



Research Article

Functionality improvement of virgin coconut oil through physical blending and chemical interesterification

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Abstract

In recent years, virgin coconut oil (VCO) has been gaining dramatic growth in food markets and is one of the most clinically studied edible oils. However, owing to its low plasticity and stiff nature, VCO could not be applied directly in edible fats production and various modification processes must be considered. In present study, physical blending with palm olein (PO) and chemical interesterification were conducted in order to improve the functional characteristics of VCO. Likewise, the alterations in chemical composition, solid fat content (SFC), slip melting point (SMP) and rheological attributes (e.g. flow behavior, strain sweep, frequency sweep and temperature sweep) of fat blends, prior and following interesterification were investigated. All blends were *trans*-free and interesterification modified the melting characteristics of fat blends through reduction of SFC and SMP. In terms of rheological attributes, a shear thinning demeanor in all fat blends was noticed and the flow data were fitted well with *Herschel–Bulkley* model. Interesterified samples were illustrated lower storage (G') and loss (G'') moduli compared to initial blends. The elastic attribute of interesterified 10:90, 20:80, 30:70, 40:60 and 50:50 blends was prevailing up to 28.89, 29.68, 31.28, 34.46 and 36.05 °C, respectively. Finally, the interesterified blends of VCO and PO revealed characteristics fitted for production of not only *trans*-free roll-in shortening but table-grade, stick and Danish margarines, as well.

Keywords Virgin coconut oil · Palm olein · Chemical interesterification · Rheology · Margarine · *Trans*-free

1 Introduction

Among the various types of lipids, bakery (shortening) and margarine fats would provide crucial eligible organoleptic attributes e.g. spreadability, favorable taste, consistency, tenderness and lubricity along with a positive effect on the geometry and structure of the final products [1]. Taking this into account, commercial margarines and shortenings are mainly developed by vegetable oils which due to their certain chemical composition and fatty acids (FAs) distribution on the glycerol backbone, at their natural state would not be suitable choices for production of margarine and bakery fats [2]. Thus, chemical (e.g. hydrogenation and interesterification) or physical procedures (such

as blending and fractionation) would be applied with the purpose of rectifying the functional attributes of vegetable oils [1].

Partial hydrogenation is among the most common modification techniques which due to enhancement of melting point, hardening of the vegetable oils would occur [3]. Though, it is eminent that partial hydrogenation would lead to the generation of *trans* FAs (TFAs), where depending on the degree of hydrogenation up till 50% TFAs could be formed [3]. There is a positive correlation between intakes of TFAs and elevated levels of low-density lipoprotein (LDL) cholesterol which would raise the risk for inflammation of the arteries, coronary heart diseases, shortening of pregnancy period and cancers.

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Consequently, the demand for healthy *trans*-free fat products is rapidly expanding which obligated the food industry toward decline or elimination of TFAs from food products [4].

Oil blending is among the best alternatives for partial hydrogenation due to its practicality, convenience and cost-efficiency. Blends of multiple vegetable oils could alter the FA profile as well as physicochemical properties of oils and hence, it could improve the techno-functionality of the final product. However, in some cases, it could change and demote the overall quality of vegetable oils through reduction of essential FAs ($\omega 3$ and $\omega 6$) [5].

Contrarily, interesterification would not alter the FA profile nor produce TFA. Thus, with utilization of *trans*-free fats and oils as the base stocks, interesterified fats will be *trans*-free, as well [6]. This procedure includes the redistribution of FAs among the triacylglycerols (TAGs), which can be conducted within the same molecule or among diverse molecules [7]. Hence, it could either enhance or reduce properties like slip melting point (SMP), oxidative stability, solid fat content (SFC) curve, crystallization and rheology which are associated to the TAG profile of fats. Moreover, interesterification could lead to consistency increment within the solid state as well as plasticity improvement of fats [1].

Virgin coconut oil (VCO) has been recognized as the oil extracted from fresh and mature coconut kernels via mechanical means, with or without the utilization of heat, particularly without any chemical refining and gaining sensational growth in the edible oils market, as a result of its excellent flavor and potential health benefits [8]. VCO is consisted of > 80% saturated FAs (SFAs), and this is notably more than most of the vegetable oils. Nutritionally, this might be accounted as a great drawback, but such simple analogies can be fallacious. When vegetable oils are hydrogenated to a similar consistency, they possess higher SFAs as well as TFAs, which various studies have displayed to be even more objectionable in terms of serum cholesterol profiles than the saturated ones [9]. Moreover, the vast majority of the VCO's total FAs are formed with medium-chain FAs (MCFAs; SFAs composed of 6–12 carbons), where lauric (46–50%) and myristic (17–19%) acids being the predominant ones [10]. MCFAs are directly absorbed into the portal vein, metabolized through the liver and withstand binding since they are not easily re-esterified. This makes them much less likely to participate in fat deposits and congealment which would lower the risk of cardiovascular diseases [11]. Diabetes and insulin sensitivity improvement, cancer inhibition, reduction of total cholesterol and LDL levels along with increasing the antioxidant enzymes, helping in foot crack recovery and scar removal are among other health benefits of VCO [11, 12].

In this regard, VCO could be a proper choice in production of bakery fats and margarines, however, owing to its poor plasticity, spreadability and rigid nature at room temperature, the utilization of VCO in fat products could be extremely challenging [13]. On that matter, as it was previously stated, blending and/or interesterification with vegetable oils containing smaller and finer β' crystals could stabilize more air and more liquid component into solid state and consequently, ameliorate the melting behavior of VCO [6, 14, 15]. The β' crystals pertain to tiny fat crystals which are accountable for the smooth texture of the shortening and margarine fats and would assist incorporation of multiple air bubbles throughout the creaming procedure [16]. The liquid fraction of palm oil known as palm olein (PO), mainly comprises β' crystals in its structure. Hence, it could be regarded as a reliable option for blending with VCO [17, 18].

Even though studies have been carried out on interesterification of coconut oil with other edible oils [3, 13, 19–24], investigations on chemical interesterification of VCO and PO are scant. From this perspective, the main objective of current study is to fill this gap and evaluate the feasibility of applying chemical interesterification (CI) to produce a structured lipid of VCO containing balanced fatty acid profile and modified physicochemical attributes. To the best of our knowledge, there was no information concerning the rheological characteristics of the interesterified blends of VCO and PO, as well. Thus, the rheology of their blends before and after interesterification were analyzed and described for the first time in this paper. Eventually, the melting attributes of the interesterified fat blends were compared with that of the commercial shortenings and margarines with the intention of identifying the potential utilization of the produced edible fats.

2 Materials and methods

2.1 Materials

A commercially available cold-pressed, centrifuged VCO (free fatty acid (FFA) content = 0.09% w/w, peroxide value (PV) = 0.39 meq/kg) was obtained from local market and refined, bleached and deodorized PO (FFA = 0.06% w/w, PV = 0.51 meq/kg) was procured from Golbahar Co. (Garm-sar, Iran). The Dry sodium methoxide (99% purity) was purchased from Sinochem Nanjing Co. (Nanjing, China). Bleaching and filter-aid earths were acquired from Khak Rangbar Abhar (Iran). Other chemicals were analytical grade and obtained from Xilong Scientific Co., Ltd., (Guangzhou, China). The raw materials were stored at -10 °C for later use.

2.2 Blend preparation

The samples were prepared as binary blends between VCO and PO (w/w) at various ratios (VCO/PO: 10:90, 20:80, 30:70, 40:60 and 50:50). This process was conducted after the samples were thoroughly melted at 70 ± 1 °C and homogenized for 10 min. The blends were refrigerated (5 ± 1 °C) until further analysis.

2.3 Chemical interesterification

For the interesterification, 400 g of the dried blends were mixed with 0.5% dry sodium methoxide and interesterified for 1 h at 90 °C under vigorous magnetic stirring (300 rpm) and reduced pressure (0.8 bar abs.). The reaction was ended by adding 2% (w/w) aqueous citric acid solution (20%, w/v) with the intention of neutralizing the catalyst. Next, the mixture was agitated for 15 min at 70 °C using magnetic stirrer (300 rpm). For the purpose of removing the excess citric acid, 1.5% bleaching earth was added to the interesterified blends and stirred via magnetic stirrer (300 rpm) at 110 °C for 15 min under reduced pressure (0.8 bar abs.). Eventually, the sample was filtered under vacuum via a filter paper (Whatman no. 4). In order to obtain interesterified fats with the minimum amount of residual soap, bleaching was carried out twice [18].

2.4 Fatty acid composition

The profile of FAs was assessed via converting the FAs into methyl esters (FAMES) in reference to the method Ce 2-66 suggested by American Oil Chemists' Society [25]. Detection and quantification of FAMES was executed based on the AOCS method Ce 1e-91 [25]. A gas chromatograph (model-GC-ATF, Shimadzu, Japan) equipped with a flame ionization detector (FID) and a rtx-wax capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.50 μ m; Restek, USA) was applied. The procedure conditions were: injection volume of 1 μ L, injector temperature at 240 °C, FID detector temperature at 300 °C, split ratio of 1:150, helium as the carrier gas, the column's temperature programmed to 30 min at 120 °C followed by a boost to 220 °C at 20 °C/min. A reference standard FAME mix (Supelco Inc., Bellefonte, PA, USA) was examined through similar operating conditions with the purpose of specifying the peak identity. The outcomes were displayed as relative percentages of the total FAs.

2.5 Atherogenicity and thrombogenicity indices

Atherogenicity index (AI) and thrombogenicity index (TI) of the samples were estimated in line with Eqs. (1) and (2), respectively, as stated via Ulbricht & Southgate [26] and

rectified by Vucic et al. [27] who contained TFA value in the sum of SFA:

$$AI = [C12 : 0 + (4 \times (C14 : 0)) + C16 : 0 + TFA] / (MUFA + PUFA) \quad (1)$$

$$TI = (C14 : 0 + C16 : 0 + C18 : 0 + TFA) / [(0.5 \times (MUFA)) + (0.5 \times (\sum \omega 6FA)) + (3 \times (\sum \omega 3FA)) + (\sum \omega 3FA / \sum \omega 6FA)] \quad (2)$$

The described parameters including: C12:0 (lauric acid %), C14:0 (myristic acid %), C16:0 (palmitic acid %), C18:0 (stearic acid %), TFA (trans fatty acid %), MUFA (monounsaturated fatty acids %), PUFA (polyunsaturated fatty acids %), $\omega 6FA$ (omega-6 fatty acids %) and $\omega 3FA$ (omega-3 fatty acids %).

2.6 Triacylglycerol composition

TAG composition of VCO and PO were collected from the literature [28, 29] and applied for TAG profile calculation of the primary blends. TAG composition of interesterified blends was measured based upon the 1, 2, 3- random theory following the probability law [1].

2.7 Slip melting point

The fat blends' SMPs were estimated by the open capillary tube, according to AOCS method Cc 3-25 [25]. The capillary tubes were loaded with 1 cm of fat melted at 10 °C above their melting point. Next, the loaded capillary tubes were chilled for 16 h at 6 ± 1 °C prior to assessments.

2.8 Solid fat content

The SFC was assayed utilizing pulsed nuclear magnetic resonance (pNMR) spectroscopy (Minispecmq 20, Bruker Corporation, Germany) based on the official AOCS method of Cd 16b-93 [25]. The direct assessment method was employed with samples read in series at 10, 20, 30 and 40 °C. Initially, fat samples were melted for 15 min at 100 °C, held for 15 min at 60 °C and then conveyed into the pNMR tube and tempered for 60 min in an ice-bath (0 °C). Finally, the samples were conditioned at the desired temperatures (10, 20, 30 and 40 °C) for 35 min. Then the SFC was assessed employing the pNMR.

2.9 Rheological characteristics

2.9.1 Flow measurements

For the purpose of studying the flow behavior of fat blends, the dynamic shear test was executed with a rheometer MCR 302 (Anton Paar GmbH, Germany) in the shear rate range of 0.01–300 s⁻¹. The obtained data were illustrated with the aid of various rheological models such as *Power-Law* (Eq. 3), *Herschel–Bulkley* (Eq. 4), *Bingham* (Eq. 5), *Cross* (Eq. 6), *Carreau* (Eq. 7) and *Casson* (Eq. 8) for the sake of identifying the best relationship between shear rate ($\dot{\gamma}$) and shear stress (τ), as displayed below;

$$\tau = k\dot{\gamma}^n \quad (3)$$

$$\tau = k\dot{\gamma}^n + \tau_0 \quad (4)$$

$$\tau = \tau_0 + \eta_p \dot{\gamma} \quad (5)$$

$$\eta_a = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (a_c \dot{\gamma})^m} \quad (6)$$

$$\eta_a = \eta_\infty + \frac{\eta_0 - \eta_\infty}{\left(1 + (\lambda_c \dot{\gamma})^2\right)^N} \quad (7)$$

$$\tau^{1/2} = k\dot{\gamma}^{1/2} + \tau_0 \quad (8)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s⁻¹), k represents the consistency coefficient (Pa.sⁿ), τ_0 indicates yield stress (Pa), n exhibits the flow index (dimensionless), η_p is the Bingham plastic viscosity, η_0 displays zero shear viscosity (Pa.s), η_∞ represents infinite shear viscosity (Pa.s), a_c and λ_c are time constants affiliated to the relaxation times of the blends, and finally m and N are dimensionless indices [30–32]. Among the rheological models applied in present study, *Power-Law* (Eq. 1) and *Herschel–Bulkley* (Eq. 2) indicated the best relationship between shear rate ($\dot{\gamma}$) and shear stress (τ) and hence, they were selected for in-depth analysis.

2.9.2 Oscillatory shear assessments

Primarily, the strain sweep test was executed (strain range of 0.01–10.00%, frequency of 1 Hz and temperature of 20 °C) with the intention of measuring the following parameters: (1) linear viscoelastic region (LVE); (2) structural strength (G' at LVE); (3) damping factor ($\tan \delta$ or G''/G' at LVE) and (4) crossover point (flow point) of G' and G'' with the aim of providing a straight look of whether the samples acted as a liquid or solid. Frequency sweep

experiments were carried out applying a frequency ramp from 0.1 to 50.0 Hz (at the constant strain of 0.05%, LVE range) at 5 °C. The *Power-Law* model (Eq. 9) was utilized for measurement of the frequency dependency of G' in the following way:

$$G' = a\omega^b \quad (9)$$

where G' is storage modulus (Pa), a is constant coefficient (dimensionless), ω is frequency (Hz) and b is flow behavior index (dimensionless) [6].

In order to examine the meltability of fat blends prior and after interesterification, dynamic temperature sweep experiments were conducted applying a temperature ramp of 5 to 40 °C with a 1 °C/min rate at a steady frequency of 1 Hz and within the LVE range (0.01%) [6]. The temperature sweep data were specified via G' , G'' , and $\tan \delta$ (an index of material's viscoelasticity, G''/G') as a function of temperature (°C).

2.10 Statistical analysis

All the experiments were run in minimum three replicates. Results were subjected to one-way analysis of variance (ANOVA) using the SPSS version 23.0 software (SPSS Inc., Chicago, IL, USA). Statistical significance of differences between samples was accepted at $p < 0.05$ using the Duncan's multiple range test. The rheological data were determined using Rheoplus software (Version 3.4, Ostfildern, Germany). The rheological models were fitted via Matlab software (R2015b, Mathwork, USA).

3 Results and discussion

3.1 Chemical characteristics

The FA composition of VCO, PO and their blends along with their AI and TI contents are exhibited in Table 1. According to published researches, interesterification has no effect on FAs composition [1, 6] and consequently, the FA profile of fat blends was not measured following the procedure. Furthermore, the fatty acid composition of the VCO and PO was in accordance with the reports in the literature [28, 29]. The amount of TFAs in fat blends was in the range of 0.18–0.29%. *Trans*-free products are specified as those comprising < 2% TFAs [33]. For this reason, all the fat blends of VCO and PO could be considered as *trans*-free fats. Lauric and myristic acids were the primary FAs of VCO (47.36 and 17.69%, respectively). Whereas, the main FAs of PO were oleic and palmitic acids (42.61 and 39.49%, respectively, Table 1). As previously mentioned, higher amounts of MCFAs would provide a proper

Table 1 Fatty acid composition (wt.% as methyl esters), atherogenicity index, thrombogenicity index and triacylglycerol content (%) of virgin coconut oil, palm olein and their blends

	Base stocks		Blends (VCO: PO)				
	VCO	PO	10: 90	20: 80	30: 70	40: 60	50: 50
Fatty acids (%)							
8:0	7.26±0.02	0	0.71±0.03	1.44±0.02	2.22±0.01	2.90±0.04	3.59±0.02
10:0	6.13±0.04	0	0.59±0.04	1.21±0.01	1.81±0.01	2.43±0.02	3.04±0.03
12:0	47.36±0.07	0.30±0.02	5.00±0.04	9.69±0.04	14.39±0.03	19.09±0.04	23.91±0.05
14:0	17.69±0.03	1.04±0.05	2.73±0.01	4.32±0.01	6.02±0.04	7.74±0.06	9.28±0.04
16:0	9.77±0.01	39.49±0.08	36.52±0.05	33.60±0.08	30.57±0.07	27.61±0.02	24.63±0.03
16:1	0	4.02±0.03	3.58±0.03	3.19±0.04	2.83±0.03	2.44±0.01	2.01±0.02
18:0	3.00±0.04	0	0.32±0.01	0.63±0.02	0.92±0.02	0.12±0.00	0.15±0.01
18:1	7.31±0.02	42.61±0.08	39.12±0.06	35.51±0.05	32.01±0.08	28.47±0.02	24.92±0.07
18:2	1.62±0.01	10.38±0.04	9.49±0.04	8.64±0.02	7.79±0.04	6.82±0.07	6.04±0.05
18:2 (tr)	0	0.31±0.01	0.22±0.01	0.18±0.02	0.15±0.00	0.11±0.02	0.08±0.00
18:3	0	0.35±0.00	0.27±0.00	0.24±0.01	0.21±0.01	0.18±0.01	0.15±0.02
18:3 (tr)	0	0.24±0.02	0.18±0.01	0.16±0.00	0.14±0.01	0.12±0.01	0.10±0.00
SFA	91.21±0.02	40.83±0.13	45.87±0.16	50.89±0.03	55.93±0.12	59.89±0.16	64.60±0.13
MUFA	7.31±0.02	42.61±0.08	39.12±0.06	35.51±0.05	32.01±0.08	28.47±0.02	24.92±0.07
PUFA	1.62±0.01	10.73±0.04	9.76±0.04	8.88±0.03	8.00±0.04	7.00±0.07	6.19±0.06
TFA	0	0.55±0.01	0.39±0.01	0.34±0.02	0.29±0.01	0.23±0.03	0.18±0.00
AI	14.32±0.04	0.83±0.01	1.08±0.00	1.37±0.00	1.73±0.01	2.19±0.01	2.76±0.01
TI	6.82±0.03	1.49±0.00	1.59±0.00	1.70±0.01	1.84±0.00	1.96±0.01	2.14±0.02
*TAG Composition (%)							
CpCC							
NIE	0.49	0	0.05	0.10	0.15	0.20	0.25
CIE	–	–	0	0	0	0.01	0.01
CpCpLa							
NIE	1.44	0	0.14	0.29	0.43	0.58	0.72
CIE	–	–	0	0	0	0.01	0.01
CpCLa							
NIE	5.26	0	0.53	1.05	1.58	2.10	2.63
CIE	–	–	0	0.01	0.03	0.08	0.16
CCLa							
NIE	19.69	0	1.97	3.94	5.91	7.88	9.85
CIE	–	–	0	0	0.01	0.03	0.07
CLaLa							
NIE	23.53	0	2.35	4.71	7.06	9.41	11.77
CIE	–	–	0	0.03	0.11	0.27	0.52
LaLaLa							
NIE	23.04	0	2.30	4.61	6.91	9.22	11.52
CIE	–	–	0.01	0.09	0.30	0.70	1.37
LaLaM							
NIE	10.41	0	1.04	2.08	3.12	4.16	5.21
CIE	–	–	0.02	0.12	0.37	0.85	1.59
LaLaO							
NIE	1.73	0	0.17	0.35	0.52	0.69	0.87
CIE	–	–	0.29	1.00	1.99	3.11	4.27
LaMM							
NIE	5.33	0	0.53	1.07	1.60	2.13	2.67
CIE	–	–	0.01	0.05	0.16	0.34	0.62
LaMO							
NIE	1.54	0	0.15	0.31	0.46	0.62	0.77

Table 1 (continued)

	Base stocks		Blends (VCO: PO)				
	VCO	PO	10: 90	20: 80	30: 70	40: 60	50: 50
CIE	–	–	0.32	0.89	1.66	2.52	3.42
LaMP							
NIE	2.70	0	0.27	0.54	0.81	1.08	1.35
CIE	–	–	0.30	0.84	1.59	2.45	3.28
LaCO							
NIE	0.83	0	0.08	0.17	0.26	0.33	0.42
CIE	–	–	0.07	0.25	0.50	0.60	1.09
LaPP							
NIE	0.47	0	0.05	0.09	0.14	0.19	0.24
CIE	–	–	2.00	3.28	4.03	4.37	4.35
MPL							
NIE	0.08	0	0.01	0.02	0.02	0.03	0.04
CIE	–	–	0.57	0.75	0.86	0.87	0.83
MPO							
NIE	0.56	0	0.06	0.11	0.17	0.22	0.28
CIE	–	–	2.34	3.09	3.53	3.65	3.42
MOO							
NIE	0.87	0	0.09	0.17	0.26	0.35	0.44
CIE	–	–	1.25	1.63	1.85	1.88	1.73
MLP							
NIE	0	0.80	0.72	0.64	0.56	0.48	0.40
CIE	–	–	0.57	0.75	0.86	0.87	0.83
MPP							
NIE	0	0.20	0.18	0.16	0.14	0.12	0.10
CIE	–	–	1.09	1.46	1.69	1.77	1.69
PPP							
NIE	0	0.80	0.72	0.64	0.56	0.48	0.40
CIE	–	–	4.87	3.79	2.86	2.10	1.49
POO							
NIE	0.20	25.40	22.88	20.36	17.84	15.32	12.80
CIE	–	–	19.37	17.24	15.10	12.97	10.83
POP							
NIE	0.18	30.60	27.56	24.52	21.47	18.43	15.39
CIE	–	–	17.96	15.99	14.02	12.04	10.07
POSt							
NIE	0	5.60	5.04	4.48	3.92	3.36	2.80
CIE	–	–	0.27	0.45	0.54	0.06	0.06
POL							
NIE	0	11.80	10.62	9.44	8.26	7.08	5.90
CIE	–	–	8.13	6.19	4.57	3.22	2.22
PLP							
NIE	0	11.00	9.90	8.80	7.70	6.60	5.50
CIE	–	–	3.80	2.93	2.18	1.56	1.10
PLL							
NIE	0	3.00	2.70	2.40	2.10	1.80	1.50
CIE	–	–	0.99	0.75	0.56	0.39	0.27
PStP							
NIE	0	0.10	0.09	0.08	0.07	0.06	0.05
CIE	–	–	0.13	0.21	0.26	0.03	0.03

Table 1 (continued)

	Base stocks		Blends (VCO: PO)				
	VCO	PO	10: 90	20: 80	30: 70	40: 60	50: 50
StOO							
NIE	0	2.88	2.52	2.24	1.96	1.68	1.40
CIE	–	–	0.15	0.24	0.28	0.03	0.03
StOSt							
NIE	0	0.50	0.45	0.40	0.35	0.30	0.25
CIE	–	–	0	0	0.01	0	0
OOO							
NIE	0.53	4.30	3.92	3.55	3.17	2.79	2.42
CIE	–	–	6.97	6.20	5.43	4.66	3.89
LOO							
NIE	0	2.10	1.89	1.68	1.47	1.26	1.05
CIE	–	–	4.36	3.27	2.39	1.66	1.13
LOL							
NIE	0	0.60	0.54	0.48	0.42	0.36	0.30
CIE	–	–	1.06	0.80	0.58	0.40	0.27
S₃							
NIE	94.09	1.50	10.23	19.35	28.48	37.60	46.73
CIE	–	–	8.44	9.91	11.42	12.99	19.45
S₂U							
NIE	4.09	48.50	44.06	39.62	35.18	30.74	26.30
CIE	–	–	26.12	25.86	25.66	24.70	23.99
SU₂							
NIE	1.07	43.00	38.81	34.61	30.42	26.23	22.04
CIE	–	–	29.90	26.05	22.37	18.46	15.08
U₃							
NIE	0.53	7.00	6.35	5.71	5.06	4.41	3.77
CIE	–	–	12.38	10.26	8.40	6.71	5.29

Values are expressed as mean \pm standard deviation; VCO, virgin coconut oil; PO, palm olein; NIE, noninteresterified; CIE, chemically interesterified; SFA, saturated fatty acids (sum of C8:0, C10:0, C12:0, C14:0, C16:0 and C18:0); MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids (sum of C18:2 and C18:3); TFA: *trans* fatty acids; AI, atherogenicity index; TI, thrombogenicity index

*TAG Composition of virgin coconut oil and palm olein was obtained from De Clercq et al. [28] and Appaiah et al. [29]. TAG profile of interesterified fat blends was estimated on the basis of the 1, 2, 3-random theory following the probability law. Cp, caprylic acid; C, capric acid, La, lauric acid; M, myristic acid; P, palmitic acid; St, stearic acid; O, oleic acid; L, linoleic acid, Ln, linolenic acid; S₃, trisaturated; S₂U, disaturated-unsaturated; SU₂, saturated-diunsaturated; U₃, triunsaturated; –, not determined

nutritional aspect to the binary blends owing to their rapid and more completely hydrolysis which eventually would decreased the storage of dietary fats in body's adipose tissues [11]. On the other hand, oleic acid has the superiority of greater oxidative durability as against PUFAs, in addition to be accountable for reducing levels of LDL cholesterol [34]. That being said, the addition of PO rich in oleic and linoleic acids would lead to blends with higher MUFAs and PUFAs than pure VCO which provided the healthier fat blends for human consumption [6]. Additionally, the main SFA of fat blends was palmitic acid (24.63–36.52%). Generally, fats with higher amount of this particular FA are more sustained in β' crystal (optimal for shortening

and margarine production) than those with low levels of palmitic acid [35]. The high oxidative stability is another subject of concern which has a major influence on the shelf life of final products. The toxic components caused by rancidity could initiate issues in the forms of tumors, brain dysfunction, heart failure and cataract [1]. As a result of superior oxidative stability of SFAs, the higher level of them can be more advantageous in fat formulations and as is shown in Table 1, the amounts of SFA in binary blends of VCO and PO were relatively high (ranging from 45.87 to 64.60%).

Another approach for estimating the fat blends' nutritional quality and potential health effects is through

specification of AI and TI parameters from the FA composition [7]. AI and TI would evaluate the incidence of pathogenic phenomena, namely atheroma and/or thrombus formation [27], and high amount of AI and TI would demonstrate undesirable impacts in context of risks for expansion of cardiovascular diseases [29]. As illustrated in Table 1, pure VCO was noted to have the highest AI (14.32) and TI (6.82) values. However, with addition of PO, the amount of AI (between 1.08 and 2.76) and TI (between 1.59 and 2.14) reduced drastically in the fat blends. That again, issues to the nutritional advantage of adding PO to VCO and accordingly, the benefit of blending process. In their study, Abramovic et al. [36] investigated the amount of AI and TI of 43 Slovenian margarines and 33 shortening fats. They found that in most margarines the AI (ranging from 0.20 to 1.40) and TI (ranging from 0.25 to 2.05) values were relatively low (quite similar to the outcomes of current study's fat blends) whilst shortenings had remarkably higher levels of AI (between 0.29 and 26.82) and TI (between 0.48 and 13.27) due to containing higher quantities of pro-atherogenic and thermobogenic FAs than margarines.

The investigations of TAG profile are true hallmarks of how the randomization process occurs and are noticeably beneficial to monitor the alteration in interesterified fats and outline particular utilizations for them [7, 37]. Correspondingly, the TAG composition of CI blends can be calculated via probability laws from their fatty acid profile [1]. The calculated TAG profile of the initial and interesterified

blends of VCO and PO is displayed in Table 1. Overall, CI led to alterations in the amounts of all types of TAGs in all binary blends. The prominent TAGs of 10:90, 20:80 and 30:70 noninteresterified fat blends were POP (27.56, 24.52 and 21.47%), POO (22.88, 20.36 and 17.84%) and POL (10.62, 9.44 and 8.26%), respectively. In noninteresterified blends of 40:60 and 50:50 the primary TAGs were POP (18.43 and 15.39%), POO (15.32 and 12.80%) and CLaLa (9.41 and 11.77%), respectively. As indicated in Table 1, CI caused considerable changes in the TAG profile of fat blends. Interesterification generated a decline in CCLa, CLaLa, LaLaLa, POO, POP, POST, POL, PLP, PLL and StOO along with an increment in LaLaO, LaMO, LaPP, MPO, MOO, MPP, PPP, OOO and LOO contents. Comprehensively, following CI a decline in the contents of trisaturated (S_3), desaturated-monounsaturated (S_2U) and monosaturated-diunsaturated (SU_2) TAGs, and contrarily an increase in the amount of triunsaturated (U_3) was noticed (Table 1). This finding was in agreement with the reports of Norizzah et al. [7] where they discovered an increment in U_3 content and a reduction in the amount of S_3 following CI in binary blends of palm oil and palm kernel oil.

3.2 Physical characteristics

SFC and SMP of fat blends, prior and after interesterification are demonstrated in Table 2. SMP is a temperature upon which a fat column in a capillary tube initiates to ascend. SMP would alter with the chain length of FAs, level

Table 2 Impact of chemical interesterification on solid fat content and slip melting point of virgin coconut oil and palm olein blends

Blends VCO: PO	SFC (%)				SMP (°C)
	10 °C	20 °C	30 °C	40 °C	
10: 90					
NIE	34.03 ± 0.06 ^a	18.80 ± 0.05 ^a	8.25 ± 0.04 ^a	1.11 ± 0.03 ^a	31.90 ± 0.20 ^a
CIE	27.28 ± 0.03 ^b	13.73 ± 0.06 ^b	2.48 ± 0.03 ^b	0.00 ^b	28.60 ± 0.10 ^b
20: 80					
NIE	36.21 ± 0.07 ^a	22.80 ± 0.10 ^a	11.16 ± 0.06 ^a	1.89 ± 0.01 ^a	33.70 ± 0.30 ^a
CIE	30.05 ± 0.09 ^b	15.41 ± 0.03 ^b	2.85 ± 0.05 ^b	0.30 ± 0.00 ^b	29.43 ± 0.06 ^b
30: 70					
NIE	38.40 ± 0.10 ^a	24.75 ± 0.05 ^a	12.41 ± 0.03 ^a	2.68 ± 0.02 ^a	34.83 ± 0.06 ^a
CIE	31.63 ± 0.06 ^b	16.88 ± 0.03 ^b	5.08 ± 0.03 ^b	0.89 ± 0.01 ^b	31.76 ± 0.11 ^b
40: 60					
NIE	41.16 ± 0.06 ^a	29.30 ± 0.10 ^a	14.19 ± 0.09 ^a	3.10 ± 0.01 ^a	37.36 ± 0.06 ^a
CIE	35.34 ± 0.09 ^b	22.48 ± 0.02 ^b	10.50 ± 0.05 ^b	1.77 ± 0.05 ^b	34.70 ± 0.10 ^b
50: 50					
NIE	45.35 ± 0.05 ^a	33.30 ± 0.05 ^a	17.51 ± 0.07 ^a	4.11 ± 0.03 ^a	38.56 ± 0.23 ^a
CIE	42.61 ± 0.03 ^b	27.75 ± 0.04 ^b	16.28 ± 0.03 ^b	2.16 ± 0.06 ^b	36.10 ± 0.10 ^b

Values are displayed as mean ± standard deviation. Values (n=3) with varied lower case letters indicates the notable effect of interesterification in the same blend at $p < 0.05$

VCO virgin coconut oil, PO palm olein, SFC solid fat content, SMP slip melting point, NIE noninteresterified, CIE chemically interesterified

of unsaturation, the amount of *trans* FAs and the site of the FAs in the glycerol backbone [38]. The SMP of initial blends enhanced with the elevation of VCO ratio, due to increment of S_3 form TAGs within blends (Table 1). The interesterified samples had less SMP than their noninteresterified counterparts ($p < 0.05$, Table 1). This could be clarified due to the decline of S_3 as well as increase in U_3 TAGs contents (Table 1). The most noticeable increases were for OOO TAGs (from 3.92 to 6.97%—blend 10:90; from 3.55 to 6.20%—blend 20:80; from 3.17 to 5.43%—blend 30:70; from 2.79 to 4.66%—blend 60:40; and from 2.42 to 3.89%—blend 50:50) and LOO TAGs (from 1.89 to 4.36%—blend 10:90; from 1.68 to 3.27%—blend 20:80; from 1.47 to 2.39%—blend 30:70; from 1.26 to 1.66%—blend 40:60; and from 1.05–1.13%—blend 50:50). This outcome was quite similar to the findings of Naeli et al. [6], Farmani et al. [18], Mahjoob et al. [38], Ribeiro et al. [39] and Masuchi et al. [40]. For instance, Ribeiro et al. [39], when assessing the SMP of fully hydrogenated soybean oil and soybean oil blends before and after CI, finds that their melting points reduced significantly ($p < 0.05$). It was observed that the amount of high-melting TAGs (S_3) significantly reduced (e.g. StStSt from 15.39 to 1.45%—blend 20:80) and the amount of low-melting TAGs (S_2U) notably elevated (e.g. PLSt from 0.52 to 8.33%—blend 20:80). Basic fat applied for production of bakery and margarine fats should melt utterly at body temperature with the aim of preventing waxy mouthfeel [6]. In that regard, the SMP of interesterified blends were in range of 28.60–36.10 °C. Hence, all

the interesterified samples could melt thoroughly in the mouth.

SFC is an indicator of the fat proportion in crystalline (solid) state to total fat at a certain temperature [41]. It is a substantial physical attribute, which straightly influences the principal characteristics of fat products including consistency, spreadability and sensorial virtues [41, 42]. SFC of fat blends at 10–40 °C, prior and after interesterification is provided in Table 2. Across all given temperatures, with a raise in the level of VCO in fat blends, the SFC enhanced noticeably ($p < 0.05$), which could be as a result of elevation in S_3 kind TAGs level (Table 1). Moreover, interesterification triggered a decline in SFC of fat blends ($p < 0.05$). It was observed in Table 1 that the interesterification enhances the level of U_3 TAGs and lowered the content of S_3 TAGs. Therefore, with increase in low-melting TAGs, the solid portion of fat would be reduced. Similar trend was noted in previous literature [6, 18, 38, 39]. Ribeiro et al. [39], reported that the reduction in SFC following CI, is related to the decline in S_3 TAGs (e.g. PStSt and StStSt) and a simultaneous elevation in amounts of SU_2 TAGs, (such as StLO). Further explanation for SFC decrement via interesterification could be related to the change of β crystals to the β' type. Smaller β' crystals melt more rapidly through the affection of temperature [43]. As reported by Norizzah et al. [44], merely β' crystals were noticeable in chemically interesterified palm stearin and PO blends. They ascribed this to the variegation of glycerides via interesterification.

Fig. 1 Flow behavior curve (apparent viscosity-shear rate) of the VCO (virgin coconut oil): PO (palm olein) blends at ratios of 10:90, 20:80, 30:70, 40:60 and 50:50 before (NIE) and after (CIE) interesterification

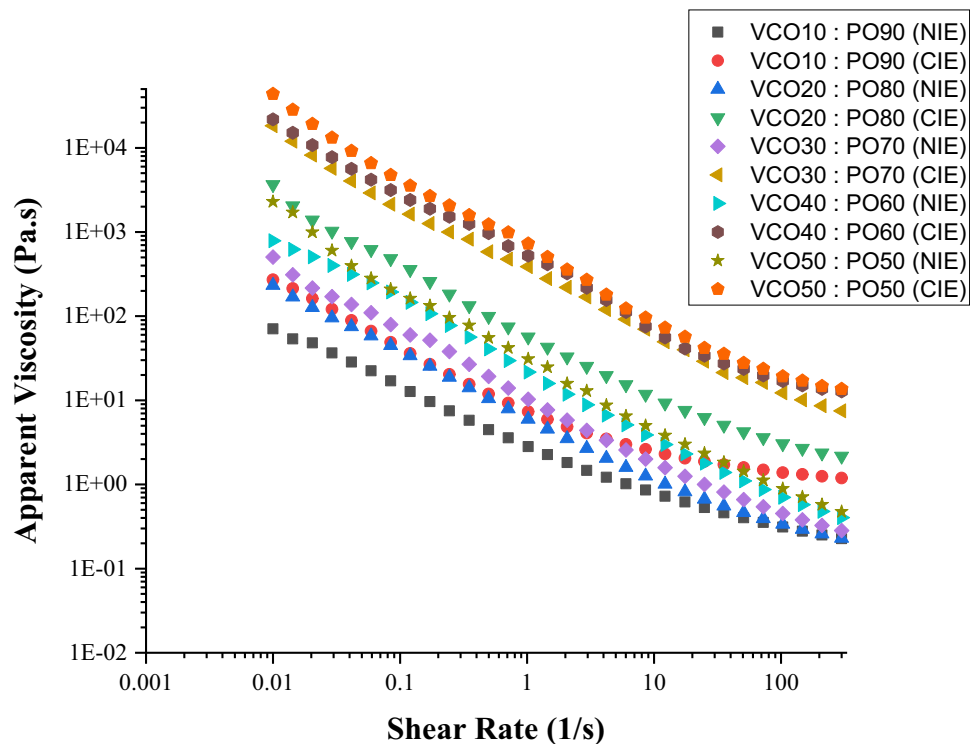


Table 3 The rheological parameters of virgin coconut oil and palm olein blends, based on *Power-Law* and *Herschel–Bulkley* models, prior and following interesterification

Blends VCO: PO	<i>Power-Law</i> parameters			<i>Herschel–Bulkley</i> parameters			
	k	n	R ²	k	n	η ₀	R ²
10: 90							
NIE	2.06 ± 0.05 ^a	0.89 ± 0.01 ^b	0.999	2.29 ± 0.08 ^a	0.80 ± 0.03 ^b	7.39 ± 1.39 ^a	1.000
CIE	0.70 ± 0.04 ^b	0.94 ± 0.02 ^a	0.999	0.95 ± 0.06 ^b	0.96 ± 0.01 ^a	3.45 ± 0.15 ^b	0.999
20: 80							
NIE	12.19 ± 1.17 ^a	0.77 ± 0.02 ^b	0.997	5.56 ± 0.66 ^a	0.70 ± 0.05 ^b	54.87 ± 6.88 ^a	0.999
CIE	1.57 ± 0.09 ^b	0.86 ± 0.04 ^a	0.999	1.04 ± 0.02 ^b	0.91 ± 0.08 ^a	3.61 ± 0.14 ^b	1.000
30: 70							
NIE	99.50 ± 16.15 ^a	0.64 ± 0.06 ^b	0.981	19.48 ± 1.17 ^a	0.50 ± 0.02 ^b	60.92 ± 7.69 ^a	0.985
CIE	3.16 ± 0.19 ^b	0.86 ± 0.05 ^a	0.998	1.70 ± 0.11 ^b	0.85 ± 0.01 ^a	7.09 ± 0.63 ^b	0.999
40: 60							
NIE	99.59 ± 20.16 ^a	0.55 ± 0.01 ^b	0.991	28.24 ± 1.19 ^a	0.41 ± 0.09 ^b	52.00 ± 7.44 ^a	0.997
CIE	7.83 ± 0.65 ^b	0.67 ± 0.04 ^a	0.995	2.79 ± 0.37 ^b	0.76 ± 0.05 ^a	18.36 ± 1.83 ^b	0.999
50: 50							
NIE	210.90 ± 20.16 ^a	0.22 ± 0.01 ^b	0.987	51.55 ± 9.67 ^a	0.36 ± 0.07 ^b	63.23 ± 9.68 ^a	0.995
CIE	13.41 ± 0.77 ^b	0.43 ± 0.01 ^a	0.997	6.13 ± 0.96 ^b	0.62 ± 0.03 ^a	19.85 ± 2.33 ^b	0.999

Values with varied lower case letters indicates the notable effect of interesterification in the same blend at $p < 0.05$

VCO virgin coconut oil, PO palm olein

3.3 Rheological characteristics

3.3.1 Flow behavior measurement

The flow curves of fat blends before and after interesterification at varied proportions of VCO are exhibited in Fig. 1. The impact of CI and various ratios of VCO on the rheological indices of fat blends based on *Power-Law* and *Herschel–Bulkley* models are demonstrated in Table 3, as well. According to Fig. 1, all fat blends expressed pseudoplastic behavior since the apparent viscosity decline upon shear rate increment (0.01 to 300 S⁻¹). This behavior is in connection with the collapse of the weak bonds between molecules or the network encircling the fat particles [45]. In all tested samples, the apparent viscosity was dependent on the amount of VCO in fat blends (Fig. 1), in such a way that the highest and lowest apparent viscosity was noticed at 50% and 10% VCO content, respectively. Similar finding was reported in the study of Irmischer et al. [46] where due to concentration enhancement of hydrogenated palm fat from 2.5 to 5.5 wt.% in canola oil-palm fat mixtures, the amount of apparent viscosity raised from 0.75 to 1.85 Pa.s at the shear rate of 39.1 s⁻¹. It was concluded that at higher palm fat ratio, greater number of crystals would be present in the oil-fat mixtures and consequently, larger number of primary bonds would be attributed to a larger number of lipid bridges between fat crystals which eventually, sintered crystals would be available. Thus, more comprehensive and powerful three dimensional lipid network

would be formed [46]. Since following interesterification, the levels of U₃ type TAGs increased (Table 1), the apparent viscosity of all interesterified samples was lower than initial fat blends (Fig. 1).

In general, the flow behavior data were fitted well with both *Power-Law* and *Herschel–Bulkley* models with high coefficient values (R² ≥ 0.981 and R² ≥ 0.985, respectively). Nevertheless, the *Herschel–Bulkley* model fitted the experimental data greater (Table 3). Flow behavior indices (n) were in ranges of 0.22 to 0.94 in the *Power-Law* model, whereas it was between 0.29 and 0.95 in the *Herschel–Bulkley* model. Since both flow indices were less than 1, it allows the conclusion that all the fat blends had shear thinning (pseudoplastic) behavior [32]. Non-Newtonian fluids do not possess absolute viscosity (as the apparent viscosity dependent on shear rate). Thus, the coefficient of consistency (k) can be regarded as an index for determining the resistance against flow [32]. The content of k measured by *Power-Law* model was 0.70-2.06, 1.57-12.19, 3.16-99.50, 7.83-99.59 and 13.41-210.90 Pa.s in blends of 10:90, 20:80, 30:70, 40:60 and 50:50, respectively. However, the k (measured via *Herschel–Bulkley* model) was ranged from 0.95 to 2.29, 1.04 to 5.56, 1.70 to 19.48, 2.79 to 28.24 and 6.13 to 51.55 Pa.s in blends of 10:90, 20:80, 30:70, 40:60 and 50:50, respectively. According to Table 3, as VCO ratio elevated, k noticeably enhanced, exhibiting the increment in consistency and hardness of the samples ($p < 0.05$). Yield stress (τ₀) is specified as the stress at a point higher than which the material initiates to flow [24]. Having

adequate information with respect to the product's yield stress level significantly supported the examination of its technological utilizations [32]. The yield stress of the samples with VCO content of 10, 20, 30, 40 and 50% was in the range of 3.45–7.39, 3.61–54.87, 7.09–60.92, 18.36–52.00 and 19.85–63.23 Pa, respectively. In accordance with Table 3, the yield point (τ_0) of fat blend samples was remarkably boosted by enchantment of the VCO concentrations within blends ($p < 0.05$).

3.3.2 Oscillatory shear assessments

Small deformation oscillatory examinations represents useful data which could be associated to fat crystal network structure and plasticity. The assessed parameters are G' or storage modulus, which offers an indication of the solid-like structure as well as G'' or loss modulus, which proposes an estimation of the fluid-like behavior in a viscoelastic substance [6].

At the primary stage of oscillatory rheological examinations, the strain sweep test was conducted for the aim of specifying the linear viscoelastic regions (LVEs) of the initial and interesterified fat blend samples (Fig. 2). As exhibited in Fig. 2, the strain sweep curve of all the fat blends can be segregated into two common areas of linear and non-linear. Within LVE, G' and G'' were nearly steady which means the structural deformation was reversible (small deformations). In non-linear area, through elevation of the strain, G' and G'' initiated to decline (large deformations) till crossing each other. Basically, the cross point of G' and G'' ($G' = G''$) is noted as the flow point of the material and it is defined as a particular strain value, at which the internal structure would break and the samples would flow [32]. It is worth mentioning that in all fat blends G' was greater than G'' merely prior the flow point. Consequently, all samples displayed a solid-like behavior within LVE. Though, following the LVE, G'' was at higher levels than G' and fat blends indicated more liquid-like demeanor.

The data of γ_{LVE} , G' in the LVE range, $\tan \delta_{LVE}$ (G''/G' at LVE), and the crossover point of G' and G'' (flow point) are exhibited in Table 4. Accordingly, through enhancement of VCO proportion in samples, γ_{LVE} was noticeably raised ($p < 0.05$), showing the increase in the strain of these samples in LVE range. However, after interesterification there was a significant decline in the amount of γ_{LVE} . Overall, a broader LVE limit implies that the samples have greater viscoelastic characteristics, maintaining their form at higher levels of strain sweep and have higher capacity for recovering their structure [32]. All fat blends in this study demonstrated low levels of γ_{LVE} , which displayed the short linear viscoelastic domains of the fats and lower strength of samples at strains below γ_{LVE} amplitude. For the purpose of providing a straight look of solid- or liquid-like

demeanor of the fat blends in the LVE limit, the $\tan \delta_{LVE}$ which is the proportion of G'' to G' in LVE was also investigated. As illustrated in Table 4, in all blends $\tan \delta_{LVE}$ of interesterified samples were less than the noninteresterified ones ($p < 0.05$). This proves the superior elastic behavior of interesterified samples at LVE domain. As a whole, by elevation of VCO content from 10 to 50%, a considerable raise in the G' at LVE and crossover point ($G' = G''$) or flow point was noted ($p < 0.05$). This might be due to increment of S_3 form TAGs and SFA contents (Table 1). Moreover, the amount of G' at LVE in interesterified samples was less than initial blends ($p < 0.05$). Certainly, changes in TAG profile upon CI tremendously impacted the rheological attributes of the blends. As previously stated, interesterified samples had higher amount of U_3 type TAGs than initial blends as well as lower S_3 , S_2U and SU_2 TAGs (Table 1). Ahmadi et al. [47] assessed the effects of CI on rheological properties of fully hydrogenated canola oil and high oleic acid sunflower oil blends and they found that there was a strong negative correlation ($r = -0.96$) between G' and U_3 TAGs content of these fat blends which verified the lower storage modulus of interesterified samples.

The frequency sweep rheograms of the fat blends prior and after interesterification are exhibited in Fig. 3, A–E. The outcomes of frequency sweep test displayed that fat blends had a quite steady trend against frequency sweep and G' was higher than G'' at all frequency ranges where no crossover was noted (Fig. 3). This verifies the solid-like (elastic) behavior of fat blends against frequency sweep. In general, samples possessing more VCO had greater G' than G'' as a function of frequency, though interesterification caused a reduction in both solid-like and liquid-like demeanors of the fat blends (Fig. 3A–E).

The variables of *Power-Law* model which revealed the frequency dependency of the fat blends' storage modulus are provided in Table 5. Accordingly, the coefficient a reveals the extent of G' modulus and the index b indicates the gradient of the relation between G' and frequency [6]. At lower frequency dependence, b approach to zero which shows G' does not alter with frequency [32]. The quantities of b value also displays the elastic attributes of the fat blends, as b nearly close to 1 indicates the formation of a viscous material, whereas b close to zero illustrates an elastic material [31]. In accordance with Table 5, the b value of all noninteresterified samples were less than 0.081 revealing that their G' would not alter with frequency and consequently have an elastic demeanor. Similar results was seen in interesterified blends with the exception of 10:90 and 20:80 blends which demonstrated the highest alteration of G' with frequency ($b = 0.149$ and $b = 0.101$, respectively) and they behaved as a relatively viscous material. Moreover, it can be seen from Table 5 that the interesterified blends had lower a value than the initial samples

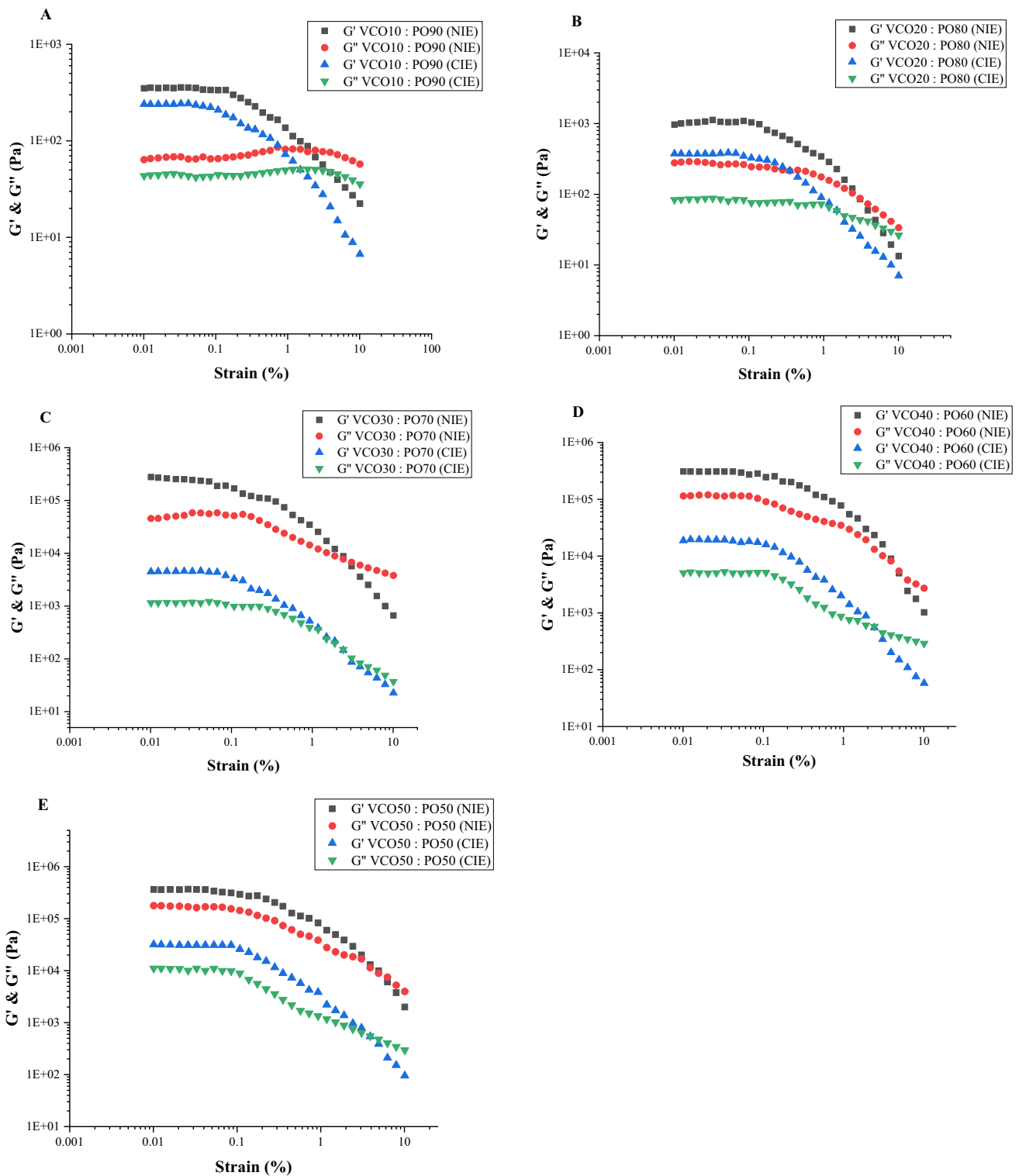


Fig. 2 Strain sweep curve of the VCO (virgin coconut oil): PO (palm olein) blends at ratios of 10:90 (a), 20:80 (b), 30:70 (c), 40:60 (d) and 50:50 (e) before (NIE) and after (CIE) interesterification

($p < 0.05$), which proves the less stiff structure of interesterified blends. It has been indicated in previous literature that the hardness of fat crystal networks is positively

correlated with the amount of G' [47]. In that regard, the effect of TAG composition on hardness can also be clarified in terms of the proportion of S_3 , S_2U , and SU_2 , and U_3 TAGs

Table 4 The rheological parameters of the virgin coconut oil and palm olein fat blends, measured using strain sweep test, prior and following interesterification

Oil blends VCO: PO	γ_{LVE} (%)		G'_{LVE} (Pa)		$\tan \delta_{LVE}$		Crossover point (%)	
	NIE	CIE	NIE	CIE	NIE	CIE	NIE	CIE
10: 90	0.06 ^{Ea}	0.05 ^{Db}	338.94 ^{Ea}	235.53 ^{Eb}	0.20 ^{Ea}	0.17 ^{Eb}	2.42 ^{Da}	1.50 ^{Eb}
20: 80	0.08 ^{Da}	0.05 ^{Db}	1089.75 ^{Da}	385.78 ^{Db}	0.24 ^{Da}	0.20 ^{Db}	3.04 ^{Ca}	1.89 ^{Db}
30: 70	0.10 ^{Ca}	0.06 ^{Cb}	168936.92 ^{Ca}	4378.34 ^{Cb}	0.30 ^{Ca}	0.26 ^{Cb}	3.04 ^{Ca}	2.40 ^{Cb}
40: 60	0.13 ^{Ba}	0.08 ^{Bb}	253369.33 ^{Ba}	17492.28 ^{Bb}	0.32 ^{Ba}	0.29 ^{Bb}	4.90 ^{Ba}	3.04 ^{Bb}
50: 50	0.17 ^{Aa}	0.10 ^{Ab}	277054.09 ^{Aa}	25925.58 ^{Ab}	0.41 ^{Aa}	0.34 ^{Ab}	6.32 ^{Aa}	3.91 ^{Ab}

Values with varied lower letters displays the notable impact of interesterification in the same blend at $p < 0.05$. Values with varied capital letters demonstrates the notable impact of virgin coconut oil ratio in the same column at $p < 0.05$

γ_{LVE} quantity of strain at linear viscoelastic range, G'_{LVE} storage modulus at the limit of viscoelastic region, $\tan \delta_{LVE}$ loss tangent value in the linear viscoelastic region, NIE noninteresterified, CIE chemically interesterified, VCO virgin coconut oil, PO palm olein

contents. Clearly, less amounts of S_3 , S_2U and SU_2 TAGs in the interesterified samples led to lower yield force (G') values and consequently softer fat. Naeli et al. [6] compared the *Power-Law* model rheology parameters of palm stearin and soybean oil at three blends of 10:90, 30:70 and 50:50 before and after interesterification via frequency sweep test (from 0.01 to 1000 Hz). They observed that interesterified 10:90 and 30:70 blends had greater a value and lower b value than noninteresterified samples, however 50:50 blend had lower a value and higher b value than initial sample ($p < 0.05$). They justified their findings through increment of S_2U type TAGs level in their 10:90 and 30:70 fat samples and the decline of it in 50:50 blend after interesterification. As a result, higher structural strength was observed in interesterified 10:90 and 30:70 blends as well as less stiff structure in interesterified 50:50 blend.

Temperature sweep test could offer beneficial information in respect of heat-induced alterations which happen to viscoelastic virtues of fats [6]. The impact of heating (from 5 to 40 °C) on storage and loss modulus of the fat blends before and following interesterification are stated in Fig. 4A–E. For the aim of gaining a straight look of whether fat blends acted as solid or liquid at each temperature, $\tan \delta$ or damping factor which is the ratio of G'' to G' was also investigated. As is illustrated in Fig. 4, with elevation of temperature, there was a decline in both G' and G'' . The interesterified 10:90, 20:80, 30:70, 40:60 and 50:50 blends had greater G' than G'' up to the 28.89, 29.68, 31.28, 34.46 and 36.05 °C, respectively, which was relatively in proportion with the decline of SFC values. The viscoelastic demeanor of interesterified fats were quite similar to that observed by Lee et al. [48] and Naeli et al. [6]. According to Naeli et al. [6], interesterified 10:90, 30:70 and 50:50 blends of palm stearin and soybean oil showed elastic demeanor up to 28.8, 37.9 and 41.8 °C, respectively. Nonetheless, as the temperature kept boosting, the interesterified samples revealed merely viscous fluid attribute after mentioned

temperatures. As reflected in Fig. 4, in all fat blends the amount of G' and G'' of interesterified samples were less than the initial ones nearly at all temperatures. This was in disagreement to the findings of Naeli et al. [6] and Soares et al. [35], which most likely could be related to differences in TAG composition of their fat blends. The damping factor ($\tan \delta$) is an advantageous index for evaluating the viscoelastic behavior of fat materials and a raise in the levels of $\tan \delta$ implies an alteration from elastic to more viscous status [6]. As evidence in Fig. 4, the alteration of $\tan \delta$ content could be segregated in two phases of initial slow raise and an ultimate rapid boost. The initial stage may display the temperature limit upon which the sample possesses SFC where in this phase fats reveals viscoelastic demeanor. The temperature upon which G' and G'' are equal ($\tan \delta = 1$) is expressed as the cross point [6], which could be an indication of fats meltability. As a whole, with enhancement of VCO ratio in blends (Fig. 4) the cross point raised. The cross point temperature of interesterified 10:90, 20:80, 30:70, 40:60 and 50:50 fat blends were 28.89, 29.68, 31.28, 34.46 and 36.05 °C respectively, which were in accordance with the SMP data of present study (Table 2). Blends with less SMP exhibited less cross point temperature, as well. Following melting point, with increment of temperature fats melts utterly and the G'' content raised rapidly which changes the nature of fats to more viscous state and consequently a rapid boost in $\tan \delta$ would occur. In case of interesterified blends, the sharp rise in $\tan \delta$ happened at lower temperatures compared to initial samples (Fig. 4).

3.3.3 Potential utilizations of interesterified fat blends

As stated earlier, the SFC is a substantial property of lipids, which straightly impacts on functional characteristics of fats e.g. spreadability and other sensorial attributes. One of the benefits of SFC curves is to assess the unique utilizations of fats [42].

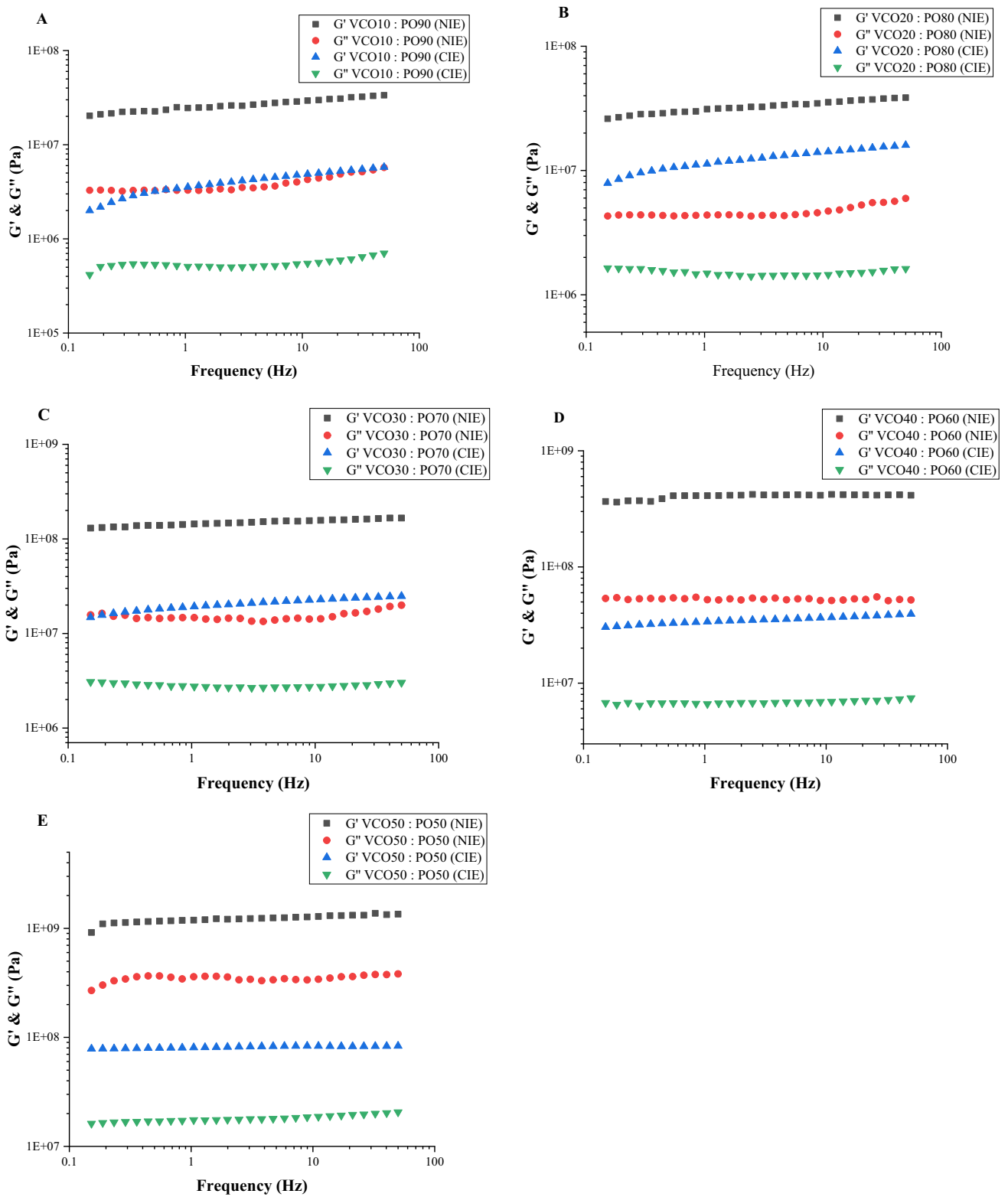


Fig. 3 Frequency sweep curve of the VCO (virgin coconut oil): PO (palm olein) blends at ratios of 10:90 (a), 20:80 (b), 30:70 (c), 40:60 (d) and 50:50 (e) before (NIE) and after (CIE) interesterification

Table 5 Power-Law model parameters of storage modulus in frequency sweep test of the virgin coconut oil and palm olein fat blends prior and following interesterification

Blends VCO: PO	$G' = a\omega^b$					
	R^2		a (Pa.s)		b	
	NIE	CIE	NIE	CIE	NIE	CIE
10: 90	0.99	0.95	24188916.34 ^{Ea}	3358558.32 ^{Eb}	0.081 ^{Ab}	0.149 ^{Aa}
20: 80	0.99	0.97	30423866.32 ^{Da}	11038561.69 ^{Db}	0.063 ^{Bb}	0.101 ^{Ba}
30: 70	0.99	0.97	142668640.25 ^{Ca}	18835323.64 ^{Cb}	0.040 ^{Cb}	0.077 ^{Ca}
40: 60	0.99	0.99	372938976.65 ^{Ba}	33461335.92 ^{Bb}	0.018 ^{Db}	0.040 ^{Da}
50: 50	0.85	0.88	1171706373.75 ^{Aa}	80599656.10 ^{Ab}	0.004 ^{Eb}	0.011 ^{Ea}

Values with varied lower letters displays the notable impact of interesterification in the same blend at $p < 0.05$. Values with varied capital letters demonstrates the notable impact of virgin coconut oil ratio in the same column at $p < 0.05$

NIE noninteresterified, CIE chemically interesterified, VCO virgin coconut oil, PO palm olein

Hence, for the purpose of determining the potential application of interesterified fat blends of VCO and PO, their SFC curves were compared with that of different kinds of commercial margarines and shortenings obtained from previous researches [49, 50]. A table-grade margarine must deliver somewhat unique physical demands in the sense that it must possess a plastic consistency with a quite sharp melting point [50]. Consumers anticipate a table-grade margarine to melt swiftly in the mouth for a complete flavor release, to be instantly spreadable out of the refrigerator and to sustain a solid consistency for extended periods on the dinner table. These attributes are presented with a blend of liquid oils or a soft base-stock with specific firm base-stocks [50]. In accordance with Fig. 5, interesterified samples containing 20–30% VCO could be potentially applied in production of table-grade margarines, as their SFC levels were in range with this particular margarine, which verifies their desirable spreadability at refrigeration temperature. Likewise, the interesterified blend of 30% VCO could be considered for the production of stick margarines, as well, since their SFC values were relatively matched. Stick margarines are another type of fat which provide slightly stiffer consistency than table-grade margarines. The utmost hardstock fat values are applied to formulate roll-in margarines (or puff pastry fats) where a plastic yet firm fat with good consistency is

required for its acceptable performance [50]. In addition to the traditional use as table foods, margarines and shortenings are also extensively utilized in baking applications e.g. in cookies and/or as roll-in fats for puff and Danish pastries. The distinguishing features of roll-in shortenings and/or Danish margarines are plasticity and firmness to an extent that they should stand as unbroken layers throughout repeated folding and rolling operations [50]. In that regard, the SFC of interesterified 50:50 blend was fitted well with both roll-in shortening and Danish margarine.

4 Conclusion

In summary, the impact of CI on physicochemical and rheological attributes of *trans*-free fats obtained via VCO and PO were studied. As a consequence of their high melting point and low elasticity, the noninteresterified samples were not appropriate for straight utilization in shortenings and margarines production. That being said, the interesterified samples had less SMP and SFC than the initial samples. Additionally, interesterification rectified the rheological virtues of fat samples through declining of the G' and G'' moduli in all blends. The damping factor in all interesterified blends were less than of initial blends, proving the betterment of elastic demeanor in fat blends. The elastic virtue of

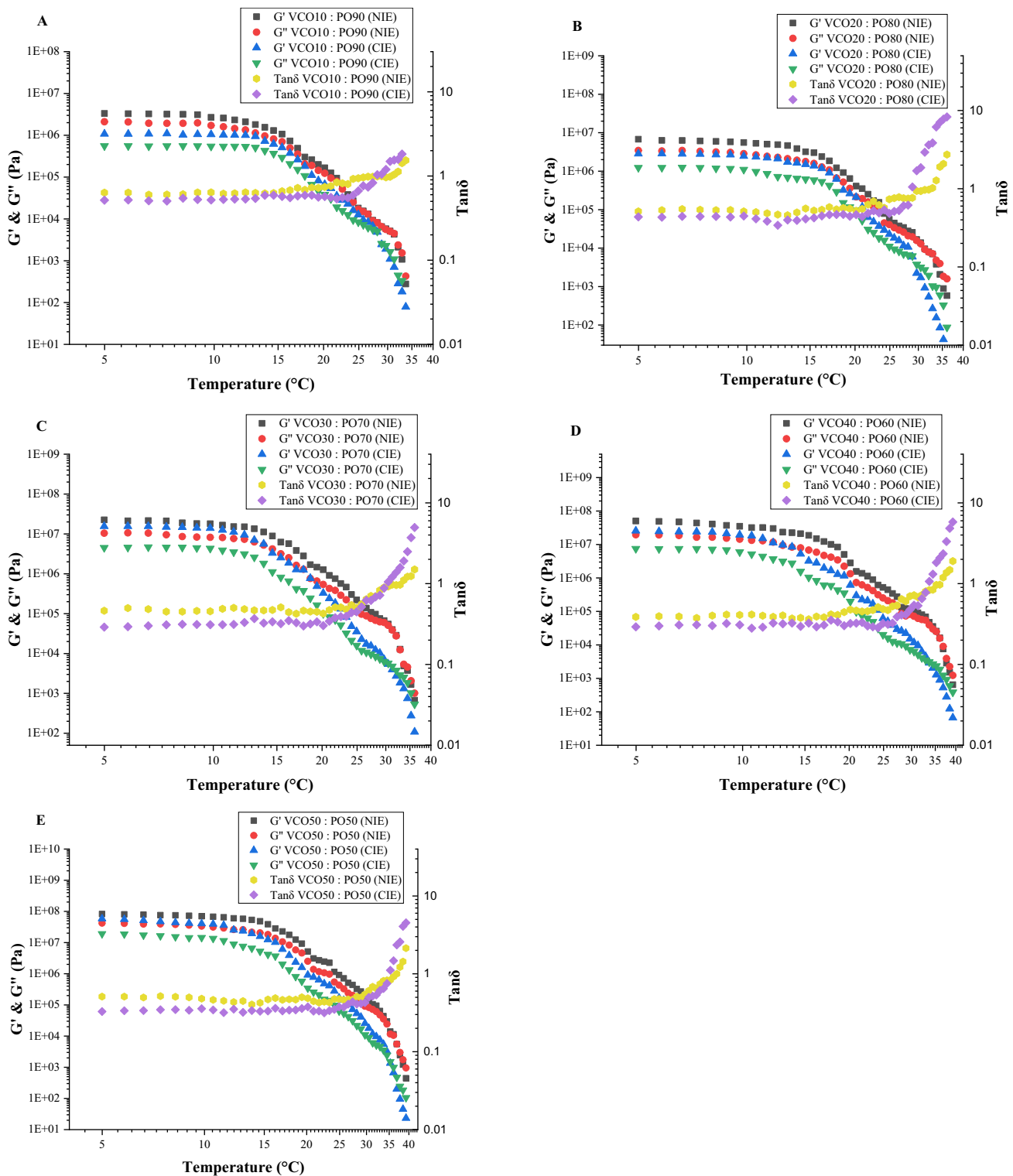


Fig. 4 G' and G'' moduli and $\tan\delta$ of the VCO (virgin coconut oil): PO (palm olein) blends at ratios of 10:90 (a), 20:80 (b), 30:70 (c), 40:60 (d) and 50:50 (e) before (NIE) and after (CIE) interesterification as a function of temperature

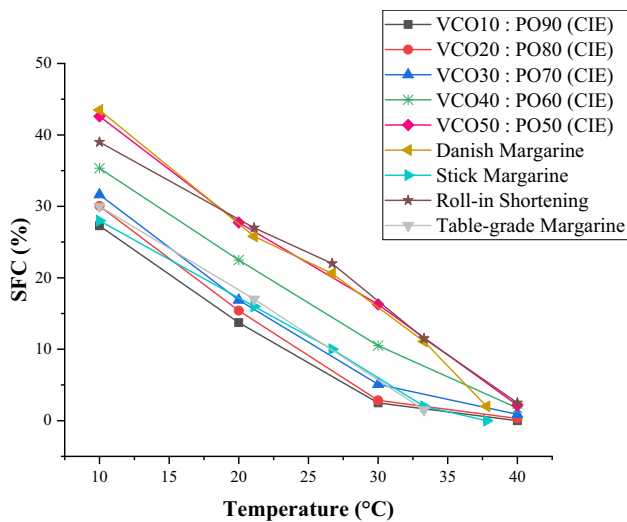


Fig. 5 Comparison of solid fat content curve of interesterified blends of VCO (virgin coconut oil): PO (palm olein) with SFC curve of commercial stick margarine [48], Danish margarine, roll-in shortening and table-grade margarine [49]

interesterified 10:90, 20:80, 30:70, 40:60 and 50:50 fat blends were superior up to 28.89, 29.68, 31.28, 34.46 and 36.05 °C, respectively. The outcomes of present study implied that the interesterified blends of VCO and PO could be employed as a substitute of partially hydrogenated stick, table-grade and Danish margarines as well as roll-in shortening.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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