Review Article

Kokum butter as a potential source of cocoa butter substitute in confectionary products: A Review

Abstract:

Cocoa butter is an important ingredient in the confectionery industry because of its unique physicochemical properties which are given by its peculiar fatty acid composition. Increasing demand and shortage of supply for cocoa butter, poor quality of individual harvests, economic advantages, and some technological benefits have induced for the development of its alternative or replacer. Kokum kernel is a byproduct of the agro-processing industry in India containing about 40–50 % fat which has the potential as a worthy cocoa butter alternative (CBA). However, inefficient extraction techniques that are practiced at the cottage level restrict its industrial applications.

Keywords: Kokum Butter, Chocolate, Cocoa butter, fatty acid composition, Kokum kernel.

Introduction:

The cocoa bean is the fatty seed found inside a cocoa pod. It is a small evergreen tree belonging to the family Malvaceae. This plant is native to the deep tropical regions of Central and South America. After harvesting the cocoa fruit, it is opened to expose the seed, then fermented for a few days to separate pulp and seed. Pulp is used in distilleries and seed is used to prepare cocoa powder or chocolate and cocoa butter. It is brittle at a temperature below 25°C, softens in the hand, and melts in the mouth having at a temperature of about 34 ^{0}C. These specific physiochemical properties make it is an important ingredient in the confectionery industry.

Moreover, cocoa butter is the only continuous fat phase in chocolate (Lannes *et al*., 2003) but it is not suitable for use in warmer or tropical climates, as cocoa butter and chocolate soften under these conditions. Also, about 30% of the world's coca crops are destroyed due to climate change. The fat content of the cocoa bean is small in amounts as compared to the other fatty crops (more than 50-58% than cocoa beans).

The cocoa plant is cultivated in a few countries and requires a tropical climate, it makes it unbalanced availability and expensive (Knapp, 2007). For example, cocoa prices plunged to a 27-year low of $714 per tonne in November 2000 and soared to a 32-year high of $3,775 per tonne in March 2011. With demand for cocoa currently exceeding supply, cocoa prices are rising. In March 2014 cocoa prices reached US$ 3,031 per tonne in New York (Anonymous -1).

Other than this to overcome some technical problems like fat bloom (Hassan et al., 1995; Moreton, 1988; Liu et al., 2007), which is directly related to the fat in chocolate products, either cocoa butter or vegetable oils. Cocoa butter represents about 95% of chocolate fat. The addition of other vegetable fats above this level means the products are named compound coatings. A bloomed chocolate is characterized by the loss of the initial gloss of the surface, giving rise to a more or less white aspect. Furthermore, the bloom can have different appearances, from a uniform dull gray to a marble aspect, as well as from small individual white points to large white spots on the chocolate. (Pierre Lonchampt et al., 2004).

So that during chocolate production it needs to find out replacer to use as cocoa butter alternatives. Therefore, researchers have been efforts to find other fats to replace cocoa butter in chocolate manufacturing for many reasons (Dewettinck and Depypere, 2011; Issara et al., 2014).

Heat resistant chocolate:

The development and production of heat-resistant chocolate (HRC) are necessary because there is a problem with chocolate that it melts in the summertime and in most warm tropical countries because Cocoa butter, the main fat constituent in chocolate, melts at 33.8 °C (DeMan, 1999). There are three main approaches to create Heat Resistant Chocolate 1) Enhancement of the microstructure of the materials 2) addition of a polymer 3) increasing the melting point of the fast phase.

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 (Jewell, G.G, Wiggall, P.H., 1981 and Padley, F.B. et. al., 1972).

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 properties 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 the 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 the physical blending of mahua and kokum fats in selected proportions.

Cocoa butter replacers (CBR) fats may be called cocoa butter extenders, or hydrogenated domestic butter because they do not replace the full amount of cocoa butter. Their compatibility with Cocoa butter is lower than for Cocoa butter equivalence (CBE) but higher than for Cocoa butter substitutes (CBS).

Kokum is a small, slender evergreen tree found in several parts of India. The fruits have 3 to 8 large, black ovoid seeds, and the kidney-shaped kernels contain about 40% hard and brittle fat (melting point 39–43 ^{0}C). Kokum seed is a good source of fat called Kokum butter that is used in the chocolate and confectionery industry as well as the pharmaceutical and cosmetic industry as a surfactant (Prajakta Jagtap et al., 2015). Kokum kernel is a byproduct of the agro-processing industry, it contains about 40-50% fat, which has the potential to be used as a cocoa butter alternative (CBA).

The utilization of natural or processed lipid can be decided using its compositional data (fatty acid composition and triacylglycerol conformation) and thermal properties such as crystallization and melting characteristics. However, the compatibility of these lipids with cocoa butter is also an important aspect that should be carried out to measure the capability of lipids to be used as cocoa butter alternatives.

However, inefficient extraction techniques of kokum butter that are practiced at the cottage level restrict its quality yield fat and industrial applications (Vidhate and Singhal, 2013). The aim of this article is to study the equivalence of fatty acid composition, rheological properties, and crystal formation of kokum butter and cocoa butter also to study the standard operation procedure (SOP) for the extraction of kokum butter.

Table 1. Fatty Acid and Triglyceride Composition in Kokum and Cocoa butter

Sr.No.		Kokum Butter	Cocoa Butter
A.	**FATTY ACIDS %**		
1	Palmitic acid (C16:0)	2.5 – 5.3	24.5-33.7
2	Stearic acid (C18:0)	49.33	33.7-40.2
3	Oleic acid (C18:1)	34 - 42	29-38
4	Elaidic acid	3.00	-
5	Linoleic acid (C18:2)	0 - 2	1.70-3.00
6	Arachidic acid (C20:0)	1.20	1.00
7	Eicosenoic acid -	2.25	-
8	Other fatty acids	2.30	-
9	Myristic acid (C14:0)	-	0-4.00
10	Lauric acid (C12:0)	-	19.68 ± 0.004
11	Palmitoleic acid(C16:1)	-	0-4
12	α-Linolenic acid	5.25	0-1
13	Undecanoic acid	-	1.69 ± 0.08
14	Free fatty acids (%)	5.64	-
B.	**Triacylglycerol**		
1	POS 1(3) palmitoyl-3(1) stearoyl-2- oleoglycerol	6	42.2
2	SOS 1(3)-distearoyl-2- oleoylglycerol	72	24.2
3	POP	<1 (Trace)	21.8

	1,3-dipalmitoyl-2- oleoylglycerol		
4	POSt rac-palmitoyl-stearoyl-2- oleoyl-glycerol	6	37
5	StOSt 1,3-stearoyl-2-oleoyl-glycerol	72	26
6	Total SOS	78	79

(Source: Talbot, 2009, Lakshiminarayana 1977)

Fatty acids:-

Cocoa butter mainly consists of triacylglycerols (97%). The remaining 3% are minor components, such as free fatty acids (FFA), mono- and diacylglycerols, phospholipids, etc. (Smith, 2001). A triacylglycerol consists of a glycerol backbone esterified with three fatty acids. In Cocoa butter, the main fatty acids (95% of total) are palmitic (C16:0, 20 to 26%), stearic (St, C18:0, 29% to 38%) and oleic acid (C18:1, 29% to 38%). Next to these fatty acids also linoleic (C18:2, 2% to 4%) and arachidic acid (C20:0, ± 1%) are present in considerable amounts. The ratio of these fatty acids varies depending on the origin of the Cocoa butter. (Talbot, 2009; Smith, 2001).

Cocoa butter has a relatively simple triacylglycerol (TAG) composition compared to other fats. According to Van Malssen et al. (1996) 70% to 88% of the total triacylglycerols present in cocoa butter are symmetrical mono-unsaturated triacylglycerols of the SatOSat-type (disaturated oleylglycerol). The main triacylglycerols are 1,3-dipalmioyl-2-oleoyl-glycerol (POP), rac-palmitoyl-stearoyl-2- oleoyl-glycerol (POSt) and 1,3-stearoyl-2-oleoyl-glycerol (StOSt). The amount of these TAGs in the cocoa butter varies with the origin of the cocoa bean, but the average amount of POSt, StOSt and POP is around 35%, 23% and 15% respectively (Afoakwa et al., 2008). Due to this triacylglycerols composition, cocoa butter quickly melts over a narrow temperature range (15-35^0C) (Talbot, 2009b). Next to these triacylglycerols also monosaturated dioleolyglycerols (SatOO) and disaturated-2- linoleoyl-glycerols (SatLSat) are present in appreciable amounts (Van Malssen et al., 1996). The triacylglycerols of cocoa butter crystallize in a high-melting fraction (mainly StOSt) and a low melting fraction (mainly POP and POSt) (Norberg, 2006).

Cocoa butter hardness depends on the saturated and unsaturated fatty acid contents bound in triglycerides, and on free fatty acids (FFA) content. The general opinion is that higher FFA content leads to a decrease in the hardness of cocoa butter (Pontillon, 1998). For reasons of quality, therefore, the directive 73/241 /EEC (EEC, 1973) limits the maximum FFA content to 1 .75% oleic acid equivalent in cocoa butter. Only illipe and kokum have total SOS contents as high as those in cocoa butter so that illipe and kokum gurgi can be used directly in cocoa butter equivalents without further processing (Talbot, G., 2009).

In Kokum butter Stearic acid is the major fatty acid (Sastri B.N. 1956). It has fatty acid and triacylglycerol compositions, tolerance toward milk fat, and solidification properties similar to those of cocoa butter (Reddy & Prabhakar, 1994). These properties are considered ideal in the confectionery industry and kokum is used as a replacement to cocoa butter in the preparation of chocolates (Reddy & Prabhakar, 1994). The fatty acid composition typical for kokum butter and cocoa butter is given in Table 1. The range of composition of fatty acids in kokum fat is stated to be Cl4 (O-4%), Ci6 (1.7-5.8%), Cis (51-61%), Cis:i (36.8415%), and Cts:(0.551.7%) (Lakshiminarayana, 1977).

It is clear from the above table regarding SOS point of view, kokum butter contains enough SOS to be able to match the levels found in cocoa butter. The oils have much lower levels of SOS that means the SOS needs to be concentrated by fractionation. Usually, solvent fractionation is used.

Physical and Chemical Characteristics:

Prior to 2003 any vegetable fat could be used, provided it met the properties mentioned above. But since, 3rd of August 2003 an amendment on the EU Directive 2000/36/EC stated that only the six vegetable fats mentioned i.e. i) Palm oil, ii) Illipe, Borneo tallow or Tengkawang, iii) Shea, iv) Sal, v) Kokum and vi) Mango Kernel can be used in chocolate. All of these oils are "rich" in some of the same type of symmetrical monounsaturated triglycerides (SOS) as are found in cocoa butter—POP, POSt, StOSt.

Table-2 shows that the melting point of the Kokum butter is much more than cocoa butter. It indicates that the kokum butter is useful for the preparation of heat-resistant chocolate.

Table 2: Physico-Chemical properties of Cocoa butter and Kokum butter.

Sr.No.	Particular	Kokum Butter	Cocoa Butter
PHYSICAL PARAMETER			
1	Colour	Pale white	soft tan/off white
2	State at room temperature	Solid	Solid
3	Melting point (ºC)	38 to 42 °C	15-35°C
CHEMICAL PARAMETERS			
1	Total fat content (% of seed)	40-50%	
2	Acid Value (mg NaOH/g of oil)	4.9	1.04-1.68
3	Saponification number (mg KOH/g of oil)	200.2	192-199
4	Iodine value (mg KOH/g)	39.4	32-35
5	Sterols	1.02	-
6	Vit. E (mg/100g)	20.01	-
7	Total Saturated FA (%)	52.78	-
8	Mono Unsaturated FA (%)	39.67	-
9	Poly Unsaturated FA (%)	5.25	-

***(Source:** Bindu Naik et al., 2014, Utpala P. et al., 2014, Jahurul et al., 2013)*

Studies have also shown that kokum butter when used along with cocoa butter increases the heat-resistance property of cocoa butter and chocolate and is helpful in preventing the heat-induced softening and loss of consistency of chocolates (Maheshwari & Reddy, 2005; Reddy & Prabhakar, 1994).

Kokum Butter Extraction Technique:

Kokum kernel is a byproduct of the agro-processing industry in India containing about 40–50% fat which has the potential as a worthy cocoa butter alternative (CBA). However, inefficient extraction techniques that are practiced at the cottage level restrict its industrial applications. Here we are discussing the various advanced techniques used for the Kokum oil extraction.

Traditional Method

Conventionally raw Kokum butter is a white-colored fat with a creamish yellow or at times even a slightly grey tint which is extracted by traditional oil mills method. In this method, the kokum seeds are collected and decorticated by wooden mallets. The final product is obtained by crushing the kernels, boiling the pulp in water and skimming off the fat from the top, or churning the crushed pulp with water. The idea here is to physically separate oil from water as these two liquids are immiscible. This process is a time-consuming process and the yield, in this case, is only about 25% of raw Kokum butter. Therefore the production cost of raw Kokum butter remains high. This is the major constraint in the extraction of kokum fat at a commercial scale.

Improved Traditional Method

In India, the kokum kernel fat is extracted by the Indian standards on oil milling industry for Grading for kokum kernels for oil milling, IS: 8557—1977, 1983 and Kokum fat IS : 8591—1977, 1986. To extract good quality kokum fat there is a need to develop the Standard Operating Procedure (SOP). Such type efforts are made to standardize the traditional processing method of kokum oil extraction by the National Agricultural Innovation Project (NAIP) on A Value Chain for Kokum, Karonda, Jamun, and Jackfruit which was implemented at Dr. Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli (Maharashtra) during 2009 to 2014. Accordingly following standard procedure was developed.

Kokum seeds were dried using a mechanical dryer at 60 ^{O}C. The dried kokum seeds were cleaned using air screen cleaner and dirt, dust, ash, stones, other crop seeds, and other impurities were separated using air screen cleaner. Then these cleaned and dried kokum seeds were shelled by using kokum seed dehuller to obtain kokum kernels. The husk was separated from kernels. For better oil extraction, the moisture content of kernels was brought to about 10%. Then the steaming was provided to the kernels prior to oil extraction for 20 min duration (temperature of the steamed kernel was 70^{O}C). The crude oil obtained was boiled in the large SS vessel to separate impurities. The scum collected at top of the oil and heavy but fine particles of cake settled at bottom of the vessel are separated from the oil. The clean oil is kept for solidification overnight (12 hrs). The next day, these oil/butter were churned in the spiral mixer to uniform mixing of butter. Then cubes or blocks of convenient size were made from this butter. The procedural details for kokum butter extraction were as shown in the flow chart given in Fig. 1.0.

The yield, in this case, is about 34 % which was only 25% in the traditional expelling method. The extracted oil was crystal clear having the uniform bright color of butter and having Acid value (6.55), Iodine value (29.85), and Safonification value (187.40).

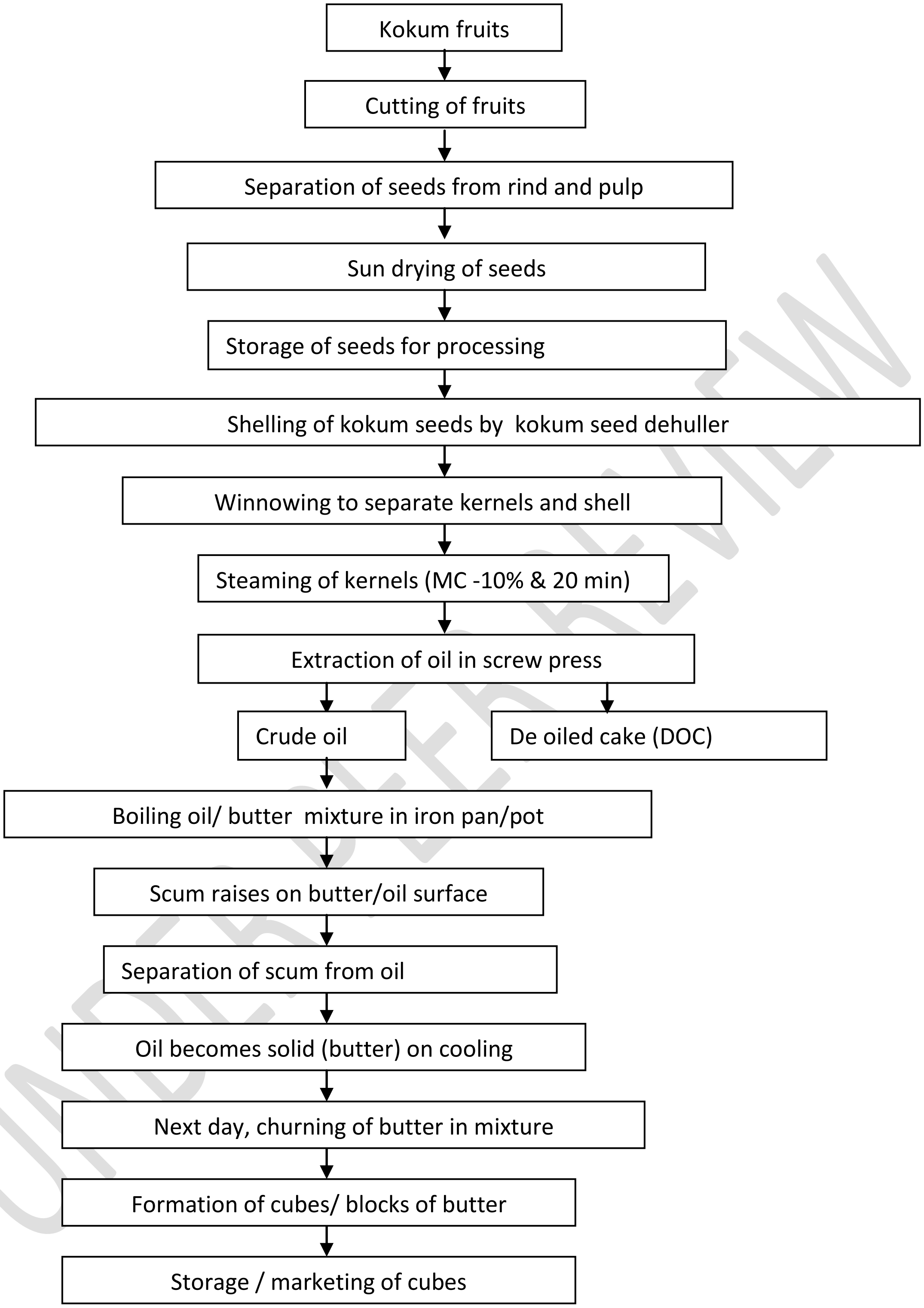

Fig. 1.0 Flow chart for Standardization of Kokum Butter extraction

Solvent extraction method

Kokum butter is also obtained by multistage solvent extraction technique by using hexane, but this technique is costly only it is economical when done at large scale. This is the easiest and the most popular way of extracting kokum oil. The yield in this case is about 44% of raw Kokum butter but such chemically processed Kokum butter is not 100% natural.

Three phase partitioning (TPP)

Three phase partitioning (TPP) is a simple novel bio-separation and purification technique in which a salt (e.g. ammonium sulphate) and water miscible aliphatic alcohol (e.g. t-butanol) are added to an aqueous solution containing proteins (Roy et al., 2005). TPP has been extensively evaluated for simultaneous separation and purification of proteins, enzymes and inhibitors from crude suspensions. The physiochemical basis of TPP is quite complex and is believed to involve ionic strength effects, kosmotropy, cavity surface tension enhancement, osmotic stress, and exclusion-crowding effects (Roy et al., 2005).

Ganesh S. Vidhate and Rekha S. Singhal, 2012 were studied the optimization of the technique of three phase partitioning (TPP) for efficient extraction of kokum kernel fat. The Kokum seeds were separated from matured kokum fruits manually, and washed with hot water 3 to 4 times to remove gummy material adhered to seeds. These seeds were then dried in a tray dryer at 70 ^{0}C to reduce the moisture content from an initial value of 27% to below 10%. The loosened shells were separated manually to obtain kernels. Dried kokum kernels were powdered in hand grinder to get fine powder of 1000 µm which would aid the extraction.

After preparation of kokum kernal powder the slurry was prepared by dispersing 1 g powder in 16 ml distilled water by gentle stirring on a magnetic stirrer. Weighed amount of ammonium sulphate (10 to 60% w/v of slurry) was added to the slurry prepared and vortexed gently, followed by addition of measured amount of t-butanol (t-butanol to slurry ratio = 0.5:1 to 3:1). This slurry of salt and solvent system was mixed properly by gentle stirring on magnetic stirrer for 30 min. In order to form three phases, system was allowed to stand at 45 ^{0}C in a water bath for 1 h. The three phases formed were separated by centrifugation at 2900 g for 10 min at 30 ^{0}C. The upper organic layer of t-butanol containing extracted fat was collected and the t-butanol was evaporated on a rotary evaporator to obtain the extracted fat. They found the a maximum recovery of 95 (% w/w) fat obtained from kokum kernels with evaluated TPP system consisting of 50 (% w/v) salt concentration, 1:1 ratio of slurry to t-butanol, and a pH of 2.0 within 2 h.

Exploiting this technology could mobilize agro-industrial wastes such as kokum kernel for value added ingredients for food and cosmetic industries.

Application of kokum fat in chocolate

The kokum fat does not need fractionation for use in cocoa butter equivalent formulation, and after refining kokum kernel fat may be directly used in chocolate. Fractionation of the kokum fat gives a very high level of stearin fractions, which were useful for chocolate filling or chocolate coating (Timms RE, 2003). The triglyceride compositions and other physicochemical properties of kokum kernel fat make it a valuable fat, which can be used as an improver to increase the hardness of chocolate, inhibits fat bloom and decreases the tempering time (Jahurul MHA, et al., 2013 and Directive 2000/36/EC).

Kokum fat, is used as an improver to increase the hardness of chocolate. Kokum fat is added in various proportions replacing cocoa butter in dark and milk chocolate formulations and its effects on rheology, hardness and triglyceride composition were studied. The results revealed that up to 5% kokum fat addition by weight of the product did not significantly affect the plastic viscosity or yield stress of milk or dark chocolate.

Table 3. Formulations of chocolate with added kokum fat

Ingredient (%)	Dark chocolate	Milk chocolate
Cocoa mass	39 .6	15 .0
Cocoa butter	21 .75	23 .5
Kokum fat	3.16	1 .6
Skim milk powder	—	18 .0
Sugar	48 .2	41 .4
Lecithin	0.4	0 .6
Percentage Kokum by weight of fat	**10 %**	**5 %**

(Source: Maheshwari, B. et al., 2005)

Maheshwari, B. et al., 2005 prepared the milk and dark chocolate products by using the formulations given in Table 3. The replacement of Cocoa butter by 10% is suitable for Dark Chocolate and 5 % for Milk Chocolate by weight of the product. All the ingredients were mixed with about 50% of added Cocoa butter and passed through a three-roll refiner (Pascal, England), three times. The mass was then conched by adding the remaining CB and lecithin for 3 h at 50–55 ^{0}C.

Rheological properties

The rheological properties of chocolate are closely related to its microstructure which is imparted by the choice of ingredients and manufacturing process. The continuous phase of chocolate is composed of cocoa butter with an added emulsifier (lecithin) in the order of one gram / 100 grams. A small fraction of the cocoa butter may be replaced by other milk fat or other fats. Emulsifier presence is important to ensure dispersion of the crystalline sugar.

The rheological behavior of chocolate followed the non-Newtonian flow, as reported in the literature, due to the presence of solids in molten fat. Also, the viscosity gradually decreased with an increase in shear rate (Beckett, S.T., 2009).

The hardness of both dark and milk chocolate increased with an increase in the addition of kokum fat. The solids fat content at and above 30 °C increased with an increase in the level of kokum fat with cocoa butter especially at and above 15%. These physical properties are due to an increase in 2 *oleodistearin* triglycerides with the addition of kokum fat with cocoa butter. The results revealed that kokum fat could be used up to 5% by the weight of the product to increase the heat-resistance property of chocolate so that it can be used in warm climates.

Economic Aspect:

Cocoa trees take approximately two years to mature and another five to bear fruit, which means that investment in cocoa farming will not pay off for nearly a decade.

Conclusion:

The compatibility of some important properties of the kokum butter like as triglycerides in terms of fatty acid constituents, slip or sharp melting points, solid fat contents, iodine value, acid value, and saponification values resulting promising alternative to cocoa butter fats. These results revealed the good potential of kokum fat as a cocoa butter improver. The fat could be used up to 5-10 % by weight of the product without affecting the taste and other properties of chocolate, which will save the cost of the chocolate manufacturing and also help to generate income for Kokum growers.

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