Food Chemistry 214 (2017) 277–284

Contents lists available at ScienceDirect

Food Chemistry

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

Effect of polyglycerol esters additive on palm oil crystallization using focused beam reflectance measurement and differential scanning calorimetry

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ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form 16 June 2016
Accepted 11 July 2016
Available online 12 July 2016

Keywords:
Palm oil crystallization
Polyglycerol esters
Crystal size distribution
FBRM

ABSTRACT

The effect of 0.1–0.7% (w/w) of polyglycerol esters (PGEmix-8) on palm oil crystallization was studied using focused beam reflectance measurement (FBRM) to analyze the in-line changes of crystal size distribution during the crystallization. FBRM results show that 0.1–0.5% (w/w) of PGEmix-8 did not significantly affect nucleation but slightly retarded crystal growth. The use of 0.7% (w/w) additive showed greater heterogeneous nucleation compared to those with lower dosages of additive. Crystal growth was also greatly reduced when using 0.7% (w/w) dosage. The morphological study indicated that the palm oil crystals were smaller and more even in size than when more additive was added. Isothermal crystallization studies using differential scanning calorimetry (DSC) showed increased inhibitory effects on palm oil crystal growth with increasing concentration of PGEmix-8. These results imply that PGEmix-8 is a nucleation enhancing and crystal growth retarding additive in palm oil crystallization at 0.7% (w/w) dosage.

1. Introduction

Palm oil is an edible oil derived from the fruits of the oil palm *Elaeis guineensis*. The physical nature of palm oil which exhibits a semi-solid state in tropical climate, allows its separation as a low melting fraction (olein) and a high melting fraction (stearin) (Deffense, 1985). The quality of the olein fraction depends on the crystallization step, whereas the quality of the stearin fraction depends on both the crystallization and separation steps (Timms, 2005). Therefore, an understanding of crystallization is very important in modifying the fractionation process to ensure good yield and quality of the products. In recent years, fractionation technology has undergone some important improvements (Saw, Chong, & Yeoh, 2015). The developments in palm oil fractionation are mainly focused on areas related to crystallization and solid-liquid separation, i.e. the development of more efficient crystallizers and high-pressure membrane filter presses (Kellens & Hendrix, 2000). These modifications served to reduce utilities consumption, increasing yield and production of higher purity fractions, thereby reducing processing cost.

The use of crystallization enhancers is another interesting area of development in palm oil fractionation. Crystallization enhancers may vary the crystal size distribution of the palm oil slurry, thus affecting the yield and quality of the products. There are numerous publications on the influence of minor components or additives on the physical properties of oils and fats during crystallization (Basso et al., 2010; De Oliveira, Grimaldi, & Goncalves, 2014; Fredrick, Foubert, De Sype, & Dewettinck, 2008; Garbolino, Bartoccini, & Flöter, 2005; Kuriyama, Miyaji, Tamura, Zaliha, & Chong, 2011; Saberi, Lai, & Toro-Vázquez, 2011; Sakamoto et al., 2003; Shimamura, Ueno, Miyamoto, & Sato, 2013; Verstringe, Danthine, Blecker, Depypere, & Dewettinck, 2013). The additives can be categorized into two types: indigenous components and added components (Smith, Bhaggan, Talbot, & van Malssen, 2011). These minor components include free fatty acids (FFA), monoacylglycerols (MAG), diacylglycerols (DAG), and phospholipids, triglycerol monostearate and polyglycerol esters (Smith et al., 2011). These additives may affect crystallization of oils and fats by influencing the nucleation, crystal growth, morphology, heat capacity, rheology and polymorphic stability (Smith et al., 2011).

Jacobsberg and Ho (1976) discussed several factors influencing the crystallization of palm oil whereby palm oil fractionation is adversely affected by the increases in the FFA, DAG content and degree of oxidation. De Oliveira et al. (2014) reported that 6.0–8.5% of DAG increased the initial crystallization rate of palm oil. In contrast to this, Saberi et al. (2011) reported a reduction in the rates of nucleation and crystal growth of palm oil with the

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http://dx.doi.org/10.1016/j.foodchem.2016.07.084
0308-8146/

addition of 5% palm-based DAG. Nonetheless, high concentration (30 and 50%) of DAG have shown a significant reduction in the induction time and an elevated Avrami constant (k), which suggested promoting effects on nucleation and crystallization rates of palm oil (Saberi et al., 2011). These differences could also be influenced by the type and dosage of DAG added, as well as the crystallization conditions. Basso et al. (2010) reported that tripalmitin increases crystallization rate of palm oil and causes the formation of larger crystals. This is because of the crystallization of the tripalmitin itself due to its high concentration in palm oil (Basso et al., 2010). The research paper also pointed out that the addition of MAG led to the formation of a large number of nuclei without changing the final solid content, accelerating the process of crystal formation, leading to the formation of smaller crystals than those found in the refined palm oil (Basso et al., 2010). Verstringe, Dewettinck, Ueno, and Sato (2014) studied the templating effects on crystallization of palm oil with 8% of monopalmitin using synchrotron radiation microbeam. The study found that monopalmitin promoted palm oil crystallization and crystal formation was oriented by the previously crystallized monopalmitin (Verstringe et al., 2014). Most of the research activities involved the use of high concentration of additives of above 5% to achieve a significant effect on crystallization, except Sakamoto et al. (2003), who reported that 1% of polyglycerol behenic acid esters promoted nucleation and inhibited crystal growth of palm oil.

The initial study investigated the effect of low concentrations of polyglycerol esters (PGEmix-8) as the additive for palm oil isothermal crystallization at 24 °C (Kuriyama et al., 2011). The additive was specially designed by Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan) for enhancing palm oil fractionation process. It is made of a mixture of fatty acids of palmitic acid, stearic acid and oleic acid, with a melting point of 42.8 °C (Kuriyama et al., 2011). Preliminary results as reported by Kuriyama et al. (2011) indicated that olein yield was increased with the use of 0.5% of the additive. The study reported that the increase of olein yield was due to better filtration efficiency, caused by more homogeneous crystals formed (Kuriyama et al., 2011). The objectives of this study were to evaluate the role of this additive in palm oil crystallization using FBRM, DSC and optical microscopy, and a possible mechanism of crystallization was predicted based on the data obtained from these techniques. The use of FBRM ensures real time and *in-situ* monitoring of particle characteristics within different physical and chemical processes such as granulation, flocculation, dissolution as well as in agitated crystallization system (Hishamuddin & Omar, 2016), which is very much comparable to the actual crystallization process in fractionation. Moreover, the device is able to detect the onset of nucleation, analyzing the in-line changes in particle dimension, concentration and population (Hishamuddin, Stapley, & Nagy, 2011). The changes in total particle count and mean particle size can be used to describe nucleation and crystal growth, respectively (Yu, Chow, & Tan, 2008).

2. Materials and methods

2.1. Materials

Refined, bleached and deodorized palm oil (RBDPO) was purchased from Moi Foods Malaysia Sdn. Bhd (Selangor, Malaysia). The GRAS graded polyglycerol esters – PGEmix-8 additive was provided by Sakamoto Yakuhin Kogyo Co., Ltd. (Osaka, Japan). It was made of a mixture of fatty acids of palmitic acid, stearic acid and oleic acid, with a melting point of 42.8 °C (Kuriyama et al., 2011).

2.2. Crystal size distribution by FBRM

The changes in chord length distribution of crystals during isothermal crystallization of palm oil and its blends with polyglycerol esters (PGEmix-8) was monitored in a 1 L stirred, jacketed glass Mettler Toledo Labmax reactor equipped with a Lasentec D600L probe (Schwerzenbach, Switzerland). The probe was used to monitor the particle counts and size distribution within the crystallizer.

Low concentrations of PGEmix-8 additive of 0.1, 0.3, 0.5 and 0.7% (w/w) were used in this study. About 700 g of the pre-melted RBDPO and the additive were first loaded into the reactor that was equipped with a glass anchor agitator and stirred at the rate of 30 rpm. The mixture was then heated to 70 °C and held at that temperature for one hour to destroy the entire crystal structures. The melt was then cooled down to 30 °C in one hour and the temperature was further reduced to 24 °C in 20 min. The isothermal crystallization was carried out at 24 °C for 120 min. During the isothermal run, data were collected using a 90 log-channel over the size range of 1–1000 μm. The chord Length distribution of crystals was recorded at every 30 s during the run. Crystal counts were categorized into five classes: 1–5 μm, 10–23 μm, 29–86 μm, 100–251 μm and 293–1000 μm. Each experiment was done in duplicate. The same procedure was conducted for RBDPO crystallization at all additive dosages. The control run was carried out without the addition of the additive.

2.3. Crystal morphology by polarized light microscope

Crystal morphology study of RBDPO and its blends with additives during the isothermal crystallization was conducted using a Leica DMLP polarized light microscope (Wetzlar, Germany). Images were captured and recorded using Leica Qwin V3 imaging system (Cambridge, UK). Samples of the slurries were collected at 20 min intervals during the 120 min isothermal crystallization and images were microscopically captured. A total of 7 samples were collected for each run. A drop of the slurry was placed onto a glass slide and covered with a cover slip. Microscope images were captured at a magnification of 100×.

2.4. Isothermal crystallization by DSC

Isothermal crystallization of RBDPO and its blends with different dosages of PGEmix-8 were performed with a Perkin-Elmer DSC (DSC 8000) equipped with an autosampler. The instrument was calibrated using indium and a temperature programme of 120 °C–180 °C at a rate of 5 °C/min. About 5–10 mg of samples was prepared in a volatile aluminium sample pans. The sample was first heated to 80 °C to erase the previous crystal history. The sample was then cooled at a fast cooling rate of 100 °C/min to the isothermal temperature (24 °C). The sample was held at the isothermal temperature for 90 min and the heat flow during the crystallization was recorded. Peak time was determined using exotherm from zero time until the exotherm reached to a maximum heat flow.

2.5. Statistical analysis

The FBRM data were analyzed using the analysis of variance (one-way ANOVA) to determine the significance of the additive dosages on overall crystal growth rate, total particle count and mean particle size at 5% (w/w) confidence level. Comparisons were made using Dunnett Method, with 0.0% (w/w) as the control. The software used was Minitab 16.2.