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Melting and Solidification Properties of Palm Kernel Oil, Tallow, and Palm Olein Blends in the Preparation of Shortening

Qingzhe Jin · Ting Zhang · Liang Shan · Yuanfa Liu · Xingguo Wang

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Abstract Ternary systems composed of palm kernel oil (PKO), tallow, and palm olein (POo) were studied in terms of their physical properties such as solid fat content (SFC), melting characteristics by DSC and polymorphism by X-ray diffraction. Ternary phase behavior was analyzed with isosolid diagrams. The results showed that as the POo content of the blends was increased the SFC value decreased, while the increase of tallow content increased the SFC value. Eutectic effects within the ternary system were confirmed from the deviation of the measured SFC from the calculated SFC for corresponding thermodynamically ideal blends. The deviation reached a maximum when the amounts of PKO and POo are both about 45%. X-ray diffraction results showed that addition of PKO into the blends promoted stabilization in the β' crystalline form.

Keywords Ternary systems · Melting characteristics · Polymorphism · Solid fat content · Compatibility

Introduction

Shortenings, which are widely used for general purpose applications, cooking, frying, and baking, are fats formulated from oil and base oil (often with a plasticizer and an emulsifier) [3]. Hydrogenation of oils and transesterification of fats used to be the preferred method for obtaining the hard fat of shortenings with specific physicochemical characteristics. However, new trends show a move towards the use of fewer modified fats and oils, because the negative role of *trans* fatty acids in some aspects of human health [9]. Therefore, researchers are starting to consider natural lipid sources, as well as lipids that undergo mild processing procedures, in order to obtain pre-designed fat products with the desired physical, chemical, and nutritional characteristics [2, 5].

The fats and oils present in natural plant sources are mixtures of different types of triacylglycerol (TAG). The complicated behavior of melting, crystallization and transformation, crystal morphology, and aggregation of real-fat systems is due in part to the physical properties of the component TAG. TAGs usually occur in three polymorphs: α, β', and β [11]. The α form is not stable. The β' polymorph, although metastable, is the most desirable form because it provides a fine arrangement and a large surface area of solid crystals, and thus stabilizes the liquid oil and water droplets most effectively. The β form, although the most stable, is not desirable in large amounts because the large crystals of this arrangement will result in a coarse and grainy texture.

When the compositions and physical properties of fats, such as phase behaviors and polymorphisms are known, it is possible to find appropriate uses for them. With this knowledge, it is possible to predict and control the final characteristics of derived products.

Isosolid diagrams are very useful tools for studying the phase behaviors of natural fats and their mixtures [5, 10], and to analyze the compatibility of them. Differential scanning calorimetry (DSC) gives information about the temperatures and enthalpy changes associated with the fusion, crystallization, and polymorphic transformations of fats. X-ray diffractometry (XRD) is a relatively more direct

Q. Jin · T. Zhang · L. Shan · Y. Liu · X. Wang (✉)
School of Food Science and Technology,
Key Laboratory of Food Science and Safety,
Ministry of Education, Southern Yangtze University,
170 Huihe Road, Wuxi 214036,
Jiangsu Province, People's Republic of China
e-mail: jacklshan@yahoo.com.cn

technique for studying polymorphism and can be the most informative. An XRD pattern is comprised of both short- and long-spacings with the former related to the cross-sectional arrangement of the crystal lattice and particularly independent of the chain length of fatty acids (FA).

Palm kernel oil (PKO), as co-product of palm oil, has very similar compositions and properties as coconut oil. The production of PKO has been increasing along with the fast growth of palm oil, and PKO has been used in margarines, shortenings, confectionary fats and so on. However, PKO has a limited compatibility with the other fats, so studying on the compatibility of PKO blending with other fats can provide a theoretical basis for the production technology of margarine and improving a product's quality.

Palm kernel oil (PKO), tallow, and palm olein (POo) are commonly used in industrial shortenings. However, not much work has been conducted on ternary blends of PKO, tallow and POo. The objective of the present study was to evaluate the physical characteristics, such as SFC, the melting properties, polymorphic forms of the ternary blends of PKO, tallow, and POo, as affected by interactions in the ternary mixture, in order to provide useful guidance for developing bakery shortenings with ternary blends of the kind.

Materials and Methods

Materials

Commercial palm kernel oil PKO, tallow, and POo were obtained from East Ocean Oils and Grains Industries (Zhangjiagang) Co., Ltd. with slip melting points (SMP) of 28.5, 24.2 and 46.5 °C, respectively, as determined according to AOCS Cc3-25. The oils were melted and mixed according to the formulations shown in Table 1. The blends were poured into plastic tubes and kept at 5 °C overnight, and then stored at room temperature for further analyses.

Table 1 Formulation of ternary mixtures of PKO, Tallow and POo

Sample code	Components (proportion w/w)		
	PKO	Tallow	POo
A	0.8	0.1	0.1
B	0.1	0.8	0.1
C	0.1	0.1	0.8
D	0.45	0.45	0.1
E	0.45	0.1	0.45
F	0.1	0.45	0.45
G	0.33	0.33	0.33

FA Compositions

Fatty acid methyl esters (FAME) were prepared by transesterification of oils with methanol [1]. FA compositions were determined by gas chromatography (GC) on a SHIMADZU (Japan) GC-14B apparatus fitted with a flame ionization detector (FID, temperature 230 °C). The operating conditions were as follows: 60 m × 0.32 mm × 0.25 μm SP-2380 capillary column (60 m × 0.32 mm i.d.), temperature 240 °C, and carrier gas (nitrogen) at 100 kPa.

Solid Fat Content

Solid fat content (SFC) of the fats was measured according to the PORIM method using a Bruker Minispec PC120 pulsed NMR instrument (Karlsruhe, Germany) [4]. The fats in the NMR tubes were melted at 70 °C for 30 min and tempered at 0 °C for 90 min prior to determination. The relative proportions of solid and liquid fats were measured in 5 °C increments between 0 and 45 °C, after holding the sample at each temperature for 30 min.

Deviations in SFC (ΔSFC) were obtained by subtracting the theoretically calculated SFC (SFCt) from the observed SFC of each blend at all temperatures. The following formula [6, 12] was used to produce SFCt:

$$\mathrm{SFCt}(x/y/z) = \mathrm{Px} \times \mathrm{SFCx} + \mathrm{Py} \times \mathrm{SFCy} + \mathrm{Pz} \times \mathrm{SFCz}$$

where Px, Py, and Pz are the partial amounts, and SFCx, SFCy and SFCz the observed SFC of each component oil (x, y, or z) in the relevant blend.

Thermal Analysis by DSC

The DSC melting profiles were determined with a Perkin–Elmer DSC-7 Thermal Analysis System calibrated with indium (99.99%). The calorimeter temperature program was: cooling to −20 °C for 2 min followed successively by heating at 10 °C min^{-1} to 80 °C and holding at 80 °C for 2 min.

Crystal Analyses by XRD

The polymorphic forms of the fat crystals in the samples were determined with a Philips X'PERT PRO Diffractometer using Cu–Kα radiation (k = 1.54056 Å, voltage 40 kV, current 30 mA), fixed 1.0°, 1.0° and 0.1 mm divergence, anti-scatter and receiving slits, respectively. The samples were kept at 5 °C for 24 h, and mounted on flat stainless steel plates with a rectangular hole

immediately before XRD analysis. Scans from 1.0° to 28° (2θ scale) were performed at ambient temperature. Each test was run twice.

Results and Discussion

Fatty Acid Composition and SFC of the Component Oils

PKO was characterized by high contents of lauric (48%) and myristic (15%) acid. POo had the highest amounts of palmitic acid (40.45%), oleic acid (42.78%) and linoleic acid (11.00%) among the three fats at the expense of lower stearic acid content. Tallow was characterized by highest concentration of stearic acid (23.77%) (Table 2).

PKO showed a sharply inclined melting curve (Fig. 1) indicating a relatively higher hardness at room temperature, a narrow melting range below human body temperature relating to a pleasant mouth feeling. The SFC versus temperature profile of the other two oils clearly demonstrated their potential as candidate major constituents of shortenings, margarines and spreads, as judged from their relatively smoother melting curves.

Ternary Phase Behavior for the Mixtures of PKO, Tallow, and POo

For an ideal mixing behavior, a straight line should be observed for each isosolid line at each temperature in the corresponding phase diagram. However, this is rarely observed for many ternary combinations, which may be due to the mixing enthalpy, in addition to enthalpy of crystallization and fusion of the mixture constituents. Besides, changes in compositions and temperatures are also responsible for poor uniformity in ternary systems [13].

Table 2 Fatty acid compositions of the component oils

Fatty acid	Contents (wt%)		
	PKO	POo	Tallow
<C10:0	4.14	–	–
C10:0	3.54	–	–
C12:0	48.16	0.20	–
C14:0	15.39	1.01	2.37
C16:0	8.14	40.45	26.58
C18:0	2.19	4.12	23.77
C18:1	15.45	42.78	36.14
C18:2	2.43	11.00	4.35
C20:0	0.11	–	–

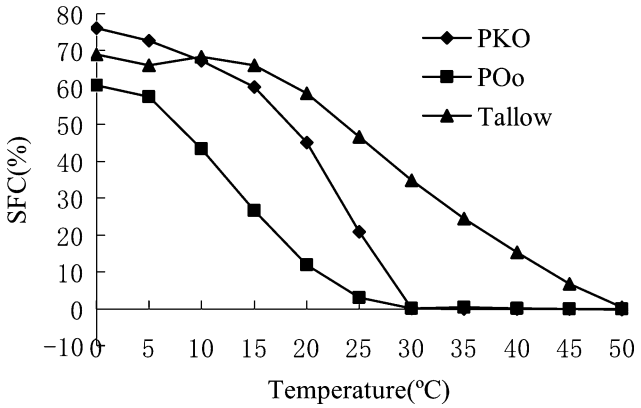

Fig. 1 Effects of temperature on SFC of PKO, tallow, and POo

In the ternary blends of the present study, minimal SFC at 20 °C was observed at point C and E in Fig. 2c. Among the fats studied, tallow possessed the highest SFC at 20 °C (58.40%), followed by PKO (45.15%) and POo (11.91%) (Fig. 1; Table 3). As the POo content of the blends was increased from 10.00% (point D) to 80.00% (point C), the SFC value at 20 °C decreased from 33.57 to 15.24%. The increase of tallow content increased the SFC value from 14.85% (point E) to 24.60% (point G) and to 48.53% (point B) at 20 °C (Table 3; Fig. 2c). However, as shown by the contour lines (Fig. 2c), the effects of tallow was less pronounced compared to that of PKO and POo. Similar patterns of isosolid lines were found at other measured temperatures (10, 15 and 30 °C, Fig. 2a, b, d).

The Compatibility of Ternary Mixtures of PKO/Tallow/POo

According to the Buning-Pfaue and Bartsch method [6, 12], higher negative values of ΔSFC are indicative of stronger eutectic effects. Eutectic effects at 20 °C in the present blends is readily be indicated evidently by the significant ΔSFC (Fig. 3). ΔSFC reached its maximum (−16.667%, point E) when the amounts of PKO and POo were both 45%, yielding curves close to the binary line of PKO/POo (Fig. 3; Table 4). Minor eutectic interaction (ΔSFC = −2.624%) is indicated at point F. More evident eutectic interaction is indicated by a depression of the lines in the blends coded A, D, E and G. PKO was indicated to be less compatible with tallow and POo (Fig. 3), which was stated to be attributable to the large amounts of lauric acid-containing triacylglycerol featured by smaller molecular size in PKO [15]. In general, the interactions in the present ternary blends (Table 4) were more noticeable at 15 and 20 °C than at other temperatures.

Melting Behaviors of the Component Oils and their Mixtures

POo displays the lowest temperature for the onset of melting (around −0.3 °C) and tallow the highest (~36 °C), while PKO shows at an intermediate temperature for the onset of melting (~18 °C). The higher melting temperature of tallow compared to PKO and POo is related to the higher contents of saturated long-chain fatty acids, namely C16:0 and C18:0, and lower contents of unsaturated long-chain fatty acids (C18:1 and C18:2) (Fig. 4).

Due to molecular species interaction among the three constituents, the blends showed different temperatures for melting onset, with curves somewhat wider for the mixtures than for their single constituents, and the maximum point of melting of the blends was displaced below that of the individual constituents or to about intermediate temperature positions in between. Ternary blends show more complicated DSC pattern with an increasing number of peaks and shoulders. Blend A, due to the dilution effects of softer fats (PKO and POo), produced a displacement towards temperatures lower than the fusion point of the harder one (tallow), despite the higher proportion of the latter.

Table 3 SFC of PKO, tallow and POo blends as measured by NMR

Code	SFC at			
	10 °C	15 °C	20 °C	30 °C
A	63.96	52.78	33.06	1.11
B	67.75	59.16	48.53	25.03
C	45.35	30.02	15.24	2.86
D	65.29	52.30	33.57	10.19
E	52.55	33.27	14.85	1.63
F	59.08	46.38	33.85	13.88
G	57.80	41.47	24.60	7.99

A previous study by DSC indicated that the melting ranges and peak shapes are the results of overlapping effects from all component oils [8]. The melting curve of POo showed a broad melting range in the lower temperature zone (0–20 °C) while PKO and tallow a single broad

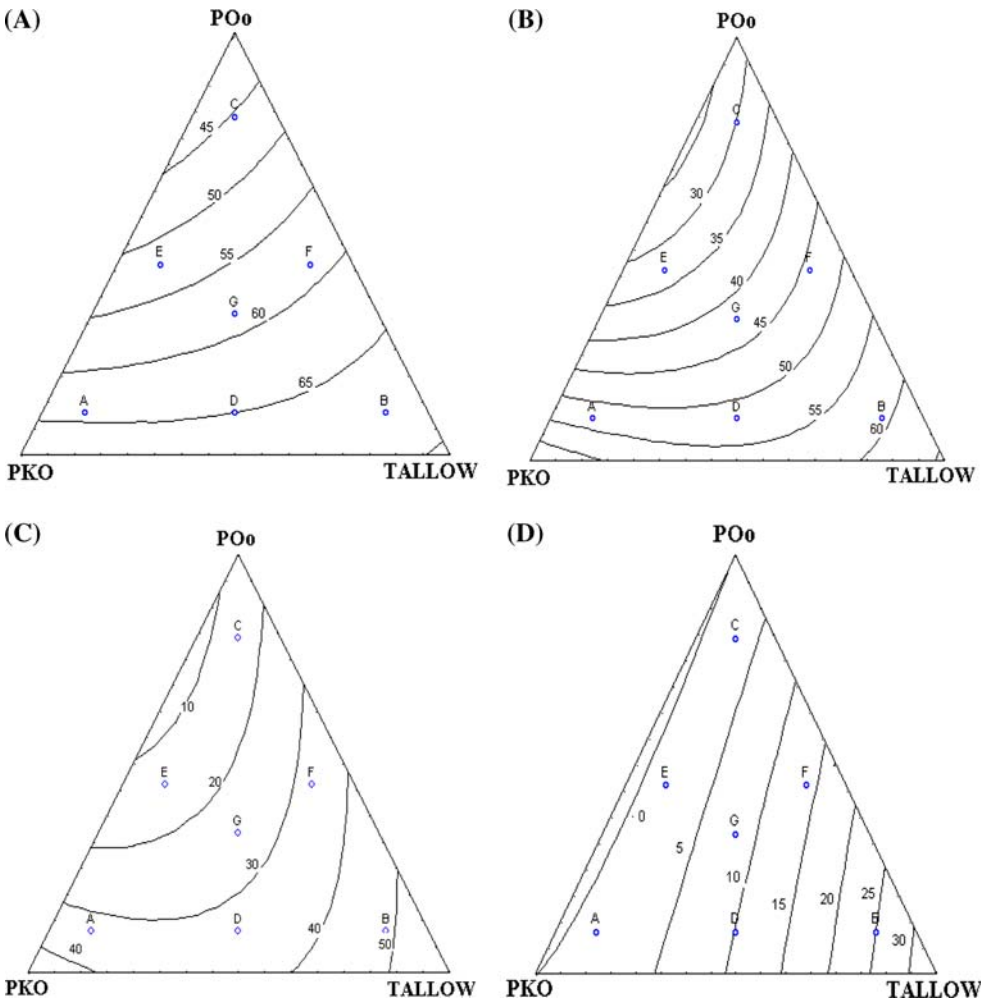

Fig. 2 Isosolid lines for PKO, tallow and POo mixtures at **a** 10 °C, **b** 15 °C, **c** 20 °C and **d** 30 °C

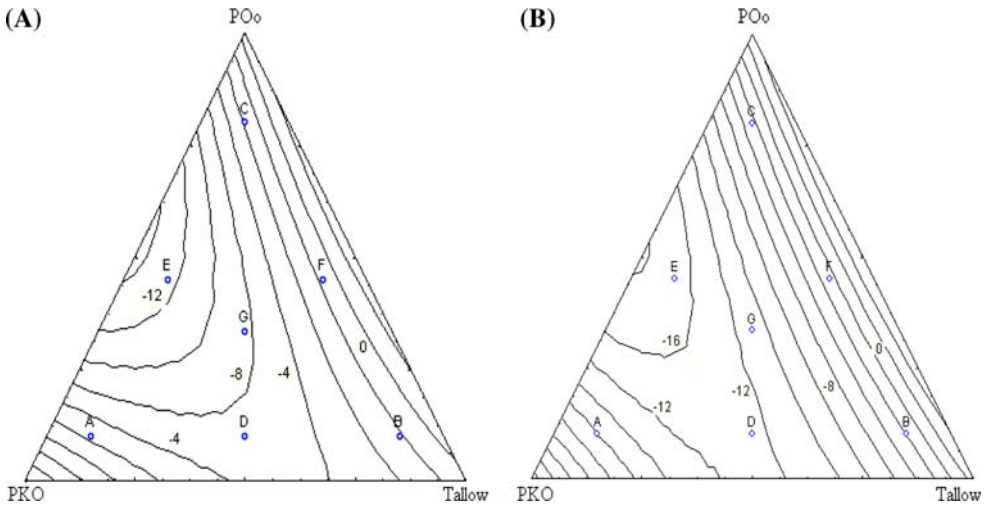

Fig. 3 Isosolid diagram of ΔSFC at **a** 15 °C, **b** 20 °C

Table 4 ΔSFC of the ternary blends

Code	ΔSFC at			
	10 °C	15 °C	20 °C	30 °C
A	−1.034	−4.536	−10.091	−2.457
B	1.951	−2.335	−3.896	−2.806
C	−2.907	−3.839	−4.643	−0.707
D	−0.106	−7.105	−14.218	−5.511
E	−4.075	−12.317	−16.667	−1.937
F	2.052	−1.297	−2.624	−1.821
G	−1.286	−8.911	−13.501	−3.550

melting peak. Sample G containing all three components of equal amounts showed a curve with an overlap of melting ranges of PKO, tallow and POo. Increasing the percentage of tallow in the formulation shifted the major melting region to higher temperatures, indicating the presence of higher melting point triglycerides (samples B, G, D).

The Polymorphic Forms in the Blends

The α short-spacings are found at 4.15, 4.2 and 3.8 Å; and β' exhibits two strong peaks near 4.2 and 3.8 Å or three strong peaks near 4.27, 3.97 and 3.71 Å. Another form which does not satisfy the above criteria is called β, which usually shows a very strong short-spacings at 4.60 Å. The quantities of β and β' crystals in the mixtures are estimated by the relative intensity of the short-spacings at 4.2 and 4.6 Å [7].

Sample F exhibited very weak short-spacings at 4.56 Å and a strong short-spacings at 4.22 Å indicating the formation of a mixture of β' and β polymorphs, with the β' form being dominant. Sample B shows medium short-spacings at 4.57 Å and weak short-spacings at 4.17 Å. The β polymorph dominates, and the β' crystals shows minor presence [14]. The blend G results in greater formation of β' than β (Table 5).

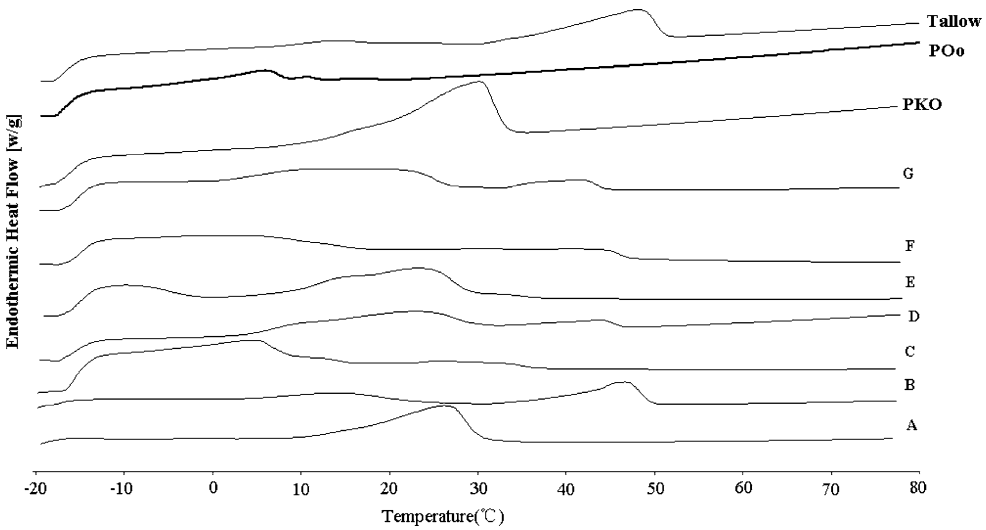

Fig. 4 Melting curves of PKO–tallow–POo mixtures

Table 5 Polymorphisms of PKO, tallow and POo blends measured by XRD

Code	Short-spacings (Å)									Polymorphic forms
	4.7	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.8	
A		4.61vw		4.40 s		4.23 s		4.04 m	3.82 s	β'
B	4.76 m		4.57 m				4.17w		3.83 m	$\beta >>> \beta'$
C		4.61w				4.24 m	4.10w		3.85 m	$\beta' > \beta$
D			4.57 m		4.38 s	4.23 s	4.12 m		3.81 m	$\beta + \beta'$
E										Liquid
F		4.65w	4.56w		4.37 m	4.22 s			3.84 s	$\beta' > \beta$
G				4.41w		4.20 s		4.01w	3.81 s	$\beta' >> \beta$

Sample A shows two strong peaks at 4.23 and 3.82 Å (Table 5), which is typical of polymorph β'. Increasing the concentration of PKO into the ternary systems increased the proportion of the β' form in the mixture. This is consistent with reported results [15] concluding that lauric fats tend to possess a stable β' polymorph because of their mixed chain-length triglycerides. In the case of PKO, it comprised about 4.1% short-chain fatty acids (<C10:0), 67.9% medium-chain fatty acids (C10–C14), and 26.1% long-chain fatty acids (C16–C20) (Table 1). When PKO, tallow and POo were blended, the triglyceride mixture of the blends became more complex, and the tendency of the blends to crystallize into β polymorphic form declined.

Conclusion

In the interactions present in the ternary blends of PKO, tallow and POo, the effects of both PKO and POo were more pronounced compared to that of tallow. Eutectic effects within the ternary system can occur with the strongest eutectic interactions reached when the amount of PKO and POo are both around 45%. Addition of PKO into the blends promotes crystal stability in the β' form. The mixture containing 10% PKO, 45% tallow, and 45% POo is a hopeful recipe for manufacturing plastic shortenings.

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