Heat-Resistant Cocoa Butter Extenders from Mahua *(Madhuca latifolia)* and Kokum *(Garcinia indica)* Fats

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ABSTRACT: Cocoa butter extenders with heat-resistant properties were prepared using mahua and kokum fats. The stearin fraction [Fraction (Fr.) 1, 77–80% yield] obtained by solvent fractionation of 50:50 blends of these fats showed a steep melting profile with a higher solid fat content (SFC) at 32.5°C than cocoa butter, even after mixing with it at 25 or 50% levels. The solidification characteristics showed that the Fr. 1 had a supercooling property similar to cocoa butter, but showed higher temperature rise with less crystallization time on the cooling curve, which is advantageous for chocolate molding. Fr. 1 was compatible with cocoa butter at all proportions, as revealed by cooling curves and isothermal solid diagrams. The stearin fraction obtained by dry fractionation of mahua/kokum blend (Fr. 2, 77% yield), though, had similar solidification characteristics and showed lower SFC compared to that of Fr. 1. Fr. 1 and Fr. 2 have high levels of 2-oleo-distearin triacylglycerols (46–51%), which are responsible for better stand-up property at high temperatures compared to cocoa butter. The suitability of the blends of mahua/kokum fats and mahua stearin/kokum fats as cocoa butter extenders was also evaluated. The isothermal solid diagrams showed complete miscibility of the two fats fractions. The results showed that a series of cocoa butter extenders with varying melting characteristics could be prepared by fractionating and by physical blending of mahua and kokum fats in selected proportions.

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Cocoa butter, though an ideal fat for use in chocolate, is not adequate for use in warmer or tropical climates. It has been reported that incorporation of certain vegetable fats or fractions rich in 2-oleo-distearin (StOSt) triacylglycerols into cocoa butter/milk fat system can produce an increase in solid fat content (SFC), and usually a slight decrease in tempering time (1–3). Borneo tallow or illipé butter and shea fraction have been reported to impart these qualities and also can be used to harden cocoa butter and chocolate products (1–4). India produces a variety of stearic acid-rich fats, such as sal, mango, dhupa, kokum, etc. In the present study, kokum fat was chosen as a stearic acid-rich fat. Kokum (*Garcinia indica*, fam. Gutiferae) is a small, slender evergreen tree found in several parts of India (5). The fruits are spherical, dark purple in color, and the pulp is edible (6). The fruits have 3–8 large, black ovoid seeds, and the kidney-shaped kernels contain about 40% hard and brittle fat (m.p. 39–43°C) (5,6), hence requiring modification before use in chocolate and confectioneries. The other fat chosen for the study was mahua. Mahua or mowrah (*Madhuca latifolia,* fam. Sapotaceae) trees are found in several parts of India. Green-colored egg-size fruits contain concave kernels (constituting about 75% of the weight of seed) that contain about 50% pale-yellow, semisolid fat (7). Preparation of cocoa butter extenders by blending kokum fat with a phulwara (*M. butyracea)* butter fraction was reported earlier (8). In the present study, cocoa butter extenders/replacers with temperature-resistant properties are prepared by fractionation and blending of mahua and kokum fats.

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MATERIALS AND METHODS

Mahua fat was purchased from M/s Sarvodaya Oil Industries (Nagpur, India) and kokum fat was from M/s Mahamango (Kudal, Maharashtra, India). The fats were refined using alkali before use. Cocoa butter was procured from M/s Campco Chocolate Factory (Puttur, India). BF_3/methanol, standard fatty acid methyl esters, and triacylglycerols were procured from Sigma Chemical Co. (St. Louis, MO). Other chemicals and solvents used were of analytical grade.

Fractionation. (i) Solvent fractionation. Mahua fat (200 g) was dissolved in 200 mL of acetone by heating to 50°C. The solution was gradually cooled to 13°C and held at this temperature for about 3 h with occasional stirring. The partially crystallized mass was filtered to separate stearin and olein fractions. The solvent from the stearin fraction was removed under vacuum and the yield was 35%.

Mahua and kokum fats were mixed in a 1:1 ratio (w/w) and heated to 50°C to get a clear liquid. The blend (200 g) was dissolved in 400 mL of acetone. The solution was gradually cooled to 18°C and held at this temperature for 3 h with occasional stirring and then filtered. The solvent from the stearin [yield 77–80%, Fraction (Fr.) 1] was removed under vacuum.

(ii) Dry fractionation. Mahua and kokum fats were mixed in equal proportions and heated to 55°C to get a clear liquid. The blend (200 g) was gradually cooled to 27°C and held at

this temperature for 2 h with occasional stirring. The stearin (yield 77%, Fr. 2) was removed by filtration under vacuum by manually pressing the material from above.

Differential scanning calorimetry (DSC). A Mettler (Griefensee, Switzerland) TA-3000 DSC system was used to obtain melting endotherms and melting profiles along with the percent liquids at various temperatures. The heat flow of the instrument was calibrated using indium. A PT-100 sensor was calibrated using indium, zinc, and lead. To ensure homogeneity and to destroy all crystal nuclei, the samples were heated to 60°C. About 15 mg of the sample was accurately weighed and placed in a standard aluminum crucible and the cover was crimped in place. An empty aluminum crucible with pierced lid was used as a reference. The samples in the pans were stabilized according to IUPAC method (9), which included keeping the samples at 0°C for 90 min, 26°C for 40 h, and 0°C for 90 min prior to introduction into the DSC cell. Thermograms of the samples were recorded by heating at a rate of 2°C/min from −5 to 50°C. The peak temperatures, heat of fusion (ΔH), and the percentage liquid at various temperatures were recorded directly using a TC-11A (Mettler) data processor. SFC was calculated by subtracting percent liquids from 100, and the melting profiles were drawn by plotting percent solids against temperature.

DSC was also used to study the solidification characteristics of the samples. About 15 mg of the molten sample was accurately weighed and placed in standard aluminum pans and the covers crimped in place. The samples were introduced into the DSC cell, maintained at 60°C for 5 min to destroy all crystal nuclei, and immediately cooled to −10°C at 5°C/min. The cooling exotherms, crystallization temperatures, and enthalpy of crystallization were recorded.

Isothermal solid diagrams. Isothermal solid diagrams were constructed by plotting the SFC at various temperatures (20, 25, 30, 32.5, and 35°C) obtained by DSC against the percentage of the blends. The compatibility or miscibility of mahua fat or its stearin with kokum fat, the blends of mahua/kokum fats, mahua stearin/kokum fat, and Fr. 1 with cocoa butter were determined by constructing isothermal solid diagrams.

Fatty acid composition. The fatty acid composition of the samples was determined by analyzing the fatty acid methyl esters by gas chromatography (GC). The methyl esters were prepared using 14% BF_3/methanol (10) and were analyzed using a Shimadzu GC-9A (Kyoto, Japan) equipped with a flame-ionization detector operating under the following conditions: column, 2.4 m × 0.3 cm, stainless steel, packed with 15% diethylene glycol succinate coated on Chromosorb W (60/80 mesh); column temperature, 180°C; injector temperature, 200°C; carrier gas, N_2, 15 mL/min and hydrogen, 20 mL/min. The peaks were identified by comparing the retention times with those of authentic standards and reported as relative percentage of individual fatty acids.

Triacylglycerol composition. The triacylglycerol composition of the samples was determined by high-performance liquid chromatography (HPLC) using a Shimadzu system controller LC-10A and refractive index detector RID-10A. A C-18 column (3.9 × 300 mm; 5 µm particle size) maintained at 36°C was used. The mobile phase was a mixture of acetone/acetonitrile (63.5:36.5, vol/vol) at the flow rate of 1 mL/min (11). The samples were purified by passage through a silica gel column and elution of pure triacylglycerols with hexane. The dried samples were dissolved in chloroform and 10 µL was injected. The peaks were identified by comparing the retention times with those of authentic standards and reported as relative percentage of individual triacylglycerols in the sample.

Cooling curves. Solidification characteristics of the samples were determined by cooling curves obtained using a Shukoff flask according to the procedure described by Wilton and Wode (12).

The cooling curve is of great value in assessing the supercooling quality and solidification behavior of cocoa butter-type fats used in chocolate products. Supercooling property means that the liquid fat, when undisturbed, will remain in the liquid state well below its melting point. The temperature minimum reached on the curve decides the supercooling capacity of the fat; a higher temperature at the minimum point is considered to reduce the fats' supercooling properties. Fats with reduced supercooling properties will be more sensitive to cold temperatures and will require chilling for an increased time during chocolate making (13).

RESULTS AND DISCUSSION

Mahua is a soft fat consisting mostly of palmitic, stearic, and oleic acids, whereas kokum fat is very hard (m.p. 40°C), containing stearic and oleic acids in equal proportions (Table 1). Mahua crystallizes slowly, whereas kokum crystallizes rapidly at high temperatures as revealed by cooling curves (Fig. 1). In addition, kokum has high SFC, even at 35 and 40°C (Fig. 2). Triacylglycerol composition shows that kokum fat consists of mainly StOSt triacylglycerols, whereas mahua consists of lower concentrations of monounsaturated (SUS) triacylglycerols compared to cocoa butter (Table 1). Hence, these fats require modification for use in chocolate as cocoa butter extenders/replacers.

Fractionation of mahua/kokum fat blends. The mahua stearin obtained after removal of up to 65% of the liquid fraction did not show such improvement in its physical or chemical properties as to make it suitable for use as a cocoa butter extender (Figs. 1, 2; and Table 1). Mahua and kokum fats were mixed in equal proportions and then fractionated. Fr.1 obtained in this way by solvent fractionation showed improved solidification and melting characteristics compared to the individual parent fats (Figs. 1 and 2). Fr. 1 had slightly reduced supercooling capacity but showed rapid crystallization as indicated by a sudden rise in temperature with less crystallization time compared to cocoa butter (Fig. 1). It has been reported that the temperature rise above the minimum point is related to the amount of crystallization, which controls the degree of contraction, and that fats with higher temperature

TABLE 1
Fatty Acid and Triacylglycerol Composition of Mahua and Kokum Fats and Their Fractions

	Fatty acids (%)[b]				Triacylglycerols (%)[b]					
Sample[a]	16:0	18:0	18:1	18:2	StOSt	POSt	POP	StOO	POO	OOO
Mahua fat	23.5	20.0	39.0	16.7	10.6	22.2	18.9	6.7	12.6	2.2
Mahua stearin	28.8	27.2	33.9	7.0	12.9	27.2	17.1	7.0	11.8	2.3
Kokum fat	2.0	49.0	49.0	0	72.3	7.4	0.5	15.1	1.3	2.1
Fraction 1	11.7	40.0	44.0	4.2	50.9	14.7	8.4	9.2	6.5 0	
Fraction 2	15.7	37.8	35.5	11.1	46.2	15.0	9.7	9.5	7.4	2.0
Mahua fat + kokum fat (50:50)	ND	ND	ND	ND	4.4	13.6	7.7	11.5	7.3	0
MS + kokum fat (50:50)	ND	ND	ND	ND	47.5	15.6	8.1	11.6	7.0	0
Cocoa butter	31.5	30.5	34.8	3.2	30.0	43.6	19.4	4.1	1.4	0

[a]Fraction (Fr.) 1 and Fr. 2, stearins (77–80%) obtained from mahua/kokum fats by solvent and dry fractionation, respectively. MS, mahua stearin (35%).
[b]P, palmitic acid; St, stearic acid; O, oleic acid. ND, not determined.

rise are better for chocolate molding (13). Also, it was reported that rapid transition from α and β_1 takes place during the temperature rise (14). Hence, Fr. 1 has potential advantages for use in chocolate. It had a steep melting profile with higher SFC at 32.5°C than cocoa butter (Fig. 2), which imparts better stand-up properties at high storage temperatures compared to cocoa butter. The melting enthalpy of Fr. 1 was slightly lower than that of cocoa butter (Table 2). The DSC cooling trace showed a single crystallization curve for Fr. 1, similar to that of cocoa butter, crystallizing slightly at a higher temperature (Fig. 3), and the heat of crystallization was similar for both Fr. 1 and cocoa butter (51 and 58 J/g), respectively.

The isothermal solid diagrams showed complete miscibility of Fr. 1 with cocoa butter, showing only the dilution effect

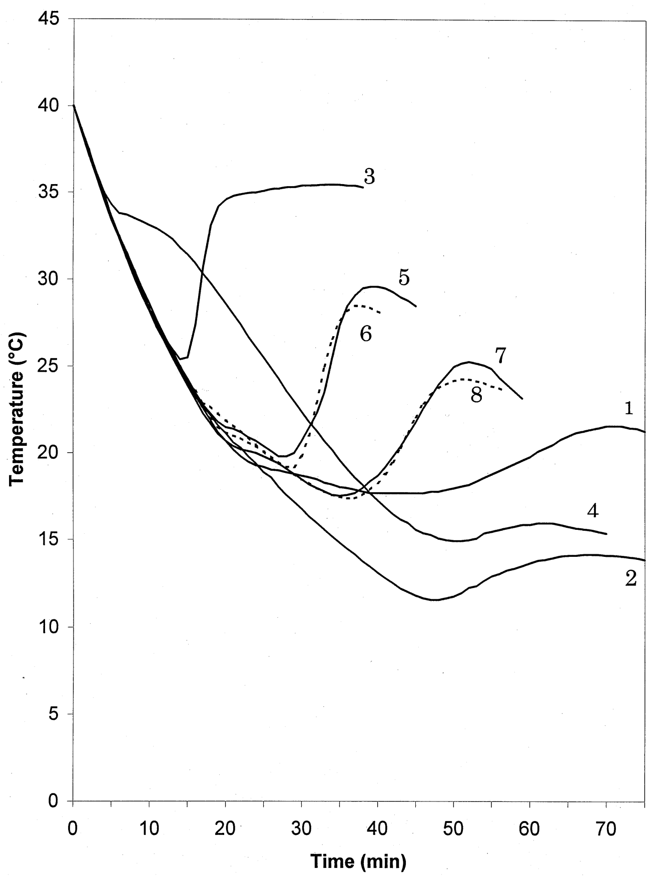

FIG. 1. Shukoff's cooling curves for (1) cocoa butter (CB); (2) mahua fat; (3) kokum fat; (4) mahua stearin; (5) Fraction (Fr.) 1; (6) Fr. 2; (7) Fr. 1 + CB (50:50); (8) Fr. 2 + CB (50:50). Fr.1 and Fr. 2, stearins (77–80%) obtained from mahua/kokum fats by solvent and dry fractionation, respectively.

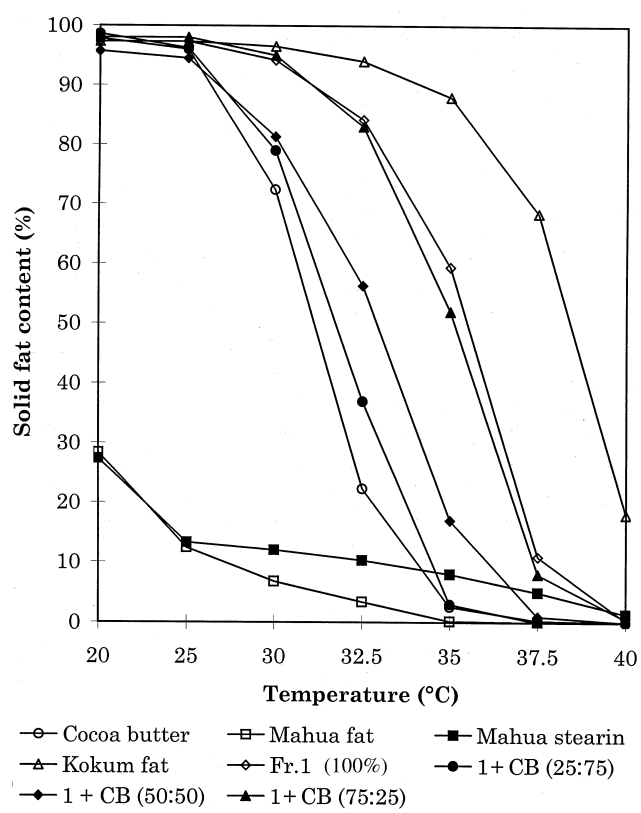

FIG. 2. Melting profiles of Fr. 1 and its mixture with CB. See Figure 1 for abbreviations.

TABLE 2
Solids Content of Mahua and Kokum Fats and Their Fractions

	Solids at °C (%)							Melting	
Sample[a]	20	25	30	32.5	35	37.5	40	Peak temp. (°C)	Enthalpy ΔH (J/g)
Fr. 1	97.3	97.3	94.2	84.2	59.4	11.0	0.3	37.0	111
Fr. 2	93.0	85.5	73.0	48.5	9.3	1.0	0	35.7	105
Mahua + kokum (50:50)	92.7	84.5	75.7	64.3	35.4	3.0	0	36.1	112
MS + kokum (50:50)	92.9	91.8	81.6	69.8	41.9	6.0	0	36.4	110
Mahua + kokum (40:60)	99.6	96.5	90.0	80.0	55.0	14.7	0	37.1	106
MS + kokum (40:60)	100	100	96.5	78.5	53.3	13.3	0	37.3	134
Cocoa butter	97.8	96.0	72.4	22.3	2.6	0	0	32.5	128

[a]See Table 1 for abbreviations.

(Fig. 4). No evidence of eutectic behavior was observed, as the lines of SFC at constant temperature were linear and there was no depression or reduction in SFC compared to the mean values of the individual samples (15). The softening effect of cocoa butter on Fr. 1 was directly related to the amount of cocoa butter present in the mixture (Figs. 2 and 4). Fr. 1 showed higher SFC at 32.5°C, even after mixing with cocoa butter at 25 and 50% levels, and showed no solids at body temperature (Fig. 2). In addition, the fraction showed better tolerance toward milk fat compared to that of cocoa butter (Fig. 5), thus allowing incorporation of milk fat in milk chocolate with less softening effect.

The stearin obtained by dry fractionation (Fr. 2) of mahua/kokum blend showed solidification characteristics similar to Fr. 1 (Fig. 1), but was softer compared to the latter (Table 2). However, Fr. 2 also showed higher SFC at 32.5 and 35°C compared to cocoa butter. Fr. 1 and Fr. 2 consist of higher stearic acid and StOSt triacylglycerols, which are mainly responsible for providing better stand-up properties at high storage temperatures similar to that reported for shea stearin or Borneo tallow (1–3). These results therefore revealed that the fractions (Fr. 1 and Fr. 2), owing to higher SFC and higher content of StOSt triacylglycerols than cocoa butter, could be used to increase the hardness of cocoa butter.

Blending of mahua and kokum fats. In order to assess the suitability of the blends containing mahua fat or mahua stearin and kokum fat without fractionating, various blends

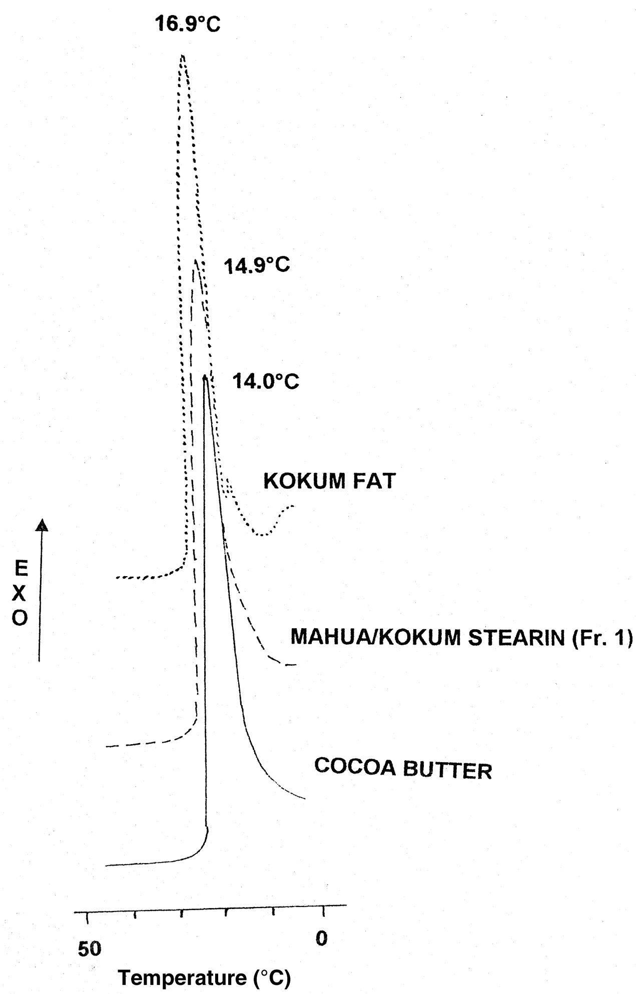

FIG. 3. Differential scanning calorimetry (DSC) cooling traces. Conditions: held for 5 min at 60°C, then cooled to −10°C at 5°C/min.

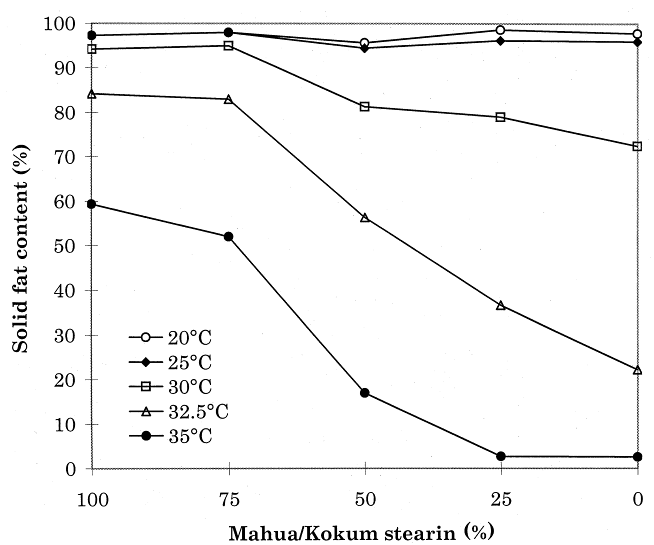

FIG. 4. Isothermal solid diagrams for mixtures of Fr. 1 and CB. See Figure 1 for abbreviations.

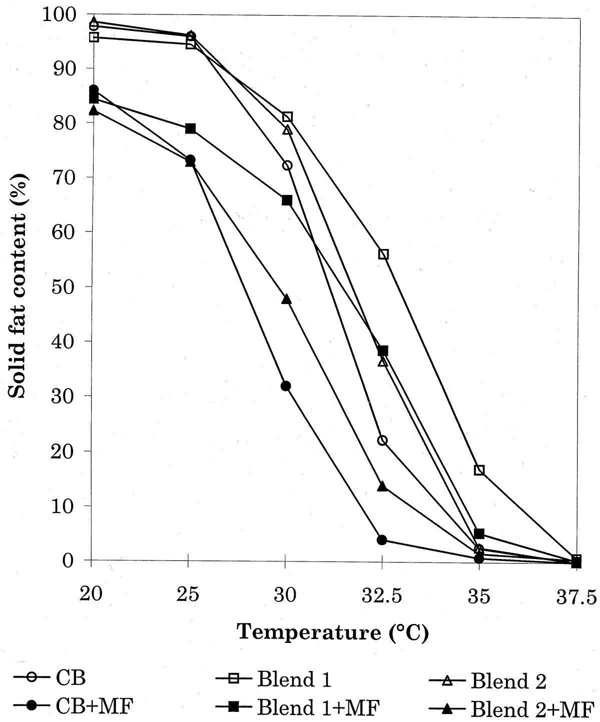

FIG. 5. Effect of milk fat (MF) on melting profiles of Fr. 1 and CB. Blends 1 and 2: Fr. 1 + CB (50:50 and 25:75), respectively; MF added at 15% level. See Figure 1 for abbreviations.

of these fats/fractions were prepared. Preparation of cocoa butter extenders by blending the least-soluble acetone fraction of mahua and kokum fats has been reported earlier (16). Isothermal solid diagrams showed that mahua fat or mahua stearin was completely miscible with kokum fat over a full range of compositions (Figs. 6 and 7). No significant changes in the nature of the solid phase or in its melting range except the dilution or dissolution effect were observed. The blends containing 10–20% kokum fat did not show an increase in SFC at

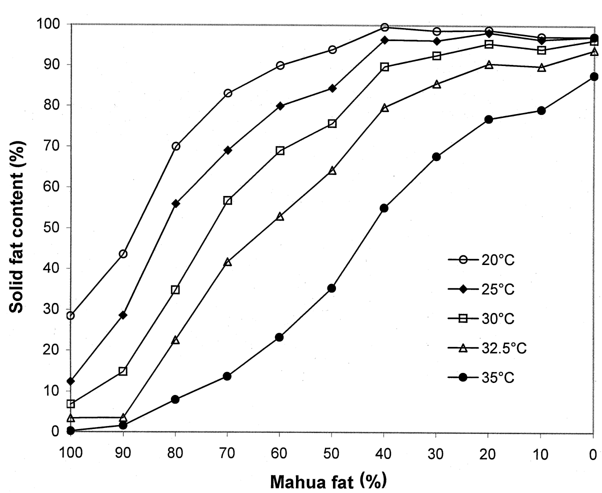

FIG. 6. Isothermal solid diagrams for mixtures of mahua fat and kokum fat.

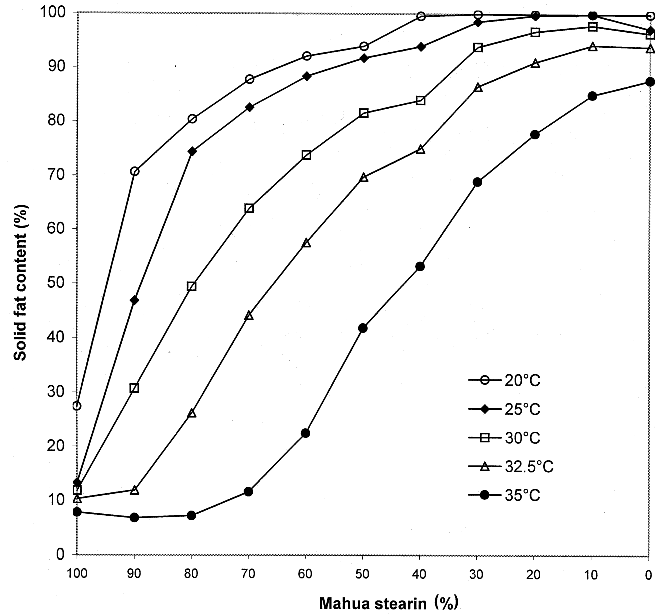

FIG. 7. Isothermal solid diagrams for mixtures of mahua stearin and kokum fat.

35°C, although they did show higher values at other temperatures (Figs. 6 and 7). However, no depression in melting peak temperatures or reduction in SFC was observed in any of the blends compared to the mean values of either of the samples. Based on the results, the blends containing 40 and 50% mahua stearin or mahua fat and 60 and 50% of kokum fat were selected for further analyses. There was only a marginal difference in SFC at any temperature between mahua fat/kokum fat and mahua stearin/kokum fat blends (Table 2). This was further confirmed by triacylglycerol composition, which showed

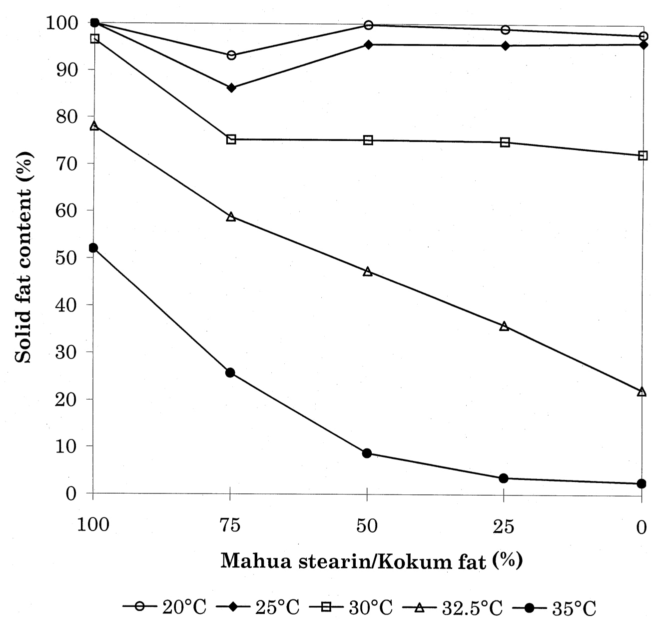

FIG. 8. Isothermal solid diagrams for mixtures of mahua stearin/kokum fat (40:60) blends with CB. See Figure 1 for abbreviation.

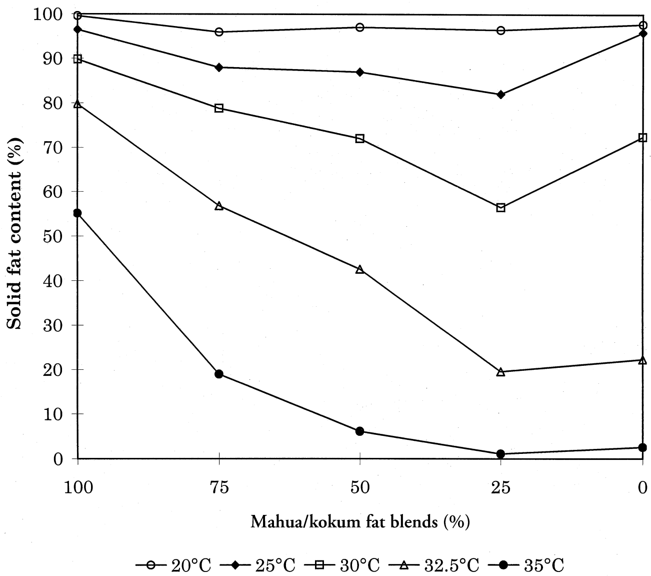

FIG. 9. Isothermal solid diagrams for mixtures of mahua fat/kokum fat (40:60) blends with CB. See Figure 1 for abbreviations.

only minor variations in the concentration of SUS triacylglycerols between the two blends (Table 1).

The 40:60 blends of mahua fat or mahua stearin with kokum fat showed SFC similar to those of Fr. 1 (Table 2). However, when admixed with cocoa butter, these blends showed lower SFC compared to those of corresponding Fr. 1/cocoa butter blends, indicating more softening effect (Figs. 4, 8, and 9). These blends, especially those containing mahua stearin, were completely miscible with cocoa butter over a full range of compositions without any significant eutectic behavior (Fig. 8). However, the blends containing mahua fat/kokum fat showed lowering of SFC at 25, 30, and 32.5°C, when mixed with cocoa butter at the 25% level, unlike those of mahua stearin/kokum blends or Fr. 1 (Fig. 9). The results revealed that the blends containing 50:50 mahua fat or mahua stearin and kokum fat are also suitable as cocoa butter extenders, though they are slightly softer than the 40:60 blends or Fr. 1. These blends also showed higher SFC at 30 and 32.5°C compared to those of cocoa butter (Table 2).

Thus, a series of cocoa butter extenders with varying melting profiles were prepared using blends of mahua and kokum fats. For instance, the stearin fractions (Fr. 1 or Fr. 2) obtained from the blends of mahua and kokum fats and the 40:60 blends containing mahua fat or its stearin with kokum fat have better stand-up properties at high temperatures, as they showed higher SFC at 30 and 32.5°C compared to cocoa butter, and for that same reason, they can also be used to increase the hardness of cocoa butter. The hardness or SFC was decreased as the proportion of kokum fat was reduced from 60 to 50% in the blend. These results therefore reveal that by blending or fractionating mahua and kokum fats, the quality of these two fats is upgraded and value added when cocoa butter extenders with temperature-tolerance properties are prepared.

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