

EFFECT OF CHEMICAL AND ENZYMATIC INTERESTERIFICATION ON THE PHYSICO-CHEMICAL PROPERTIES OF PALM OIL AND PALM KERNEL OIL BLENDS

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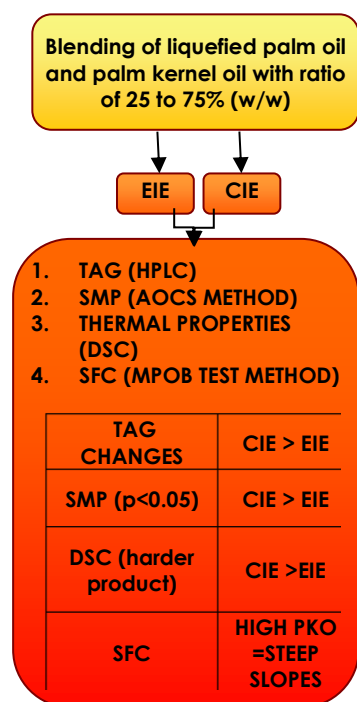
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Graphical abstract



Abstract

Palm oil (PO) and palm kernel oil (PKO) have different chemical composition and physical properties. Both oils have limited application in their natural form. To widen their commercial values, PO and PKO were modified by blending and subsequently followed by interesterification (IE). Interesterification is the rearrangement of fatty acids within and among different triacylglycerols, using enzyme or chemical as the catalysts. Palm oil with iodine value (IV) of 52.6 and PKO (IV = 17.5) were mixed in different ratios from 25:75 to 75:25 (%wt/wt) at 25% increment. The blends were subjected to chemical and enzymatic interesterification using sodium methoxide and Lipozyme TL IM as catalysts, respectively. The effects of chemical and enzymatic interesterification on the triacylglycerols (TAG) composition, thermal properties, solid fat content (SFC) and slip melting point (SMP) were investigated. Chemical interesterification (CIE) caused significant changes in the TAG composition of the oil blend compared to enzymatic interesterification (EIE). This changes led to a significantly higher ($p < 0.05$) SMP for the chemically-interesterified than the enzymatically-interesterified blends. The differential scanning calorimetry (DSC) melting thermograms confirmed that harder product with higher final complete melting temperature was obtained from the chemically-interesterified blends. Similar SFC profiles for all oil blends were observed with steep SFC slopes for blend with high proportion of PKO. Chemical interesterification reduced the eutectic interactions that occurred at 5 to 25°C in the non-interesterified and enzymatically-interesterified blends. Thus, CIE caused significant changes in physicochemical properties of the PO and PKO blends compared to EIE. Results from this study could improve the existing PO and PKO properties and widen their usage in food and non-food applications.

Keywords: Chemical interesterification, enzymatic interesterification, palm oil, palm kernel oil, physicochemical properties

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1.0 INTRODUCTION

Palm oil (PO) is derived from the mesocarp of the fruits of the oil palm species *Elaeis guineensis*. Currently, Malaysia and Indonesia with about 34.2% and 50.5% global palm oil production respectively, are the world's leading palm oil producer [1]. As the main exporter of

palm oil, Malaysia has an important role in fulfilling the global need for oils and fats. The growth of palm oil in the world market has led to many studies, particularly into its physicochemical, crystallization behaviour and nutritional values.

Palm kernel oil (PKO) is produced from an oily, dull white endosperm of the palm fruit's true seed. It has narrow melting range (27-30 °C) and is known as 'lauric oil'

because of the high proportion of lauric acid [2]. Most fats and oils have limited applications in their natural forms due to unrandomised arrangement of fatty acids and this does not optimise the use of fats and oils for industrial purposes. By subjecting fats and oils to modification, the physicochemical properties may be altered thus widen their applications [3, 4, 5 & 6].

Interesterification is one of the methods used to change the physicochemical properties of fats and oils. It is a reaction which involves the rearrangement of fatty acids within and among different TAG [7]. There are two types of interesterification namely chemical interesterification and enzymatic interesterification.

Enzymatic interesterification (EIE) used enzyme lipase as catalyst and this enzyme can be either random or specific. Enzymatic interesterification does not involve the use of heat thus acquiring milder conditions and producing regiospecific product. Chemical interesterification is more preferable in modifying fats and oils because of the lower investment and production costs of finished products [8]. It is a tried-and-true approach as it has been around for a long time since 1940s where it was applied to improve the spreadability and baking properties of lard plus, the existence and availability of industrial procedures and equipment [7].

By applying the modification techniques, new product such as oil suitable for edible purposes can be obtained. Hence, the objectives of this study are to determine the physicochemical properties of palm oil as affected by blending with palm kernel oil at different ratios and to compare the effect of CIE and EIE on the melting properties of PO and PKO blends.

2.0 METHODOLOGY

Refined, bleached and deodourised PO (IV = 52.6) and PKO (IV = 17.5) were obtained from Golden Jomalina (M) Sdn. Bhd, Klang. Commercial immobilized *Thermomyces lanuginosus* lipase (Lipozyme TL IM) was obtained from Novozyme (Denmark). The oils were stored at 0 °C prior to use. The chemicals used were either analytical or high-performance liquid chromatography (HPLC) grade.

Palm oil and palm kernel oil were melted at 70 °C prior to use. Oil blends were prepared by mixing liquefied PO and PKO in the following ratios: PO:PKO = 100:0, 75:25, 50:50, 25:75 and 0:100. The non-interesterified, enzymatic interesterified and chemical interesterified oils are abbreviated as NIE, EIE and CIE, respectively.

The interesterification process was carried out according to the MPOB Test Method [9]. Sodium methoxide was used as catalyst in chemical interesterification (CIE). For enzymatic interesterification (EIE), fresh Lipozyme TL IM was pre-treated for de-activation and dried in a vacuum batch reactor at 70 °C

for 30 minutes. A melted sample was interesterified with the readily pre-treated enzyme dose of 4% of substrate. Sampling was conducted for 6 hours.

The triacylglycerol (TAG) composition was analysed in reversed-phase HPLC (Gilson, Villiersel-Bel, France) equipped with a refractive index detector. A Lichrosphere RP-18 column (Merck, Darmstadt, Germany) was used. The acetone:acetonitrile (75:25; v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. Identification of TAG was done by comparison of retention times with those of commercial TAG standards.

Slip melting point was determined using capillary tubes according to AOCS Method Cc.3.25 [10]. The value recorded is the mean of triplicates.

Determination of solid fat content was conducted based on the MPOB Test Method [9] using a Bruker Minispec pulsed Nuclear Magnetic Resonance (pNMR) spectrometer. Measurement was carried out at 5 °C to 50 °C with interval of 5 °C and the result was expressed as mean value of triplicates.

Thermal properties were determined using DSC-7 Perkin Elmer Differential Scanning Calorimeter (Norwalk, CT). The sample was heated to 70 °C in order to destroy any crystal memory and then cooled to -40 °C. After holding for 10 minutes, the melting profile was obtained by heating to 70 °C at 5 °C/min.

The statistical results presented were obtained using a one-way analysis of variance (ANOVA) to determine significant differences among the samples at a confidence level of 95%. Data analysis was performed using SPSS program version 17.

3.0 RESULTS AND DISCUSSION

Intesterification altered the TAG composition of oil blends as shown in Figure 1. After interesterification, the relative concentration of several TAG experienced both decreases and increases, depending on the ratio of PO:PKO in the blend.

Chemical interesterification resulted more prominent changes in the TAG composition as compared to EIE due to random rearrangement of the fatty acid on the glycerol backbone. In contrast, EIE was very selective as Lipozyme TL IM attack only at 1,3-position and thus did not result in much changes as compared to their corresponding NIE blends.

Major decreased of the low melting TAGs such as LaLaLa and LaLaM were observed after CIE with the increased in the medium melting fractions such as LaOM, LaPM, MLP and OLO. Changes in TAG composition affected the melting profile of PO and PKO blends as indicated by the increment in their SMP as shown in Figure 2.

The addition of PKO in the binary blends decreased the SMP. This was due to the medium-chain fatty acids in PKO such as lauric acid, capric acid and caprylic

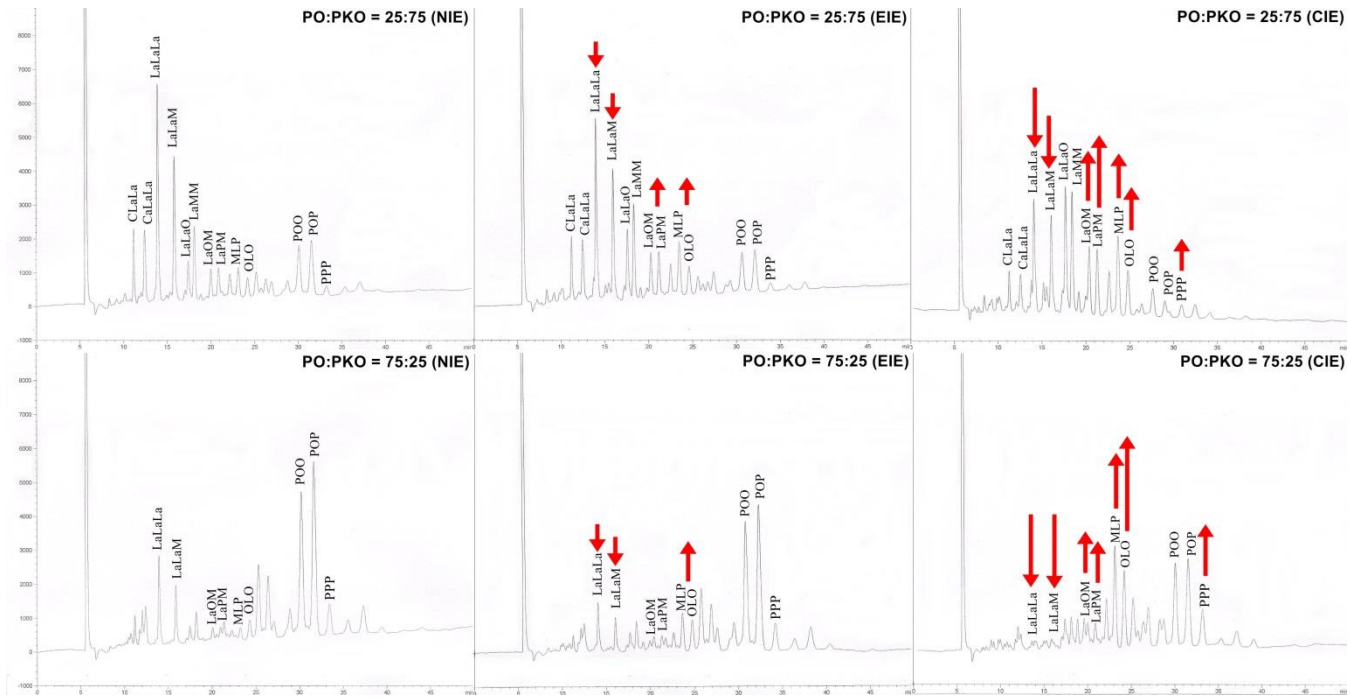


Figure 1 Triacylglycerol (TAG) profiles of non-interesterified (NIE), enzymatic interesterified (EIE) and chemical interesterified (CIE) 25:75 and 75:25 PO:PKO blends.

acid. On the other hand, high-melting TAG in PO, like tripalmitin, resulted in increment of the SMP. Hence, the SMP increased with chain length of fatty acids, high concentration of high-melting TAG and saturation of TAG.

Chemical interesterification (CIE) showed a significantly higher SMP ($p < 0.05$) as compared to their original blends (NIE), except for 100% PKO. The same behaviour was also demonstrated with the addition of more than 50% PO in EIE. However, there were no significant changes ($p > 0.05$) in SMP of enzymatically interesterified oil blends with 50% PO or lesser. As known, CIE caused a major change of fatty acids distribution while EIE was very selective. However, blends with high amount of PO (above 50%) contributed to the presence of fatty acids of various chain lengths after interesterification as compared to blends with high proportion of PKO. Thus proportion of PO in the oil blends also influenced an increase in SMP due to a diversification of the fatty acids in the glycerols fraction as well as high melting point of long chain fatty acids in PO.

Figure 3 shows similar trends of solid fat content (SFC) profiles for all oil blends where the %SFC declined with increased in temperature. The CIE increased the SFC as compared to their corresponding NIE blends, except for 100% PKO. The single blend of PKO generated only few changes in TAG after CIE as compared to their blends. This apparently due to intraesterification and randomisation of same proportion blend and thus, did not result in much alteration in the TAG composition. Oil blends with a

high proportion of PKO showed SFC profiles with steep slopes indicating the dilution effect of PKO occurred.

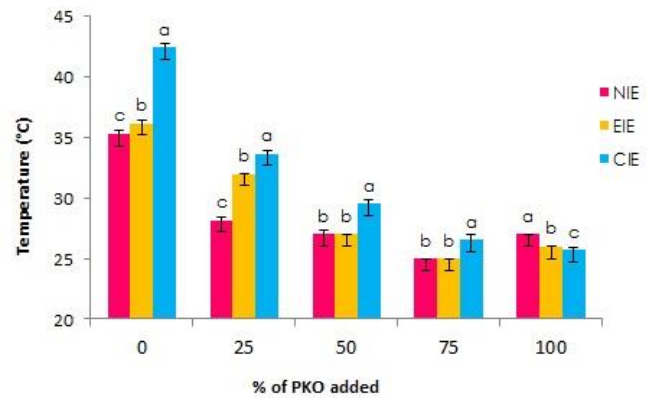


Figure 2 Slip melting point of NIE, EIE and CIE of palm oil (PO), palm kernel oil (PKO) and their binary blends. abc-Comparisons between NIE, CIE and EIE blends. Means with different letters are significantly different ($P < 0.05$).

The largest reduction was observed in the SFC from 15 °C to 30 °C, which was most likely due to the large proportion of TAG that liquefied and solubilised between these temperature ranges. The SFC at 35°C is related to the extent of melting that takes place in the mouth which is below human body temperature. Oil blends with PO:PKO = 50:50 melted completely at 35 °C after interesterification for both CIE and EIE.

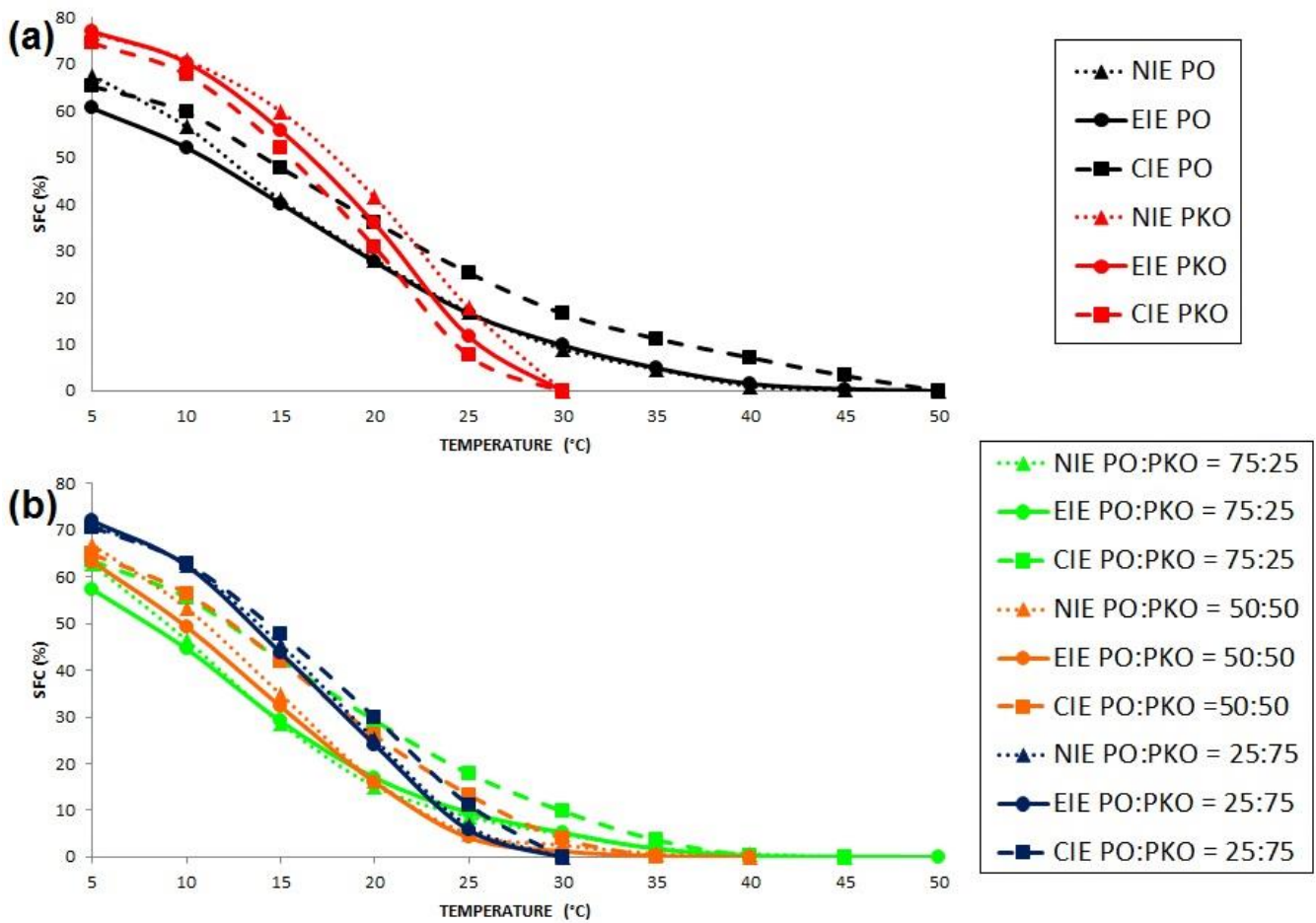


Figure 3 SFC (%) of NIE, EIE and CIE as a function temperature for (a) PO and PKO (b) PO:PKO = 75:25, 50:50 and 25:75.

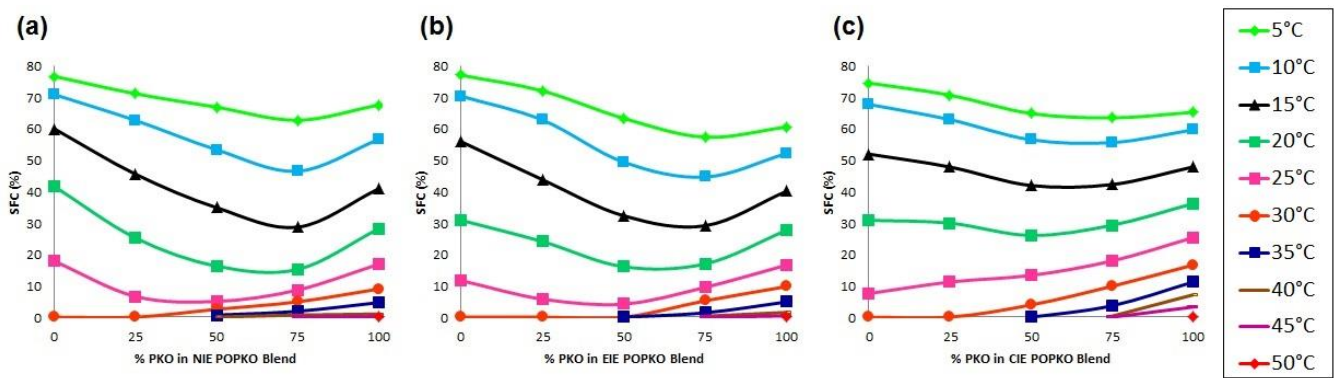


Figure 4 Eutectic effects of (a) NIE, (b) EIE and (c) CIE of PO and PKO blends at various temperature.

Hence this blend could be suitable for the manufacture of margarines or shortenings.

Figure 4 demonstrates a comparison of eutectic effect among the NIE, EIE and CIE blends. At 5 °C to 25 °C, a eutectic interaction was observed in NIE and EIE blends containing 25 to 75% PKO. This behaviour was due to the incompatible mixture of PO and PKO in the oil blend, which indicates the differences in the melting point of these two oil blends.

At those temperatures range (5°C to 25°C), short chain fatty acid, particularly in PKO, melted first and hence immiscible with the higher melting fraction of PO. This was reflected in the TAG composition of PO and PKO which lead to intersolubility in the system. The eutectic effect occurs due to the differences in the molecular size of the TAG and the polymorph of the crystals of the two types of fat [11]. However, less prominent eutectic effect was observed for CIE blends. Thus, CIE promoted TAG of PO and PKO compatible with each other that crystallised together. This result is in accordance with the findings by Grimaldi *et al.* [12], Norizzah *et al.* [13] and Timms [11], whereby interesterification would eliminate eutectic interactions due to the presence of residual amounts of TAG with long and short chain fatty acids, respectively.

Figure 5 shows the changes in the melting properties of PO and PKO before and after interesterification. There were several peaks observed in the PO thermogram as compared to the PKO thermogram showing its specific melting behaviour. The melting curve of PKO showed only one peak with small

shoulders reflected that the lower melting TAG overlapped with the higher melting TAG, resulted the PKO to melt at a faster rate than PO. The endothermic region become narrower as the proportion of PKO increased and peak shifted to lower temperature due to the dilution effect of PKO, and this is aligned with the SMP and SFC observation. A transition temperature from a peak shifted to a higher temperature and the disappearance of the small shoulder peaks after CIE as compared to NIE and EIE, which indicated a thorough randomisation of oil blends. of PO. This was reflected in the TAG composition of PO and PKO which lead to intersolubility in the system. The eutectic effect occurs due to the differences in the molecular size of the TAG and the polymorph of the crystals of the two types of fat [11]. However, less prominent eutectic effect was observed for CIE blends. Thus, CIE promoted TAG of PO and PKO compatible with each other that crystallised together. This result is in accordance with the findings by Grimaldi *et al.* [12], Norizzah *et al.* [13] and Timms [11], whereby interesterification would eliminate eutectic interactions due to the presence of residual amounts of TAG with long and short chain fatty acids, respectively.

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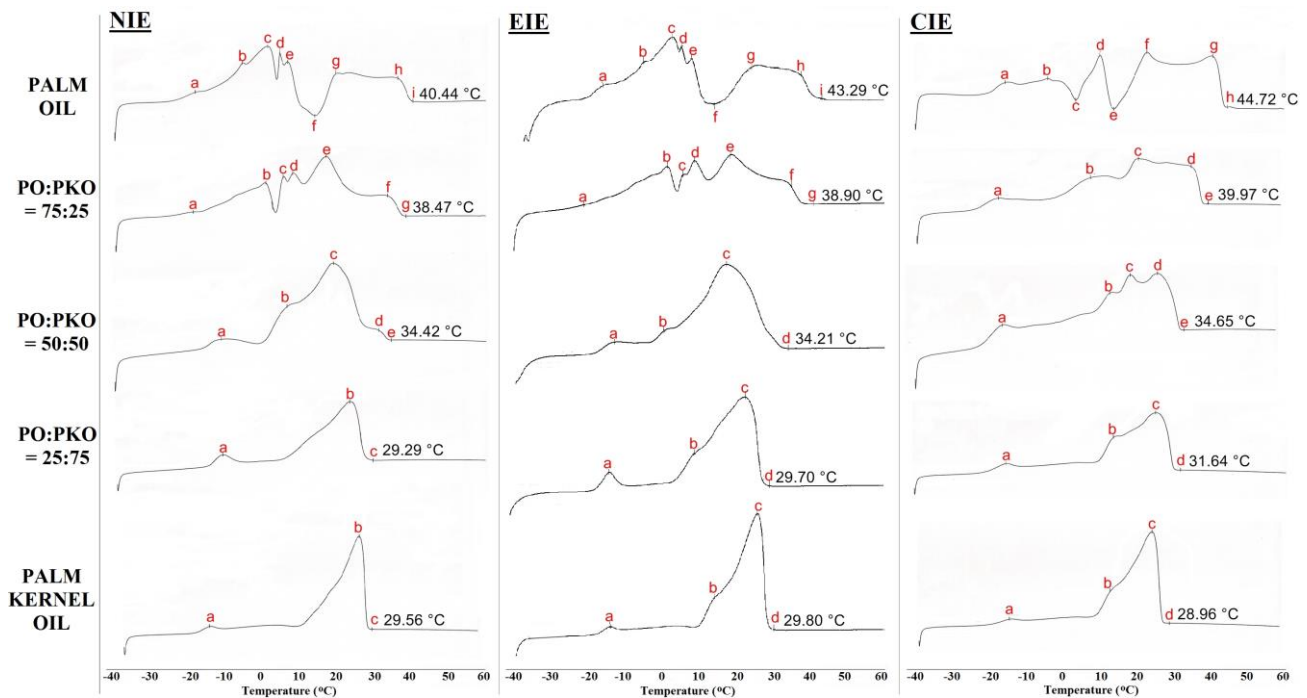


Figure 5 DSC melting thermogram of palm oil (PO) and palm kernel oil (PKO) blends before (NIE) and after interesterification (EIE and CIE).

overlapped with the higher melting TAG, resulted the PKO to melt at a faster rate than PO. The endothermic region become narrower as the proportion of PKO increased and peak shifted to lower temperature due to the dilution effect of PKO, and this is aligned with the SMP and SFC observation. A transition temperature from a peak shifted to a higher temperature and the disappearance of the small shoulder peaks after CIE as compared to NIE and EIE, which indicated a thorough randomisation of oil blends.

4.0 CONCLUSION

Blending of PO with 25 to 75% PKO significantly reduced the SMP, SFC and caused the disappearance of numerous peaks in the melting thermogram due to the dilution effect of PKO. Chemical interesterification resulted in more pronounce changes in the triacylglycerol composition as compared to enzymatic interesterification due to random rearrangement of fatty acids on the glycerides, which caused a significant increased ($p < 0.05$) in the SMP, SFC and harder product obtained with higher DSC complete melting point. Chemical interesterification eliminated eutectic interaction between PO and PKO at 5 to 25 °C resulted in the oil blends to be compatible with each other. Thus, chemical interesterification caused a significant change in the physicochemical properties of the blends as compared to their corresponding enzymatic interesterified blends.

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