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Exploration on the thermal behavior, solid fat content and hardness of rambutan fat extracted from rambutan seeds as cocoa butter replacer

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Abstract

Fat content and macroscopic properties of fat network formulation result in final products in chocolate industry. The knowledge of physical properties is required in regard to stability of final food products resulting to quality. The study was carried out to investigate the thermal behavior, solid fat content and hardness of Rambutan fat (RF), cocoa butter and mixtures between two fats. The results found that the mixtures can be compatibility; the cocoa butter indicated the higher of solid fat content at room temperature more than RF and other mixtures. The RF had the highest melting point in both non-stabilized and stabilized form among cocoa butter and their mixtures. The hardness behavior showed lower in the mixture 1 and RF. For the phase behavior of crystallization exhibited the similar for all samples whereas the time of crystallization and temperatures were different. Therefore, the RF might be possible source of cocoa butter substitute with suitable proportion in the manufacturing chocolate and confectionery products.

Introduction

Cocoa butter (CB) is important ingredients in chocolate and confectionery industries. Moreover, cocoa butter is a continuous fat phase in chocolate production. The volatile compound such as aromas was no attempt for characterization of cocoa butters (Lipp and Anklam, 1998). In general, 25-36% of CB present in chocolate which affect to smooth texture, contractibility, flavor release, and gloss of the product. But due to the increased of cocoa price in 2006 was on average 1590 US $ per ton while in 2011 the price had doubled to 3140 US $ per ton and the trend of cocoa price is continuously increasing until present day (Issara *et al*., 2014). The melting profile of the fat crystals play key roles in determining properties such as texture, stability, spreadability, and mouth feel. The texture of products such as chocolate, shortenings, and especially butter is determined by the concentration, morphology, and interactions of fat crystals (Depypere, 2011). Therefore, the industries have been made their effort to find other fats to replace the cocoa butter in chocolate and chocolate like products (Lannes *et al*., 2003).

Rambutan (*Nephelium lappaceum* L.) is a seasonal fruit native of west Malaysia and Sumatra. It is cultivated widely in Southeast Asian countries. This fruit is customarily consumed freshly and for production of Rambutan canned (Solís-Fuentes *et al*., 2010). The Rambutan fruits are deseeded during processing and these seeds are treated as by-product of the canning industry. Some studies had reported that Rambutan seed possesses high amount of antioxidant and other nutrients. It also showed that Rambutan has relatively high amount of fat (between 17% and 39%) and these fats are similar to those of cocoa, although they showed difference in some physical properties (Sirisompong *et al*., 2011; Zzaman and Yang, 2013). The extracted fat from Rambutan seed not only could be used for manufacturing candles, soaps, and fuels, but it also has a possible to be a source of natural edible fat with feasible proportion (Solís-Fuentes *et al*., 2010).

Physical properties of oil or fat are critically necessary to determine its potential usage. Fat and oil are used in various forms to produce final products. The physical properties such as the phase behavior of crystallization and melting point that encompass both solid fat content and polymorphic behavior (Oliviero *et al*., 2009; Asmaa *et al*., 2015). Moreover, cocoa butter itself existed in different crystal modifications under diversified conditions (Hagemann, 1988). A vigilant tempering of the chocolate is needed in order to obtain the fine crystals in the correct form

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(β-modification). Without this tempering, cocoa butter is inclined to crystallize in rather coarse crystals, with the tendency to blooming which it described the unfavorable occur of big white fat crystals on the surface of the chocolate (Bricknell and Hartel, 1998; Zzaman *et al*., 2014).

Differential scanning calorimetry (DSC) is an instrumental method that measured the electrical power required to keep the temperature of a sample equal to that of an air reference (Talbot *et al*., 2005). The DSC used to measure the crystallization and melting point of pure forms of the triglycerides present in cocoa butter and also determined the solid fat content (Minifie, 1989; Lannes *et al*., 2003). The interactions between cocoa and rambutan fat could be interest to confectionery and chocolate industry as a potential source of cocoa butter replacer (Lannes *et al*., 2003). As a result, the properties of cocoa butter and rambutan fat are necessary to investigate its compatibility together in the manufacturing chocolate and confectionery products. The aim of this study was to analyze the interactions between cocoa butter and rambutan seed fat in term of phase behavior of crystallization, melting point, solid fat content and hardness index.

Materials and Methods

Raw sample collection

Cocoa butter (Grade-A) was purchased from Indonesian Coffee and Cocoa Research Institute, Indonesia. Rambutan seeds (average weight: 2.5 ± 0.12) were collected from rambutan pulp-canning production industry where the seeds were still covered by a small amount of rambutan pulp. Rambutan seeds fat extraction was carried out using KOMET screw oil expeller DD 85 IG (IBG Monforts Oekotec GmbH and Co. KG, Germany). Prior to screw-pressing, dried rambutan seeds were dehusked and heated at 60˚C for 30 minutes. Screw-pressing processing resulted in rambutan seed butter which was a viscous mixture of rambutan seeds butter and RSF. Separation of RSF from rambutan seed butter was done through filtration in a heated condition (60˚C). The RSF was then collected and transferred into inert-screw-cap bottle and stored at -4˚C until used for analysis.

Experimental design

Interaction experiments were conducted with mixtures between cocoa butter (CB) and rambutan fat (RF). The mixtures proportions were as Mixture 1 (10% CB with 90% RF), Mixture 2 (90% CB with 10% RF), Mixture 3 (70% CB with 30% RF), Mixture 4 (30% CB with 70% RF), Mixture 5 (50% CB with 50% RF) and Mixture 6 (100% CB with 0% RF). The samples were prepared in the triplicate for all analysis.

Analysis of thermal behavior

The samples were analyzed according to the method of Solís-Fuentes et al. (2010) with some modification. Non-stabilized mixtures was prepared by storing the mixtures in room temperature until solidified, whereas stabilized mixtures was prepared following the method of Solís-Fuentes and Durán-de-Bazúa (2004) by tempering it at room temperature for 24 hours followed by storing at 5 ˚C for 2 weeks. The equipment was used DSC Q200 equipped with RC90 refrigeration system (TA Instrument, New Castle, DE, USA). The DSC data was retrieved using TA Q series Thermal Analysis 2000. Prior to analysis, the device was calibrated with indium (melting point 156.6˚C). Approximately 4 ± 0.5 mg of the samples were weighed in aluminum pan and then covered with aluminum lid and hermetically sealed. An empty sealed pan was used as reference. The temperature programs in the calorimeter were set in three steps as i) Isothermal heating at +90˚C for 10 min to erase thermal history of the samples. ii) Cooling at 10 ˚C/min from +90˚C to -80˚C, the crystallization profile, enthalpy of crystallization and the phase changes were recorded. iii) Heating from -80˚C to +90˚C at 10˚C/min, the melting profile, enthalpy and phase changes were recorded. Data was analyzed by using TA Universal Analysis 2000 (TA Instrument- DMA Q800, New Castle, DE, USA) including crystallization and melting temperature ranges, and enthalpy calculation.

Determination of solid fat content (SFC)

Solid fat content measurement was carried out according to Solís-Fuentes *et al.* (2010). The measurements were carried out in stabilized and stabilized condition. The mixtures and CB were stabilized under room condition for 24 hours prior to storage at 5˚C for 2 weeks. The quantification was done according to previously acquired DSC data using TA Universal Analysis 2000 (TA Instrument-DMA Q800, New Castle, DE, USA). The integration of the data was made considering that at -80˚C the fat was complete solid and at +90˚C the samples were 100% liquid.

Texture measurement (hardness)

The method used to determine the hardness of samples was adapted from Lannes e*t al.* (2003). Hardness was measured using texture analyzer with

the cone probe. Condition was set to penetrate 10.0 mm with speed of 2.0 mm/s, in triplicate. The results were used to create the hardness diagram.

Statistical analysis

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

Results and Discussion

Determination of melting point

Fats are customarily mixed with triglycerides where each of triglyceride had its own melting point (Özdemir and Devres, 2000). Each fat having a range of melting point depended on types of triglycerides present in fat (Issara *et al.*, 2014). The study found that the melting point was relative to the percentage of fat content presented in Figure 1. The rambutan fat had a higher melting point in both non-stabilized and stabilized condition than the cocoa butter and their mixtures. The melting point in stabilized condition showed higher than non-stabilized samples of rambutan fat, cocoa butter and their mixtures.

Phase behavior of crystallization

The crystallization velocity of the fats was obtained by cooling curve termed phase behavior of crystallization using DSC (Lannes *et al*., 2003, 2004). Crystallization finished when the maximum temperature was reached. The main transition temperature point, phase behavior to crystallization and fusion enthalpies of non-stabilized for solid to liquid phase changed in all mixtures is summarized in Table 1. Though the profiles of the cooling curves were similar for all samples, the time of crystallization and temperatures were different. In this study, the lower solid fat content sample (mixture 1) showed more slow crystallization than higher solid fat content. The peak maxima of M1, M3 and M5 were observed at 24.44˚C, 19.64˚C, and 21.06˚C, respectively. On the other hand, mixtures M2 and M4 exhibited more simple melting profile which quite similar with the melting profile of CB. Peak maxima of M2, M3 and CB were observed at 22.06˚C, 22.76˚C, and 22.64˚C, respectively. Therefore, the study concluded that rambutan fat was softer than cocoa butter because of low solid fat content. Consequently the quality of rambutan fat may better than cocoa butter and their mixtures based on crystallization behavior. Researcher observed that the rate of crystallization was a key parameter

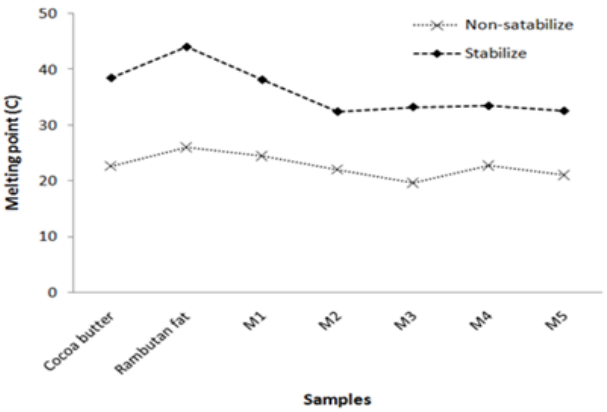

Figure 1. Melting point of the cocoa butter, rambutan fat, and their mixtures

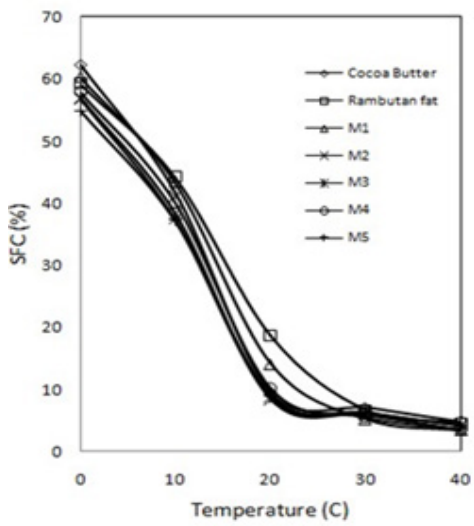

Figure 2. Solid fat content curves of cocoa butter, rambutan fat and their mixtures for non-stabilized

of the fat which useful to observe the polymorphic behavior of fats (Narine and Marangoni, 1999; Sato, 2001). According to Frankel (2005), vegetable origin lipids (fatty acids, acylglycerides, and fats and oils) showed polymorphism, and in general, and with more frequency, solidified in three different crystalline forms: α, β', and β, with correspondingly higher fusion temperatures. Polymorph α (lowest fusion point) was generally present after rapid cooling processes from melted fat. The form β' was a higher melting or fusion point than the previous one, generated through solidification of fat under certain conditions of temperature or due to transition from α form. Polymorph β, the most stable crystalline form in the fat sample because it was produced from the other two forms by incubating at slightly higher fusion temperatures than α form (Nakaf *et al*., 2000). The changes in fatty acid and TAG composition may be the main factor that affecting the crystallization and melting profile of mixtures. As mentioned previously by Lannes *et al.* (2003), the proportion of

Table 1. Transition points temperature, crystallization and fusion enthalpies for unstabilize condition of cocoa butter, rambutan fat and their mixtures.

Sample	Phase change	Temperature if the phase transition point (ºC)						Total ΔH (J/g)
		To	1	2	3	4	*Tr*	
M1	Crystallization	23.06	19.77	1.79	-45.03		-60.64	41.02
	(a) Fraction I	23.06	19.77					36.36
	(b)Fraction II	3.80		1.79				0.71
	(C)Fraction III	-42.74			-45.03			3.95
	Melting	-35.54	-30.76	-8.66	6.43	24.44	35.73	117.2
M2	Crystallization	17.32	13.11	-11.60	-37.33		-56.72	60.02
	(a) Fraction I	17.32	13.11					57.65
	(b)Fraction II	-7.26		-11.60				0.77
	(C)Fraction III	-21.67			-37.33			1.60
	Melting	-34.32	-6.44	22.06			33.38	119.2
M3	Crystallization	18.73	13.89	-17.03	-49.00		-58.58	56.12
	(a) Fraction I	18.73	13.89					54.63
	(b)Fraction II	-4.85		-17.03				0.47
	(C)Fraction III	-46.13			-49.00			1.02
	Melting	-37.60	-32.83	-3.82	19.64		33.74	117.3
M4	Crystallization	21.14	16.85	-45.88	-71.04		-73.87	75.86
	(a) Fraction I	21.14	16.85					72.46
	(b)Fraction II	-43.29		-45.88				3.08
	(C)Fraction III	-70.92			-71.04			0.32
	Melting	-44.33	-30.30	3.33	22.76		34.84	105.3
M5	Crystallization	19.42	14.84	-47.22	-73.06		-74.20	69.50
	(a) Fraction I	19.42	14.84					67.40
	(b)Fraction II	-44.14		-47.22				1.91
	(C)Fraction III	-72.66			-73.06			0.19
	Melting	-42.70	-30.60	21.06				110.7
Cocoa butter	Crystallization	17.71	12.78	2.45	-11.54		-21.66	44.62
	(a) Fraction I	17.71	12.78					43.22
	(b)Fraction II	4.08		2.45				0.03
	(C)Fraction III	-5.20			-11.54			1.37
	Melting	-25.97	-0.35	22.64			37.73	116.2
Rambutan fat	Crystallization	26.81	20.02	2.49	-44.67		-61.20	39.22
	(a) Fraction I	26.81	20.02					34.48
	(b)Fraction II	4.97		2.49				1.32
	(C)Fraction III	-42.20			-44.67			3.42
	Melting	-34.87	-30.42	7.67	26.01		38.95	113.7

T_0 : onset temperature; T_f : offset temperature; 1, 2, 3, 4 : transition temperature points for cooling and heating; ΔH : transition heat.

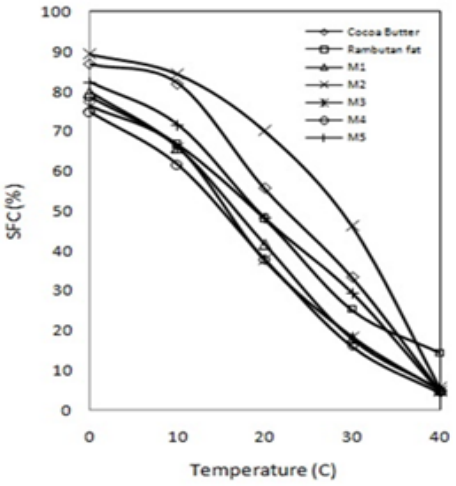

Figure 3. Solid fat content curves of cocoa butter, rambutan fat and their mixtures for stabilized

different fat affected the properties of mixtures such as phase behavior, crystallinity and hardness.

Determination of solid fat content (SFC)

The profiles of the solid fat content for non-stabilized samples are shown in the Figure 2. The cocoa butter had the highest the solid fat percentage than other samples, while the mixture 5 (50% of cocoa butter: 50% of rambutan fat) showed the lowest percentage of SFC. It meant that the mixture was smoother than cocoa butter, rambutan fat and other mixtures. According to Lannes *et al*. (2003) the rambutan fat would be useful in filled chocolate manufacture as a softer filling fat compatible with cocoa butter. The stabilized condition for SFC curve is shown in the Figure 3. Similarities observed in the behaviour of the solid and liquid phases of the fats due to the temperature effect, when subjected to stabilization. Rambutan fat was softer than cocoa butter and other mixtures at low temperatures and had a harder consistency at higher temperatures, except mixture 2. This behaviour is probably due to the compositional differences in rambutan fat and cocoa butter. The lowest SFC in fats almost used in the chocolate industry resulting in the softest of the products. If chocolate was made with softer fat, less crystals was formed. The SFC profile also affected to the relative tendency of chocolate hardness resulting in the pure fat system. (Solís-Fuentes *et al*., 2004).

Texture measurement (hardness)

The hardness and crystalline behavior is influenced on the mixture proportion of samples used (Kealy, 2006). The hardness diagram for the mixtures of the cocoa butter and rambutan fat in non-stabilized and stabilized samples is shown in Figure 4. The study found that the both fats were not entirely combined together. The trend of hardness in all samples presented similarities behavior in the both stabilized and un-stabilized condition. The cocoa butter showed the highest hardness behavior due to higher solid percentage. In the other hand,

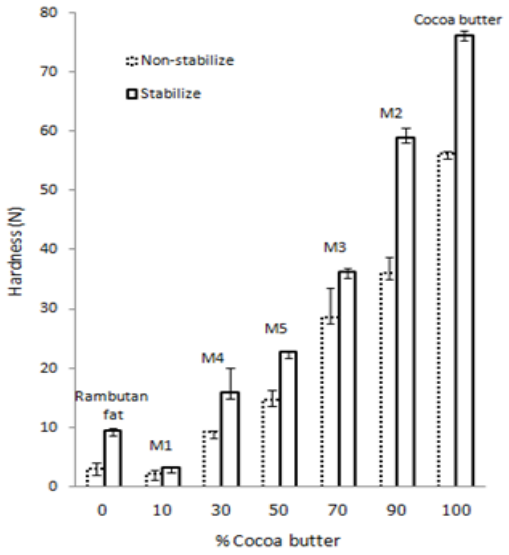

Figure 4. Hardness diagram for non-stabilized and stabilized of mixtures between cocoa butter and rambutan fat

the mixture 1 had the lowest of hardness, where the mixture containing 90% RF mixed with 10% CB. Moreover, the results of other mixture also exposed to the harder texture when the ratio of cocoa butter was increased in the sample mixtures.

Conclusion

The phase behavior of crystallization showed nearly similar in rambutan seed fat and cocoa butter whereas indicated differences with time and temperature of crystallization. Rambutan fat and their mixtures found lower solid fat content than cocoa butter as a result to softer texture. Furthermore, the cocoa butter and rambutan fat exhibited compatibility on thermal behavior in their mixture samples. The mixture 2 (90% CB with 10% RF) presented the highest compatibility on thermal behavior among all samples. Rambutan fat would be useful in filled or substitute cocoa butter to produce chocolate and confectionery products as a softer filling fat compatible with cocoa butter. The finding concluded that ranbutan seed fat can be used as a cocoa butter substitute to produce better quality chocolate and confectionery products. There are several aspects that also need to be studied further considering incorporation of RF into chocolate formulation, to check the compatibility and stability of the chocolate, fermentation and roasting to flavor optimization as well as toxicity assay for feasibility for human consumption.

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