LWT - Food Science and Technology 86 (2017) 492–500

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Shea olein based specialty fats: Preparation, characterization and potential application

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ARTICLE INFO

Article history:
Received 30 May 2017
Received in revised form
16 July 2017
Accepted 12 August 2017
Available online 14 August 2017

Keywords:
Shea olein
Crystallization rate
Compatibility
Oil-in-water emulsion

ABSTRACT

To expand low melting point “liquid” base oil categories of plastic fats, the soft fat named SheaOL25 as a byproduct of shea butter with a melting point of 25.5 °C was achieved *via* solvent fractionating of shea butter, and abounded in oleic acid and stearic acid/oleic acid/oleic acid (SOO) type triacylglycerols. The compatibility test with palm-based oil and coconut oil showed the desirable linear relationship of isothermal curve. At temperatures above 25 °C, SheaOL25 exhibits good compatibility and could serve as a blending base oil for preparing specialty fats. Compared with palm olein, blending SheaOL25 and palm stearin can significantly expedite crystallization rate and retard crystallization rate after interesterification, thereby stabilizing the β′ crystal form in the system. Further exploration of SheaOL25 as “liquid” oil in oil-in-water emulsion system revealed that SheaOL25 as the oil phase can significantly improve the system's stability compared with the control groups of soybean oil and palm olein towards maintaining the particle size and emulsion stability under high temperatures.

1. Introduction

Shea has become the second largest natural source of symmetrical stearic-rich triacylglycerols (TAGs) and is increasingly popular as a component of cosmetic formulations and a cocoa butter substitute in the chocolate industry (Alaba, Sani, Mohammed, Abakr, & Daud, 2017; Segman, Wiesman, & Yarmolinsky, 2012). However, only the hard fraction (shea stearin) is utilized by the food industry in past years. Shea olein, a byproduct of shea stearin production, is obtained after the fractionation of shea butter, and proves to be a rich source of bioactive compounds (Lovett, 2015). Depending on the fractionation condition, shea olein with melting points of 25–30 °C can be obtained (Lovett, 2014) and these products hold much potential for applications. Adhikari and Hu (2012) modified the mixtures of rice bran oil, shea olein, and palm stearin by interesterification, and reported that margarine/shortening formulation with shea olein can enhance the whipping properties.

Saturated fat is commonly used in food industry (Co & Marangoni, 2012) but its excessive consumption is considered highly unhealthy. As a consequence, a lot of research efforts have been focused on seeking functional liquid oil as alternatives (Floter, 2012). Particularly, compared with the conventional palm olein (POL) which abounds in palmitinic acid, shea olein is rich in unsaturated fatty acids (USFAs) including stearic acid and oleic acid. Therefore, shea olein, which is a kind of “liquid” oil, could be adopted in the oil-in-water (O/W) emulsion system to reduce saturated fats as a substitute for plastic fats. Xu et al. reported that shea olein based cold soluble powder fats obtained *via* the interesterification of shea olein and palm kernel stearin could be ideal alternative fats to the reduction of saturated TAGs, and shea olein could also be considered as a frying oil and confectionary fats (Xu et al., 2016).

This study aims to prepare shea olein as a functional oil, explore its application in oil blends and oil chemical interesterification (CIE), and analyze its compatibility with traditional palm-based oil (PO) and medium-carbon chain oils. The rate of crystallization was

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http://dx.doi.org/10.1016/j.lwt.2017.08.035
0023-6438/

recorded according to the solid fat content (SFC) method by *p*-NMR. CIE experiments using shea olein were introduced to study the SFC and crystal form changes. Besides, shea olein is used in an O/W emulsion system which was prepared by adding mono stearin emulsifying agent to mixtures of certain oil and water. The formed solid-fat-like product was featured by low contents of saturated fatty acid and fat compared with the existing margarine and shortening. To our knowledge, there is very little published information about the application of shea olein. Therefore, the findings in this work will contribute to the preparation of specialty fats based on shea olein as a new low melting point “liquid” base oil and raise its potential industrial application value.

2. Materials and methods

2.1. Materials

Shea butter, coconut oil (CNO), soybean oil (SBO), palm stearin (PST, Iodine value = 33–35), and palm olein (POL, 24 °C) were provided by PGEO Co., Ltd. (Pasir Gudang, Johor, Malaysia). Sodium methoxide (MeONa), oleic acids, *n*-hexane and acetone (>99.5%) were purchased from Fuyu Chemical Co., Ltd. (Tianjin, China). Sodium stearyl lactate (SSL) and monostearate (MS) were purchased from Danisco (China) Holding Co., Ltd.

2.2. Solvent fractionation of shea butter

300 g Shea butter was melted in a beaker followed by the addition of 1500 mL *n*-hexane. The beaker was put in a thermostatic water bath, and the temperature was set at 25 °C. A mechanical impeller with a plastic paddle rotating at 200 r/min was used to stir the mixture. After 30 min, the mixture was filtered. The solid fat was collected and dried, and the filtrate was concentrated under vacuum to get the liquid oil. The solid fat and the liquid oil were marked as shea stearin (SheaST25) and shea olein (SheaOL25), respectively.

2.3. Chemical interesterification of SheaOL25 with palm-based oil

150 g of SheaOL25 and 150 g PST (or POL) were melted and added in a three-necked round-bottom flask (500 mL), and heated in a thermostatic oil bath, while being stirred at 400 r/min. When the temperature reached 105 °C, 0.9 g MeONa (0.3 wt.% of the oil mass) was added. The reaction was conducted under vacuum (~2000 Pa) for 0.5 h. After reaction, the mixture was cooled, neutralized by citric acid, and then washed by hot water. The interesterified oils was then dried and analyzed by gas chromatography (GC).

2.4. O/W emulsion system preparation

120 mL deionized water (40.0 wt.%) was added in a beaker, immersed and heated to 80 °C in a thermostatic water bath. 18.0 g MS (6.0 wt.%) and 1.5 g SSL (0.5 wt.%) were added to 160.5 g oil phase (53.5 wt.%) as emulsifiers in the other beaker, and then heated to melt. The O/W emulsion system was prepared by adding the melted oil phase to the water dropwise with a high-shear mulser to mix.

2.5. Fatty acid, acylglycerols analysis, and TAGs composition

The composition of fatty acids (FAs) of samples was analyzed as fatty acid methyl esters (FAMEs) by a GC system with a capillary column (CP-Sil88, 100 m × 0.250 mm i.d., 0.2 μm in film thickness, Agilent Technologies Inc., Palo Alto, CA, USA) (Zhang et al., 2015). The glycerolysis products were analyzed by a GC system equipped with a capillary column (DB-1HT, 15 m × 0.25 mm i.d., 0.1 μm in film thickness, Agilent Technologies Inc., Palo Alto, CA, USA). The yields of acylglycerols were expressed as the percent content of the corresponding peak area response compared with the total peak area using a flame ionization detector (Wang, Wang, & Hu, 2011). TAGs compositions of samples were conducted using the above GC with column (Rtx-65TG, 30 m × 0.25 mm i.d., 0.1 μm in film thickness, RESTEK, USA). TAGs composition was analyzed before deacidification and identified using available standard (Adhikari & Hu, 2012). All determinations were performed in three replicates and the means ± standard deviations were reported.

2.6. Characterization of the samples

2.6.1. Solid fat contents (SFC) and crystallization rates

SFC was determined according to the AOCS Official Method Cd 16-81 (AOCS, 2009d) on a Bruker PC/20 Series NMR analyzer, Minispec (Bruker Optics, Milton, On, Canada). Samples were tempered at 60 °C for 30 min, followed by 0 °C for 60 min and finally for 30 min at each temperature of measurement. SFC was measured at intervals of 5 °C from 10 °C up to 40 °C. All determinations were performed in duplicate and the means were reported.

Crystallization rates were measured at intervals of 2 min from 2 min up to 12 min according to the SFC value at 10 °C. The increase rate of SFC value was defined as crystallization rate.

$$\text{Crystallization rate(T)} = \frac{\text{SFC(T)(\%)}}{\text{SFC }(10\,^{\circ}\text{C})(\%)}$$

where SFC (T): SFC value of the melted sample at 10 °C for a certain time, SFC (10 °C): SFC value of the sample at 10 °C.

2.6.2. Compatibility test

The compatibility of dualistic mixtures of SheaOL25 with palm-based oil (PO) which contains 80%POL+20%PST and with coconut oil (CNO) was studied by ΔSFC. *ΔSFC = practical SFC (P-SFC) − theoretical SFC (T-SFC)*, while *T-SFC = SFCx X% + SFCy Y%* which was calculated in computer according to the SFC value of single oil. X%, and Y% were the percentages in mixture total mass of x-oil and y-oil respectively. The closer to zero of ΔSFC, the better compatibility of oil blends. When the ΔSFC value is above zero, blends are monotectic, otherwise eutectic (Willimas, Ransom, & Hartel, 1997).

2.6.3. Melting and crystallization behaviors

A differential scanning calorimetry (DSC) system was used to monitor the melting and crystallization behavior of the products. The exotherm was obtained by holding the samples for 5 min at 80 °C followed by cooling to −40 °C by 5 °C/min. To obtain endotherm, the samples were heated to 80 °C at 5 °C/min (Bouzidi, Boodhoo, Humphrey, & Narine, 2005; Zhang et al., 2015). All determinations were performed in three replicates and the means ± standard deviations were reported.

2.6.4. Crystal structure

Polarized light microscope (PLM) techniques were applied to characterize the structures of crystallization after smeared and 24 h ripening at 20 °C. The products were characterized by X-ray diffraction (XRD) (Cerdeira, Martini, Candal, & Herrera, 2006).

2.6.5. Particle size analysis

A laser particle size analyzer (LS13-320, Beckman Coulter) was used to measure the particle size changes of O/W samples during