring temperature for 30 min prior to measurement (PORIM, 1995). Melting, chilling and holding of the samples were carried out in pre-equilibrated thermostatted water baths, accurate to 0.1 °C. SFC was measured in the temperature range 5–50 °C.

2.6. Melting characteristics

Melting characteristic was followed using a differential scanning calorimeter DSC-7 (Perkin Elmer, Norwalk, CT). Calibration was carried out using an indium standard for the high temperature range and *n*-decane for the sub-ambient temperature range. A sample weighing 3–5 mg was hermetically sealed in an aluminium pan with an empty pan serving as a reference. The samples were heated to 80 °C for 10 min to destroy crystal memory. The samples were then cooled from melt (80 °C) at 5 °C/min to −50 °C and held for 15 min before being heated to 80 °C again at 5 °C/min for the melting thermograms.

2.7. Crystal polymorphism by X-ray diffraction

The polymorphic forms of fat crystals in the blends were determined by X-ray diffraction, using an Enraf Nonius Model FR592 (Delft, The Netherlands). The instrument was fitted with a fine copper X-ray tube. The sample holders were flat stainless-steel plates with rectangular holes. Samples were melted at 70 °C and tempered at 20 °C for 30 min. Short spacings on the X-ray film were measured with a Guinier viewer (Enraf Nonius, Delft, The Netherlands). The short spacings of the β' form are at 4.2 and 3.8 Å and that of the β form is at 4.6 Å (D'Souza, deMan, & deMan, 1991). Levels of β' and β crystals in mixtures were estimated by the relative intensity of the short spacings at 4.2 and 4.6 Å.

2.8. Triglyceride (TG) profiles

The TG profiles of the interesterified and non-interesterified PS and PKOo blends were analysed in a reversed-phase high-performance liquid chromatograph (Gilson, Villiers-el-Bel, France). A Lichrosphere RP-18 column (250 mm × 4 mm) of 5-μm particle size (Merck, Darmstadt, Germany) with acetone/acetonitrile (75:25% v/v) as the eluent at a flow rate of 1.0 ml/min and a refractive index detector was used. Identification of TG was done by comparison of retention time with those of commercial TG standards.

2.9. Crystal morphology by polarized light microscope

A small droplet (about 10 μl) of melted fat was placed on a glass slide and covered with a glass slip. The sample was first heated to 70 °C for 10 min and then rapidly cooled (50 °C/min) to 20 °C. The sample was tempered at 20 °C for 30 min prior to measurement. A Leica DMLP polarized light microscope (Wetzlar, Germany) equipped with a Linkam THMS 600 temperature controller stage and a JVC 3-CCD colour video camera was used. Temperature was thermostatically controlled by a Linkam TP 94 multiramp temperature programmer and LNP automatic cooling system (Linkam, Tadworth, Surrey, United Kingdom). Liquid nitrogen was used as the coolant. The photomicrograph of the crystal was taken at 200× magnification.

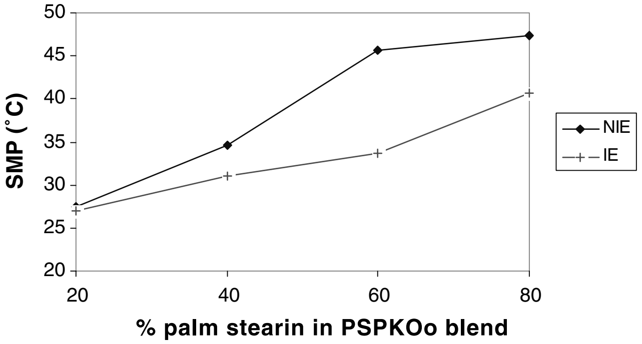

Fig. 1. Slip melting points of interesterified and non-interesterified palm stearin and palm kernel olein (PSPKOo) blends.

3. Results and discussion

3.1. Slip melting point

The SMP of the interesterified and non-interesterified PS and PKOo blends are shown in Fig. 1. The interesterified blends had lower SMP than their non-interesterified blends at all ratios analysed. The decrease in SMP of the interesterified blends indicated that PS (IV 40.3) mixed with PKOo (a liquid oil of shorter saturated fatty acids) resulted in blends with lower slip melting points than the non-interesterified blends. The SMP increased with an increase in the amount of PS in the blends due to the high amount of high-melting TGs, such as POP and PPP, in palm stearin. The largest increase in SMP was observed in non-interesterified blend with 40–60% PS added. All the interesterified blends, except for the blend containing 80% of PS, had SMPs

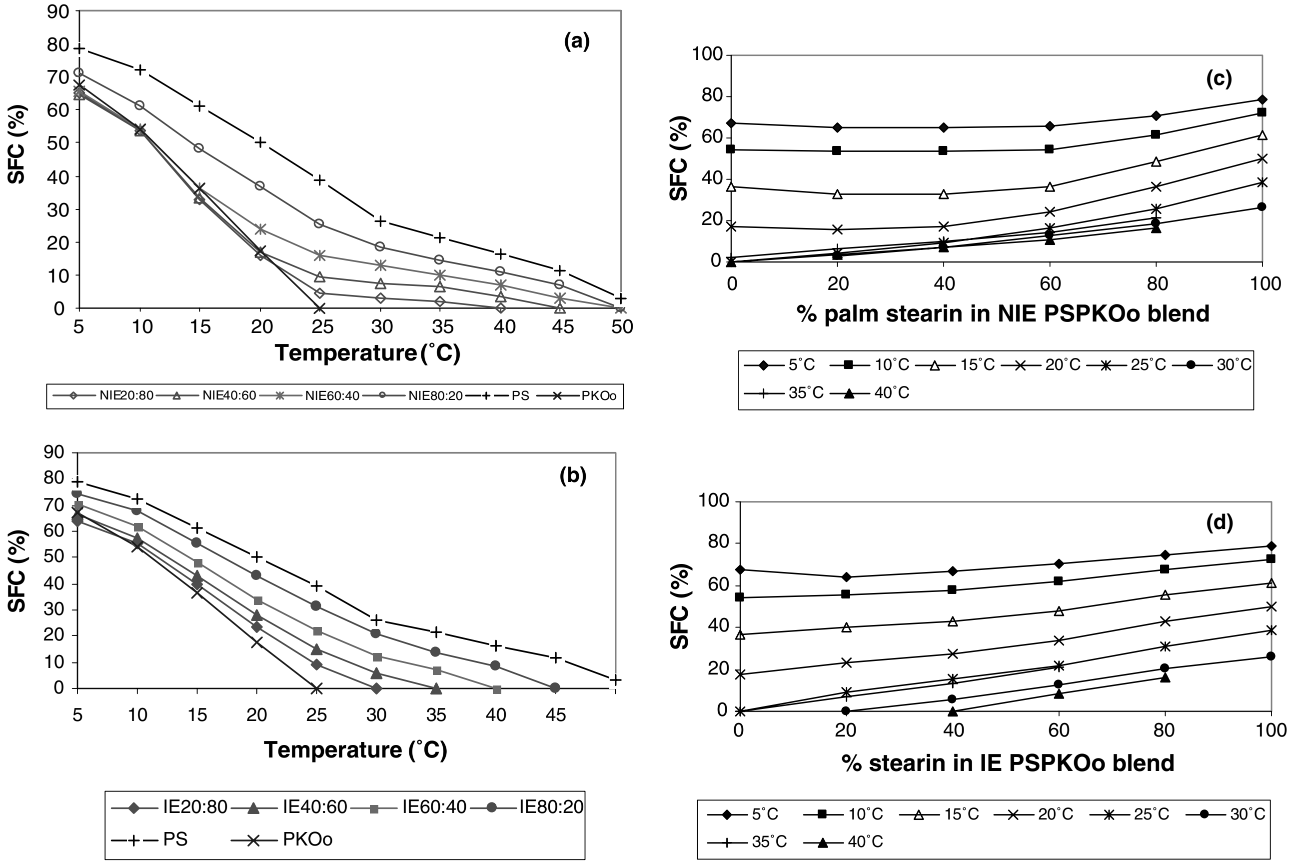

Fig. 2. (a) Solid fat content profiles of palm stearin, palm kernel olein, and non-interesterified palm stearin and palm kernel olein blends. (b) Solid fat content profiles of palm stearin, palm kernel olein, and interesterified palm stearin and palm kernel olein blends. (c) Eutectic effects of non-interesterified palm stearin and palm kernel olein (PSPKOo) blends at different temperatures. (d) Eutectic effects of interesterified palm stearin and palm kernel olein (PSPKOo) blends at different temperatures.

well below body temperature. The biggest drop in SMP was observed in blend 60:40.

3.2. Solid fat content

Figs. 2(a) and (b) show the SFC profiles of the non-interesterified and interesterified blends as a function of temperature, respectively. The two blends had similar SFC profiles and their SFC increased with increasing amounts of PS in the blends. Addition of palm kernel olein to PS lowered SFC at all measured temperatures. Generally, all the interesterified blends are completely melted (SFC = 0%) at lower temperatures than their non-interesterified blends and this is in line with the SMP observation above. This could be due to the rearrangement of fatty acids in the TGs after interesterification, to form a medium melting fraction (MMF) and a low melting fraction (LMF).

Before interesterification, the blends contained high proportions of higher melting glycerides, such as POP, POS, PPS and PPP in the palm stearin, as shown in Fig. 3(a). After interesterification, their levels were reduced (Fig. 3(b)) and mixed glycerides containing lower melting TGs were formed. The largest drop in SFC, from 10 to 15 °C, remains the same in the non-interesterified and the interesterified blends. The interesterified stearin and PKOo blends containing 20–60% stearin have less steep SFC slopes and lower melting points, which are below body temperature. These blends might be suitable for margarine and shortening, non-tempered confectionery fats, whipped cream and similar products which require a more gentle melting profile, below body temperature, for a proper mouthfeel.

Fig. 2(c) shows there was a slight eutectic interaction in the non-interesterified PS and PKOo blend at 5–20 °C. Eutectic behaviour occurs in the non-interesterified blends due to the differences in the molecular size of the TGs and the shape and polymorph of the crystals between the two types of fat. This shows that the PS and PKOo are incompatible with each other. After interesterification, eutectic interaction was only observed at 5 °C, as shown in Fig. 2(d). At this temperature, the reduced eutectic behaviour is due to the presence of residual amounts of TG with long and short chain fatty acids, respectively. This result is consistent with Timms (1984) findings, whereby interesterification would eliminate or reduce eutectic interactions in a eutectic mixture. The eutectic effect is desirable if this blend is going to be used for the production of margarine and shortening (Timms, 1984).

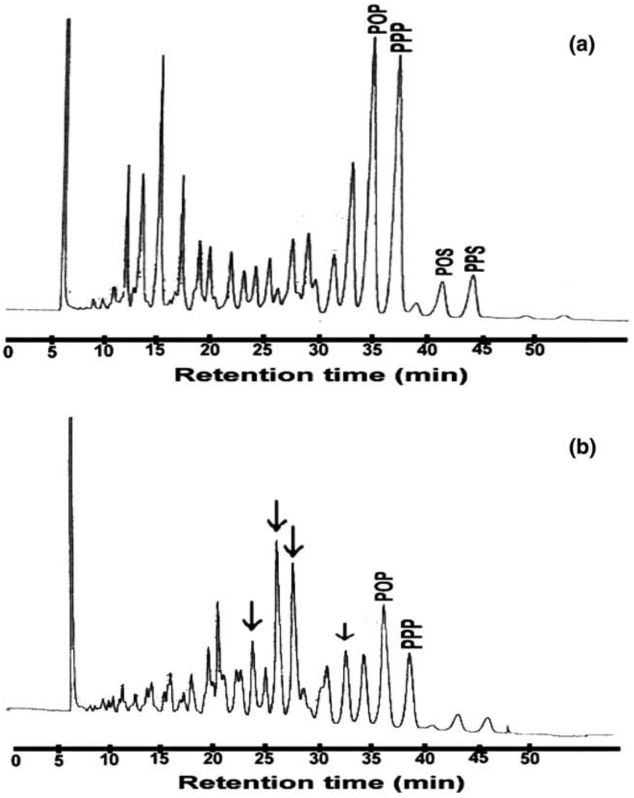

Fig. 3. HPLC Chromatograms of (a) non-interesterified and (b) interesterified palm stearin and palm kernel olein blend (60:40) Arrows indicate triglycerides which increased in concentration (P, Palmitic; O, oleic acid; L, linoleic; S, stearic acid).

3.3. Polymorphic forms

Table 1 shows the polymorphic forms of the various blends of the interesterified and non-interesterified PS and PKOo blends. The non-interesterified blends of PS and PKOo contained mixtures of both β and β' polymorphic forms with the β form dominating except in the 80:20 blend. PS is a β-tending fat due to its high concentration of tripalmitin. It contains 10–32% of tripalmitin, depending on the fractionation conditions (deMan & deMan, 1995). On the other hand, PKOo consists exclusively of the β' crystalline form, as reported by Timms (1984, 1990). This is due to the presence of fatty acids of various chain lengths. Hence, in NIE blends, both oils will tend to crystallise in their own polymorphic form. In the 80:20 NIE blend, both the β and β' polymorphic forms are present in roughly the same concentrations. However, as the concentration of the β'-tending PKOo was increased, the β polymorphic

Table 1
Polymorphic forms of the interesterified and non-interesterified palm stearin and palm kernel olein blends

%PS:PKOo	Polymorphic form (s)	
	Non-interesterified	Interesterified
20:80	$\beta \gg \beta'$	β'
40:60	$\beta \gg \beta'$	β'
60:40	$\beta \gg \beta'$	β'
80:20	$\beta = \beta'$	β'

form was observed to be dominant even in the 20:80 NIE blend. This could be either due to the dilution effect, as observed by deMan and deMan (1994) where the β polymorphic form tends to dominate the more the fat is diluted with a liquid oil, or because the amount of β′ polymorphic form is too low in concentration to exert any influence.

After interesterification, only the β′ crystals were observed to be present in all the blends. This is due to the randomization of fatty acids in PS glycerides with the fatty acids in PKOo glycerides leading to a diversification of the fatty acids in the glycerides of the resulting blends. Palmitic acid, which is present in large quantities in PS, could have been interchanged with lauric acid, the main fatty acid present in PKOo. This is in accordance with deMan and deMan's (1995) observation that a diversification of fatty acid chain lengths in solids and high melting glycerides tends to promote β′ stability.

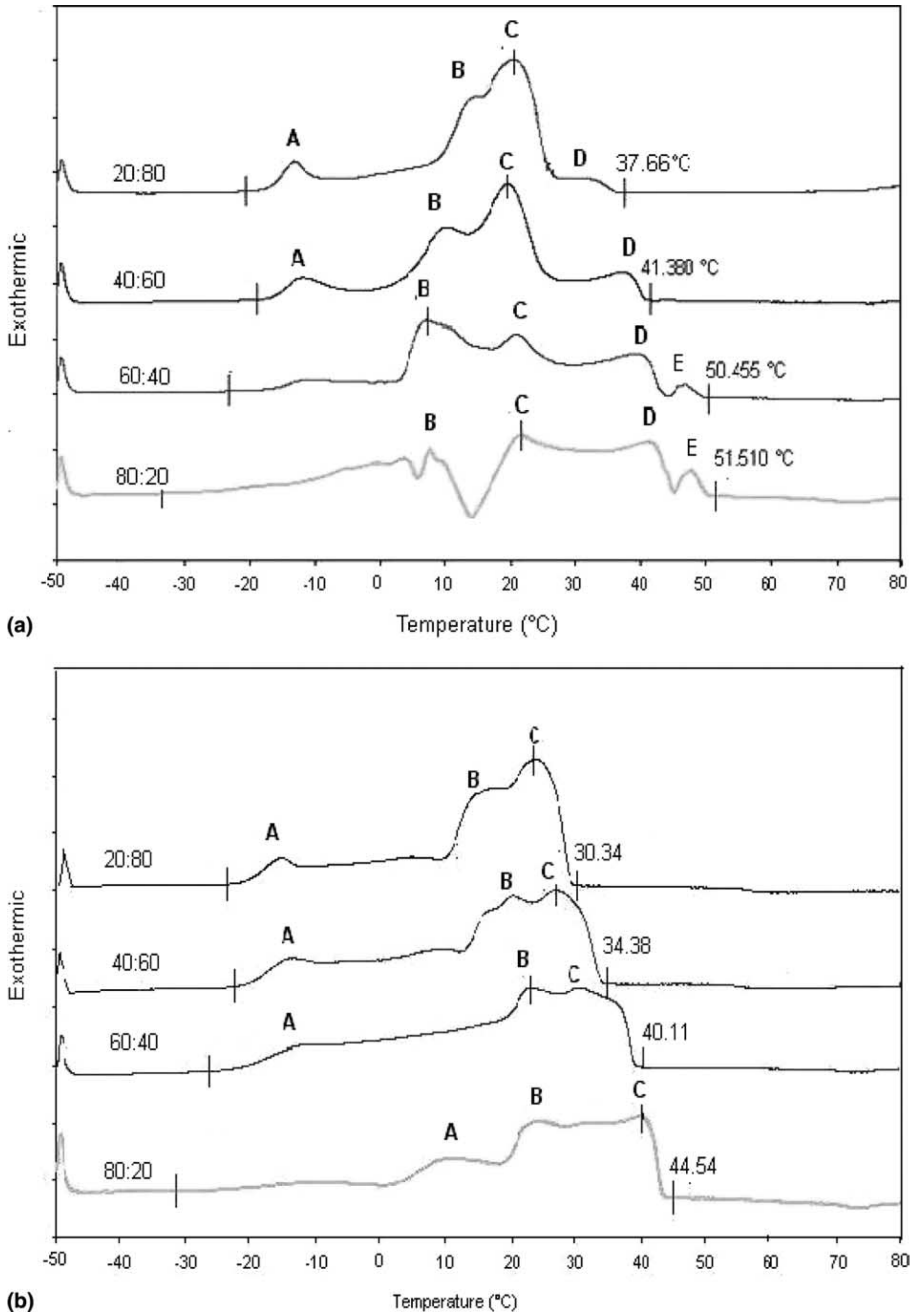

Fig. 4. DSC melting thermograms of (a) non-interesterified and (b) interesterified palm stearin and palm kernel olein blends at heating rates of 5 °C/min.

3.4. Triglyceride profiles

Interesterification altered the TG profiles of the fat blends as shown in Fig. 3. After interesterification, the relative concentrations of several TGs increased (as indicated by arrows in Fig. 3(b)), while others such as POP, PPP, POS and PPS were observed to decrease. The results obtained were similar to previous findings by several researchers (Chu, Ghazali, Lai, Yaakob, & Yusof, 2002; Ghazali, Maisarah, Yusof, & Yusoff, 1995; Lai, Ghazali, & Chong, 1998; Liew, Ghazali, Long, Lai, & Yazid, 2001; Zainal & Yusof, 1999). Such considerable increase or decrease in the amount of specific TG, observed in the oil blends evaluated, was due to random rearrangement of the fatty acids during interesterification. Changes in the TG profiles are usually accompanied by changes in the physical characteristics, such as SMP and SFC of the oil blends. Since the concentrations of the high melting TGs, such as PPP and POP, were reduced after interesterification, a softer product was obtained, as shown by the reduction in their SMPs (Fig. 1).

3.5. Melting thermograms

Fig. 4 shows the melting thermograms of interesterified and non-interesterified PS and PKOo blends. Chemical interesterification changes the melting profile of the blends. The melting thermograms of the non-interesterified blends show that peak A, which represents the low melting TG of PKOo, gradually disappeared, while peaks D and E, which indicate the high melting TG of PS, increased in size as the amount of stearin in the blends increased. The final

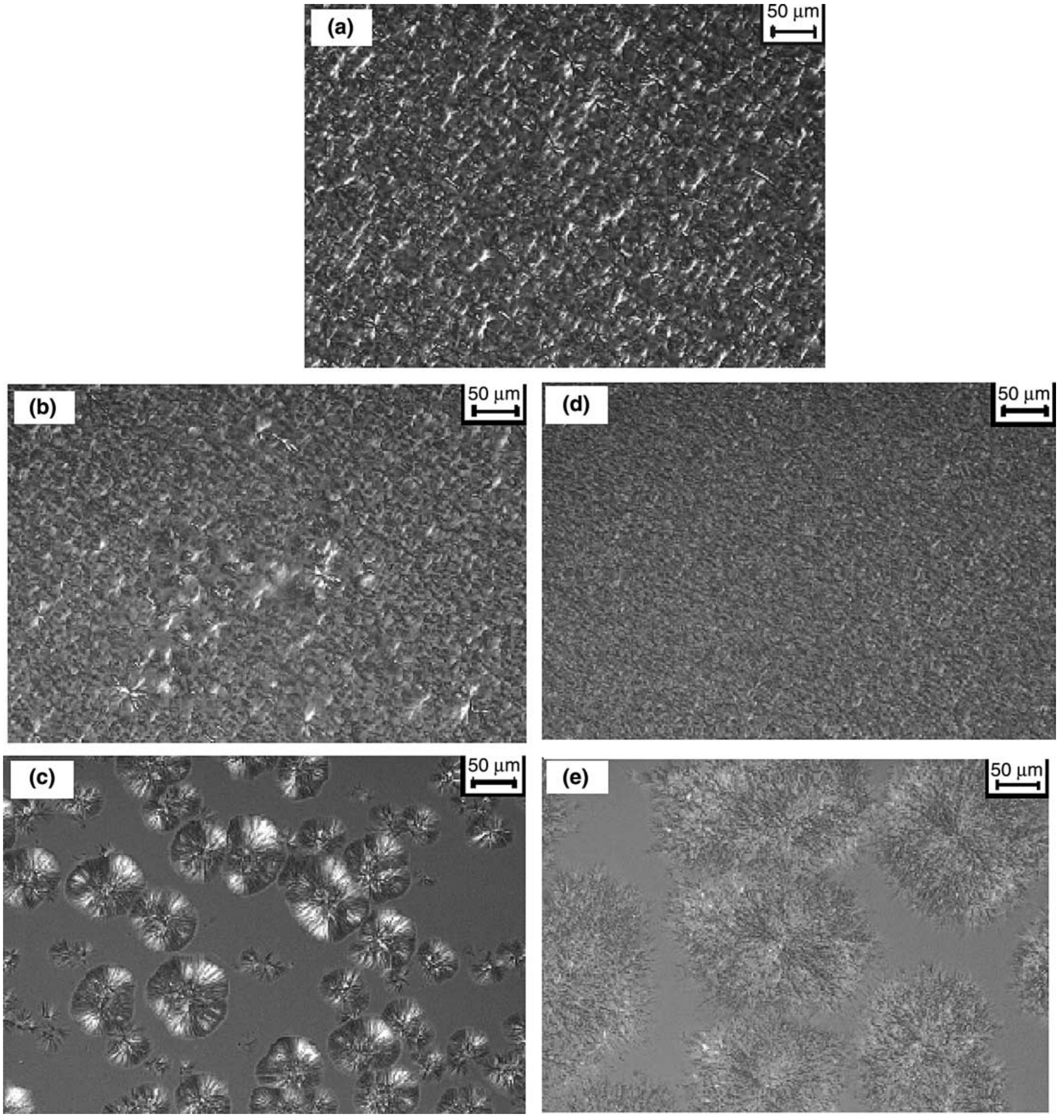

Fig. 5. Polarized light microscopy photomicrographs of palm stearin, non-interesterified and interesterified palm stearin and palm kernel olein blends tempered for 30 min at 20 °C; (a) palm stearin; (b) NIE80:20; (c) IE80:20; (d) NIE20:80 and (e) IE20:80 Scale bar = 50 µm; Magnification = 200×.

peak melting temperatures also increased from the 20:80 (37.7 °C) to 80:20 (51.5 °C) blends. This shows a harder product being formed with an increase in the stearin content, as confirmed by the SMP results shown in Fig. 1. After interesterification, peaks D and E of the non-interesterified blend disappeared, indicating a softer product being formed as a result of the randomization of the fatty acids present in the glycerides of both oils. This is also consistent with the SMP results shown in Fig. 1.

3.6. Microscopic observation

Crystal network density, crystal size and crystal morphology of palm stearin were greatly influenced by blending and interesterification with PKOo. Fig. 5(a) shows that PS consists of a dense network of fine plate-like structure. Addition of PKOo to PS resulted in mixtures of plate-like and spherulitic crystals. Figs. 5(b) and (c) showed that incremental addition of PKOo to PS leads to the formation of large and loosely packed crystals. Chemical interesterification of the blends leads to the formation of finer spherulitic crystals than that of non-interesterified blends, as shown in Figs. 5(d) and (e). This result is in line with X-ray diffraction polymorphic study which showed that only the β' form is present in the interesterified blends. These results also agree with those of Rousseau, Hill, and Marangoni (1996), who found that blending butterfat with canola oil, and subsequent interesterification, modified the crystal morphology of butterfat.

4. Conclusion

Chemical interesterification of PS and PKOo blends produced an oil with lower SMP and SFC due to changes in the TG profile. The interesterified oil was observed to be β'-tending and have a very fine spherulitic crystal network. Oil exhibiting a stable β' form tends to be smooth, provide good aeration and have excellent creaming properties. Therefore the PS and PKOo interesterified blends produced by chemical interesterification could be used for the production of margarine and shortenings, non-temper type confectionery fats, whip creams and similar products, as they impart smooth texture to the product with a slight lingering mouthfeel.

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