CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106174

Physicochemical Properties and Crystallisation Behaviour of Fat Blends for a Margarine Formulation

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This study aimed to investigate the physicochemical properties and crystallisation behaviour of fat blend to obtain a stable formulation of margarine. Liquefied palm oil (PO), palm stearin (PS) and palm kernel oil (PK) were mixed in four different ratios and the properties were analysed based on physicochemical properties (fatty acid composition, solid fat content (SFC) and slip melting point (SMP) and crystallisation behaviour as compared to a commercial margarine. The percentages of fatty acid (FA) composition were varied depending on the variation of type of fat and percentage of fat added. The result showed that PO:PS:PK blends of 70:10:20 gave the closest SMP (39 °C) with commercial margarine followed by 72:8:20, 75:5:20 and 70:15:15. SFC of 72:8:20 and 70:10:20 blends showed the closest to commercial margarine in the temperature range of 20–35 °C. The SFC percentage decreased significantly between 20–25 °C. From the crystallisation behavior, 70:10:20 and 70:15:15 showed the closest behaviour with commercial margarine. From the result, the blend with ratio of 70:10:20 was the most suitable fat basis formulation as it has the most similar properties and behaviour with commercial margarine. This formulation can be used as the basis for a stable margarine formulation with addition of anthocyanins from plant-based extract such as roselle extract.

1. Introduction

Margarine is a food consists of fatty acid that has similar appearance, nature and composition with butter. It is an emulsion which consists of a mixture of liquid and oil and crystalline fat (Fomuso and Akoh, 2001) which is formed by a matrix of three-dimensional fat crystals or crystal aggregates. Commonly vegetable oils are used to produce margarine with the required characteristics (Pande et al., 2013). Production of margarines is mainly using partial hydrogenation process that turns liquid oils into solid fats for application in margarines. This solidification process produces trans fatty acids (TFA) as part of the products which is a type of unsaturated fat that have double bond in the chain. High consumption of TFA may cause increased in low-density lipoprotein (LDL), decreased in high-density lipoprotein (HDL), and increased in total HDL cholesterol (Mozaffarian and Clarke, 2009) and may triggered cancer (Michels et al., 2021). The increasing awareness towards the implication of TFA motivates many government health agencies globally to minimise the amount of trans-fats in food intake. US Food and Drug Administration has recommended that saturated fatty acid content in food should be less than 33 % and TFA of less than 1 % (Food and Drug Administration, 2022).

One of the main factors in formulation of margarine is the ratio of solid to liquid at a desirable amount, type of oil used achieved by hydrogenation and blending, type of process used in blending and crystallisation process and parameter control such as temperature, pH and time for blending and crystallise. Margarine oil phase is a

Paper Received: 05 March 2023; Revised: 25 July 2023; Accepted: 11 October 2023
Please cite this article as: Sahat N.S., Jusoh Y.M.M., Hashim Z., Muhamad I.I., Dailin D.J., Zainol N., Nor N.F.A., Kassim A.S.M., Zaidel D.N.A., 2023, Physicochemical Properties and Crystallisation Behaviour of Fat Blends for a Margarine Formulation, Chemical Engineering Transactions, 106, 1039-1044 DOI:10.3303/CET23106174

blend between vegetable oil and fat or it can also be blends of edible oils and hard stock fat such as palm oil and palm stearin. Palm oil (PO) is a commonly used in margarines and shortenings as hard stock due to its properties that produce plasticity, body, and mouthfeel (Podchong et al., 2018). Palm stearin (PS) is collected by crystallisation of PO under controlled conditions and mainly consists of solid fat (Ming et al., 1999) while palm olein is the liquid fraction of PO. The PS contains palmitic acid (47–74 %), oleic acid (16–37 %), stearic acid (4–6 %), linoleic acid (3–10 %) and myristic acid (1–2 %) (Tang and Pantzaris, 2009). PS is a good source of a hard fat component for food products for example margarine and shortening since it has slip melting point (SMP) range between 44 and 56 °C. In order to produce low-trans hard fat that is used for shortenings, stick or tub-type margarines, PS can be added to the formulation at a certain amount to inter-esterified fats to improve product stability and meltability (Podchong et al., 2018). Saadi et al. (2012) has reported that binary fat blends of margarine using ratio of PO%: PS% (wt/wt) formed smoother emulsions with higher PO content compared to lower PO content. The margarine with higher PO content showed low workability force and more frail network structure.

Palm Kernel Oil (PK) is a fat produced from the kernel of the fruit of the oil palm by mechanical expression or solvent extraction. Addition of palm kernel oil influences many properties of the fat blend. Margarine fat blends have to be formulated with adequate solids content of hard stock fat. This condition is crucial to produce a margarine that is suitable for application as stick margarine and tub margarine for table spread. However, the solid content should be reserved at a low percentage to provide a smooth, easy spreadability on bread when user want to use the margarine directly from refrigerator. POs are normally blended with PK or palm kernel olein (PKO) to improve solid fat content profile and margarine stability (Dian et al., 2017). Margarines should melt easily at body temperature (37 °C) to have smooth feeling in the mouth and less stickiness. Palm kernel oil was chosen to provide a good-oral melt-down at 37 °C and produce a wide range of fatty acid especially short chain fatty acid. Palmitic acid content (C16:0) is another factor that must be taken into consideration in the formulation of margarine, which influence the crystal stability of the final margarine. The ratios between these different types of fat are important to produce margarine with high quality in terms of the physical and chemical properties. The objective of this study was to investigate the physicochemical properties and crystallisation behaviour of fat blend consists of different ratios of PO, PS and PK to obtain a good formulation of margarine. In this study, a commercial margarine is used as the comparison for the good formulation of margarine.

2. Materials and methods

2.1 Materials and chemicals

Food grade refined, bleached and deodorized palm oil (PO), palm stearin (PS) and palm kernel oil (PK) were kindly provided by Sime Darby Research Centre Sdn. Bhd. Distilled monoglyceride and butter flavouring were from Matrix Oleochem Sdn. Bhd. All reagents and solvents are of either HPLC or analytical grade. Planta was bought at a local supermarket and used as a commercial margarine.

2.2 Preparation of fat blend

The fat blend was formulated referring to Ming et al. (1999) with slight modification. Ming et al. (1999) only used palm stearin and sunflower oil or oil blend whereas three types of fat were used in this study. Liquefied PS, PO and PK were mixed in four different ratios according to Table 1 (according to mass ratio). The margarine was prepared according to Zaidel et al. (2017). The water and fats were separately heated to 60 °C. The water and fats were mixed vigorously for 60 min using a table top homogenizer (Ultra-Turrax T-25).

Table 1: Fat blend in mass ratio

Blend	PO (%)	PS (%)	PK (%)
1 (OSK701515)	70	15	15
2 (OSK75520)	75	5	20
3 (OSK72820)	72	8	20
4 (OSK701020)	70	10	20

2.3 Analysis of fatty acid composition

Fatty acid (FA) composition of the primary fats and the fat blends was performed following Zaidel et al. (2017) with modification using an analytical gas chromatograph Clarus 500 (Perkin–Elmer, USA) coupled with an Supelco, capillary column (30 m × 0.25 mm id; 0.25 μm film thicknesses). 50 mg sample was taken from the blend system, and was melted and weighed out individually. Hexane (950 μL) and methoxide solvent (50 μL) were added to the sample. The solution was shaken by using vortex mixer and left to stand for 5 min. The top layer of the solution was taken carefully (about 1 µL) and injected manually at 20 °C. The compositions of FAs were identified and quantified by using the TAG standards retention time as the reference (St. Louis, MO, USA).

2.4 Analysis of solid fat content

Analysis of SFC was performed following the method by Zaidel et al. (2017) for the primary fats and fat blends. The sample was tempered for 30 min at 70 °C, followed by chilling for 90 min at 0 °C. The chilled sample was kept at the desired temperatures (20, 25, 30 and 35 °C) for 30 min prior to measurements.

2.5 Analysis of slip melting point

SMP was determined for the primary fats and fat blends according to a standard method (ISO International Standard, 2002). The capillary tubes were placed in cold water. It was heated at 0.5°C/min until the level of the fat rises in the capillary tube. The melting temperature was measured.

2.6 Measurement of crystallisation behaviour

SFC was measured at various time from 1 min until 3,600 min. A graph of crystallisation behaviour of the fat blends was plotted using Microsoft Excel from the data of SFC against time.

3. Results and discussion

3.1 Fatty acids composition

FA composition of the primary fats (PO, PS and PK) are shown in Table 2. PO has a high content of palmitic acid (C16) which was about 45 % and oleic acid (C18:1) about 38 %. High amounts of palmitic acids help to impart the β’ crystal formation. Fats containing mainly β’ crystals promote a smooth, continuous and homogeneous texture and mouthfeel to margarines whereas β crystals promote grainy texture (Nguyen et al., 2020). β’ crystals are relatively small crystals which enhances the ability to incorporate in the crystal network with large amount of liquid oil. No trans-fatty acids were detected. PS has a higher content of palmitic acid (C16) than PO which was about 57% and oleic acid slightly lower than PO (29.8 %). The high content of palmitic acids also noted to contributes in formation of smooth texture. The major FA in PK were lauric acids (61.7%) and myristic acids (12.6%). Both of these FA are saturated fatty acid and have a shorter chain length.

Table 2: Fatty acid compositions of palm oil, palm stearin and palm kernel oil

Fatty acid / Fat	C12	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	C20
PO	0.722	1.835	45.368	0.272	3.378	38.540	9.136	0.323	0.292
PS	0.313	1.434	57.171	0.129	4.601	29.879	5.823	0.234	0.360
PK	61.729	12.643	4.200	0.011	0.739	5.683	0.982	0.032	0.030

Figure 1 shows the FA composition of the blend that consist of PO, PS and PK. The percentages of FA composition were varied followed with the variation of type of fat and percentage of fat added. These values of FA were within the ranges as reported in previous study (Podchong et al., 2018). PK were added in the blend as it contains high C12 and C14 to imitate the high percentage of C12 and C14 in Planta. PK also helps to provide shiny texture to the margarine. However due to economical and availability factors, the addition of PK was restricted to 20 % maximum. The percentage of PO added was higher as PO consists of balanced FA composition and addition of excessive PS may lead to β crystal tending (Podchong et al., 2018). Blend OSK75520, OSK72820 and OSK701020 showed the closest C12 percentage with Planta which was 15.051 %. For the percentage of C16 and C18:1, OSK75520 and OSK701020 have the closest percentage with Planta which was 33.554 % and 30.779 %. The percentage of C12 and C14 of all four blends increase drastically and closer with Planta. The percentage of C16 and C18:1 gradually decreased as the portion of PO and PS decreased. Addition of PK affected all range of FA of the blends because it contains high percentage of short FA.

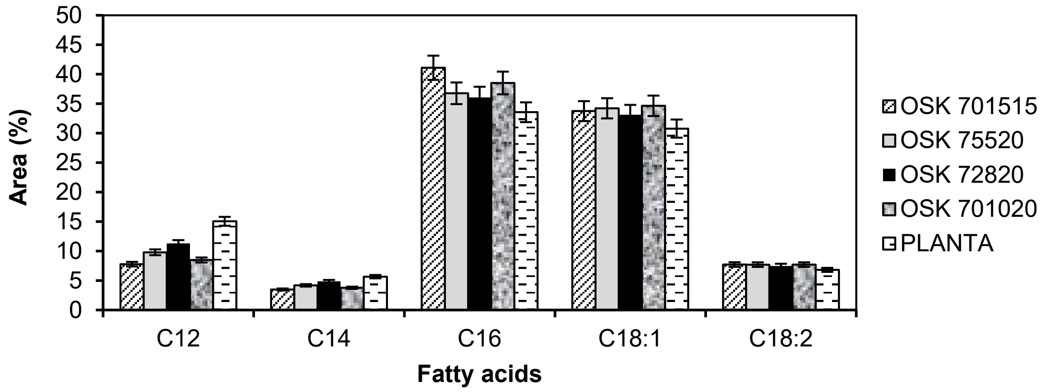

Figure 1: Fatty acid compositions of fat blends in comparison to Planta

3.2 Solid fat content

Figure 2 shows the SFC analysis for the primary fats and the four fat blends. The values of SFC below 25°C indicate the product's hardness and values between 25 and 30°C show the heat resistance properties. In between 27 to 33°C, the product melts which create a cooling sensation in the mouth and flavour releasing (Torbica et al. 2016). PS has high solid fat content percentage (68% at 25 ºC and 25% at 35 ºC). This indicates that PS is a hard fat. PS is helpful in providing structure and strength to the margarines and helps to prevent margarines from melting whenever there are fluctuations of temperatures during handling and storage by maintaining the products' structure and shape (Podchong et al., 2018). PO starts with lower solid fat content percentage at 25 ºC which is about 30% and gradually decreased to 5% at 35 ºC. PO presented naturally as semi-solid at ambient room due to the balanced FA composition presents (Dian et al., 2017). The amounts of unsaturated and saturated FAs are in equal amount in PO. PK has different characteristics of solid fat content which is completely melt at 30 °C, which influenced the SFC of the blends. The SFC percentage of the four blends decreases drastically from 20 to 25 °C. This could be because at this temperature range the larger proportion of TGs liquefy (Ming et al., 1999). Out of the four blends, OSK72820 and OSK701020 showed the closest SFC percentages with Planta. Mixture containing palm kernel oil contributes to higher percentages of short chain fatty acids for instances lauric acid (C12) and myristic acid (C14) hence blends prepared will melt completely at low temperature. It has been reported that SFC of a margarine should be approximately 15–35 % at 25 °C, for desired texture and spreadability and it should be more than 10 % at 20 °C for a better stability and to avoid separation of oil (Rao et al., 2001).

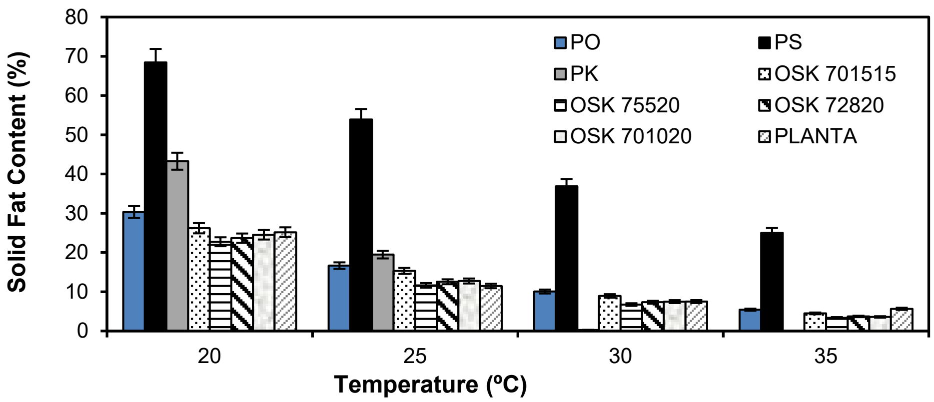

Figure 2: Solid fat content analysis of the fat and four fat blends at different temperatures

3.3 Slip melting point

Figure 3 shows the SMP analysis of the primary fats and the four tertiary blends and Planta. PS shows the highest slip melting point at about 51 ºC. Melting temperatures are influenced by the FA chain length and the number of unsaturated bonds in the FAs. As PS is mainly composed by palmitic acids, it contributes to the high melting temperature. PO showed high SMP at approximately 42 ºC which is also due to high amount of palmitic acid. PK shows the lowest slip melting point at about 28 ºC since PK contains mainly short chain length compared to PO and PS. This result showed that the shorter the fatty acid, the lower the melting temperature. The result of OSK701020 showed the closest SMP point with Planta followed by OSK72820 and OSK701515 and lastly OSK701515. The SMPs were varied depend on the degree of saturation of fatty acid content in the mixture. Margarines undergone a conversion from the β' to the β-form. The formation of β-form crystals that has a firmer structure due to higher SMP indicates stronger formation of crystal network (Nguyen et al., 2020). The standard range for melting point of margarine are between 28 and 34 °C in order for the margarine to be firm at room temperature for good spread-ability and melt rapidly in the mouth (Zaidel et al. 2017).

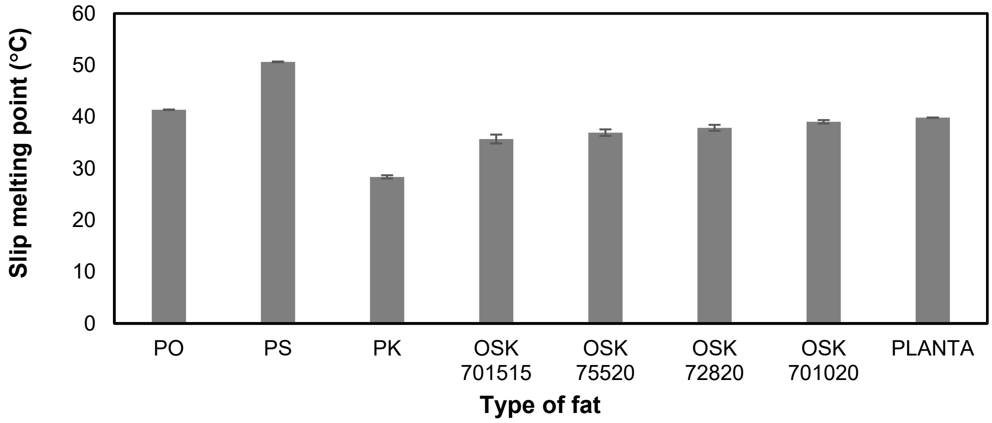

Figure 3: Slip melting point temperature of primary fats and four fat blends in comparison to Planta

3.4 Crystallisation behaviour

Figure 4 shows the crystallisation behaviour of the four blends. OSK701515 shows higher solid fat content than Planta at certain temperatures and OSK701020 have a lower solid fat content compared to Planta at certain temperatures. These were due to the higher percentage of PS added in the blend. Palm stearin contributes to higher solid fat content as it contains high percentage of long chain fatty acid so it takes a longer time to melt (Saadi et al., 2012). OSK75520 and OSK72820 mainly have lower SFC compared to Planta because these blends have low percentage of PS. This behaviour was similar to the result reported by Saadi et al. (2012). It indicates that different fat blends affect the hardness of margarine due to the different crystalline networks (Zhu et al. 2020). Overall, the blends OSK701020 and OSK701515 show the closest crystallisation behaviour with Planta. This indicates that these blends have a firm structure as close as to the commercial margarine.

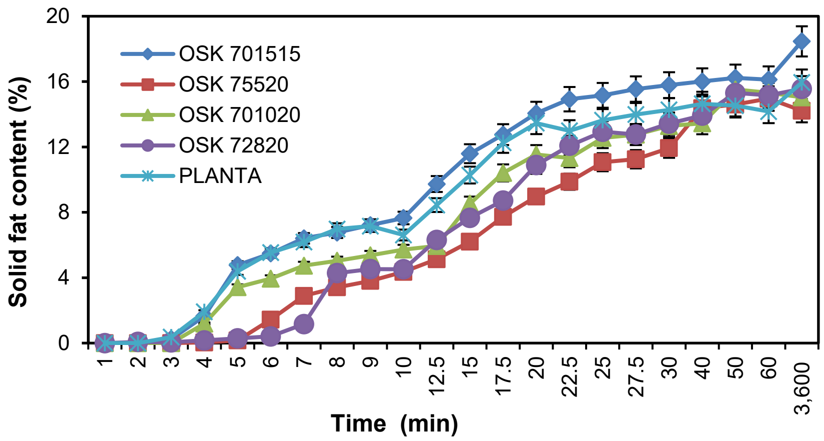

Figure 4: Crystallisation behaviour of the four blends

4. Conclusions

From this study, blend OSK701020 was chosen as the most suitable fat formulation for margarine formulation containing three fats with ratio of 70% palm oil, 10% palm stearin and 20% palm kernel oil, as it has the most similar properties with a commercial margarine in terms of fatty acid composition, solid fat content percentages, slip melting point and crystallisation behaviour analysis. These physicochemical properties are the most basic indicators for a good formulation of margarine. This formulation can be used for further formulation of margarine with addition of natural bioactive compounds for example natural colourant or plant-based antioxidant. Further analysis on stability of margarine should be studied in terms of the peroxide values, volatile oxidation products and sensory evaluation to produce a high quality and stable margarine formulation.

Acknowledgments

The authors would like to acknowledge the funding from Ministry of Higher Education Malaysia and Universiti Teknologi Malaysia under the UTM Fundamental Research Grant (Q.K130000.3843.21H95).

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