Palm-Pressed Mesocarp Fibre Oil as an AlternativeCarrier Oil in Emulsion

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Abstract: Refined palm-pressed mesocarp fibre oil (PPFO), which can be obtained from one of the by-products of palm oil milling, palm-pressed mesocarp fibre, is categorized as palm sludge oil. So far, it has been given less attention and underutilized until some recent scientific reports revealing its high content of phytonutrients, carotenoids and vitamin E, which have been proven scientifically to possess anti-oxidant activity. The study evaluated the stability of PPFO as a carrier for plant-based emulsion. PPFO was extracted and examined for its positional distribution of fatty acids, saturation levels and iodine value (IV) using NMR spectroscopy. The PPFO-based emulsion was then prepared and subjected to stability tests, including temperature variation, centrifuge test, cycle test, pH and slip melting point for 28 days. Phase separation was observed from PPFO-based emulsion stored at 40°C from day-21 onwards while no creaming found in all the palm olein-based emulsions stored at the three storage temperatures. Nevertheless, results indicated that the PPFO-based emulsion passed all the tests above showing insignificant phase separation (p > 0.05) compared with those of palm olein commonly used in emulsion preparation. The findings suggested that PPFO enriched with valuable phytonutrients could be used as an alternative carrier oil in emulsion formulation, which is an important component in personal care products.

Key words: palm-pressed mesocarp fibre oil, oil palm biomass

1 Introduction

Palm oil milling process includes seven main processes which are fresh fruit bunches reception, sterilization, threshing, digestion, mashing and pressing, crude oil clarification and palm kernel recovery which have resulted in tremendous by-products. The available by-products, in various forms or types, are palm oil mill effluent, empty fruit bunches, palm oil mill sludge, decanter cake, palm kernel shells and palm-pressed mesocarp fibres1. A number of approaches to process the substantial amounts of palm oil mill by-products into value-added products have been implemented and reported, such as mechanical2-4 and thermo-chemical5-7 conversion methods. Previous studies showed that many of these materials can be utilized to produce organic fertilizers8, fuels9, animal feeds10, biodegradable plastics11, methane12, paper and pulp13, etc.

Mesocarp fibre is one such by-product generated from a palm oil mill which has been highly used as a fuel for palm oil extraction. It contains 5-6% of residual oil (dry basis)14. The oil can be extracted from the pressed mesocarp fibre during the mashing and pressing processes in the mill and the extracted oil is termed crude palm-pressed mesocarp fibre oil. Crude palm-pressed mesocarp fibre oil has limited applications because it contains gums, waxes, trace metals and free fatty acids. Therefore, it is commonly used in animal feed formulations (non-food). Its use for human consumption is avoided unless it is further processed to meet the required specifications. In fact, it could be refined by removing the undesirable components in order to obtain higher quality fibre oil. Nevertheless, it has been proven to possess significant amounts of phytonutrients, including phytosterols, carotenoids and vitamin E14. To date, there are limited number of research articles reported on the utilization of refined palm-pressed mesocarp fibre oil (PPFO).
In 2006, Lau and coworkers reported the differences in quality and efficiency of fibre oils extracted using supercritical carbon dioxide and solvent. A few years later, Neoh et al. (2011) compared the recovery rate and the fatty acid compositions of fibre oils extracted using three different methods, i.e. soxhlet, reflux and cold hexane extractions. A recent study conducted by Lau and coworkers indicated that the crude palm-pressed mesocarp fibre oil consists of high concentration of carotenoids and vitamin E. In 2019, Sulihatimarsyila and coworkers reported that both phytonutrients remain in PPFO after pre-treatment. Palm olein is widely used in food industry is particularly restricted due to this down-grading. Value addition of the palm oil milling by-product, specifically the PPFO, is required to create awareness on the goodness of the oil, since it is enriched with valuable phytonutrients for either food or non-food uses. Our aim was to evaluate the stability of PPFO in an oil-based formulation attempted as a personal care ingredient. Palm oil and its derivatives are widely used in cosmetic and personal care industries and literature data showed that palm olein-based emulsion exhibited good emulsion stability, therefore palm olein (PO) was used as a control in this study for comparison purpose.

2 Materials and Methods

2.1 Materials

PO was sourced from local supermarket. Hexane, polyoxyethylene(20) sorbitan monostearate (Tween 60), polyoxyethylene(20) sorbitan monooleate (Tween 80) and cetyl alcohol were purchased from R&M Chemicals (Malaysia). Deuterated chloroform was purchased from Sigma Aldrich (Switzerland). Stearic acid was purchased from Merck Millipore (Darmstadt, Germany). Glycerol monolaurate was purchased from Hangzhou GengYang Chemical Materials Co., Ltd. (China).

2.2 Production of refined palm-pressed mesocarp fibre oil (PPFO)

Crude palm-pressed mesocarp fibre oil was supplied by a palm oil mill. The oil was degummed, bleached and deacidified at MPOB to obtain the PPFO. The carotene and vitamin E contents of the PPFO were 1192 ppm and 1404 ppm, respectively. The free fatty acid (FFA) of the PPFO and PO was 1.29 wt% and 0.12 wt% (as palmitic acid), respectively. The peroxide value (PV) of the PPFO and PO was 2.32 and 1.56 meq/kg, respectively.

2.3 Product characterization

The positional distribution of fatty acids, saturation level and iodine value (IV) of the PPFO and PO were recorded using a NMR spectrometer, JEOL ECZ-600 MHz. In brief, 0.5 mL of deuterated chloroform was used to dissolve 0.1 g of oil. The oils were analyzed by 13C-NMR for the positional distribution of fatty acids and saturation level as described by Teh et al. (2016). The percentage of saturated, oleic, linoleic and linolenic fatty acids of each oil was calculated as described by Olatunya et al. (2016). The IV of these oils was calculated according to AOCS method. The total carotene content of the oils was determined using a UV-Vis Spectrometer, U-2001, Hitachi Instruments Inc., Tokyo, Japan according to MPOB Test Method p2.6:2004 at an absorbance of 446 nm. Vitamin E content was analyzed using a high-performance liquid chromatography (HPLC) on a C18 column (150 mm × 4.6 mm i.d.) coupled to a fluorescence detector (Agilent Technologies, Palo, CA). The mobile phase used was acetonitrile/methanol (50:50, v/v) at a flow rate of 1.0 mL/min. The FFA of oils was analyzed using titrimetric method according to AOCS Official Method Ca 5a-40. PV of the oils was analyzed by iodometric method as given in the international method ISO 3960. All the analyses were performed in triplicate for each oil.

2.4 Preparation of emulsion

The emulsions were prepared according to Teh et al. (2018). In brief, oil-soluble ingredients, stearic acid (20 g), cetyl alcohol (20 g) and glycerol monolaurate (30 g) were first added into 300 g of PPFO, then mixed and heated at 70°C until fully dissolved. Both emulsifiers, Tween 60 (10 g) and Tween 80 (10 g) were added into 700 g of distilled water, then mixed and heated at 60°C until fully dissolved. The oil and water-phase mixtures were cooled down and maintained at 35°C. Both mixtures were homogenized with IKA T25 Digital Ultra-Turrax at 6000 rpm for 15 minutes. The final product (emulsion) was then kept at room temperature for 48 hours (baseline, t0) for stabilization purpose. All the steps above were repeated by replacing PPFO with PO.

2.5 Stability tests

2.5.1 Temperature variation test

Temperature variation test was performed to determine stability of emulsion according to Fernandes et al. (2013) with some modifications. The stabilized emulsions were stored at 4°C (in a fridge), 27°C and 40°C (in an oven) for 28 days. These emulsions were evaluated at intervals of 0, 1, 7, 14, 21 and 28 days for their stability. Each test was carried out in triplicate.
2.5.2 Accelerated thermal stability test

2.5.2.1 Centrifuge test

Phase separation was recorded after each emulsion was centrifuged at 4000 rpm and room temperature for 15 minutes using Universal 32R Centrifuge.

2.5.2.2 Cycle test

Changes of emulsions were recorded after storing the emulsions in a 5-cycle freeze/thaw system. Three cycle systems designed in this study were −5°C (in a fridge) for 24 hours, 27°C for 24 hours and 40°C for 24 hours.

2.5.3 Chemical characteristics

All the emulsions from different time intervals were subjected to slip melting point (SMP) and pH analyses. The SMP of emulsions was carried out according to MPOB Test Method p4.2:2004: Determination of slip melting point. The pH of emulsions was measured using a calibrated pH meter.

2.5.4 Statistical analysis

All the data were presented in mean and performed statistically using GraphPad Prism 5. Data were analyzed by one-way ANOVA, followed by Tukey’s Multiple Comparison Test. The p value ≤ 0.05 was considered to be statistically significant.

3 Results and Discussion

The stability assessment of any finished personal care products is mandatory to warrant the safety and functionalities of the products during storage under huge variation of temperatures and times. It is also used to estimate the shelf life of a product[28].

The quantitative 1H-C-NMR analysis performed on both the oils is useful to examine the positional distribution of fatty acids and their saturation levels. The results (Table 1) show that PPFO and PO have comparable saturation levels of total fatty acids with PPFO possessing slightly higher percentage of saturated fatty acids (SFA). This is because PPFO has not undergone any fractionation process during the refining step. Hence, PPFO retains both the high and low melting point components, which are stearin and olein, respectively. IV is commonly used to assess the degree of unsaturation levels in oils and fats. The finding was consistent with the IV analyzed via 1H-NMR. The calculated IV for PPFO and PO was 50.5 and 55.9, respectively, implying a higher saturation level of PPFO than that of PO.

The longevity of the emulsions was assessed by temperature variation test[29]. There was no separation of layer observed throughout the experimental period in all the emulsions stored at 4, 27 and 40°C. The results implied that both the emulsions were stable under heat up to 40°C. Moreover, all the emulsions exhibited good stability at accelerated temperature with evidences of no noticeable phase separation. As such, the emulsions were consider-

| Groups          | Types of fatty acids | Composition (mole/100 mole total fatty acids) |
|-----------------|----------------------|--------------------------------------------|
|                 |                      | sn-1,3 | sn-2 | sn-1,2,3 |
| SFA             | 68.4 ± 0.0           | 15.9 ± 1.3 | 50.5 ± 1.3 |
| PPFO            | MUFA                 | 28.1 ± 0.6 | 62.5 ± 2.6 | 39.9 ± 1.6 |
|                 | PUFA                 | 3.5 ± 0.6 | 21.6 ± 1.4 | 9.6 ± 0.4 |
| PO              | MUFA                 | 27.9 ± 1.1 | 70.3 ± 0.1 | 42.2 ± 0.5 |
|                 | PUFA                 | 4.5 ± 0.1 | 22.6 ± 0.9 | 10.5 ± 0.4 |

Note: SFA represents saturated fatty acids; MUFA represents monounsaturated fatty acids; PUFA represents polyunsaturated fatty acids; p > 0.05 between two groups.

The emulsions were tested for accelerated temperature stability using a 5-cycle freeze/thaw system. Three cycle systems designed in this study were −5°C (in a fridge) for 24 hours, 27°C for 24 hours and 40°C for 24 hours. The results implied that both the emulsions were stable under heat up to 40°C. Moreover, all the emulsions exhibited good stability at accelerated temperature with evidences of no noticeable phase separation. As such, the emulsions were consider-

ably stable even though undergoing drastic change of temperature.

Mechanical force, which is also known as centrifugal force, was applied to all the emulsions derived from PPFO and PO to assess the creaming phenomenon. The phenomenon reflects a decrease in the quality of emulsion as separation occurs[20]. There was no creaming found in all the PO-based emulsions stored at the three storage temperatures, i.e. 4, 27 and 40°C. For the stored PPFO-based emulsions, no creaming was observed at 4 and 27°C. However, phase separation was observed from PPFO-based emulsion stored at 40°C on day-21 and day-28 as emulsions are typically thermodynamically unstable. The PV of PPFO was higher than that of PO which led to its relatively instability as PV is used to evaluate lipid oxidation[31]. The result is in good agreement with Mosca and coworkers which reported that lipid oxidation is one of the factors that promote emulsion instability due to the oil droplet aggregation[32]. In addition, the instability of PPFO-based emulsion might be due to a higher saturated fat content; causing less interaction between the oil and the emulsifiers as SFA is less polar compared to the unsaturated fatty acid. In this case, the formulation becomes less stable when subjected to centrifugal force. Literature data showed that creaming was observed in vegetable oils including olive, safflower, grape seed, soy bean and sunflower oils-based emulsions that kept at 40°C after a 14-day of the experimental period[23]. The data postulates that the stability of PPFO-based emulsion is superior to the vegetable oil-based emulsions though the performance of PPFO-based emulsion is a little poor compared to that of PO-based emulsion.

It is well known that emulsion stability is much dependent on availability of interfacial film, where in turn is affected by pH[32]. Smaoui and co-workers revealed that an ideal pH for human skin should be 4.5 to 6.0[32]. The pH of

Table 1  Positional fatty acid compositions (mole/100 mole total fatty acids) of refined palm-pressed mesocarp fibre oil (PPFO) and palm olein (PO).

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the PPFO-based emulsions obtained in this study was found to fall in the range of 5.50 to 6.00 while that of the PO-based emulsions was 5.85 to 6.09 (Table 2). The results showed that both the fresh emulsions had acceptable pH levels. The pH of the stored emulsions was desirable too except for the PO-based emulsion stored at 4°C on day-21, 27°C on day-7, as well as 40°C on day-7 and day-28 which had slightly exceeded the ideal pH range as mentioned earlier. The pH value for PPFO-based emulsion with storage temperature of 40°C decreased on day-14 and become constant after that day might due to the FFA (1.29 wt% as palmitic acid) in the oil. Other than this, the pH dropped might due to the formation of FFA as well as the generation of mono- and di-acyl glycerols via acyl migration. The formations above might be one of the factors that affect the stability of the PPFO-based emulsions as phase separation was observed from the emulsion stored at 40°C on day-21 and day-28. Nonetheless, there was no significant differences in terms of pH values detected among all the emulsions under the influence of temperature up to 40°C. There wasn’t any drastic pH drop in these emulsions, implying no significant formation of FFA throughout the experimental period. Probably, the high percentages of SFA in both the PPFO and PO had managed to make them susceptible to oil degradation and stabilize them upon storage.

Lastly, both the emulsions derived from PPFO and PO had comparable SMP ranging from 1.0 to 2.2°C throughout the experimental period (Table 3). This might be due to the similar degree of saturation levels between the two emulsions as shown in Table 1.

### 4 Conclusion

Phase separation was observed from PPFO-based emulsion stored at 40°C from day-21 onwards while no creaming found in all the PO-based emulsions stored at the three storage temperatures. Nevertheless, both the PPFO- and PO-based emulsions possessed comparable stability with no significant oil and water phase separation throughout the 28-day stability study at three temperature variations, centrifuge and cycle tests. The PPFO-based emulsion formulated was therefore stable. The results suggested that PPFO could be served as an alternative carrier oil in personal care products formulations.

### Conflict of Interest

None of the authors had a conflict of interest.
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