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Thermal profiles, crystallization behaviors and microstructure of diacylglycerol-enriched palm oil blends with diacylglycerol-enriched palm olein

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ABSTRACT

To elucidate the possible interaction mechanisms between DAG-enriched oils, this study investigated how mixtures of DAG-enriched palm-based oils influenced the phase behavior, thermal properties, crystallization behaviors and the microstructure in binary fat blends. DAG-enriched palm oil (PO-DAGE) was blended with DAG-enriched palm olein (POL-DAGE) in various percentages (0%, 10%, 30%, 50%, 70%, 90%, 100%). Based on the observation of iso-solid diagram and phase diagram, the binary mixture of PO-DAGE/POL-DAGE showed a better compatibility in comparison with their corresponding original blends. DSC thermal profiles exhibited that the melting and crystallization properties of PO-DAGE/POL-DAGE were distinctively different from corresponding original blends. Crystallization kinetics revealed that PO-DAGE/POL-DAGE blends displayed a rather high crystallization rate and exhibited no spherulitic crystal growth. From the results of polarized light micrographs, PO-DAGE/POL-DAGE blends showed more dense structure with very small needle-like crystals than PO/POL. X-ray diffraction evaluation revealed when POL-DAGE was added in high contents to PO-DAGE, above 30%, β-polymorph dominated, and the mount of β' forms crystals was decreasing.

1. Introduction

In recent decades, studies have indicated that diacylglycerol (DAG) oils are considered as a novel functional lipid. Due to the distinctive molecular structure and metabolic characteristics of DAG in contrast to triacylglycerol (TAG), DAG has been certified to have the functionality to decrease postprandial lipid levels and suppress body fat accumulation, thus it is conducive to inhibiting obesity in spite of providing almost equivalent energy values and similar digestibility compared to TAG (Flickinger & Matsuo, 2003; Taguchi et al., 2000). Moreover, DAG cooking oil is not only confirmed by Ministry of Health and Welfare in Japan, but also classified into "Generally Recognized as Safe" (GRAS) by the Food and Drug Administration. Functional DAG oils containing 80% of DAG commercially produced from soybean oils and canola oils are currently marketed in the USA and Japan (Lo, Tan, Long, Yusoff, & Lai, 2008).

Abundant resources of oils and fats such as rapeseed oil (Danthine & Deroanne, 2003), lard (Cheong, Zhang, Xu, & Xu, 2009) and palm oil (Farmani, Safari, & Hamedi, 2006; de Oliveira, Grimaldi, & Gonalves, 2014) have been applied to produce DAG oils. Lipozyme TLIM is a commercial immobilized lipase manufactured by Novozymes, which is sn-1,3-specific lipase and widely used to catalyze the production of partial glycerides (Yeoh et al., 2014). Palm oil as world leader raw materials and its derivatives palm olein are extensively applied in plastic fats (Aini & Miskandar, 2007). As consumers increasingly pursue healthier food, it is urgently to exploit some healthful palm-based DAG (P-DAG) fat products. So far, although the crucial information available for P-DAG oils was insufficient, they were still attractive not only for their capacity to alleviate obesity, but also for their unique physico-chemical properties suitable for application in plastic fats. Particularly, P-DAG oil has been investigated blending with corresponding original oils and some other oils or fats (Ng et al., 2014; Saberi, Kee, Oi-Ming, & Miskandar, 2011; Saberi, Lai, & Miskandar, 2012). As a hydroxyl group presented in the molecular, P-DAG oil behaved rather differently compared to corresponding palm-based oil, not only in their physico-chemical features such as crystal polymorphism and solid fat content, but also in textural and viscoelastic features (Saberi, Kee, et al., 2011; Xu, Wei, Zhao, Chen, & Dong, 2015). These unique physico-chemistry properties

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could qualify P-DAG oils for utilization in plastic fats, which could provide P-DAG oils with a potential as a fresh parameter for fat modification. Several researches suggested that plastic fats including margarine (Cheong, Tan, Long, Yusoff, & Lai, 2009; Saberi et al., 2012) and bakery shortenings (Cheong, Tan, Long, Affandi Yusoff, & Lai, 2010; Latip et al., 2013) manufactured by P-DAG as the dominant components (more than 40%) in blends with various oils is feasible. And they were found to have desirable textural and viscoelastic properties. Nevertheless, to our best knowledge, literature concerning about interaction between two or more DAG-enriched oils is limited. Hence, further investigation should be conducted to illuminate interaction mechanisms between DAG-enriched oils.

Although P-DAG oils were detected to have broader SFC range and higher slip melting point (SMP) applicable to plastic fats in contrast to their original oils, they were primarily characteristic of β polymorphism undesirable for most plastic fats. Mixing P-DAG oils with their corresponding TAG oils instead of being applied individually probably would be a good solution (Saberi, Kee, et al., 2011), not only providing healthful benefits, but also reducing the production cost. Additionally, oil blending is the simplest and an effective measure for modified oils and fats for certain utilizations. Shortening is a blending of diverse oils/fats. It is critical to illustrate the effect of molecular interaction between DAG-enriched oils for the shortening products application.

This paper was thus to investigate the complicated interaction between DAG-enriched palm-based oils, aiming at exploring how blending of DAG-enriched oils influenced the physico-chemical properties in a solid fat system. In the present study, various ratios of DAG-enriched palm oil (PO-DAGE) and DAG-enriched palm olein (POL-DAGE) mixtures were investigated. We aimed to investigate the phase behavior, crystallization kinetics, thermal behavior and microstructure of DAG as a dominant component in the blends. These informative data will contribute for some approach more applied to discover a suitable interaction mechanism for DAG-enriched blends as well as for application of P-DAG as a functional ingredient to produce DAG-enriched plastic fat in the future.

2. Material and methods

2.1. Materials

Palm oil (PO) and palm olein (POL) were kindly provided by Yihai Jiali Grain and Oil Industry Co., Ltd. (Shanghai, China). Lipozyme TL IM was purchased from Novozymes A/S. All other reagent were analytical grades or chromatographically pure.

2.2. Sample preparation

According to the method of Xu et al. (2015), P-DAG was produced through enzymatic glycerolysis of palm oil (PO) or palm olein (POL) using Lipozyme TL IM in a 1 L scale enzymatic reactor and purified by short path distillation. Purified PO diacylglycerol (PO-DAG) was melted and mixed with PO to obtain DAG-enriched PO (PO-DAGE) with DAG concentration of 50% (wt/wt). Equally, POL-DAGE was prepared by blending purified POL-DAG with POL. All the samples were stored at −18 °C for further evaluation.

2.3. Blend preparation

Mixtures of PO-DAGE and POL-DAGE as well as blends of PO and POL were prepared by entirely melting the samples at 80 °C for 30 min and subsequently mixed in various ratios. The ratios of PO-DAGE/POL-DAGE as well as PO/POL were labeled as follows (wt/wt): A(100:0), B(90:10), C(70:30), D(50:50), E(30:70), F (10:90), G(0:100). All the blends were stored at −18 °C for further evaluation.

2.4. Solid fat content (SFC)

A pulsed nuclear magnetic resonance (pNMR) Oxford Instruments (MQC, Oxford, UK) was applied to measure the SFC values, according to Official Method Cd 16b-93 (AOCS, 1989). The samples (2–3 g) were loaded into NMR tubes and held in a water bath at 85 °C for 30 min, followed by chilling to 0 °C and held for 90 min before measurement. The SFC was determined from 0 to 50 °C (with 5 °C intervals) and equilibrated for 30 min at measurement temperatures prior to determination. Measurement was conducted in triplicates.

2.5. Slip melting point (SMP)

SMP was measured on basis of AOCS Method Cc 1-25 (AOCS, 1993).

2.6. Thermal behavior

The thermal properties of the oil samples were analyzed using TA Q2000 DSC (TA instruments, Delaware, USA). The weighted sample (8–10 mg) was sealed in an aluminum capsule. The crystallization behavior was detected through heating the sample at 80 °C for 8 min and then cooling to −40 °C at 10 °C/min. To analyze melting behavior, the sample was chilled at −40 °C for 8 min, followed by heating to 80 °C at 10 °C/min. Crystallization onset and offset (T_{oc} and T_{fc}), melting onset and offset (T_{om} and T_{fm}), crystallization and melting enthalpy (ΔH_c and ΔH_m) were calculated using TA Universal Analysis software. Determination was repeated three times.

2.7. Isothermal crystallization

Isothermal crystallization of DAG-enriched blends and original blends were conducted through an Oxford pNMR instruments (MQC, Oxford, UK). Each weighted sample (2–3 g) was firstly melted in a water bath at 85 °C for 30 min to entirely eliminate residual crystals, followed by instantly shifting to a water bath at the measurement temperature (T_m) of 10 °C, 15 °C, 20 °C, and 25 °C for isothermal crystallization, respectively. The SFC values were measured at a suitable time interval during 60 min. The obtained data were fitted to the Avrami equation by nonlinear regression to quantify the kinetic parameters (Marangoni, 1998; Singh, Bertoli, Rousset, & Marangoni, 2004). Following is presented the Avrami equation:

$$\frac{F(t)}{F(\infty)} = 1 - \exp^{-kt^n} \quad (1)$$

where $F(t)$ is SFC at time t, $F(\infty)$ is SFC as time approaches infinity. Avrami constant (k) represents crystallization rate and crystal growth mechanism is indicated by Avrami exponent (n).

$t_{1/2}$ is half-time of crystallization, which is calculated on the basis of Eq. (2):

$$(t_{1/2})^n = 0.693/k \quad (2)$$

2.8. Polymorphism analysis

A Bruker D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu Kα radiation (λ = 1.54056 Å) was applied to analyze the polymorphism. The samples were monitored at a 2θ range of