BLENDING OF BAMBANGAN KERNEL FAT-STEARIN, PALM OIL MID-FRACTION AND PALM STEARIN TO FORMULATE COCOA BUTTER EQUIVALENT

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DECLARATION

I declare that I wrote this thesis and that this research work is my own unless otherwise mentioned in the text. This work has not been submitted for any other degree or professional qualification except as described.

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ABSTRACT

Pure vegetable fats and oils often had unsatisfactory properties in speciality fat applications such as cocoa butter equivalent (CBE). There have been substantial studies showing that fat modification using fractionation and blending improves the properties of the pure fats and yields a product with desirable properties. Therefore, this study aimed to determine the effects of blending fractionated bambangan kernel fat-stearin (BKF-SS) with palm oil mid-fraction (POMF) and palm stearin (PS) in CBE formulations on their physicochemical, thermal, morphological properties and their compatibility with cocoa butter (CB). The results showed that all blends at five varying ratios (90:10, 85:15, 80:20, 75:25, and 70:30 %) have similar physicochemical properties with CB. Nevertheless, only the blend containing 70% BKF-SS and 30 % POMF (PMF5) and PS (PS5) showed a remarkable resemblance to CB's composition. Both PMF5 and PS5 mimic the fatty acids of CB with 18.87 – 21.73 % palmitic, 38.23 – 38.92 % stearic, and 31.12 – 34.05 % oleic acid with improved thermostabilities (high solid fat content (SFC) at 30 ºC but reached to 0 % at 40 ºC). The fatty acids and TAG composition of the blends were significantly different ($P<0.05$) compared to the individual BKF-SS, wherein BKF-SS, the stearic acid, and 1,3-distearate-2-oleate-glycerol (SOS) content were higher. The changes in the composition could be attributed to high palmitic acid and 1,3-dipalmitate-2-oleate-glycerol (POP) content in the palm fractions that reduced the stearic composition. In addition, it showed low rancidity values, which indicates these blends are stable and have better quality. The results also featured similar melting and crystallisation profiles. They exhibited β and β' polymorphic forms, which correspond to a mixture of disc-shaped crystals with a needle-like crystal structure of 40 – 50 μm diameter. These morphological features indicated similar textural attributes to CB; hence, they were analysed for compatibility with CB. Although the 1-palmitate-2-oleate-2-stearate (POS) content in the blends is slightly lower, PMF5 and PS5 have comparable POP (10.35 -12.07 %) and SOS (29.57 – 30.22 %) content with CB. The TAG profiles, SFC, morphology features and straight line on the iso-solid diagram indicates that the BKF-SS blended with POMF and PS has better compatibility with CB than the individual BKF-SS. The results obtained in this study proposed that BKF-SS integrated with palm fractions, especially POMF at 70:30 % ratio (PMF5), showed better resemblances properties and showed potential application as CBE. In conclusion, this palm fraction successfully improves the composition, thermal and morphological properties of BKF-SS and increases the compatibility of the fractionated BKF-SS with CB.

ABSTRAK

PENCAMPURAN STEARIN LEMAK KERNEL BAMBANGAN, PECAHAN TENGAH MINYAK SAWIT DAN STEARIN SAWIT UNTUK FORMULASI SETARA MENTEGA KOKO

Lemak dan minyak sayuran tulen sering mempunyai sifat yang tidak memuaskan dalam aplikasi lemak khusus seperti setara mentega koko (CBE). Terdapat kajian besar yang menunjukkan bahawa pengubahsuaian lemak menggunakan pecahan dan pencampuran meningkatkan sifat-sifat lemak tulen dan menghasilkan produk dengan sifat-sifat yang diingini. Oleh itu, kajian ini bertujuan untuk mengetahui kesan pencampuran pecahan stearin lemak kernel bambangan (BKF SS) dengan pecahan tengah minyak sawit (POMF) dan stearin sawit (PS) dalam formulasi CBE terhadap sifat fizikokimia, haba, sifat morfologi dan keserasiannya dengan mentega koko (CB). Hasil kajian menunjukkan bahawa semua campuran pada lima nisbah yang berbeza-beza (90:10, 85:15, 80:20, 75:25 dan 70:30 %) mempunyai sifat fizikokimia yang sama dengan CB. Walau bagaimanapun, hanya campuran yang mengandungi 70% BKF-SS dan 30% POMF (PMF5) dan PS (PS5) menunjukkan kemiripan yang luar biasa dengan komposisi CB. Kedua-duanya menyerupai asid lemak CB dengan 18.87 – 21.73 % asid palmitik, 38.23 – 38.92 % asid stearik dan 31.12 – 34.05 % asid oleik serta keupayaan termostabil yang lebih baik (kandungan lemak pepejal yang tinggi (SFC) pada 30 ºC tetapi mencapai 0% pada 40 ºC). Komposisi asid lemak dan TAG bagi campuran ini adalah berbeza secara signifikan ($P < 0.05$) berbanding dengan BKF-SS secara individu; di mana kandungan asid stearik dan 1,3 distearat-2-oleat-gliserol (SOS) bagi BKF-SS adalah lebih tinggi. Perubahan dalam komposisi boleh dikaitkan dengan kandungan asid palmitik dan 1,3-dipalmitate-2-oleate-gliserol (POP) yang tinggi dalam pecahan sawit yang mengurangkan komposisi asid stearik. Selain itu, ia menunjukkan nilai ketengikan yang rendah, yang menunjukkan adunan ini stabil dan mempunyai kualiti yang lebih baik. Hasil kajian juga memaparkan profail lebur dan penghabluran yang serupa, mereka mempamerkan bentuk polimorfik β dan β′, yang sepadan dengan campuran kristal berbentuk cakera dengan struktur kristal seperti jarum dengan diameter 40 – 50 µm. Ciri morfologi ini menunjukkan sifat tekstur yang serupa dengan CB; oleh itu, mereka dianalisis untuk keserasian dengan CB. Walaupun kandungan 1-palmitate-2-oleate-2-stearate (POS) di dalam campuran ini adalah lebih rendah, campuran PMF5 dan PS5 mempunyai kandungan POP (10.35 – 12.07 %) dan SOS (29.57 – 30.22 %) yang sebanding dengan CB. Garis lurus pada rajah iso-pepejal juga menunjukkan bahawa BKF-SS yang dicampurkan dengan POMF dan PS mempunyai keserasian yang lebih baik dengan CB berbanding BKF-SS secara individu. Keputusan yang diperolehi dalam kajian ini mencadangkan BKF-SS yang dicampurkan dengan pecahan sawit, terutamanya POMF pada nisbah 70:30 % (PMF5), menunjukkan sifat keserupaan yang lebih baik dan menunjukkan potensi aplikasi sebagai CBE. Kesimpulannya, pecahan sawit ini berjaya menambah baik komposisi, sifat terma dan morfologi BKF-SS serta meningkatkan keserasian pecahan BKF-SS dengan CB.

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LIST OF SYMBOLS

α	-	Alpha
β	-	Beta
β'	-	Beta-prime
°	-	Degree
γ	-	Gamma
λ	-	Lambda
μ	-	Micro
θ	-	Teta
Å	-	Angstrom

LIST OF ABBREVIATIONS

AV	-	Acid value
ANOVA	-	Analysis of variance
AOCS	-	American Oil Chemists Society
BKF	-	Bambangan kernel fat
BKF-SS	-	Bambangan kernel fat stearin
BKP	-	Bambangan kernel powder
CB	-	Cocoa butter
CBA	-	Cocoa butter alternatives
CBE	-	Cocoa butter equivalent
CBI	-	Cocoa butter improver
CBR	-	Cocoa butter replacers
CBS	-	Cocoa butter substitutes
CO	-	Coconut oil
DPPH	-	2-Diphenyl-1-picrylhdrazyl
DSC	-	Differential scanning calorimetry
FA	-	Fatty acid
FAMEs	-	Fatty acid methyl ester
FFA	-	Free fatty acid
FRAP	-	Ferric reducing antioxidant power
GC-FID	-	Gas Chromatography-Flame Ionization Detector
HOHS	-	High oleic high stearic
HOSO	-	High oleic sunflower oil
HSHO	-	High stearic high oleic
HPLC	-	High performance liquid chromatography
HPMF	-	Hard palm oil mid-fraction
IB	-	Illipe butter
IP	-	Inter-esterified blends
IV	-	Iodine value
KF	-	Kokum fat
KI	-	Potassium iodide
KOH	-	Potassium hydroxide

LDL	-	Low density-lipoprotein
MKF	-	Mango kernel fat
MKF-TS	-	Mango kernel fat third stearin
MMF	-	Fractionated MKF
MSF	-	Mango seed fat
MUFA	-	Monounsaturated fatty acid
NaOH	-	Sodium hydroxide
NMR	-	Nuclear magnetic resonance
OO	-	Olive oil
OOA	-	1,2-dioleate-3-arachidate-glycerol
PH	-	Partially hydrogenated
PLM	-	Polarised light microscopy
pNMR	-	Pulsed-nuclear magnetic resonance
POMF	-	Palm oil mid-fraction
PPP	-	tripalmitin
PS	-	Palm stearin
PKO	-	Palm kernel oil
PO	-	Palm oil
POO	-	1-palmitate-2,3-dioleate-glycerol
POP	-	1,3-dipalmitate-2-oleate-glycerol
POS	-	1-palmitate-2-oleate-2-stearate
PUFA	-	Polyunsaturated fatty acid
RBDPKO	-	Refined, bleach, deodorised palm kernel oil
RBDPS	-	Refined, bleach, deodorised palm stearin
RKF	-	Rambutan kernel fat
RI	-	Refractive index
SFA	-	Saturated fatty acid
SHS	-	Sunflower hard stearin
SMP	-	Slip melting point
SO	-	Sunflower oil
SOA	-	1-stearate-2-oleate-3-arachidate-glycerol
SOO	-	1-stearate-2,3-oleate-glycerol

SOS	-	1,3-distearate-2-oleate-glycerol
SS	-	Shea stearin
SUS	-	Symmetrical unsaturated
SUU	-	Symmetercial disaturated
SFC	-	Solid fat content
TAG	-	Triglycerides
UFA	-	Unsaturated fatty acid
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Cocoa butter (CB) is the main ingredient for confectionery products such as coatings, fillings, chocolate, and candies (Nirupam, Yuen, Chin, Sivaruby, & Lee 2017). It has unique physicochemical properties that are responsible for the desired processing properties and remarkable mouthfeel effect, with melting properties of body temperature (32 to 33 ºC for (V) β and 35-36 ºC for (VI) β form) (Zhang, Song, Lee, Xie, & Wang, 2020). These properties allow the production of stable confectionery products without a waxy mouthfeel. CB are mainly consist of 24.5 to 33.7 % palmitic, 33.3 to 40.2 % stearic, and 26.3 to 36.5 % of oleic acid (Gunstone, 2011; Sonwai, Kaphueknngam,& Flood, 2014; Kadivar, De Clercq, Mokbul, & Dewettinck, 2016; Norazura, Sivaruby, & Noor Lida, 2020). This unique composition results in the presence of three dominant triglyceride (TAG) such as 1,3-dipalmitate-2-oleate-glycerol (POP), 1-palmitate-2-oleate-2-stearate (POS), and 1,3-distearate-2-oleate-glycerol (SOS), which dominate their melting profiles and SFC.

When CB is eaten, the continuous fat phase is also responsible for providing the texture, melting characteristics, flavour, desired β polymorphism, and cooling or smooth-mouthfeel effect (Campos & Marangoni, 2012; Talbot, 2017). This behaviour correlates to the presence of the V (β) polymorph form, which has the optimal melting properties. However, CB is expensive due to the shortage of supply and declining production that exceeds the global demand. Products produced from pure CB, such as pure chocolate, is more expensive than compound chocolate (a chocolate product that uses more than 5% of other vegetable fats and oils). Thus, the industry is keen to find cost-effective and compatible alternatives with CB without changing the physical attributes of the final product. The targeted fat should contain 70-80% of monounsaturated TAG with high POS percentages to mimic CB so that it has a similar eating quality.

CB-like fat, or cocoa butter equivalent (CBE), is a low-cost vegetable fat and oil similar to CB. It is frequently used as a substitute for natural CB in the chocolate industry. It can be produced by fractionation and physical blending of different vegetable fats (Jahurul *et al.*, 2014a; Sonwai *et al.*, 2014; Jin *et al.*, 2017a; Nirupam *et al.*, 2017; Huang *et al.*, 2021). Fractionation is the oldest separating technique, which is the pioneer of today's edible oil and fat processing industry (Saw, Chong, & Yeoh, 2015). The separating method is particularly essential in the palm oil sector since palm oil contains almost equal levels of saturated and unsaturated fatty acids. The physical constitution of palm oil, which exhibits a semi-solid condition in the Malaysian tropical climate, allows its separation into a low-melting fraction (olein) and a high-melting fraction (stearin) (Gijs *et al.*, 2007; Kellens *et al.*, 2007).

The separation process also allows the fractions to be used separately based on their functionality and properties. Moreover, fractionation has become the only lipid modification process permitted by the European Union (Directive 2000/36/EC) for CB improver (CBI) and CBE manufacturing due to food safety concerns (Jin *et al.*, 2017b). It has also been employed by the fats processing industry to broaden the applications of pure fats and oils and to replace chemical modification techniques entirely or partially (Kellens, Gibon, Hendrix, & De Greyt, 2007). For instance, fats with specific functions or speciality fat, such as CB alternatives (CBA) or chocolate applications, can also be produced by isolating the fats using a fractionation process. Therefore bambangan kernel fat-second stearin (BKF-SS) produced from multi-stage fractionation is regarded as high-quality fat.

The symmetrical unsaturated-TAG (SUS-TAG) from BKF-SS fractions is also suitable as a blending component with palm oil fractions for the production of CBE (Bootello *et al.*, 2012; Tran *et al.*, 2015). Blending fat with SUS-TAG with other fats will yield CBE with appropriate POP, POS, and SOS-TAG composition. The blending technique improves fats and oils' composition, thermal, and morphological attributes. It results in novel fat mixtures with acceptable properties for food manufacturing, especially in the confectionery application (Jahurul *et al.*, 2014b; Ramli, Said, Mizan, Tan, & Ayob, 2014; Chiavaro, 2015; Bahari & Akoh, 2018a,b). Moreover, blending or mixing is the industry's most straightforward and less expensive method to combine fats and oil with different properties. Therefore, the blended product is applicable for the application in which it is not practical in its present form.

Physical blending also produces a fat blend compatible with CB and can be partially or wholly integrated into CB. CBE is commonly produced by combining POP-rich fats like palm oil mid-fraction (POMF) and palm stearin (PS) with SOS-rich fats such mango kernel fat, shea stearin, and high oleic-high stearic sunflower stearin (Kaphuekngam *et al.*, 2009; Salas *et al.*, 2011; Kang *et al.*, 2013a; Jahurul *et al.*, 2014a,b; Sonwai *et al.*, 2014; Watanabe *et al.*, 2021). POMF has a high POP level with values of 51.8%, resulting in its steep SFC properties and is commonly used as a confectionery fat resource (Bootello, Hartel, Garcés, Martínez-Force, & Salas, 2012; Biswas *et al.*, 2017; Shin, Heo, & Lee, 2019; Norazlina *et al.*, 2021). It has a distinct melting behaviour, allowing it to be used in various confectionery applications. POMF is also commonly blended with SOS-rich fats to produce CB substitutes (CBS) and CBE.

PS is similarly a POP-rich fat resource, containing about 71.82 % POP-TAG, greater than POMF (Jahurul *et al.*, 2019). It's also a solid fat fraction with a high melting point (44 to 56 ºC) produced by palm oil (Oliveira, Rodrigues, Bezerra, & Silva, 2017). These properties cause PS to have incomplete melting and low plasticity properties at body temperature, but it is an excellent palmitic donor. Moreover, POMF and PS is more economical and less expensive ingredient, applicable for compound chocolate and confectionery fillings application than other palm oil products (Nirupam *et al.*, 2017; Jahurul *et al.*, 2019). High POP content in these fractions makes it desirable for blending with POS or SOS-rich fat sources to resemble CB's triglyceride (TAG) composition (Sonwai *et al.*, 2014).

BKF-SS was obtained from the crude of bambangan kernel fat (BKF) by multi-stage fractionation with more than 70% of fractionation yield, resulting in solid fat with high stearic acid (48.50%) and SOS (64.70%) content (Norazlina *et al.*, 2020a, b). BKF-SS is cost-effective since the kernel, which accounts for about 27% of the