

Storage stability studies on interesterified blend-based fast-frozen special fats for oxidative stability, crystallization characteristics and physical properties

Ting-wei Zhu^a, Xia Zhang^{a,b}, Min-hua Zong^a, Robert J. Linhardt^c, Hong Wu^{a,b,*}, Bing Li^{a,b,*}

^a School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, China

^b Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, Guangzhou 510640, China

^c Department of Chemical and Biological Engineering, Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

ARTICLE INFO

Keywords:

Intesterified blend-based fast-frozen special fat
Oxidative stability
Crystallization behavior
Physical property
Constant temperature storage

ABSTRACT

The storage stability of two kinds of interesterified blend-based fast-frozen special fats (PS:SO-IBSF, PS:RO-IBSF) with varied triacylglycerols (TAGs) compositions under different temperatures for 4 weeks was investigated. Rancimat and peroxide values experiments indicated that both IBSFs display good oxidation stability throughout a 4-week storage. As for the physical properties of both IBSFs, the solid fat content and hardness decreased with the increase of storage temperature, and IBSFs still exhibited a viscoelastic solid-like behavior. X-ray diffraction results showed that crystal transformation from β' - to β -form was more serious when stored at 25 °C. The more content of ECN 50-type TAGs in PS:RO-IBSF is helpful to reduce its crystal transformation from β' - to β -form compared to PS:SO-IBSF. On the other hand, storage at 4 °C was beneficial for both IBSFs to keep their crystal network integrity, and the PS:RO-IBSF maintained better quality under the same storage conditions.

1. Introduction

The fast-frozen special fat, which is defined as a type of plastic fat, is extensively applied in the preparation of traditional Chinese fast-frozen foods such as sweet dumpling balls (rice balls) and dumplings, and exhibits a significant role in providing these food products with desirable textural properties (Zhu et al., 2017; Zhu, Weng, Zhang, Wu, & Li, 2018). Conventionally, fast-frozen special fats used in the fast-frozen foods preparation are all-purpose plastic fats, such as margarines and shortenings, which are generally prepared using refined animal and/or vegetable fats and oils, hydrogenated vegetable oil, or their physical blends as a base oil (Zhu et al., 2018). However, these base oils are rich in abundant saturated fatty acids and the granular crystals in the refined animal fat-formulated margarines and shortenings that is related to the β polymorph transformation impairs the consistency, plasticity and mouth-feel of fat products in the applications (Meng et al., 2010). Moreover, trans-fatty acids are inevitably generated in the partial hydrogenation of vegetable oils and the intake of these could increase the

risk of coronary heart diseases (Fernández, Tonetto, Crapiste, & Damiani, 2007). Enzymatic interesterification, one potential alternative in oil and fat modification technology, has already been applied to the preparation of fast-frozen special fats with quite a good quality (Zhu et al., 2017; Pande & Akoh, 2013).

In previous studies, it has been demonstrated that an interesterified blend with a slip melting point (SMP) of 45 °C, prepared by lipozyme TL IM-catalyzed interesterification of palm stearin (PS) and soybean oil (SO), had more β' crystal and wide plastic range, and the resulting interesterified blend-based fast-frozen special fat (IBSF) exhibits good performance in its application for fast-frozen food production (i.e., low cracking rate, better boil-resisting ability and mouth feel) (Zhu et al., 2017). In addition, compared to the corresponding physical blend-based fast-frozen special fat (PBSF), an IBSF stored at 4 °C for 8 weeks still maintained good quality when applied in the preparation of fast frozen sweet dumplings (Zhu et al., 2018). The molecular composition of triacylglycerols (TAGs) has important effects on the crystallization behavior and the crystallization behavior of special fats critically

Abbreviations: PS, palm stearin; SO, soybean oil; RO, rapeseed oil; IBSF, the interesterified blend-based fast-frozen special fat; PS:SO-IBSF, PS:SO 7:3 blend-based IBSF; PS:RO-IBSF, PS:RO 7:3 blend-based IBSF; ECN 50-type TAGs, ECN 48-type TAGs, ECN 42-type TAGs, the equivalent carbon number (ECN) of the TAGs were 50, 48, 42, respectively. (ECN = CN-2DB, where CN is carbon number of triacylglycerol (TAG) and DB is a total number of double bonds in TAG). The TAGs of fat can be separated by HPLC according to its equivalent carbon number (ECN)

* Corresponding authors School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, China.

E-mail addresses: bbhwu@scut.edu.cn (H. Wu), bli@scut.edu.cn (B. Li).

<https://doi.org/10.1016/j.foodchem.2019.125563>

Received 2 March 2019; Received in revised form 26 August 2019; Accepted 17 September 2019

Available online 04 October 2019

0308-8146/ © 2019 Elsevier Ltd. All rights reserved.

influences their physical properties (Brunello, McGauley, & Marangoni, 2003; Martini et al., 2013). The more favorable performance exhibited in IBSF during storage can be attributed to its characteristic TAG composition which is different from PBSF. Albeit the effect of temperature on the crystallization behavior and physical properties of PBSF and IBSF during storage has been investigated, there is few systematic study about the storage behaviors of IBSFs with varied TAGs molecular structure. Additionally, there is also a limited mechanistic insight into the relationship between TAGs and crystallization in IBSFs during storage. Herein, an in-depth understanding of the storage property changes of IBSFs with different specialty TAGs is important and would be helpful in the developing high quality IBSF in various applications.

In the previous studies of fast-frozen special fat, we found that for most interesterified blends of PS and SO (PS:SO), the content of SPP/PSP (P: palmitic; S: stearic) TAG decreased when the SMP decreased from 45 °C to 41 °C, while for most interesterified blends of PS and rapeseed oil (RO) (PS:RO), the POO/OPO (P: palmitic; O: oleic) TAG content increased under the same conditions. The decrease of ECN 42-type (ECN, equivalent carbon number) and ECN 48-type TAGs and the increase of ECN 50-type TAGs, significantly enhanced the formation of β' crystal after interesterification (Zhu et al., 2018). The interesterified blend PS:RO had more β' crystal content than PS:SO due to the different TAGs. However, the property changes between the two IBSFs (PS:SO-IBSF and PS:RO-IBSF) during storage are largely not understood. Therefore, to afford a deeper insight into the storage stability of IBSFs with different TAGs molecular structure, two types of IBSFs (PS:SO-IBSF and PS:RO-IBSF) with 41 °C and 45 °C SMP were chosen in this study. Their oxidative stability, crystallization characteristics and physical properties at different temperature (-20 °C, 4 °C, 25 °C) over 4 weeks of storage were investigated. The oxidative stability was studied by determining peroxide values (POV) index and induction period (IP) index of IBSFs using iodometric procedure method and Rancimat method, respectively. Their relevant physical properties including solid fat content (SFC), hardness and viscoelasticity were monitored through low-resolution pulse nuclear magnetic resonance spectrometer (pNMR), texture analyzer and rheometer, respectively. The crystal polymorphism and crystal microstructure of IBSFs were determined by XRD and polarized light microscopy (PLM), respectively. Finally, the schematic mechanism of microscopic crystalline network of IBSFs during storage was established.

2. Materials and methods

2.1. Materials

Palm stearin (PS) with a SMP of 52 °C (iodine value: 40.6 g I/100 g) was supplied by Shenzhen Jingyi Co. (Shenzhen, China), and soybean oil (SO) and rapeseed oil (RO) were obtained from a local grocery store. Lipozyme TL IM (1,3-specific immobilized lipase, 1130 U/g) was purchased from Novozymes (China) Biotechnology Co., Ltd. (Guangzhou, China). All other reagents and solvents which were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) were of chromatographic grade.

2.2. Preparation of interesterified blend-based fast frozen special fats (IBSFs)

Fig. S1† showed the specific steps for the preparation of IBSF with enzymatic interesterified blend as base oil. First, the enzymatic interesterification was carried out in a self-made fluidized-bed reactor (column length 35 cm, internal diameter 1.2 cm) and 10 g immobilized lipase lipozyme TL IM was added into the internal column. A peristaltic pump was used to feed the substrate mixture of 210 g PS and 90 g RO (PS:RO, 7:3 wt%) or 210 g PS and 90 g SO (PS:SO, 7:3 wt%) into the reactor and the flow rate was controlled at 0.25–8.50 mL/min. The reaction temperature was 60 °C. The blend drained out of the fluidized-

bed reactor was collected. Then, 168 g of the above interesterified blend, 30 g water and 2 g emulsifier (Span-60:trimethylene glycol ester:soybean lecithin 5:3:2, wt. %) was fully mixed at 60 °C and 2000 rpm for 20 min. After that, the resulting mixture was maintained at 40 °C for 10 min, and then kept at -20 °C for 120 min followed by maintaining at 25 °C for 48 h. Finally, the IBSF was obtained and the IBSFs were stored at constant temperature (-20 °C, 4 °C, 25 °C) for 4 weeks, respectively.

2.3. Oxidative stability

Peroxide value (POV): The peroxide value was collected according to the method of iodometric procedure (Tsiaka, Christodouleas, & Calokerinos, 2013).

Induction period (IP): the IP can be measured by using Rancimat (Farhoosh, 2007). The sample was first weighed 3.0 g into the reactor tube of the instrument. The reaction temperature was 120 °C and the airflow rate was 20 L/h.

2.4. Solid fat content (SFC) determination

The SFC was determined by using a low-resolution pulse nuclear magnetic resonance (pNMR) spectrometer (Bruker, Germany) according to AOCS Official method Cd 16b-93 (AOCS, 2004).

2.5. Hardness analysis

A TA.XT-Plus texture analyzer (TA Instrument Inc., U.K.) was used to determine the hardness of the sample. The hardness result was defined by the maximum-recorded force (g).

2.6. Rheological properties

The sample (5 g) was conducted to dynamic oscillatory measurement using a controlled strain rheometer (DISCOVERY, TA Instruments Ltd., Leatherhead, UK). Plate-plate geometry with 20 mm diameter and 2 mm gap was used for the measurement. The amplitude scanning was performed to determine the linear viscoelastic region of the sample to protect the structural integrity of the sample during the measurement process. Amplitude sweeps were performed from 10^{-2} to 10^2 . Stress sweeps were then conducted. Finally, the software and firmware of the instrument was used for outputting the values of storage modulus (G') and loss modulus (G'').

2.7. X-ray diffraction (XRD) spectroscopy

Polymorphisms data was collected by a XRD (D8 Advance, Bruker Ltd., Germany) equipped with Cu KR radiation and a Ni filter (voltage 40 kV; current 40 mA). Then the XRD analysis was obtained by scanning the sample from 10 to 30° (2 θ scale) at a rate of 2.0°/min.

2.8. Polarized light microscopy (PLM)

The morphology of crystallized fat was observed by PLM (Axioskop40pol, Leica, Germany) with Canon A640 digital camera (Canon, Tokyo, Japan) attached. Approximately 50 mg sample was placed on a carrier glass slip and then the cover glass slip was then placed parallel to the plane of the carrier slide. The photomicrograph of the crystal was captured at a 500 \times magnification. Finally, the photomicrograph was imaged at a 500 \times magnification.

2.9. Statistical analysis

All experiments were determined at least in triplicate, and the data were presented as means \pm standard deviations (SD). Statistical analysis was performed using one-way analysis of variance (ANOVA) with

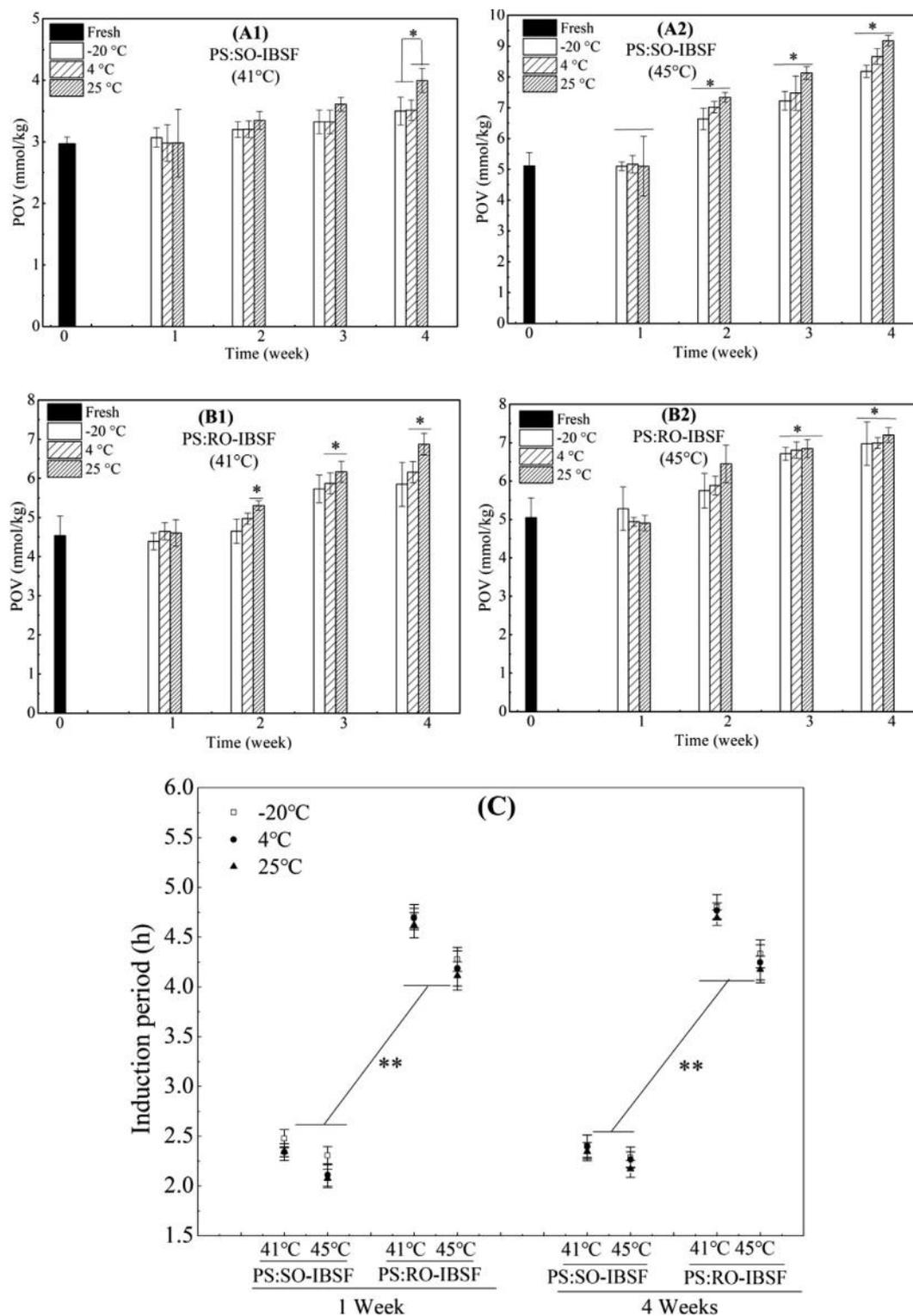


Fig. 1. Oxidative stability of different interesterified blend-based fast-frozen special fats during storage. * $P < 0.05$, ** $P < 0.01$.

Duncan's test. $P < 0.05$ was considered significant.

3. Results and discussion

3.1. Oxidative stability of IBSFs during storage

Two approaches were utilized in this paper to investigate the oxidative stability of IBSFs during storage. Since the most common way of detecting the degree of lipid oxidation is peroxide values (POV) (Tsiaka

et al., 2013), the POVs of IBSFs were firstly examined during storage and the results were showed in Fig. 1. The storage temperature did not have a significant effect on the POV changes of IBSFs ($P > 0.05$). With the increase of storage time (from 1 week to 4 weeks), the POV increased but these values were all less than 10.0 mmol/kg, which corresponds to the safety limit enacted by Codex Alimentarius Commission (CAC). Additionally, the IBSF with 45 °C SMP (Fig. 1(A2, B2)) had higher POV than IBSF with 41 °C SMP (A1, B1) under the same storage conditions. This could be attributed to the different interesterification

degrees. In addition to the POV, the induction (IP) was determined by the Rancimat method to better estimate lipid oxidation (Shim & Lee, 2011). The results were presented in Fig. 1(C). The storage time and storage temperature had no significant effect on the IP of IBSFs, indicating that this storage conditions had little effect on the oxidation stability of IBSFs ($P > 0.05$). The IP of a fat can be used as a parameter to evaluate its antioxidant capacity. The greater the IP value, the more stable a fat (Shim & Lee, 2011). The IP values of PS:SO-IBSF and PS:RO-IBSF were about 2.0 h (45 °C) to 2.5 h (41 °C), about 4.0 h (45 °C) to 5.0 h (41 °C), respectively, indicating that PS:RO-IBSF has better oxidation stability than PS:SO-IBSF and the IBSFs with lower SMP (41 °C) exhibited excellent oxidation stability under the same conditions. This is possibly due to the different base oil used, in which indigenous antioxidants existed in RO. These results were also consistent with the POV results.

3.2. Physical properties of IBSFs during storage

3.2.1. SFC

The SFC could impact the properties of plastic fat including spreadability and oil exudation (Cheong, Tan, Long, Mohdsuria & Lai, 2009). The SFC changes of IBSFs during 4-week of storage were showed in Table 1. It was found that there were no significant changes in the SFC of samples with increased storage time at a given temperature ($P > 0.05$). On the contrary, the SFC decreased with the increase of storage temperature (from -20 °C to 25 °C). After 4 weeks of storage, the SFC values of PS:SO-IBSF and PS:RO-IBSF reduced from approximately 55%-60% to 16%-19%, from 55% to 60% to 13%-16%, respectively, when the storage temperature increased from -20 °C to 25 °C. Obviously, storage at low temperature (≤ 4 °C) would markedly improve the SFC of the IBSFs, which was due to the completely melting of low melting point TAGs and the partly melting of the high melting point TAGs at high temperature (25 °C). A similar phenomenon has also been reported in the previous researches (Meng et al., 2010; Zhang et al. (2014)). Moreover, the value of SFC, more than 10% at room temperature (between 20 °C and 25 °C), is good for preventing oiling off (Lai, Ghazalia, Cho, & Chong, 2000). The SFC values of both IBSFs were about 13–19% even stored at 25 °C, which indicated that the IBSFs

Table 1

SFC of different interesterified blend-based fast-frozen special fats during storage.

Sample	Time (week)	Temperature (°C)		
		25	4	-20
PS:SO- IBSF (41 °C)	0	15.42 ± 0.43 ^b	–	–
	1	15.11 ± 0.22 ^b	41.31 ± 1.11 ^b	52.17 ± 0.63 ^c
	2	16.73 ± 0.17 ^b	42.11 ± 0.58 ^b	55.76 ± 1.03 ^b
	3	15.65 ± 0.31 ^b	42.01 ± 0.32 ^b	55.76 ± 0.18 ^b
PS:SO- IBSF (45 °C)	0	20.93 ± 0.44 ^a	–	–
	1	21.43 ± 0.63 ^a	42.08 ± 1.12 ^b	62.17 ± 1.65 ^a
	2	20.73 ± 0.17 ^a	44.16 ± 1.14 ^a	60.94 ± 0.62 ^a
	3	20.65 ± 0.23 ^c	47.79 ± 1.30 ^a	61.76 ± 1.14 ^a
PS:RO- IBSF (41 °C)	0	12.33 ± 0.21 ^c	–	–
	1	11.77 ± 0.03 ^c	40.07 ± 0.03 ^b	50.06 ± 0.67 ^a
	2	12.45 ± 0.04 ^c	40.66 ± 0.90 ^b	55.72 ± 1.76 ^b
	3	13.65 ± 0.23 ^c	39.79 ± 1.30 ^b	55.70 ± 3.08 ^b
PS:RO- IBSF (45 °C)	0	16.37 ± 0.17 ^b	–	–
	1	16.07 ± 0.03 ^b	45.74 ± 0.91 ^a	57.73 ± 0.26 ^{ab}
	2	16.27 ± 0.02 ^b	45.14 ± 1.73 ^a	60.67 ± 0.75 ^a
	3	16.32 ± 0.06 ^b	44.30 ± 0.87 ^a	59.70 ± 3.08 ^a
	4	16.75 ± 0.08 ^b	44.22 ± 0.31 ^a	59.48 ± 0.47 ^a

Note: The same letter in the individual column indicates no significant difference ($P > 0.05$) between each parameter tested.

still maintained a good consistency after storage.

3.2.2. Hardness

The hardness results of IBSFs during storage were presented in Fig. 2. Under these storage conditions, the hardness of both IBSFs decreased with increased of storage temperature from -20 °C to 25 °C. The reduction in the degree of hardness was about 72.3% to 56.9% when the temperature increased from -20 °C to 4 °C, while the hardness decreased by 90.9% to 75.1% when temperature increased from 4 °C to 25 °C. In addition, the hardness of all IBSFs significantly increased when IBSFs were stored at -20 °C and 4 °C for 4 weeks ($P < 0.05$), but the duration of storage time did not generate significant differences in their hardness when they were stored at 25 °C ($P > 0.05$). These results can be attributed to the occurrence of an aggregated crystal network in fat during storage. When TAGs in fats are exposed to supercooled conditions, the part of crystals are aggregated into a larger crystal aggregate in the crystalline network, which was lead to the hardness changes of fat products (Brunello et al., 2003; Campos, Narine, & Marangoni, 2002). An increase of temperature can lead to the melting and transformation of crystals because of the insufficient supercooling conditions. The varying degrees of destruction in crystalline network structure might result in the decrease of hardness.

Moreover, the hardness has a certain relationship with crystalline structure and crystal size. The plastic fat with completed and compacted crystalline network structure exhibits high hardness values under the same SFC value (Maruyama, Wagh, Gioielli, da Silva, & Martini, 2016; Martini, Suzuki, & Hartel, 2008). Combined with the SFC results, it is suggested that hardness changes are caused by different crystalline networks and the SFC. So, it is necessary to research the crystalline network changes of IBSFs during storage.

3.2.3. Viscoelasticity

Viscoelasticity not only exhibits viscous flow behavior of fat samples, but these also behave somewhat as elastic solids. The viscoelasticity can be expressed in terms of the storage modulus (G'), a measurement of elasticity, and loss modulus (G''), a measurement of viscosity (Cheong, Tan, Long, Affandi Yusoff, & Lai, 2010). The G' and G'' modulus of IBSFs during storage are presented in Fig. S2(a) and Fig. S2(b), respectively.

As shown in Fig. S2(a), the storage time (≤ 4 weeks) had no significant effect on the G' value of IBSFs during storage. On the whole, the G' and the G'' values decreased with the increase of storage temperature and the G' values were decreased by about 1×10^1 times and 1×10^2 times when the storage temperature increased from -20 °C to 4 °C and 4 °C to 25 °C, respectively (Fig. S2†). These behaviors, a typical solid-like behavior, can also be found in other plastic fats, including bakery shortenings and margarine (Bell, Gordon, Jirasubkunakorn, & Smith, 2007). Furthermore, for all IBSFs, the G' values were higher than the G'' values during the storage, showing a more elastic food system, and high G' and low G'' indicated the viscoelastic solid-like behavior (Cheong et al., 2010; Doublier & Durand, 2008). The storage time (≤ 4 weeks) had no effect on the viscoelastic properties of IBSFs. These above results were also consistent with the results of hardness. Moreover, the G' of PS:SO-IBSF was more sensitive to storage temperature than that of PS:RO-IBSF. The results indicated that IBSFs, especially the PS:RO-IBSF, had a stable crystalline network structure under the same storage condition. Therefore, the microscopic crystallization behavior changes of IBSFs during storage were further investigated in the following study.

3.3. Crystallization characteristics of IBSFs during storage

3.3.1. Crystal polymorphism

The crystal polymorphisms can be characterized according to the short spacings by using X-ray diffraction (XRD) and the polymorphisms with the short spacing at near 4.15 Å is for α -form, 4.6 Å is for β -form,

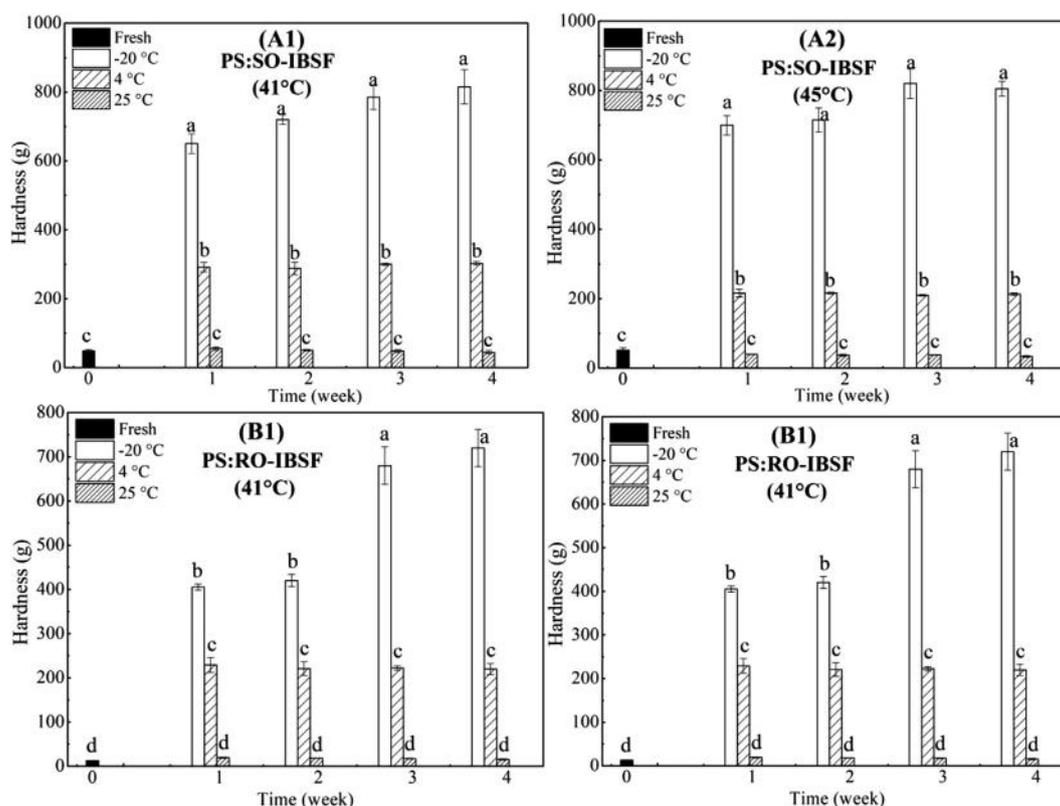


Fig. 2. Hardness of different interesterified blend-based fast-frozen special fats during storage. Different lowercase letters above the column indicate significant difference ($P < 0.05$).

and 3.8 and 4.2 Å is for β' -form, respectively (Deman, 1992; Jennings & Akoh, 2010). In addition, three short spacing at about 3.6, 3.9 and 4.5 Å is for sub- β form (Lee, Akoh, & Lee, 2008; d'Souza, Deman, & Deman, 1990). The crystal polymorphisms of the two IBSFs (PS:SO-IBSF, PS:RO-IBSF) during storage were exhibited in Fig. 3. The peaks at near 4.60 Å, 4.20 Å, and 3.81 Å were appeared in both IBSFs before storage, indicating the concomitance of β' - and β -form in all fresh IBSFs. During the storage, an obvious change was occurred in the short spacing peak of IBSFs during the selected storage temperatures. At low temperature (≤ 4 °C), the peak at 4.2 Å gradually disappeared and the intensity of the peak near 3.8 Å was gradually decreased with the increase of storage time, suggesting the polymorphism transformation from β' - to β -form was occurred and the amount of β -form increased. The crystal transformation from β' - to β -form was more serious in the IBSFs when stored at high temperature (25 °C), which was the reason that the SFC and hardness decreased when IBSFs at 25 °C.

Furthermore, for PS:SO-IBSF, during storage, the transformation rate from β' - to β - crystal became greater when the SMP of the special fat was increased from 41 °C to 45 °C. The possible reason might be their distinct changes of TAGs profiles that more content of SPP/PSP (P: palmitic; S: stearic) was present in the IBSF when its SMP increased from 41 °C to 45 °C (Zhu et al., 2018). For PS:RO-IBSF, there also existed the crystal transformation from β' - to β -form during storage. However, compared to PS:SO-IBSF, the transformation rate from β' - to β -crystal in PS:RO-IBSF was low, which was due to the presence of more β' -crystal in which before storage. In our previous study, it was found that the TAGs composition had notable influence on the crystallization profile of blends, especially the increase of ECN 50-type TAGs would significantly enhance the formation of β' -crystal ($P < 0.05$) (Zhu et al., 2018). Other research also reported that the PLO (P: palmitic, L: linoleic, O: oleic) and PPS (P: palmitic, S: stearic) which belonged to the ECN 50-type TAGs were tended to form β' crystal (Adhikari et al., 2009; Liu et al., 2018). The PS:RO-IBSF had higher content of ECN 50-type TAGs and more β' -form crystal was existed in the PS:RO-IBSF than the PS:SO-

IBSF, suggesting that the more content of ECN 50-type TAGs in PS:RO-IBSF is helpful to reduce its crystal transformation from β' - to β -form. Furthermore, the fatty acids on the ECN 50-type TAGs skeleton tend to form relatively diversified arrangement, which is beneficial for forming the β' -form crystal. It is well known that small β' -crystal could supply good texture and physical properties to the special fats, and the transformation from β' - to β -crystal impairs the consistency and plasticity of special fat (Meng et al., 2010). Therefore, the PS:RO-IBSF could maintain better quality under the same storage conditions.

3.3.2. Microstructure

The size and density of crystals in crystalline network could affect the hardness and viscoelasticity of plastic fats. Therefore, the crystalline network microstructures of IBSFs, during storage, were observed by PLM and the results were showed in Fig. 4. Some significant differences were occurred among the IBSFs during storage including the changes of crystal size, density and crystal morphology. Before storage, in all IBSFs, a large amount of spherical crystals with small size were uniformly appeared in the crystalline network. During the high constant temperature storage (25 °C), for PS:SO-IBSF (Fig. 4(A1, A2)), the crystals with different sizes were evenly distributed in the whole crystalline network even with the increase of storage time (≤ 3 weeks). After 4 weeks of storage, the crystal size increased and some fluffy crystals were appeared. But these different crystals were still uniformly dispersed in the crystalline network and the crystalline network became loose. During the low constant temperature storage (≤ 4 °C), the crystalline network of PS:SO-IBSF showed obvious improvements, especially, when IBSFs was stored at 4 °C, a large number of tight and orderly small crystals were present throughout the crystalline network. Throughout the whole storage process, the destruction levels of storage condition on the crystalline network including the crystal size, shape and distribution showed the following order: 4 °C < -20 °C \ll 25 °C.

In addition, for PS:RO-IBSF, the change rules of crystalline network

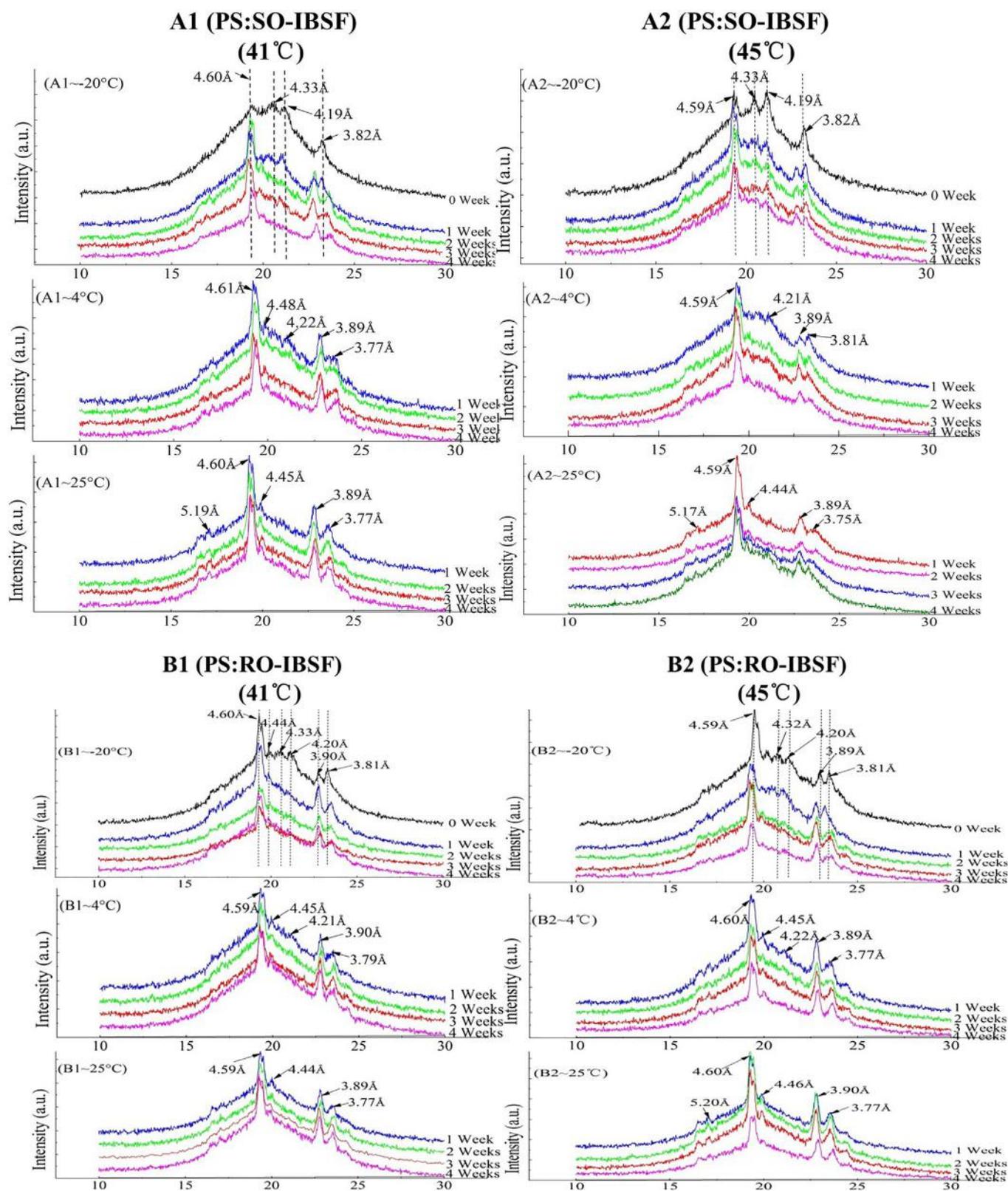


Fig. 3. X-ray diffraction spectra of different interesterified blend-based fast-frozen special fats during storage.

during the storage process were similar with that of the PS:SO-IBSF under the same storage condition. However, compared to PS:SO-IBSF, the crystalline network structure of PS:RO-IBSF was more compact. Meanwhile, the crystal size became larger and these homogeneous crystals were still tightly and uniformly dispersed in the crystalline network. On the whole, for IBSFs, the good uniformity and density of

crystals arranged in the crystalline network showed the following order: $4^{\circ}\text{C} > -20^{\circ}\text{C} \gg 25^{\circ}\text{C}$, PS:RO-IBSF > PS:SO-IBSF. Accordingly, the PLM observation results were also consistent with the hardness results. Crystal size and morphology showed effect on the consistency and acceptability of the plastic fat products (Fauzi, Rashid, & Omar, 2013). Therefore, the IBSFs could keep its good qualities in applications during

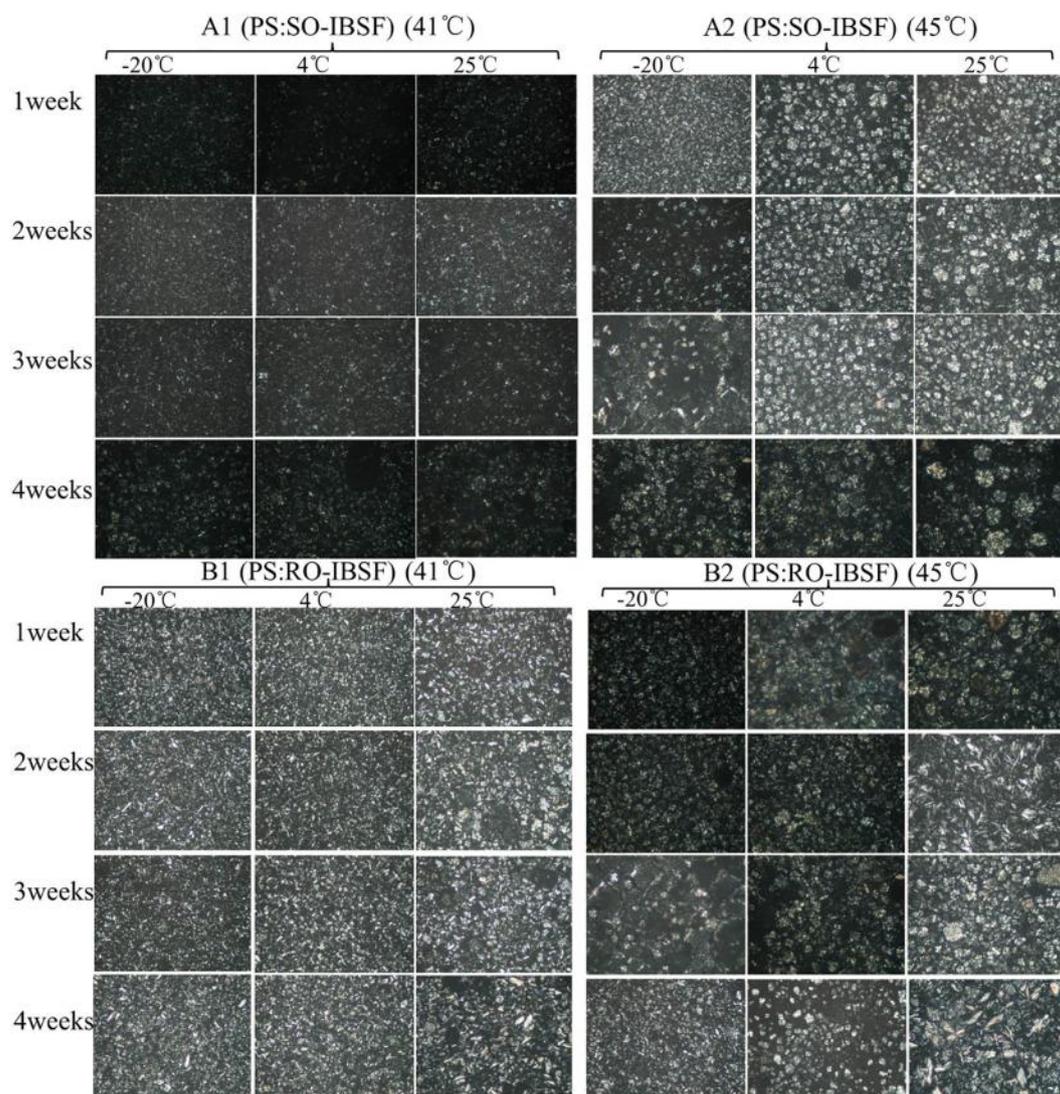


Fig. 4. Polarized light micrographs of different interesterified blend-based fast-frozen special fats during storage.

the low temperature storage (4 °C), in particular PS:RO-IBSF exhibits better properties under the same conditions.

3.4. Schematic mechanism of microscopic crystalline network of IBSF during storage

Based on the changes of crystallization characteristics of IBSFs under constant temperature storage, a schematic mechanism of microscopic crystalline network of IBSFs was prepared (Fig. 5). In the early stages of low temperature storage (−20 °C, 4 °C), some new crystals were formed under super-cooling condition and were dispersed uniformly in the crystalline network without obvious crystal transformation. When IBSFs were stored at a high temperature (25 °C), the crystal polymorphism was partly transformed from β' - to β -form. The distribution of crystals in the crystalline network was loose, and some crystals begin to aggregate at the same time. Some fluffy crystals were appeared in the crystalline network of IBSFs during the anaphase storage (4 weeks). The PS:RO-IBSF had more content of β' -form during the storage and a higher filling degree existed in the crystalline network.

4. Conclusions

Different changes were occurred in PS:SO-IBSF and PS:RO-IBSF during storage, because of their different molecular composition of

TAGs. Both IBSFs still had good oxidative stability after 4 weeks of storage, and the POV of the two kinds of IBSFs were less than 10.0 mmol/kg. The physical properties of PS:SO-IBSF and PS:RO-IBSF showed similar changes during the storage. These were that the SFC values decreased when the temperature increased and storage time (≤ 4 weeks) had no significant effect on SFC. Moreover, the hardness and viscoelasticity results were also consistent with the results of SFC. However, for the two types of IBSFs during storage, the rate of crystal transformation from β' -form to β -form in PS:SO-IBSF was faster than that in PS:RO-IBSF. Furthermore, the good uniformity and density of crystals arranged in the crystalline network after storage showed the following order: 4 °C > −20 °C \gg 25 °C, PS:RO-IBSF > PS:SO-IBSF. These results suggest that PS:RO-IBSF can maintain better quality during the storage, and the storage condition at 4 °C is more suitable for IBSFs keeping its high quality.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

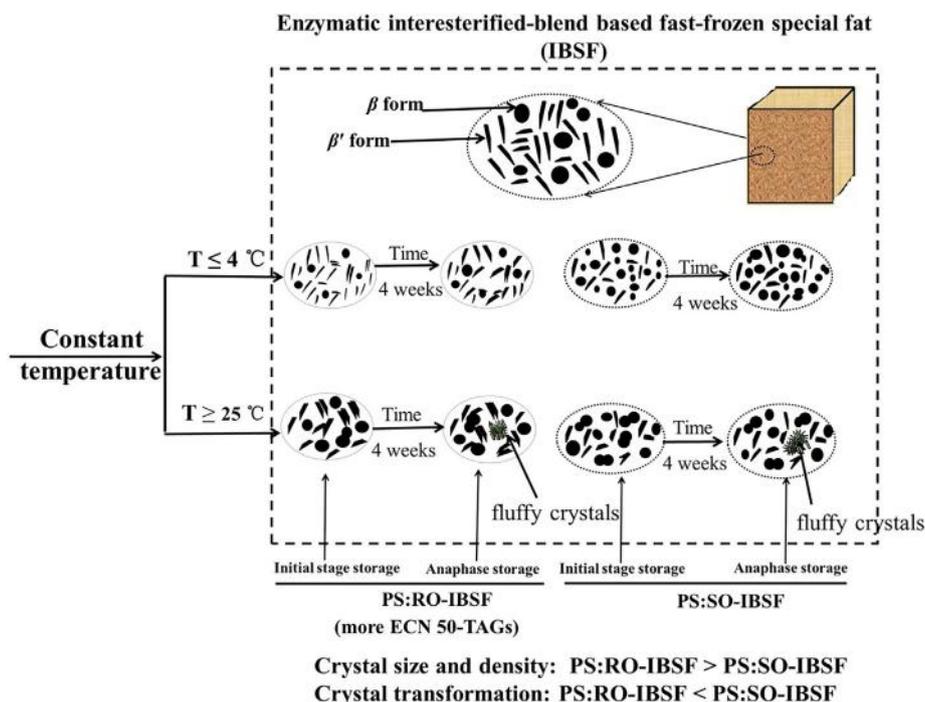


Fig. 5. The possible variation mechanism model of crystallization network in interesterified blend-based fast-frozen special fats during storage.

Acknowledgements

We acknowledge the National Natural Science Foundation of China (NSFC)-Guangdong Joint Foundation Key Project (No. U1501214), the National Natural Science Foundation of China (No. 31671852, 31871758, 31401660) and the Pearl River S&T Nova Program of Guangzhou (No. 201806010144) for financial supports.

References

- Adhikari, P., Shin, J. A., Lee, J. H., Hu, J. N., Hwang, K. T., & Lee, K. T. (2009). Enzymatic production of trans-free hard fat stock from fractionated rice bran oil, fully hydrogenated soybean oil, and conjugated linoleic acid. *Journal of Food Science*, *74*(2), E87–E96.
- AOCS (2004). Official methods and recommended practices of the American oil chemists' society. *American Oil Chemists' Society: Champaign, Cd*, 16b–93.
- Brunello, N., McGauley, S. E., & Marangoni, A. (2003). Mechanical properties of cocoa butter in relation to its crystallization behavior and microstructure. *LWT-Food Science and Technology*, *36*(5), 525–532.
- Bell, A., Gordon, M. H., Jirasubkunakorn, W., & Smith, K. W. (2007). Effects of composition on fat rheology and crystallisation. *Food Chemistry*, *101*(2), 799–805.
- Campos, R., Narine, S. S., & Marangoni, A. G. (2002). Effect of cooling rate on the structure and mechanical properties of milk fat and lard. *Food Research International*, *35*(10), 971–981.
- Cheong, L. Z., Tan, C. P., Long, K., Suria Affandi Yusoff, M., & Lai, O. M. (2009). Physicochemical, textural and viscoelastic properties of palm diacylglycerol bakery margarine during storage. *Journal of the American Oil Chemists' Society*, *86*(8), 723–731.
- Cheong, L. Z., Tan, C. P., Long, K., Affandi Yusoff, M. S., & Lai, O. M. (2010). Physicochemical, textural and viscoelastic properties of palm diacylglycerol bakery shortening during storage. *Journal of the Science of Food and Agriculture*, *90*(13), 2310–2317.
- Doublier, J. L., & Durand, S. (2008). A rheological characterization of semi-solid dairy systems. *Food Chemistry*, *108*(4), 1169–1175.
- Demian, J. M. (1992). X-ray diffraction spectroscopy in the study of fat polymorphism. *Food Research International*, *25*(6), 471–476.
- d'Souza, V., Demian, J. M., & Demian, L. (1990). Short spacings and polymorphic forms of natural and commercial solid fats: A review. *Journal of the American Oil Chemists' Society*, *67*(11), 835–843.
- Farhoosh, R. (2007). Shelf-life prediction of edible fats and oils using Rancimat. *Lipid Technology*, *19*(10), 232–234.
- Fauzi, S. H., Rashid, N. A., & Omar, Z. (2013). Effects of chemical interesterification on the physicochemical, microstructural and thermal properties of palm stearin, palm kernel oil and soybean oil blends. *Food Chemistry*, *137*(1–4), 8–17.
- Fernández, M. B., Tonetto, G. M., Crapiste, G. H., & Damiani, D. E. (2007). Revisiting the hydrogenation of sunflower oil over a Ni catalyst. *Journal of Food Engineering*, *82*(2), 199–208.
- Jennings, B. H., & Akoh, C. C. (2010). Trans-free plastic shortenings prepared with palm stearin and rice bran oil structured lipid. *Journal of the American Oil Chemists' Society*, *87*(4), 411–417.
- Laia, O. M., Ghazalia, H. M., Cho, F., & Chong, C. L. (2000). Physical and textural properties of an experimental table margarine prepared from lipase-catalysed trans-esterified palm stearin: Palm kernel olein mixture during storage. *Food Chemistry*, *71*(2), 173–179.
- Lee, J. H., Akoh, C. C., & Lee, K. T. (2008). Physical properties of trans-free bakery shortening produced by lipase-catalyzed interesterification. *Journal of the American Oil Chemists' Society*, *85*(1), 1–11.
- Liu, C., Meng, Z., Cao, P., Jiang, J., Liang, X., Piatko, M., ... Liu, Y. (2018). Visualized phase behavior of binary blends of coconut oil and palm stearin. *Food Chemistry*, *266*, 66–72.
- Martini, S., Cardona, J. R., Ye, Y., Tan, C. Y., Candal, R. J., & Herrera, M. L. (2013). Crystallization behavior of high-oleic high-stearic sunflower oil stearins under dynamic and static conditions. *Journal of the American Oil Chemists' Society*, *90*(12), 1773–1786.
- Maruyama, J. M., Wagh, A., Gioielli, L. A., da Silva, R. C., & Martini, S. (2016). Effects of high intensity ultrasound and emulsifiers on crystallization behavior of coconut oil and palm olein. *Food Research International*, *86*, 54–63.
- Martini, S., Suzuki, A. H., & Hartel, R. W. (2008). Effect of high intensity ultrasound on crystallization behavior of anhydrous milk fat. *Journal of the American Oil Chemists' Society*, *85*(7), 621–628.
- Meng, Z., Liu, Y. F., Jin, Q. Z., Huang, J. H., Song, Z. H., Wang, F. Y., & Wang, X. G. (2010). Characterization of graininess formed in all beef tallow-based shortening. *Journal of Agricultural and Food Chemistry*, *58*(21), 11463–11470.
- Pande, G., & Akoh, C. C. (2013). Enzymatic synthesis of trans-free structured margarine fat analogs with high stearate soybean oil and palm stearin and their characterization. *LWT-Food Science and Technology*, *50*(1), 232–239.
- Shim, S. D., & Lee, S. J. (2011). Shelf-life prediction of perilla oil by considering the induction period of lipid oxidation. *European Journal of Lipid Science and Technology*, *113*(7), 904–909.
- Tsiaka, T., Christodouleas, D. C., & Calokerinos, A. C. (2013). Development of a chemiluminescent method for the evaluation of total hydroperoxide content of edible oils. *Food Research International*, *54*(2), 2069–2074.
- Zhu, T. W., Zhao, Y. L., Zong, M. H., Li, B., Zhang, X., & Wu, H. (2017). Improvement of physical properties of palm stearin and soybean oil blends by enzymatic interesterification and their application in fast frozen food. *RSC Advances*, *7*(55), 34435–34441.
- Zhu, T. W., Weng, H. T., Zhang, X., Wu, H., & Li, B. (2018). Mechanistic insight into the relationship between triacylglycerol and crystallization of lipase-catalyzed interesterified blend of palm stearin and vegetable oil. *Food Chemistry*, *260*, 306–316.
- Zhang, X., Li, L., Xie, H., Liang, Z., Su, J., Liu, G., & Li, B. (2014). Effect of temperature on the crystalline form and fat crystal network of two model palm oil-based shortenings during storage. *Food and Bioprocess Technology*, *7*(3), 887–900.