

Research Article

Rheological and physicochemical properties of palm oil products with cocoa butter

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Abstract

Physico-chemical and rheological properties of binary blends of palm oil products with deodorised cocoa butter (DCB, IV 32.7) from 10 to 90% (w/w) were evaluated. Cocoa butter equivalent (CBE, IV 32.4) showed full compatibility with DCB at all concentrations and crystallised to form a strong β in a mixture of $\beta + \beta'$ polymorphic form. The solid fat content (SFC) and slip melting point (SMP) results showed that the addition of more than 20% palm-mid fraction (PMF, IV 41) and cocoa butter substitute (CBS, IV 0.3) with DCB showed eutectic effects and crystallised to form a strong β' in a $\beta + \beta'$ mixture. This is due to the higher amount of C12:0 and C16:0 in the blends containing CBS and PMF, respectively. The DSC melting thermograms of CBE and DCB blends showed a single melting peak at $\pm 19.5^\circ\text{C}$. There are two prominent melting peaks observed in blends containing more than 20% both PMF and CBS. Addition of 10% of CBE with DCB resulted in an increase in G' (storage modulus) and the blends became more elastic and highly structured. However, the addition of CBS and PMF caused the blends to be less viscous and softer.

Keywords: cocoa butter equivalent (CBE), cocoa butter substitute (CBS), palm-mid fraction (PMF), fatty acid composition, storage modulus, polymorphic form, chocolate, Malaysia.

Introduction

Cocoa butter fat has a complex polymorphism which is manifested in six polymorphs called forms I to VI [1]. Cocoa butter is a fat phase material used in product like chocolate. It accounted for about 28 to 38% of the ingredients in chocolate production [2]. This fat is important for successful production as well as in obtaining a high quality product for consumers [3]. The crystallisation and melting properties of cocoa butter are of major importance for the production of chocolate and confectionery. A steep melting profile with high solid fat content at 30°C , fully melted at mouth

temperature, will result in a glossy chocolate with good mouthfeel, flavour release and easy demoulding [4].

Vegetable fats that have very similar chemical and physical properties to cocoa butter and are able to replace certain amounts of cocoa butter in chocolate and confectionery products without any effects upon processing or product quality are known as cocoa butter equivalents (CBE) and cocoa butter substitute (CBS). They help to reduce the raw material cost as these fats are much cheaper than cocoa butter [5]. According to Fediol [6], the prices of CBE can vary from approximately 30% cheaper than cocoa butter. However, the addition of different fats resulted in changes to physical, chemical and rheological properties of the finished products. Therefore, the degree of compatibility between these vegetable fats and cocoa butter is important to ensure that a high quality chocolate and confectionery products could be produced. Incompatibility of the fat blends may give rise to bloom formation and poor quality products. In this study, the degree of compatibility of binary blends of CBE, CBS and PMF derived from palm oil with cocoa butter was investigated. The binary blends of CBE, CBS and PMF with DCB (10 - 90%) were analysed for their slip melting point (SMP), solid fat content (% SFC), DSC melting characteristics and polymorphic form.

Materials and Methods

Materials

Cocoa butter equivalent CBE (IV 32.4) CBS (IV 0.3) and PMF (IV 41) were purchased from Soctek Edible Oils Sdn. Bhd, Pasir Gudang, Johore. Cocoa butter (IV 32.7) was obtained from Kepong Koko Sdn. Bhd. Klang, Selangor, Malaysia.

Sample preparation

The samples were melted at 80°C for 30min in an oven to destroy all the crystal history. Binary blends of CBE:DCB, CBS:DCB and PMF:DCB within the range of 10 to 90% wt-% were prepared. The blends were subjected to the various analyses described below. Triplicate measurements were carried out for each analyses.

Slip melting point (SMP)

The slip melting point was measured according to the official AOCS method [7]. The slip melting point (SMP) is the temperature at which a column of fat of specified length rises in an open capillary tube under the specified condition of the test. The capillary tubes (o.d. 1.4 – 1.7 mm; i.d. 1.1 – 1.3 mm; length, 50 – 60 mm), open at both ends were dipped into a completely liquid sample of fat until the column of fat was approximately 1 cm high. The tubes were then chilled at 10°C ± 1°C for 16 hours. The tubes were subsequently attached with a rubber band to a thermometer and immersed to a depth of 3 cm in a beaker containing boiled distilled water. The water bath was stirred and heated until the fat column rose in the tubes. The temperature at which each column rises is obtained and the average values were obtained from at least three readings for each sample.

Fatty acid composition (FAC) by gas chromatography (GC)

Fatty acid composition of the blends was determined as methyl esters, which were prepared according to MPOB Test Methods [8]. Analysis was conducted using a capillary column (60 m x 0.25 mm i.d.) with a split ratio of 1:100 and flow rate of 0.85ml N₂/min and oven temperature of 230°C. Analysis was under isothermal conditions on a Hewlett-Packard 5890 Gas Chromatograph (Avondale, PA). Fatty acid methyl ester (FAME) was prepared by dissolving 50 mg of fat blend in 950 µL hexane (Merck, Darmstadt, Germany) in a 2-ml screw-capped vial. 50 microlitres of 1M sodium methoxide (Merck, Darmstadt, Germany) was added and the mixture was then mixed

vigorously with a vortex mixer for 5 min. 1 millilitre of distilled water was added and the mixture was mixed thoroughly. The mixture was then allowed to settle and separate into two distinct layers. The clear supernatant layer (FAME) was decanted and a small amount of anhydrous sodium sulphate (Merck, Darmstadt, Germany) was added to remove traces of moisture.

Solid fat content (%SFC)

The solid fat content of the blends at various temperatures was measured according to MPOB test methods [8]. Sample was melted at 70°C for 30 minutes to erase all crystal memory. Approximately 3.0 g of melted samples were pipetted into pNMR tubes (10.0 mm diameter, 1.0 mm thickness and 180 mm height). The tubes were chilled at 0°C for 90 min, and kept at the desired temperatures for 30 minutes prior to measurements.

Crystal polymorphism by x-ray diffraction

The polymorphic form of the blends was analysed using an Enraf Nonius model FR 592 (Enraf Nonius, Delft, The Netherlands) X-ray diffractometer. The instrument was fitted with a fine focus copper X-ray tube. The sample holders were flat stainless-steel plates with rectangular holes. Samples were melted at 70°C and then tempered at 10°C for 1 hour. The short spacings of the β' form are at 4.2 and 3.8Å and that of the β form is at 4.6Å [9]. Levels of β' and β crystals in the mixtures were estimated by the relative intensities of the short spacings at 4.2 and 4.6Å. Measurements were carried out in duplicate.

Thermal properties by differential scanning calorimeter (DSC)

Thermal properties of the samples were measured using a differential scanning calorimeter DSC-7 (Perkin-Elmer, Norwalk, CT). Calibration was carried out using an indium standard for the high temperature range and *n*-decane for the sub-ambient temperature range. Samples, weighing 3-5 mg were hermetically sealed in aluminium pans with an empty pan serving as a reference. The samples were heated to 70°C for 10 min to destroy crystal memory. The samples were then chilled at 0°C for 90 minutes, and kept at 26°C for 40 hours before being transferred to the desired temperatures for 30 minutes prior to measurements. The melting thermograms were recorded.

Viscoelastic properties by RS 600 rheometry

The rheological properties of the blends were determined using a Rheostress RS 600 Rheometer (Thermo Haake Karlsruhe, Germany) fixed with a water circulator at the base of a 35.0 cm serrated parallel measuring plate. For the sample preparation, round plastic moulds with thickness of 2 mm and a diameter of 35 mm were used. Samples were melted at 70°C in an oven for 30 minutes before being pipetted into the round moulds. The moulds were immediately transferred into controlled temperature incubators to be kept for one day prior to measurements.

An oscillatory stress sweep was performed to determine the linear viscoelastic region (LVR) at a frequency of 1 Hz, followed by frequency sweep tests from 1 to 20Hz at constant stress (in the LVR) to evaluate the storage (G'). All the tests were carried out in duplicate.

Results and Discussion

Solid fat content (%)

Figures 1, 2 and 3 show the solid fat content of the blends at various temperatures. There were no changes in the SFC of CBE:DCB blends at all measured temperatures. However, the SFC of the CBE:DCB blends were drastically reduced from 73% at 25°C to 0.5% at 35°C as shown in Figure

1. This could be due to the steep melting profile of DCB and CBE which is required for the manufacturing of a good chocolate. According to Willer and Wiber [10], the requirement for high quality PMF as a CBE fat component should have a very steep melting curve for solid fat content with values of at least 40% at 30°C and no tailing above 37°C.

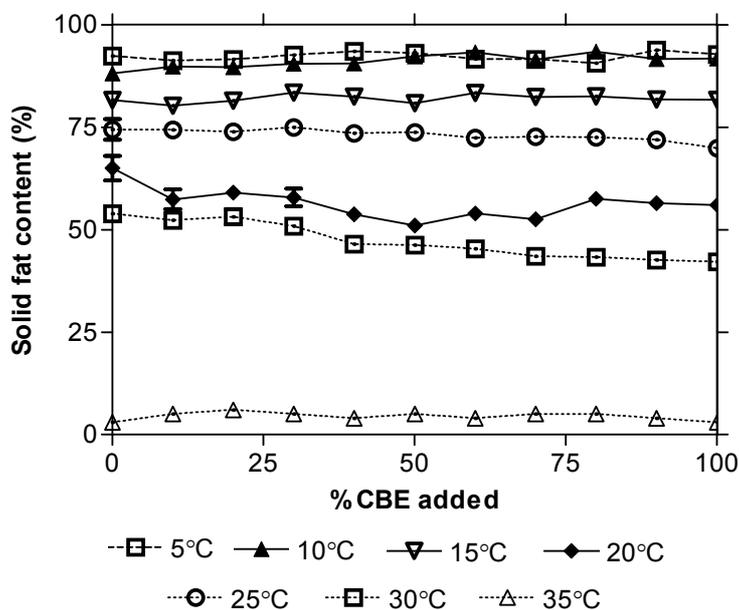


Figure 1. Solid fat content (%SFC) of CBE:DB blends at various tempering temperatures.

For the CBS:DCB blends, the addition of 20 to 60% of CBS at 25°C resulted to a decrease in SFC from 37% to 29% and gradually increased with higher amount of CBS added. The eutectic effect was obviously observed at 20 and 30°C. However, for the PMF:DCB blends, the SFC decreased when more than 10% of PMF added and this blends show eutectic effects at all measured temperatures. The eutectic effects could be due to the different types of triacylglycerols present in the blends, the incompatibility of the two oils used and their intermolecular packing. According to Timms [11], eutectic effect is desirable if the blend is going to be used for the production of margarine and shortening. Therefore, the SFC result of both CBS and PMF from this work showed their compatibility with DCB is only up to 20%. Table 1 shows the fatty acid composition of the blends.

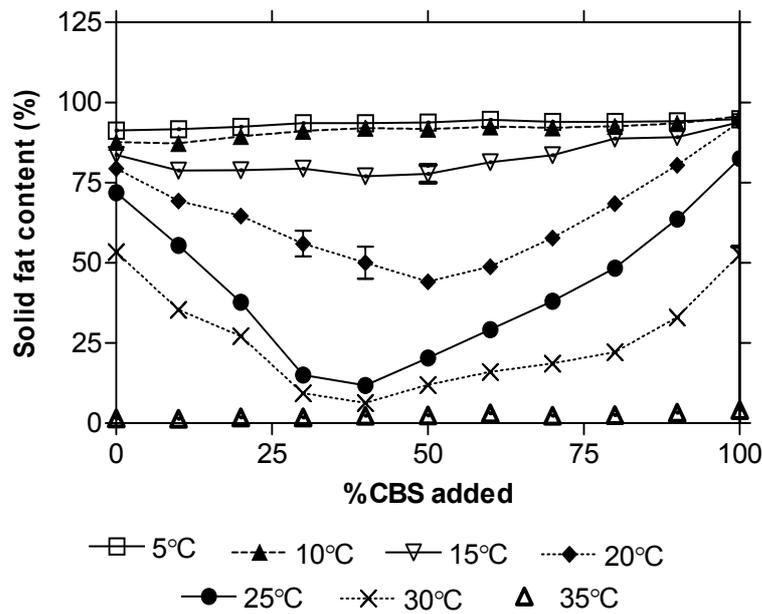


Figure 2. Solid fat content (%SFC) of CBS:DCB blends showed eutectic effects at 15°C to 30°C with the addition of CBS.

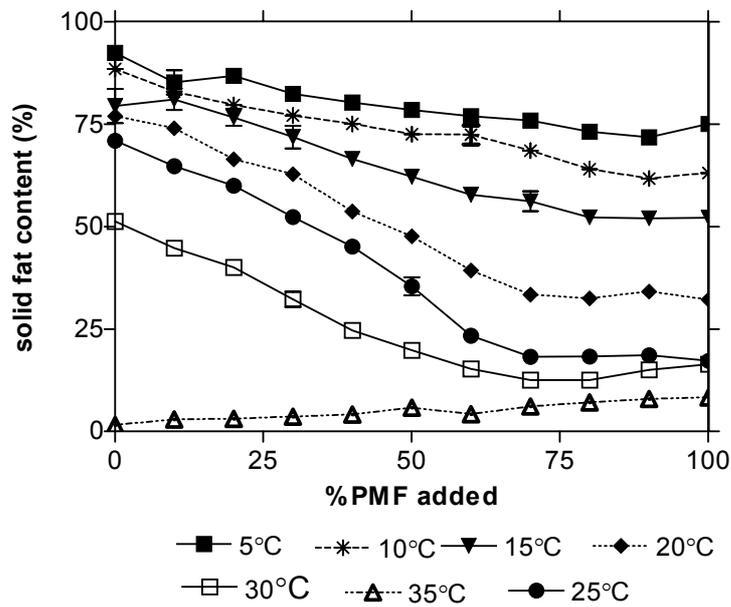


Figure 3. Solid fat content (%SFC) of PMF:DCB blends shows eutectic effects at all crystallization temperatures with addition of PMF.

Table 1. Fatty Acid Composition (FAC) and Slip Melting Point of the blends.

Sample	12:0	16:0	18:0	18:1	SMP
CBE:DCB					
0:100	0.1	34.2	28.0	34.0	26.7
10:90	-	26.5	36.1	32.7	27.0
20:80	-	27.4	35.1	32.9	27.5
40:60	-	28.7	33.4	33.3	25.4
50:50	-	30.2	33.4	33.2	25.3
80:20	-	32.6	29.9	33.5	25.3
100:0	-	25.2	37.4	32.6	24.7
CBS:DCB					
0:100	52.8	10.1	11.3	-	26.7
10:90	6.6	26.1	32.4	29.0	31.8
20:80	11.0	23.3	30.4	26.7	30.2
40:60	21.5	19.8	26.41	18.9	29.2
50:50	27.1	18.5	23.4	15.5	31.6
80:20	44.0	12.9	15.3	5.9	33.8
PMF:DCB					
0:100	0.2	47.4	4.8	36.9	26.7
10:90	-	27.5	33.7	33.1	36.8
20:80	-	29.6	30.5	33.9	36.1
40:60	0.1	34.0	24.0	34.7	34.5
50:50	0.1	36.4	20.8	35.1	32.5
80:20	0.2	42.9	11.1	36.1	30.0

Each value is the means of 3 measurements.

C12:0 Lauric; C14:0 myristic; C16:0 palmitic; C18:0 stearic; C18:1 oleic.

Polymorphic forms

Table 2 shows the polymorphic forms of CBE:DCB, CBS:DCB and PMF:DCB blends at various concentration. The CBE:DCB blends crystallised to form a strong β in a mixture of $\beta + \beta'$ polymorphic form. For CBS:DCB and PMF:DCB blends they crystallised to form a strong β' in a mixture of $\beta + \beta'$ polymorphic forms. This is due to CBS and PMF which are β' tending and crystallized out earlier to dominate the crystallisation process.

Table 2. Polymorphic form of the blends.

Sample ratio (w/w)	Polymorphic form		
	CBE:DCB	CBS:DCB	PMF:DCB
0:100	$\beta + \beta'$ ($\beta > \beta'$)	$\beta + \beta'$ ($\beta > \beta'$)	$\beta + \beta'$ ($\beta > \beta'$)
20:80	$\beta + \beta'$ ($\beta = \beta'$)	β'	$\beta' >>> \beta$
40:60	$\beta + \beta'$ ($\beta >> \beta'$)	β'	$\beta' >>> \beta$
50:50	$\beta + \beta'$ ($\beta >> \beta'$)	β'	$\beta' >>> \beta$
80:20	$\beta + \beta'$ ($\beta = \beta'$)	β'	β'
100:0	$\beta + \beta'$ ($\beta = \beta'$)	β'	β'

DSC melting characteristics

Figure 4 shows the DSC melting thermograms of CBE and cocoa butter (CBE:DCB) blends. There were no changes in terms of their peak maxima ($\pm 19.5^{\circ}\text{C}$) and melting temperature ($\pm 27.5^{\circ}\text{C}$) for all concentrations. Hence, the addition of CBE did not affect the melting behaviour of the cocoa butter which indicated that they are compatible to each other. On the other hand, Figures 5 and 6 show the incompatibility of CBS and PMF with cocoa butter as indicated by the present of two prominent melting peaks at higher concentration. The peak maxima (broader peak) started to change and melted at higher temperatures with the addition of 20% of CBS and PMF into DCB.

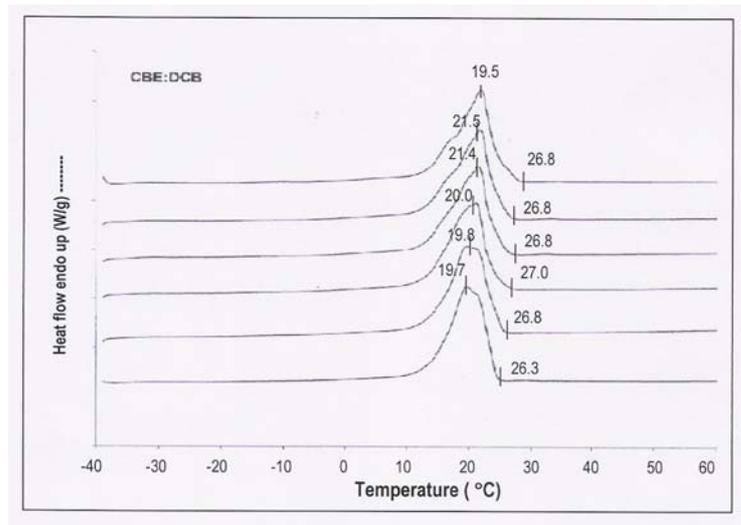


Figure 4. DSC melting characteristics of CBE:DCB blends shows their full compatibility at all ratios.

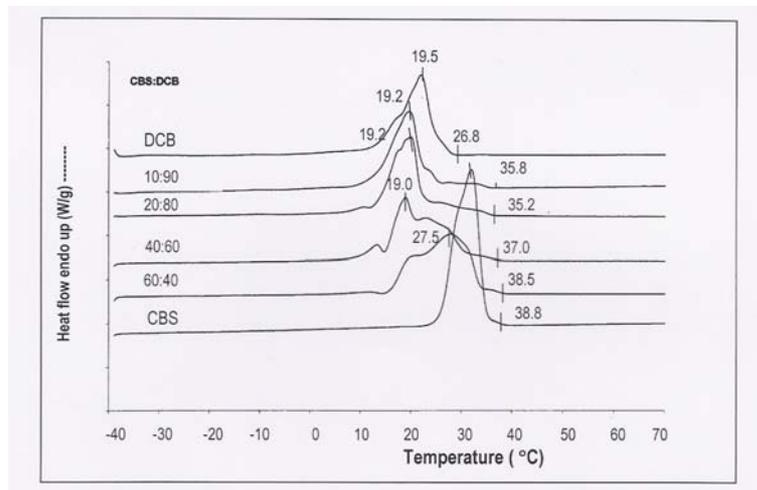


Figure 5. DSC Melting characteristic of CBS:DCB blends, shows their compatibility up to 20% of CBS added.

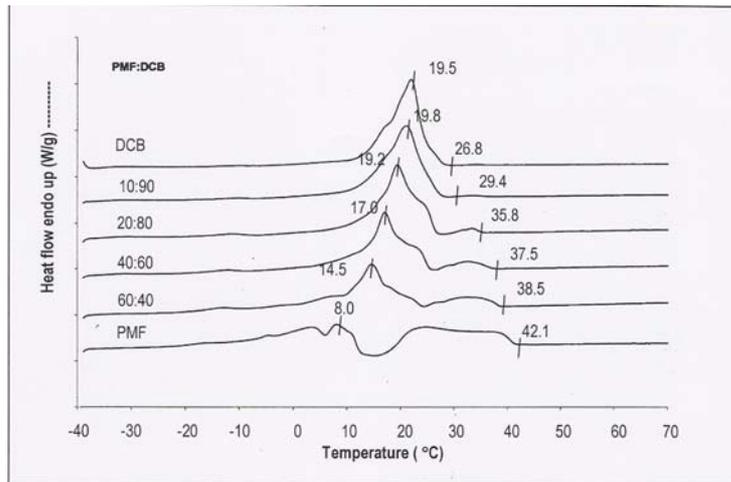


Figure 6. DSC Melting characteristics of PMF:DCB blends, shows their compatibility up to 20% PMF added.

Viscoelasticity

Measurements on rheological properties of CBE (cocoa butter equivalent), PMF (palm-mid fraction) and CBS (cocoa butter substitute) with cocoa butter at 20°C were carried out. Based on the linear viscoelastic region study by oscillatory stress sweep test, the addition of CBS caused the blends (CBS:DCB) to be more elastic by showing a linear relationship at higher shear stress (>2000 Pa) whereas the CBE and PMF blends showed a linear relationship at lower shear stress (<1000 Pa).

Figure 3.6a shows the G' (storage modulus) under oscillatory frequency sweep test at 20°C for the palm-mid fraction, cocoa butter, cocoa butter equivalent and cocoa butter substitute. All the samples were measured at frequencies of 0.1 to 20Hz. The results showed that cocoa butter (DCB) crystal network was the most elastic and highly structured network, followed by those of PMF, CBE and CBS in that order.

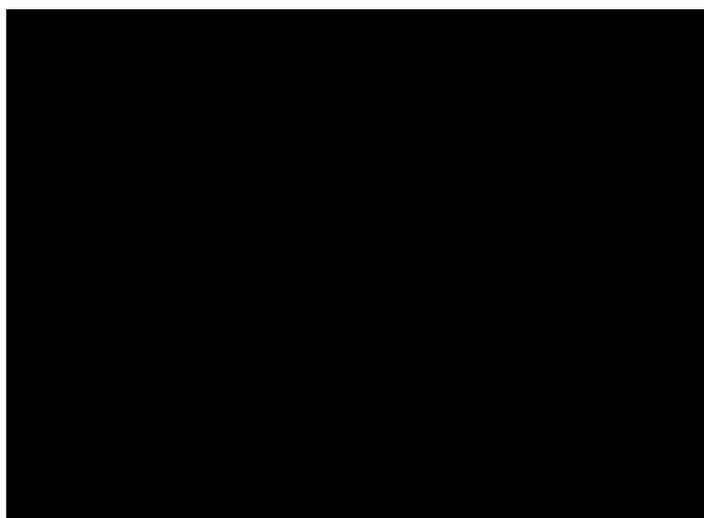


Figure 7. G'(storage modulus) of the original oils before blending at 20°C under oscillatory frequency sweep test.

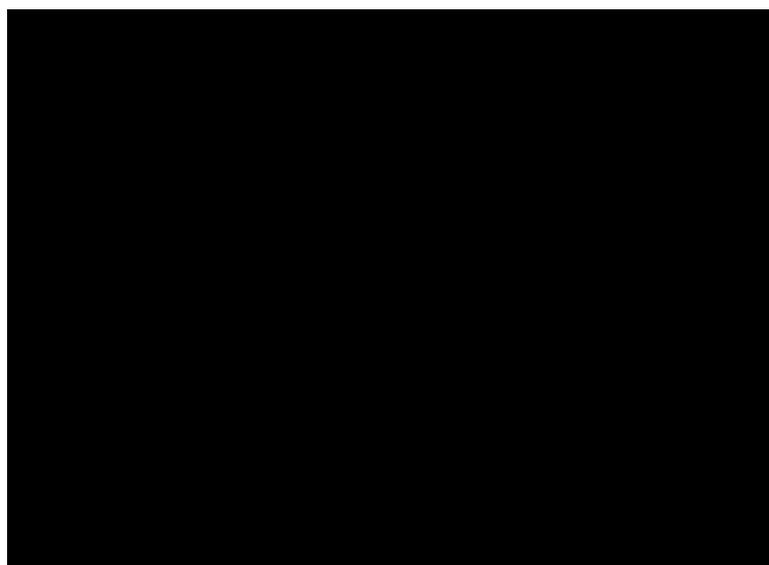


Figure 8. Viscoelasticity of the DCB, CBE and DCB:CBE blend, shows their incompatibility even with 10% CBE added.

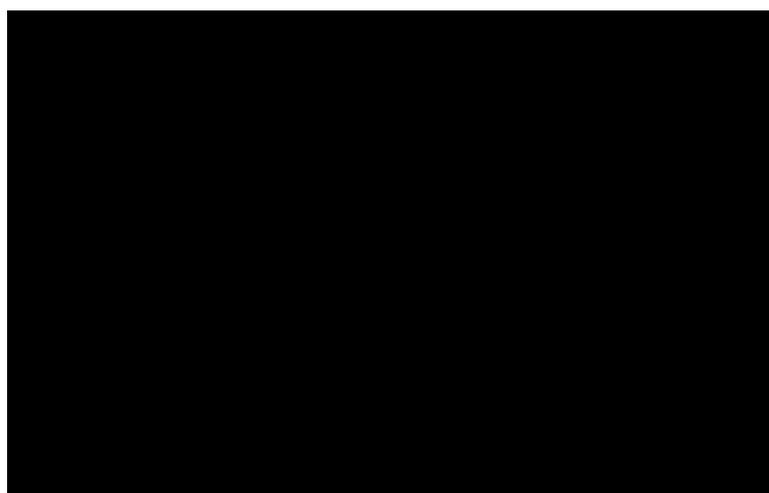


Figure 9. G' (storage modulus) of the PMF:DCB system at 20°C under oscillatory frequency sweep test.

The addition of 10% (wt/wt) of CBE with DCB resulted in an increase in the G' of the blend. This implies that with the addition of 10% CBE into cocoa butter, the blend became more elastic and highly structured compared to the original PMF and DCB samples. Addition of 10% PMF and CBS caused the crystal networks to be less elastic and softer. This could be due to the eutectic effect and agrees with the reduction of solid fat content as shown earlier.

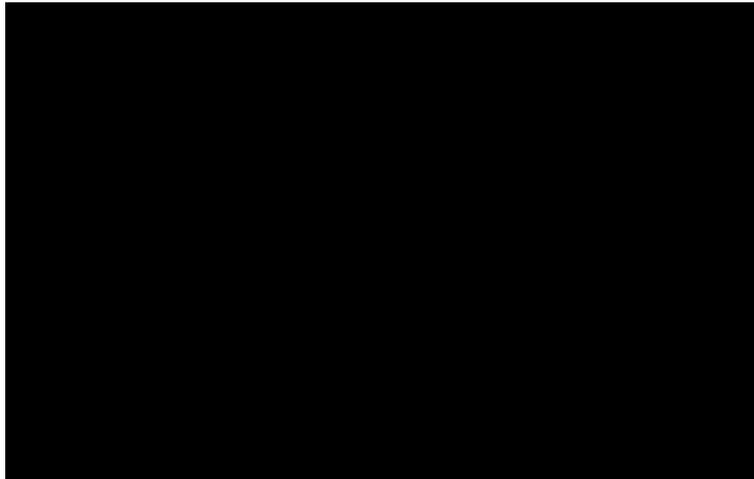


Figure 10. G' (storage modulus) of the CBS-:DCB system at 20°C under oscillatory frequency sweep test.

Viscosity

Figures 11, 12, 13 and 14 show the viscosities of the various samples and blends. The results indicated that blends of CBE and CSB with cocoa butter have higher viscosity than the original CBS and CBE but lower than DCB when measured at a frequency of 20 Hz during the frequency sweep test.

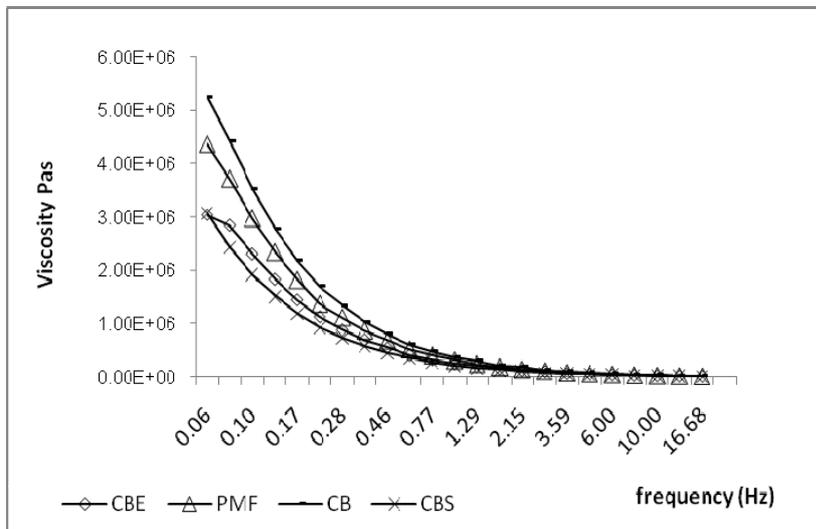


Figure 11. Viscosity (η) of the CBE, CB, PMF and CBS at 20°C under oscillatory frequency sweep test.

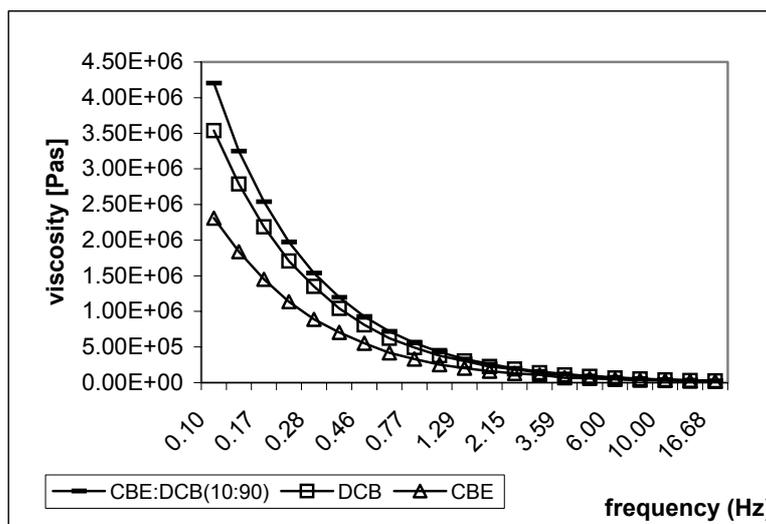


Figure 12. Viscosity (η) of the CBE:DCB system at 20°C under oscillatory frequency sweep test.

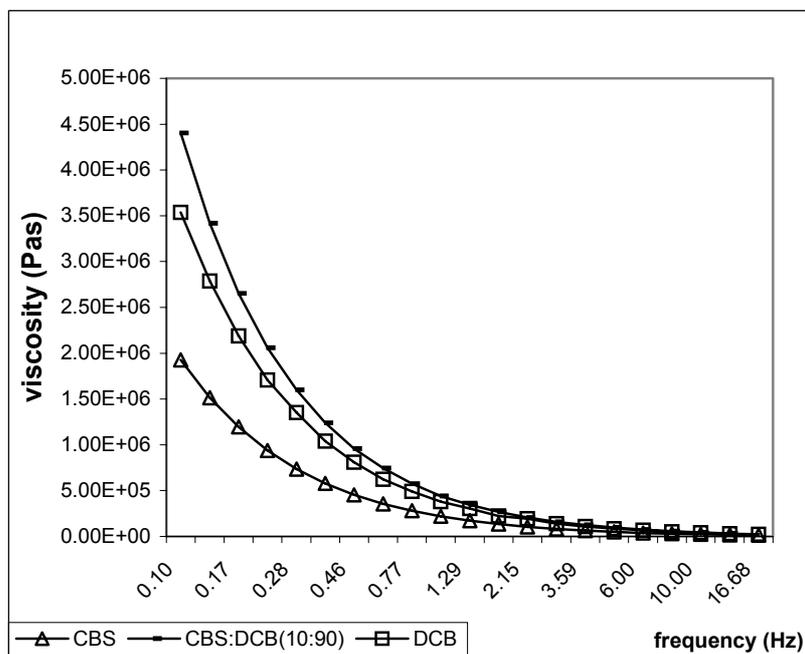


Figure 13. Viscosity (η) of the CBS:DCB system at 20°C under oscillatory frequency sweep test.

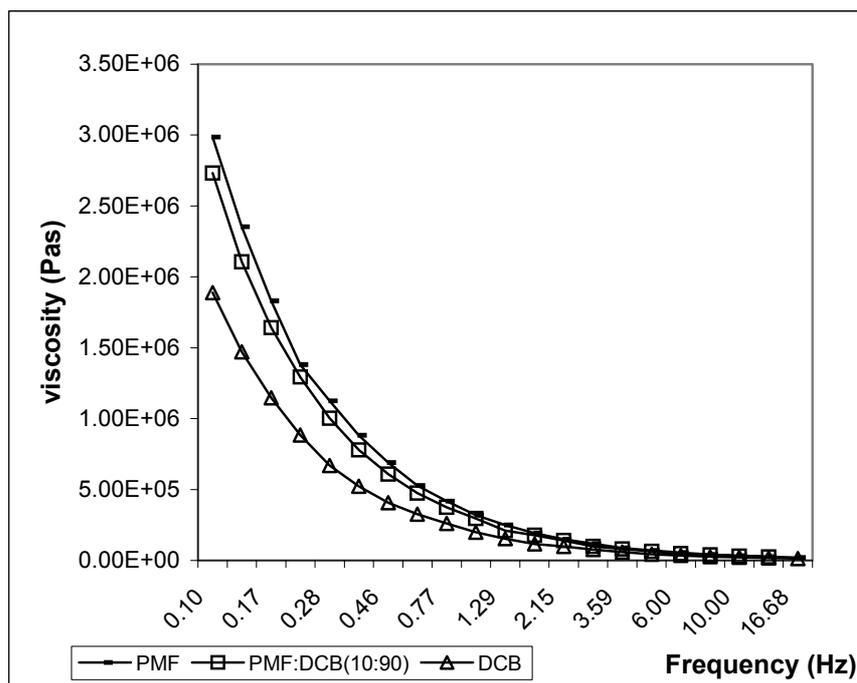


Figure 14. Viscosity (η) of the PMF:DCB system at 20°C under oscillatory frequency sweep test.

Conclusion

Based on this study, CBE was observed to be fully compatible with cocoa butter. Palm mid fraction and CBS was observed to show compatibility up to 20% concentration in the blend. Above such concentration an eutectic behaviour i.e. non-compatibility was evident. Hence for the production of a good chocolate product, PMF and CBS is recommended to be added up 20% only. However, based on the rheological properties, the result showed that the eutectics effects have occurred with 10% CBS and PMF added. Such formulations can be used as winter formulations in temperate countries. Rheological test is an important tool and recommended for investigating structural mechanisms and compatibility study of the cocoa butter and palm products. The better understanding of the complex relationship between the overall rheological, physicochemical properties and concentration of each type of oil and fat in the blends enables the manufacturers to optimize the processing conditions needed to produce high quality and reliable products.

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