International Food Research Journal 21(3): 1019-1023 (2014)
Journal homepage: *http://www.ifrj.upm.edu.my*

Fatty acid composition, rheological properties and crystal formation of rambutan fat and cocoa butter

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Article history

Received: 24 November 2013
Received in revised form: 18 January 2014
Accepted: 20 January 2014

Keywords

Fatty acid
Rheology
Cocoa butter
Rambutan fat
Chocolate

Abstract

The study was conducted to investigate fatty acid composition, rheological properties and crystal formation of rambutan fat and cocoa butter. The results showed that lauric acid, palmitic acid, and stearic fatty acid in rambutan fat were less than cocoa butter, but oleic acid found almost the same. The crystal formation of cocoa butter was not complex at 25°C, while rambutan fat and their mixture shown complicated network of crystal form. The Newton, Bingham and Casson plastic rheological models was used to describe fat flow in this experiment and the result showed that rambutan fat had higher viscosity than cocoa fat. Based on the results the study recommended that mixture proportion up to 30% rambutan seed fat can be used as a cocoa butter substitute whereas higher proportion completely alters original cocoa butter properties. Therefore, there is feasibility of using the rambutan fat to substitute cocoa butter and the mixtures of the two fats in suitable proportion in chocolate manufacturing.

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Introduction

In general, a natural fats and lipids resources are obtained from vegetable and animal fats and oils which it having different some chemical and physical properties (Sato, 2001; Lannes *et al*., 2004). Cocoa butter (CB) is a major ingredient in practically all types of chocolates. Chocolate is a processed, typically sweetened food produced from the seed (*Theobroma cacao*) of the tropical tree (Zzaman and Yang, 2013). Moreover, cocoa butter is the only continuous fat phase in chocolate (Lannes *et al*., 2003). Nowadays; the cocoa price is increasing continue day by day. 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). Rambutan (*Nephelium lappaceum* Linn.) is a fruit native in Southeast Asian countries especially in west Malaysia and Sumatra. The rambutan fruits are deseeded during processing and these seeds around 4-9 g/100 g are a waste by-product from canning industry. Some studies had reported that rambutan had relatively high amount of fat around 17-39% in the rambutan seed (Morton, 1987; Sirisompong *et al*., 2011). Therefore, the extracted fat from rambutan seed or other source of seed fat are important to be used for food manufacturing such as candles, soaps, and fuels, and it also has a possible to be a source of natural edible fat (Solis-Fuentes *et al*., 2011).

In food industry, the macroscopic properties of the fat network will be important as resulting to the texture of final product, which the texture of fat-containing products strongly depends on the texture of fat-containing in products stably (Rohm and Weidinger, 1993). These properties resulting as occur the snap of a sweet product such as chocolate. So, plastic solid to a brittle solid was obtained from different physical state of a fat and liquid viscous fluid (Myhan *et al*., 2012). Lipp and Anklam (1998) previously mentioned that the utilization of natural or processed lipids as CBA can be decided using its compositional data (fatty acid composition and triacylglycerol conformation) and thermal properties such as crystallization and melting characteristic. However, the compatibility of these lipids with cocoa butter is also important aspect that should be carried out to measure the capability of lipids to be used as cocoa butter alternatives.

The rheological properties are usefulness for various applications of food materials (Kealy, 2006). Many investigators have begun to examine the importance of rheological flow properties in the quality of liquid and semi-solid foods. Moreover

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notes that rheology technique can use for shelf life determination and measuring texture (Labuza, 2000). In part of steady flow characteristics of foods, when decrease the applied stress, the yield stress of a liquid structured was original point. Newtonian-plateau viscosity can be described this creep behavior for structured liquids at the lowest stresses. On the other hand, as increased the stress the flow behavior was changed into a power-law dependence of steady-state shear rate on shear stress (Barnes *et al*., 1999). The aim of this study was to investigate fatty acid composition, rheological properties and crystal formation of rambutan fat and cocoa butter.

Materials and Methods

Cocoa butter

Cocoa butter (Palmer's, Grade 1) derived from cocoa beans (Theobroma cacao) was purchased from Indonesian Coffee and Cocoa Research Institute, Indonesia.

Rambutan seed

Rambutan seeds (*Nephelium lappaceum* L.) were collected from pulp-canning production industry at Penang and then the seeds were dried in the over at 60°C for 30 minute as a indicator of moisture content around 3% wet basis. After peeling fat was extracted using screw-pressed (IBG Monforts Oekotec GmbH & Co. KG, Germany) and then the extracted fat were filtered using muslin cloth before transferred into inert-screw cap-bottle and stored at -4°C.

Experimental design

Interaction experiments were conducted with mixtures between cocoa butter and rambutan fat (not treated) made as following ratios shown in Table 1.

Statistical analysis

The experimental data was subjected to analysis of variance by Turkey HSD, at 5% level of significance. The analysis was performed using an SPSS package (SPSS 16.0 for window, SPSS Inc, Chicago, IL).

Preparation of fatty acid methyl esters (FAME)

Fatty acid composition was determined according by transmethylation of fatty acids into fatty acids methyl esters. FAME was prepared following the method with some modifications (Pe´rez-Martı´nez *et al*., 2005). Melted samples (0.05 g) were trans-esterified by using 2 ml of borontrifluoride (BF_3)-methanol (20:80) reagent and heated at 90-100°C for 30 minute in water bath. The heated solution was cooled at room temperature. After cooled, 2 ml of n-hexane and 8 ml of distilled water were added and agitated vigorously for 1 minute. Separation of hexane soluble and insoluble layer was done using centrifugation at 3500 rpm for 2 minute. Upper hexane soluble layer was collected and transferred into glass container that used for chromatographic analysis.

Table 1. Experimental mixtures proportion between cocoa butter and rambutan fat

Mixtures of CB & RF	Proportions (%)	
	CB[a]	RF[b]
Mixture 1	100	0
Mixture 2	90	10
Mixture 3	70	30
Mixture 4	50	50
Mixture 5	30	70
Mixture 6	10	90
Mixture 7	0	100

[a]CB = Cocoa butter, [b]RF = Rambutan fat

Gas chromatographic analysis

Gas Chromatography (GC) analysis was done using GC 2010 plus- FID (flame ionization detector) (Shimadzu Corp., Nagakyo-ku, Kyoto, Japan) equipped with SGE BPX70 (90% Cyanopropylphenyl Polisiloxane, 0.32mmID × 0.25μm × 30m) column (SGE Analytical Science Pty Ltd, Victoria, Australia). The condition of GC during the analysis was set as follows: The injection port was set using split mode (split ratio = 1:10) at temperature 250°C employed Helium (He) as carrier gas (Mondello *et al*., 2006). The column temperature was set at 70°C maintained for 1 min then increasing to 150°C at 20°C/min ramp and then increasing to 250°C at 10°C/min ramp. The final temperature was maintained for 15 min.

Polarized light microscopy

Microstructure analysis was performed following method with slight modification (Perez-Martinez *et al*., 2007). Rambutan fat samples were heated at 80°C for 30 minutes to completely melt the fat crystal in the samples. One drop of melted fat was placed on already pre-heated (70°C for 10 minutes) microscope slide and covered with the cover slips. The slides were stored in storage at room temperature for 24-48 hours (depend on formation of fat crystal). Crystal formation at 25°C of both fats was studied under polarized light microscope at 40X magnification. The pictures were recorded by using a digital video camera mounted to the microscope.

Rheological properties (Rheometer)

The rheological parameters were measured using a Rheometer AR1000-N with thermostatic bath at a temperature of 40°C. The 4 cm Flate plate was used. The test was conducted by controlled stress (500 1/s), for 120 sec (Rohm and Weidinger, 1993). The flow was described using rheological models (Newton, Bingham and Casson).

Results and Discussion

Many different lipids or fat contain in cocoa butter. According to Lannes and Gioielli (1997) described that a primary triacylglycerols that combined in the cocoa butter including; palmitic, stearic, and oleic fatty acids. Saturated and unsaturated acids are obtained from many fats and lipids combination of the fatty acids, which half of them are heterogeneous.

The fatty acids composition (%) in the cocoa butter and rambutan fat is shown in Table 2. The result found that Palmitic acid in the rambutan fat was present in much smaller amounts (8.83%) than cocoa butter (28.16%); and stearic acid in rambutan fat also showed like a palmitic acid (6.66% and 21.53%), respectively. The results showed that the palmitic acid was found 7.11% and the stearic acid and oleic acid were 6.66% and 25.32% respectively. The lauric acid content in cocoa butter was higher (19.68%) than rambutan fat (4.17%). Moreover; Arachidic acid and other saturated fatty acid such as gondoic, behenic found in rambutan seed but those fatty acids was absence in cocoa butter, which may affect to high melting point and high viscosity of rambutan seed fat (Zee, 1993; Solis-Fuentes *et al.*, 2010).

The microscope that used with polarized light was very useful tool in this study to observe crystal structures (Narine and Marangoni, 1999). Crystallization at 25°C of cocoa butter and rambutan seed fat was viewed under the microscope at 40X magnification. The result of crystal formation of each sample is shown in Figure 1. The study cocoa butter was big crystal and had small needle around the center of crystal, while rambutan seed fat found small size and many crystal because of fatty acids or different type of triglyceride (Bricknell and Hartel, 1998; Narine and Marangoni, 1999). The first visible of crystal formation is seen like a few tiny, needle shaped crystals appear scattered throughout the field. The next observation on the formation of a crystalline layer of the crystal was much more obvious and the types of these crystals grow faster than formation of a new single crystal (Lannes *et al.*, 2004). Eventually, a bundle of the needles observed around each original, single crystal and growth continues until the bundles join up to form a solid mass and appropriate crystallization of fat was described to quality of finished product. Therefore, the behavior of melting point, crystallization and crystal formation of fat are partly due to the physical properties, phase lipid in the natural resources that compose different triglyceride component (Bricknell and Hartel, 1998).

The temperature of storage, thermal processing such as pasteurization, cooling rate after pasteurization

Table 2. Fatty acids composition (area %) in the cocoa butter and rambutan fat

FATTY ACID (%)			
Type & Name of fatty acid		Cocoa butter*	Rambutan fat*
$C_{8:0}$	Caprylic acid	1.27 ± 0.002	1.08 ± 0.003
$C_{10:0}$	Capric acid	-	1.14 ± 0.004
$C_{11:0}$	Undecanoic acid	1.69 ± 0.008	1.92 ± 0.011
$C_{12:0}$	Lauric acid	19.68 ± 0.004	4.17 ± 0.015
$C_{13:0}$	Tridecanoic acid	-	4.63 ± 0.013
$C_{14:0}$	Myristic acid	-	2.80 ± 0.016
$C_{15:0}$	Pentadecanoic acid	-	3.81 ± 0.017
$C_{16:0}$	Palmitic acid	28.16 ± 0.004	8.83 ± 0.020
$C_{16:1}$	Palmitoleic acid	-	13.66 ± 0.240
$C_{18:0}$	Stearic acid	21.53 ± 0.007	6.66 ± 0.021
$C_{18:1\ cis}$	Oleic acid	22.78 ± 0.008	25.32 ± 0.070
$C_{18:1\ tran}$	Elaidic acid	-	3.53 ± 0.012
$C_{18:2\ tran}$	Linolelaidic acid	4.88 ± 0.003	-
$C_{20:0}$	Arachidic acid	-	16.39 ± 0.050
$C_{20:1}$	Cis-13-eicosenoic acid	-	4.46 ± 0.014
$C_{22:0}$	Behenic acid	-	1.22 ± 0.004

*Mean ± Standard deviation

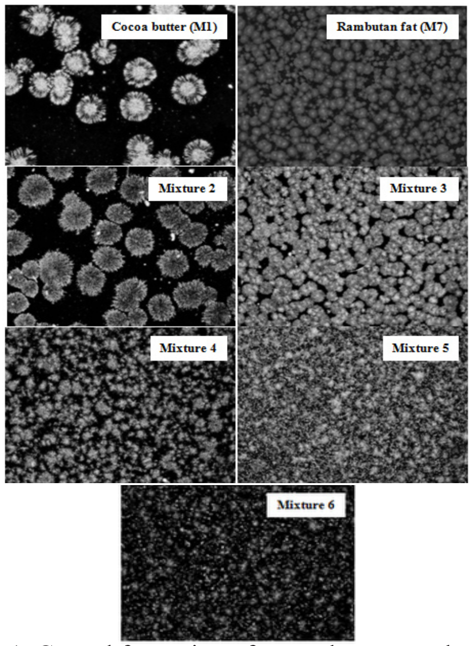

Figure 1. Crystal formation of cocoa butter, rambutan fat and their mixture at 25°C (40X magnification)

and including other processing may affect the rheological properties of the fat. Although oils are normally Newtonian but at very high shear rates there may be a curvature towards the shear rate axis in the shear stress x shear rate diagram, which is referred to as pseudoplasticity (Lannes *et al.*, 2004). According to Lannes *et al.* (2004) noted that characterized by the melting of fat crystals is defined as the level of fat in a reticular structure which are typically structured in the form of β' that conducted lead to higher viscosity more than β form structure that given their smaller size, higher surface area and potentially increased interfacial viscosity in emulsions. However, the Newtonian linear relationship of π/γ (τ = shear stress; γ = shear rate) were found in many food stuff which exhibit a yield stress τ_o and are said to show plastic behavior]. As the stress is increased, the flow behavior usually changes into a power-law dependence of

Table 3. Rheological models of the experimental mixtures

Rheological models	Mixtures						
	M1 (CB) (100 : 0)	M2 (90 : 10)	M3 (70 : 30)	M4 (50 : 50)	M5 (30 : 70)	M6 (10 : 90)	M7 (RF) (0 : 100)
Newton							
η (Pa.s) $\tau = \mu . \gamma$	bc 0.0479±0.0008	c 0.0474±0.0015	abc 0.0485±0.0007	bc 0.0478±0.0009	abc 0.0493±0.0001	ab 0.0512±0.0005	a 0.0516±0.0005
Bingham							
τ (Pa)	d 0.2132±0.0116	b 0.3270±0.0006	b 0.3360±0.0007	b 0.3173±0.0076	a 0.3758±0.0019	c 0.2564±0.0007	e 0.1813±0.0018
η (Pa.s) $\tau = \eta . \gamma + \tau_o$	bc 0.0479±0.0007	c 0.0475±0.0015	abc 0.0484±0.0007	bc 0.0479±0.0009	abc 0.0493±0.0000	ab 0.0510±0.0005	a 0.0515±0.0004
Casson							
τ (Pa)	b 0.0590±0.0003	e 0.0400±0.0007	d 0.0454±0.0008	c 0.0539±0.0022	a 0.0719±0.0005	de 0.0417±0.0007	f 0.0308±0.0012
η (Pa.s) $\tau^{0.5} = (\tau_O)^{0.5} + k^1(\gamma)^{0.5}$	c 0.0468±0.0008	bc 0.0473±0.0013	abc 0.0484±0.0007	bc 0.0478±0.0010	abc 0.0492±0.0001	ab 0.0502±0.0011	a 0.0513±0.0005

[a,b,c,d,e,f] same letter in the same line denotes are not statistical different.
Where:
η = apparent viscosity
k= consistency index
τ = shear stress
τo= yield stress
γ= shear rate

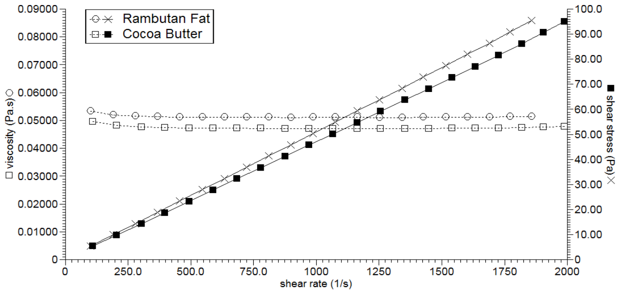

Figure 2. Flow curve of rambutan fat and cocoa butter (viscosity x shear rate and shear stress x shear rate)

steady-state shear rate on shear stress. However, for liquids structured, this behavior generally gives way to Newtonian behavior at the highest stresses. For liquids structural changes of very high viscosity (creep) to the liquid this mobile can often take more than a single order of magnitude of the stress. This behavior is based on a linear to a reasonable belief that the material yield stress and many cases of the flow curve, the simple linear equation of the Bingham-withintercept seems to describe adequately, but if you focus on the logarithm basis, equally simple Newtonian / power-law / Newtonian equations of Newton can be explained more clearly. Turkey HSD, at 5% of significance for variance analysis was elaborated to verify the difference between samples at the same rheological model parameter. The viscosities value of each model for all mixtures in Table 3 showed small differences in values and differed significantly in the same line denotes. Cocoa butter had a lower viscosity than rambutan fat, which can be explained by type and long chain structure of fatty acid and triacylglycerol composition (Narine and Marangoni, 1999). The flow curve (viscosity x shear rate and shear stress x shear rate) from Rheotest of cocoa butter and rambutan fat is shown in Fig. 2.

Conclusions

From the results obtained in this study, it is useful for basis to study other properties of rambutan seed fat before use to substitute cocoa butter. Generally the rheological of fat was study in the solid state, but the behavior of two fats and their mixtures in liquid state were studied along with testing the rheological models. For study of chemical composition (free fatty acid) of CB and RF found that it affected the crystal characteristic due to each of fat containing different of fatty acid. Up to 30% rambutan seed fat can be used with cocoa butter as a potential ratio of CB and RF for the application in chocolate manufacturing. The study concluded that ranbutan seed can be used as a cocoa butter substitute to improve and get the good quality in products. There are several aspects that need to be studied further such as optimum fermentation and roasting condition as well as toxicity assay for feasibility for human consumption.

Acknowledgments

We would like to thank to Food Technology Division, School of Industrial Technology, Universiti Sains Malaysia for laboratory facilities to carry out the experiment.

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