

EFFECT OF SUPERFATTING AGENTS ON SOAPS PROPERTIES

SYLVIA E BENJAMIN* and AMIR ABBASS**

ABSTRACT

Advancements in soap technologies have improved the quality of life worldwide. Several new products have flooded the market encompassing laundry, beauty and dermatology. Over the years, palm oil (PO) has made an invaluable contribution in the global market. The use of palm stearin (POs) in soap making is well recognised due to its cost competitiveness. However, incorporation of POs in high amounts can cause cracking of soaps. The present studies focused upon the use of POs with palm kernel oil (PKO) in ratio of 60:40. This work is novel: i.e., pure distilled fatty acids (DFA) were incorporated as superfatting agents to upgrade soap properties. Neat soap was prepared by direct neutralisation and then superfatted with pure DFA of lauric, myristic, palmitic and stearic in proportions of 2%. Moisture content (MC) is an important controlling parameter during soap processing which effects the solubility and final texture of soaps. It is evidenced that superfatted (SF) soaps showed constancy in total fatty matter (TFM), free fatty acids (FFA), iodine value (IV) and peroxide value (PV) as the MC percentage declined with time. The stability of SF soaps persisted upon exposure at an elevated temperature of 100°C for seven days. Also, the moisturising ability and foamability enhanced with the addition of superfatting agents. These soaps also exhibited improved resistance to cracking.

Keywords: palm stearin, palm kernel oil, superfatting.

Date received: 24 May 2017; **Sent for revision:** 17 July 2017; **Received in final form:** 8 November 2018; **Accepted:** 30 April 2019.

INTRODUCTION

Versatility of soap making, *i.e.*, at home on small scale and also at industrial level has added astute and innovative trends in soap technology to meet the needs of ever growing populations after food and shelter. Over the years, attempts have been made to achieve high quality toilet and anti-bacterial soaps (Awang *et al.*, 2001; Mak-Mensah and Firempong, 2011) through sagacious formulations and hybridisation of modern and primitive technologies (Maghraby and Tolba, 2015). Marketed

soaps are thoroughly scrutinised by researchers to study the link between the consumer response and the products' functional properties (Onyango *et al.*, 2014; Warra *et al.*, 2010; Okolei *et al.*, 2014).

Traditionally, the triglycerides of fats or oils are reacted with lye to form sodium salt of fatty acid(s), *i.e.*, soap (Cavitch, 1995). Triglycerides are the mixture of different fatty acids which possess carbon chain length ranging from C8 to C20. Soap properties depend on the type and the amount of fatty acids in the oil. Best soap properties are achieved with fatty acids having C12 to C18 carbon chains. The most important fatty acids are palmitic acid, lauric acid, myristic acid, stearic acid, oleic acid, linoleic acid, linolenic acid. Different fats and oils are utilised to prepare soaps of required characteristics through slight technological modifications (Gupta and Weise, 2012).

* Department of Chemistry, Forman Christian College - A Chartered University, Gulberg II, Lahore 54600, Pakistan. E-mail: s_e_benjamin@yahoo.com

** Pentagram LLC, Naif Road, P. O. Box 94351, Deira, Dubai, United Arab Emirates.

Fatty acids can be saturated or unsaturated. These are blended to gain the required hardness of soap. Mutton tallow, lard and palm oil (Marikkar *et al.*, 2001) contain longer chain saturated fatty acids in excess and soaps made from these fats are firm, slowly soluble and milder with good detergency. Lauric like coconut oil (CNO) and palm kernel oil (PKO) are shorter chain fatty acids which form hard soaps that lather fully but dry the skin. Soft oils like cotton seed oil and rice bran oil contain more unsaturated fatty acids that produce softer, less white and less stable soaps. Toilet soaps usually contain 10% to 30% lauric oils, *i.e.*, CNO and PKO, *etc.* CNO which contains lauric, capric, and caprylic fatty acids is considered as the most important vegetable oil in soap manufacture. It improves solubility and foam properties of soap with moisturising and anti-bacterial action on skin. CNO is thus a cost-effective ingredient that imparts lather when mixed with other non-lauric oils like animal fat, fractions of other vegetable oils, marine oils, hydrogenated oils, *etc.*

Soft oils are hardened by catalytic hydrogenation and then bleached to improve the colour of soap. Hydrogenation and bleaching may cause loss of natural antioxidants in oils, making it rancid (Shahidi and Wanasundara, 2008). Excess linoleic and linolenic fatty acids in soap oil blends are therefore, not advisable as these develop rancidity at a faster rate.

The raw material selection in soap making is based on the requisite quality characteristics endeavoured at the lowest possible cost. The important controlling parameters are saponification value, acid value (AV), titer value, iodine value (IV), peroxide value (PV) and the Lovibond colour, *etc.* Essentially, a well thought blend of oils and fats can furnish desired properties at a complemented price.

PO industry is expanding fast and it is expected that PO and PKO can replace tallow and CNO (Abdullah and Wahid, 2010). The chain lengths of the fatty acids present in the triglycerides of PO fall within a very narrow range of 12 to 20 carbons. PO has balanced percentage of saturated and unsaturated fatty acids that give an IV of about 53, conferring some stability against oxidation as compared to other vegetable oils. On average, PO contains mainly palmitic acid – C16 (44%-45%), oleic acid (39%-40%), with linoleic acid (10%-11%) and only a trace amount of linolenic acid. Low level of linoleic acid and weak amount of linolenic acid makes the oil relatively stable to peroxide formation.

Palm stearin (POs) is the solid fraction of PO obtained after crystallisation at ambient temperatures. POs use is rising due to its excellent soap making properties and low cost. It has some limitations *e.g.*, when high proportions are incorporated into toilet soap formulations, hard soaps are produced which tend to crack under dry and wet conditions (Kuntom *et al.*, 1999). POs mainly

contains myristic acid – C14 (49.8%-68.1%), oleic acid – C18 (20.4%-34.4%) with linoleic acid (5%-8.9%) and trace amounts of linolenic acid (Koushki *et al.*, 2015). It has an IV of 27.8-45.1 (MS815:2007). POs is sold at a discount price as compared to PO, and its price falls into the range of inedible tallow (Moulay *et al.*, 2011). PKO contains lauric acid – C12 (48.5%), myristic acid (16.2), palmitic acid (8.4%) and oleic monounsaturated C18:1 (15.3%). Palm kernel stearin (PKS) mainly contains lauric acid (54.1%-58.2%), myristic acid (21.1%-24.1%), palmitic acid (7.2%-8.6%) with oleic acid (4.6%-6.8%) and trace amounts of linoleic acid (PORIM 1995). It has a low IV (5.8-8.1) which makes the soaps hard.

PO and PKO blends show better properties than the traditional tallow and CNO blend. The soap is white with good lathering properties (Ahmed, 1984). Superfatting is the addition of fatty materials in an amount more than the stoichiometric proviso for neutralising alkali. According to patent (Megson *et al.*, US 3,576,749, 1971), free fatty acids (FFA) in soap bars produce rich and creamy lather while keeping resistance to smear. Superfatting of soaps with oils reported in literature is mostly patent.

The main objective of this work was the utilisation of POs and PKO blend for quality soap preparation. It was envisioned that soap properties can be enhanced through superfatting with pure distilled fatty acid (DFA) of lauric acid, myristic acid, palmitic acid and stearic acid in a cost-effective manner. The studies particularly focused upon on the physico-chemical properties of superfatted (SF) soap bars as the function of moisture content varying with time and temperature.

MATERIALS AND METHODS

All materials and methods used in the present investigations do not pose any threat to human beings and animals.

Pre-treatment of Samples

For oils, the samples were inverted several times to release all sediments adhering to the walls of container ensuring uniform distribution. The solid and semi solid samples were softened by gentle heating and then mixed thoroughly for the determination of moisture and volatile matter. The samples were melted in drying oven at a temperature which was at least 10°C above the melting point of the sample. Tests that required moisture free conditions (*e.g.*, IV) were treated with anhydrous sodium sulphate (1-2 g/10 g sample). Both oil and fat samples were held at 50°C in an oven, then stirred vigorously and filtered. Turbid samples were stirred vigorously and filtered inside the oven at 50°C. All samples were placed in a cool

dry place and protected from light and air to avoid rancidity of fats and oils (Lück, 2000).

Testing of Raw Materials

Iodine value. POs and PKO were analysed for the degree of unsaturation by Wijs solution method *i.e.*, iodine monochloride (ICl) solution in glacial acetic. This method confers IV as the weight of iodine (I_2) absorbed by 100 g of an oil or fat (AOAC, 1984) and tells the degree of unsaturation in fats and oils. Sample (0.5 g) was dissolved in 25 ml carbon tetra chloride (CCl_4) in a conical flask fitted with a ground stopper. Wijs's solution (25 ml) was added to it. The solution was swirled and placed in dark for 1 hr. Blank solution was also treated likewise. The excess of ICl was treated with a fresh solution of 15 ml of 10% potassium iodide (KI), freshly boiled and then cooled water (100 ml) was added with rinsing of the stopper also. Liberated I_2 was estimated by titration against standard 0.1 mol litre⁻¹ sodium thiosulphate ($Na_2S_2O_3$) solution using 2% starch solution as an indicator.

$$\text{Iodine value} = 12.69 (B - S) \times \frac{N}{W}$$

where, B is the standard $Na_2S_2O_3$ solution used for blank (ml), S is the standard $Na_2S_2O_3$ solution used for sample (burette reading) (ml), N is the normality of the standard $Na_2S_2O_3$ solution and W is the weight of the sample taken (g).

Moisture content (MC). The MC of fats and oils is the loss in mass of sample on heating at 105°C under specific conditions. Air oven method was used in the present studies (ISI, 1984). Thoroughly mixed sample (10 g) was taken in a pre-weighed metal container (7 cm diameter and 3 cm deep) with a slip cover. It was heated in an oven at 105°C with a loose cover for 1 hr. The container with cover were cooled in desiccators containing phosphorus pentoxide and weighed. This process was repeated till the change in weight between two successive observations was found to be < 1 mg. This ensured maximum moisture removal.

$$\text{Moisture and volatile matter \%} = W_1 \times \frac{100}{W}$$

where W is the weight of material taken (g) and W_1 is the loss of material on drying (g).

Melting point (MP). Open tube capillary slip method was used for testing the MP of oils (ISI, 1984a). Heated and filtered samples were sucked to a height of 10 mm inside a 50 mm long double open ended capillary tube having an inside diameter of 1 mm and outside diameter of 1.2 mm. The tube was firstly chilled with ice and then placed in a refrigerator at a temperature of 4°C to 10°C for 1 hr.

The chilled sample in capillary tube was attached to a thermometer with its lower end levelled with the bulb. These were immersed in water held at 10°C in a Thiele tube. The side tube of the Thiele tube was gradually heated at a rate of 2°C min⁻¹, till the temperature reached 25°C, and thereafter, at the rate of 0.5°C min⁻¹. The temperature at which the sample started to rise in the capillary was noted. An average of five consecutive readings was taken.

Colour. The colour was checked by Lovibond glasses of known colour characteristics. The colour is expressed as the sum total of yellow and red slides used to match the colour of oil in a cell of specific size in the Lovibond Tintometer (ISI, 1984). Transparent clean test sample was filled in a clean and dry glass cell of 1 cm length and placed in the tintometer. Its colour was matched by sliding red, yellow and blue colours. The colour of oil is reported in terms of Lovibond units as follows:

$$\text{Colour reading} = (a Y + 5 b R) \text{ or } (a Y + 10 b R) \\ \text{in (* cell)}$$

where, a is the total sum of the various yellow slides (Y) used, b is the total sum of the various red (R) slides used, $Y + 5R$ is the mode of expressing the colour of light coloured oils and $Y + 10 R$ is the mode of expressing the colour of dark coloured oils. Any personal errors due to yellow and red for the samples were compensated by applying a composite factor on the sum total of the yellow (Y) units and 5 or 10 times the total of red units as stated for the oil or fat.

Peroxide value (PV). Oil/fat sample (5 g) was dissolved in 50 ml glacial acetic acid and chloroform mixture (3:2) in a titration flask with stopper maintaining the temperature at 30°C. Saturated KI (0.5 ml) solution was added and the solution was kept in dark for a minute and supplemented with 30 ml distilled water. The solution was occasionally swirled to liberate all the I_2 from the chloroform layer. Free I_2 is titrated against standard $Na_2S_2O_3$ (0.01 N) solution using a few drops of starch (0.5%) as an indicator (AOAC, 2000). The amount of I_2 produced is directly proportional to the PV. The titre value of the sample is noted as V_s . A blank is also run for each determination noted as V_b . The PV is expressed in milli equivalents of active oxygen kg⁻¹:

$$\text{PV m.} \frac{\text{eq}}{\text{kg}} = (V_s - V_b) N \times 1000/w$$

where, W is the weight of sample (g) and N is the normality of $Na_2S_2O_3$ solution.

Acid value (AV). It is the number of milligrams of potassium hydroxide (KOH) required for the neutralisation of FFA present in 1.0 g of fat (ISI, 1984).

Thoroughly mixed cold oil/fat (0.1 g) was dissolved in 25 ml of freshly neutralised hot ethyl alcohol. The 1 ml Phenolphthalein indicator (1%) was added and the mixture was boiled for 5 min. While hot, the solution was titrated against 0.5 N KOH solution.

$$AV = \frac{56.1 V \times N}{w}$$

where, V is the volume of KOH used (ml), N is the normality of KOH and W is the weight of sample taken (g).

Preparation of Oil Blend

POs and PKO carbon composition was determined by gas liquid chromatography (GLC) (Agilent 7860S series, USA). POs and PKO were taken in ratio of 60:40. The blend was split into glycerol and fatty acids by the action of steam in the splitting column at a steam of pressure 2.5 bars. Glycerol was separated from the bottom and the fatty acids were distilled at 240°C and then separated. These were converted to methyl esters. The DFA composition was determined by GLC. The method of preparation of methyl esters and GLC is given in proceeding sections.

Preparation of Neat Soap

The 450 g of the separated DFA was mixed with 63 g of PKO in a 1000 ml beaker. Saponification of this mixture was done with slow addition of 32.4% NaOH (250 g) with vigorous stirring. When the reaction reached equilibrium, other ingredients (1.25 g each), *i.e.*, sodium silicate, magnesium sulphate, ethylene diamine tetra acetate and NaCl were added one by one. Demineralised water (30 g) was added at the end with vigorous stirring. This batch presented the neat soap.

Superfating of soap. Neat soap (200 g) was SF with 4 g of lauric acid, myristic acid, palmitic acid and stearic acid with vigorous stirring in separate beakers.

Preparation of soap bars. SF soap samples of 2% lauric acid, myristic acid, palmitic acid and stearic acid were placed in a rolling machine which had a mesh like opening at the end. It transformed the soap mass into soap noodles. Glycerin (2.5 g) was added slowly to the four portions of test noodles and mixed thoroughly. The noodles were again put in the rolling machine and transformed into large pieces of soap under pressure. These large pieces were shaped into soap bars in a molding machine. Soap bars SF with lauric acid were designated as SF-Lc, myristic acid as SF-Mc, palmitic acid as SF-Pc and stearic acid SF-Sc, respectively.

Tests on SF Soap Bars

SF-Lc, SF-Mc, SF-Pc and SF-Sc (three bars each) were taken for tests conducted in open at room temperature for 0, 20, 30 and 40 days. The same SF soap samples were again tested after seven days at 100°C making the total duration of tests 47 days. The results are reported as the average of triplicate determinations.

Total fatty matter (TFM). Ground SF soap sample (5 g) was completely dissolved in hot distilled water (100 ml) in a 250 ml beaker. Sulphuric acid (5 ml) was added to make the solution slightly acidic. The beaker was heated on a water bath until the fatty acids started to float as a layer on the top. The mixture was cooled suddenly. The fatty acids layer was separated and weighed (W_1). Diethyl ether (50 ml) was added to the remaining solution to dissolve any fatty matter left in the mixture. It was separated from the water soluble content by a separating funnel. Fatty matter content was obtained by evaporating the diethyl ether portion at 45°C in a pre-weighed porcelain dish (AOAC, 2000) and weighed (W_2). TFM was calculated as follows:

$$TFM \% = \frac{W_1 + W_2}{5} \times 100$$

Free fatty acids. SF soap sample (5 g) was thoroughly dissolved in dried methanol (50 ml) in a 250 ml conical flask. The solution was titrated against alcoholic 0.1 N KOH using phenolphthalein (two drops) as an indicator.

$$FFA (\%) = \frac{R \times 0.1 \times 56.1 \times 100}{\text{Sample weight}} \times 1000$$

where, R is the burette reading.

Moisture content (MC). The method used for MC percentage estimation was the same as adopted by Dalen and Mamza (2009) and described earlier for the testing of raw materials. The MC was also checked by moisture analyser (MB35 series America Ohaus). Thoroughly ground SF soap (0.5 g) was inserted in the analyser and the MC was noted on the display. The results obtained through both the techniques were in close agreement.

Iodine value. The IV of SF soaps was determined by Wij's solution as described earlier for oils.

Peroxide value. The oxidative stability of SF soaps was conducted by the titration method as given earlier.

Tests at 100°C. After 40 days, the SF soap bars of each type, were placed in an oven at 100°C for further seven days and analysed for FFA, MC, IV, MP, PV and AV.

pH. The pH values of SF soaps were determined by making 10% solution of ground powdered soap dissolved in double distilled water. The pH values were read on pH meter (PHS-25CW).

Foamability. Foamability of SF soaps was tested by the procedure followed by Edoga (2009). Powdered SF soap (0.5 g) was thoroughly dissolved in water and transferred to 1000 ml cylinder and shaken vigorously with a plunger. The rising of foam in cylinder was noted at 30 s and at 5.5 min. The ratio of the foam volume at 5.5 min to that at 30 s (V_5/V_0) represents the foam stability.

The colour of SF soaps was determined by Lovibond Tintometer.

Gas Liquid Chromatography

The FFA compositions of POs, PKO and the prepared SF soaps were done by GLC. Methyl esters of oils and SF soaps were prepared using methanol (pre purged with N_2 gas) and KOH, boiled and extracted with heptane. These were separated by GLC using flame ionisation detector. The 0.1-2 μ l heptane solution (5%-10%) of methyl esters was injected through the septum of inlet port. The injection system was heated to a temperature of 20°C-50°C higher than the column temperature at 185°C operating in an inert atmosphere of N_2 gas. Twin glass columns were used. The detector temperature was kept at 200°C. The patterns of methyl esters were elucidated on the basis of retention time and identified by comparison with authentic oils (IUPAC, 1979). The retention time increases with ascending number of carbon atoms and unsaturation.

RESULTS AND DISCUSSION

Ogoshi and Miyawaki (1985) have mentioned that high quality toilet soaps can be prepared from POs and PKO and also from tallow and CNO via

a new process. This process engaged fatty acid methyl ester and α -sulpho fatty acid methyl ester of POs. Kuntom and Kifli (1996) studied soaps made from blends of distilled POs and PKO fatty acids. Since, these soaps were hard they suggested a blend using a small amount of soft oils. In the present investigations, POs and PKO were mixed in ratios of 60:40 and then SF with 2% pure palmitic, myristic, stearic and lauric fatty acids. This blend was expected to compromise for soap properties, e.g., hardness, low solubility and low foamability of harder fats in palm blend.

The physico-chemical analysis of POs and PKO used in the present studies is shown in Table 1. The FFA % content in POs and PKO was close, i.e., 0.12% and 0.14%, respectively. The fatty acids were distilled, separated and converted to methyl esters. The carbon compositions of the major constituents of DFA in POs and PKO done by GLC are presented in Table 2. The analyses of POs revealed that it contained both saturated and unsaturated fatty acids with carbon number ranging from C12 to C18. Palmitic acid $CH_3(CH_2)_{14}COOH$ (C16) and oleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ (C18:1) were present in the highest amount. PKO had higher content of lauric acid $CH_3(CH_2)_8COOH$ along with a reasonable amount of C16 and myristic acid $CH_3(CH_2)_{12}COOH$.

POs and PKO (60:40) mixture was analysed (Table 3). The analyses showed that the physico-chemical properties of the mixture were closer to POs as expected due to its larger share in the blend.

Neat soap was prepared from DFA of POs and PKO mixture. Four separate portions of neat soap were SF with myristic, stearic, palmitic and lauric fatty acids. The DFA (obtained from TFM) were converted into the corresponding methyl esters of sodium for the evaluation of major components in the SF soaps by GLC. The results are presented in Table 4. The carbon composition showed that C16 component was the highest in all the SF soaps. The C16 content varied as SF-Sc < SF-Mc < SF-Lc < SF-Pc. The C18:1 component was the highest in the

TABLE 1. PHYSICO-CHEMICAL ANALYSES OF PALM STEARIN AND PALM KERNEL OIL

Raw materials	FFA (%)	IV (mg/100 g)	MC (%)	MP (°C)	PV (m.eq kg ⁻¹)	Colour (R)
Palm stearin	0.12	43.2	0.10	51.5	6.87	5.0
Palm kernel oil	0.14	19.3	0.097	27.5	2.87	2.5

Note: FFA – free fatty acid. IV – iodine value. MC – moisture content.
MP – melting point. PV – peroxide value.

TABLE 2. CARBON COMPOSITION OF PALM OIL STEARIN AND PALM KERNEL OIL

Raw materials	Carbon chain (%)						
	C12	C14	C16	C18	C18:1	C18:2	C18:3
Palm stearin	9.57	1.21	47.07	3.57	30.24	5.74	0.31
Palm kernel oil	51.35	22.97	20.06	-	-	-	-

order SF-Lc > SF-Mc > SF-Sc > SF-Pc. It is seen that 2% superfatting appeared as a non-proportional increase of the added DFA component in the prepared soaps.

The Mc of soaps is a very important parameter. During shaping of soaps the MC level is optimised to control soap quality and to avoid waste and losses. It also affects the shelf-life of the product. The SF soap bars were kept on open shelves for 0, 20, 30 and 40 days at room temperature and then at 100°C for another seven days, thus simulating long-term exposure conditions. The MC and the corresponding melting point as the function of time is given in Table 5.

The neat soap had 50% MC. The prepared SF soaps had an initial MC of 24%-31%. Soaps dried with time on open shelf with MC reducing to 4%-6% on the 40th day. Keeping at 100°C for further seven days, *i.e.*, till 47th day, MC further decreased to

<2%. The *Encyclopedia of Industrial Chemical Analysis* specifies 10%-15% MC for toilet soaps. All the SF soaps showed MP in the range of 44°C-44.5°C. This range is closest to the MP of lauric acid. Important to note is that PKO that constituted 40% share in the neat soap, had 50% lauric acid in it. For the entire duration of tests, no appreciable change in the MP of the SF soaps was observed. All soaps were stable at 100°C. Only SF-Lc showed a slight decline from 45°C to 43°C. This soap may develop tendency to soften especially in consistent hot and humid conditions due to a lower number of carbon atoms and lower melting point of lauric acid.

The impact of moisture loss with time on soap properties was studied. It is expected that evaporation of water will result in subsequent increase of TFM, FFA and PV.

The TFM of SF soaps is presented in Figure 1. An inverse relation between MC and TFM was seen

TABLE 3. PHYSICO-CHEMICAL ANALYSES OF DISTILLED FATTY ACIDS

IV (mg/100 g)	MC (%)	MP (°C)	PV (m.eq kg ⁻¹)	Colour (R)	Acid value
43.0	0.12	45	6.85	6.0	211.9

Note: MC – moisture content. MP – melting point. PV – peroxide value.

TABLE 4. CARBON COMPOSITION ANALYSES OF THE SUPERFATTED SOAPS BY GAS LIQUID CHROMATOGRAPHY

Soap	Carbon chain (%)						
	C12	C14	C16	C18	C18:1	C18:2	C18:3
SF-Lc	9.53	1.83	44.04	5.05	32.85	5.95	0.74
SF-Mc	7.0	4.77	43.81	5.92	31.89	5.87	0.73
SF-Pc	7.63	1.88	46.82	5.96	31.37	5.61	0.73
SF-Sc	7.62	1.78	43.18	9.04	31.86	5.77	0.75

Note: SF-Lc – soap bars superfatted with lauric acid.
 SF-Mc – soap bars superfatted with myristic acid.
 SF-Pc – soap bars superfatted with palmitic acid.
 SF-Sc – soap bars superfatted with stearic acid.

TABLE 5. MOISTURE CONTENT AND MELTING POINT OF SUPERFATTED SOAPS AS THE FUNCTION OF TIME AND TEMPERATURE

Soaps	Test duration (day)							
	0 RT		20 RT		40 RT		+7 days at 100°C	
SF-Lc	25.7	(45.0)	16.0	(45.0)	4.0	(45.0)	1.91	(43.0)
SF-Mc	24.6	(44.0)	18.6	(44.5)	4.0	(45.0)	1.45	(44.0)
SF-Pc	30.9	(45.0)	19.3	(45.5)	5.3	(46.0)	1.97	(45.5)
SF-Sc	27.4	(45.0)	17.4	(44.5)	5.7	(45.0)	2.1	(44.5)

Note: Moisture content (%). Melting point °C (in parenthesis).
 RT – room temperature.
 SF-Lc – soap bars superfatted with lauric acid.
 SF-Mc – soap bars superfatted with myristic acid.
 SF-Pc – soap bars superfatted with palmitic acid.
 SF-Sc – soap bars superfatted with stearic acid.

for all the SF soaps. The TFM (*Figure 1*) of all the SF soaps at RT increased b/w 62%-88% with time, while the MC systematically declined. Keeping at 100°C for further seven days, reduced the MC to 2% without an appreciable change in TFM, *i.e.*, it stayed around 90%. The SF soaps did not show any visible cracks. Low TFM in fresh soaps indicates free alkali (Awang *et al.*, 2001). The high MC in fresh soaps triggers the reaction of alkali with unsaponified fat forming FFA and glycerol. *Figure 1* shows that as the MC decreased the TFM rose per total mass making it good for a dry skin (Mak-Mensah and Firempong, 2011). These soaps will thus have lubricating properties on skin even after long time as evidenced by simulated temperature exposure tests. Habib *et al.* (2016) have reported similar TFM values of 73.37%-100% in soaps with higher MC % of 9.5%-11.8%. Our SF soaps had stable TFM content at low MC that signifies good lubricating properties and a superior shelf life.

FFA of all the SF soaps increased slightly in a systematic manner with time as the MC decreased (*Figure 2*). SF-Pc had the lowest while SF-Lc had the highest FFA content. All SF soaps showed the same FFA % when tested at 100°C for further seven days. FFA fluctuations are expected as saponification is a reversible reaction and it does not proceed to 100% completion. MC of 30% in the start hydrolysed unsaponified fat to FFA in our SF soaps. Subsequently, changes at all MC levels are small confirming stability of soaps, *i.e.*, resisting degradation.

The IV is a measure of the degree of unsaturation in a fat or oil. Saturated fats have low and unsaturated fats have high IV. There are a few exceptions, but

usually fats with high IV, make softer soaps and fats with low IV, make harder soaps. A range of 29 to 54 is satisfactory for this soap quality. The IV of the SF soaps fluctuated but stayed in the range subscribed for normal soaps for the entire duration of tests (*Figure 3*).

The IV increased slightly on 20th day but on average the IV varied b/w 39 to 42, indicating fat stability. SF soaps showed no degradation even at 100°C (for seven days), showing the typical characteristic of soaps made with saturated fatty acids. Similar, IV are reported by Mishra (2013) for soaps made with CNO and castor oil in the ratio 3:1, producing hard toilet soaps with excellent properties.

The PV of SF soaps increased slowly in a narrow range of 0.8 – 2.0 m.eq kg⁻¹ as the MC declined from 25% to 4.5% on average, showing weak oxidation. The PV values are presented in *Figure 4*.

Lower the unsaturation, more stable is the compound, and slower is the peroxide formation. Higher content of POs has imparted saturation and henceforth, stability to SF soaps. Koushki *et al.* (2015) have emphasised upon the high oxidative stability of PO (long shelf-life) due to high saturated fatty acids content. Fatty acids break into small chain aldehydes, ketones or carboxylic acid groups. This has impact on smell and lubricating properties of soaps. To achieve stability, antioxidants are generally added to soap. Our SF soaps have shown good oxidative resistance without the addition of antioxidants.

The PV increased when stored at 100°C for further seven days showing an inverse relationship with MC. Oxygen attacks, especially the unsaturated

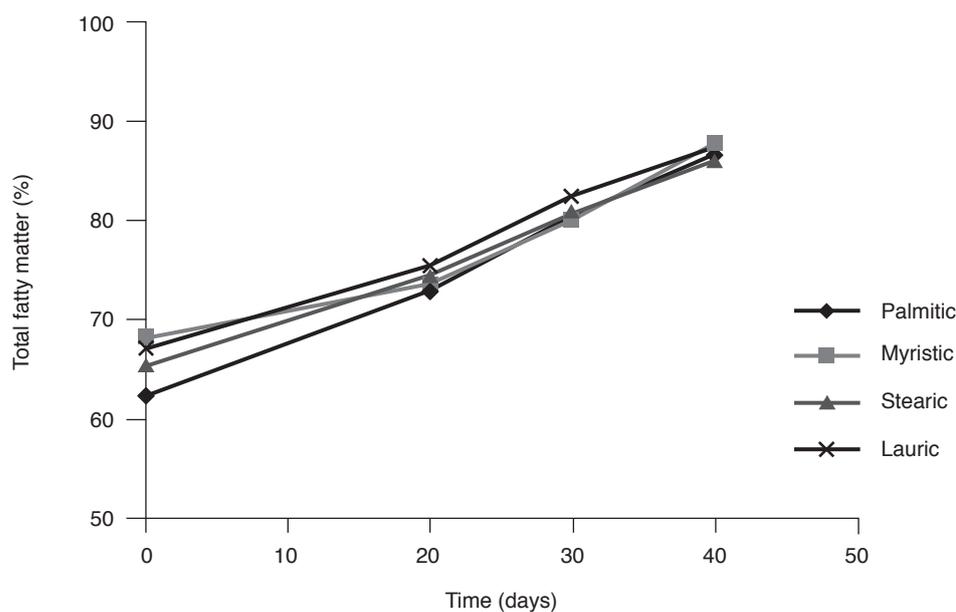


Figure 1. Changes in total fatty matter (TFM) of superfatted soaps with time at room temperature.

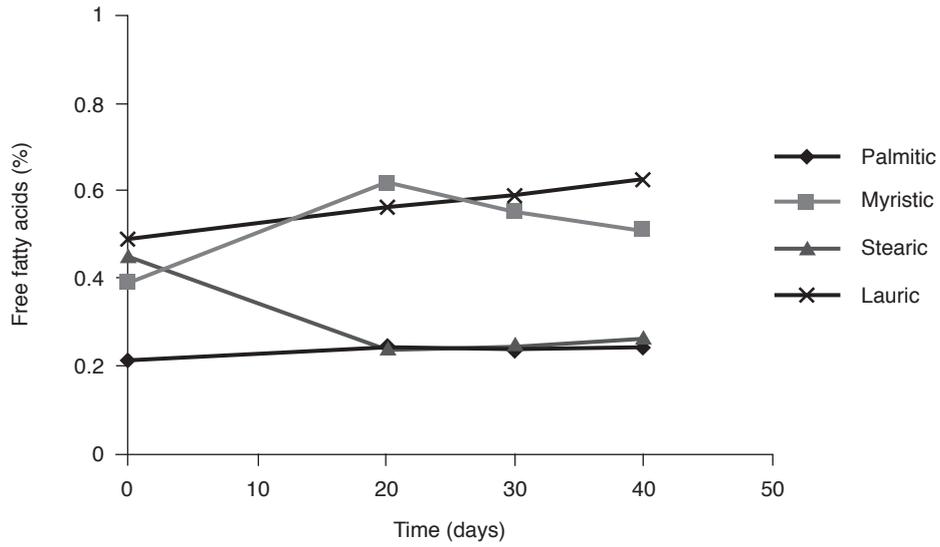


Figure 2. Changes in free fatty acids (FFA) of superfatted soaps with time at room temperature.

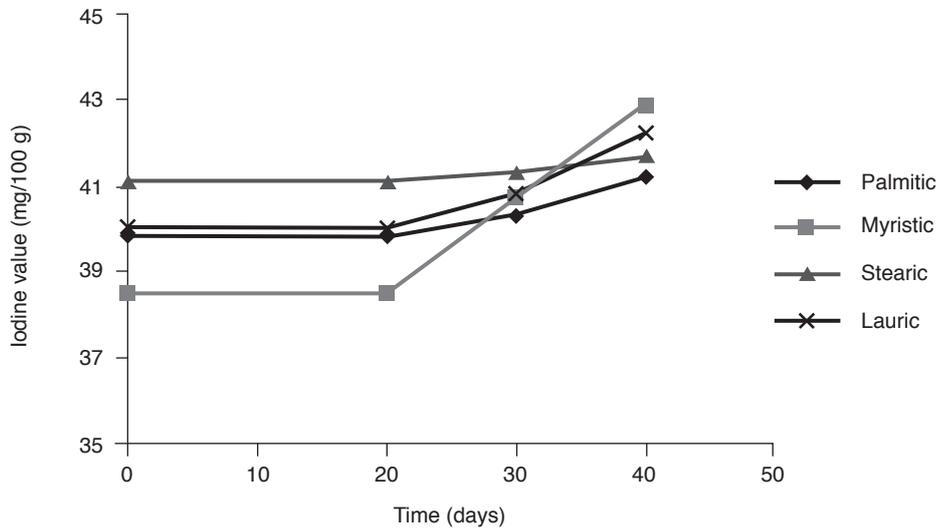


Figure 3. Changes in iodine values (IV) of superfatted soaps with time at room temperature.

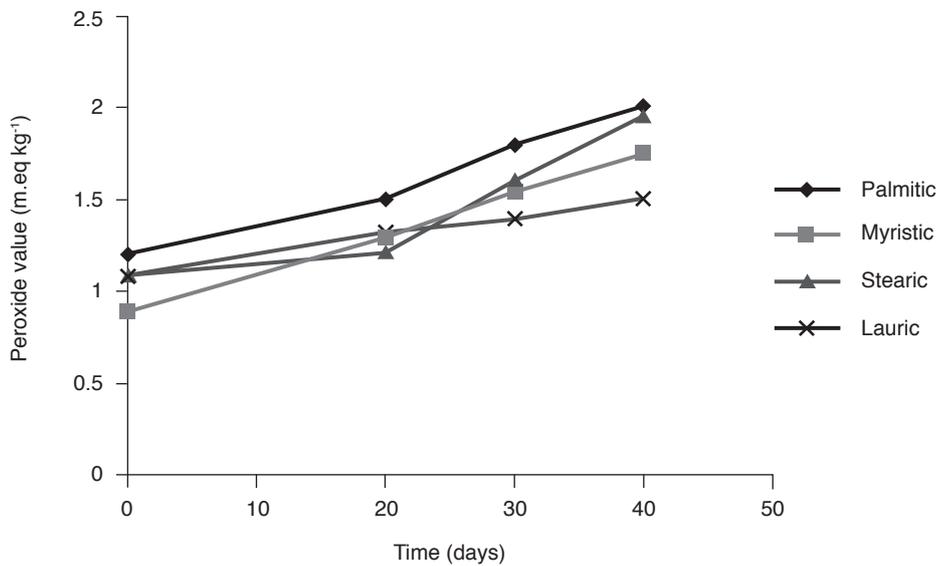


Figure 4. Changes in peroxide values (PV) of superfatted soaps with time at room temperature.

fatty acids, forming hydroperoxide (Frank, 1984). Oxygen is eight times more soluble in fatty acids than in water. MC reduction to < 2% together with rise in temperature supports a faster rate of reaction. It is planned to explore the oxidative resistance of SF soaps with MC < 2% at room temperature at prolonged periods of time in future studies.

Physical analyses of SF soaps done after 47 days with seven days at 100°C inclusive, are presented in Table 6.

The pH of SF soaps varied in the range of 9.82 to 9.9. Incomplete hydrolysis from saponification gives rise to a higher pH medium in soaps which is unfriendly to human skin. Warra *et al.* (2011) have emphasised that superfatting agents lower the harshness of soaps. Oluwatoyin (2011) evaluated some commercial soaps prepared by saponification

portions above the soap formulation improve soap properties. This study has given a smart direction for quality soap production in a cost-effective manner.

CONCLUSION

A combination of POs and PKO in 60:40 ratio and superfatting with 2% saturated oils having a carbon hydrogen ratio of 2 produce quality soaps with a durable shelf-life. Neutralisation is a more cost-effective method due to minimum glycerol production. POs and PKO blend neat soap SF with DFA of lauric, myristic, palmitic, and stearic have good functional properties and henceforth, offer higher marketing prospects especially in hot and dry regions of the world.

TABLE 6. PHYSICAL PROPERTIES OF SUPERFATTED SOAPS

Test	Superfatted soaps			
	SF-Lc	SF-Mc	SF-Pc	SF-Sc
pH	9.90	9.85	9.82	9.94
Foamability	540/452	554/462	536/446	532/434
Bar hardness	35.0	41.0	44.0	32.0
Leathering	Good	Good	Good	Good
Cracks	Nil	Nil	Nil	Nil
Effect on skin	Slightly dry	No effect on skin	No effect on skin	No effect on skin

Note: SF-Lc – soap bars superfatted with lauric acid.

SF-Mc – soap bars superfatted with myristic acid.

SF-Pc – soap bars superfatted with palmitic acid.

SF-Sc – soap bars superfatted with stearic acid.

of different types of oils. These soaps showed pH in the range of 10.27-10.55. Dove soap, prepared by Rebath process had a lower pH (7.94) exhibiting best moisturising properties. Similarly, Tarun *et al.* (2014) analysed 63 soaps. Fifty-three soaps out of 63 had pH 9.01-10 which is similar to our SF soaps. Thus, direct neutralisation followed by superfatting with palmitic acid, myristic acid, stearic acid and lauric acid produced soaps that are mild to skin as not being lye heavy. Only SF-Lc had a slightly drying effect on skin.

All the SF soaps were white in colour and showed good foamability and lathering properties. Generally, cracking of soaps occurs in hot and dry conditions. Kuntom *et al.* (1999) prepared soaps from palm oil blend and PKO and SF with neutral oils or glycerin containing 10% MC. They reported improvement in soap properties (with the exception of canola oil), *i.e.*, soaps were free of cracks with 1%-2% superfatting agents. We used DFA as superfatting agents for soap blend and none of the SF soaps showed cracks even at 100°C with MC of 1%-2%. These results confirmed that an increase in DFA

REFERENCES

- Abdullah, R and Wahid, M B (2010). World palm oil supply, demand, price and prospects: focus on Malaysian and Indonesian palm oil industry. *Oil Palm Industry Economic J. Vol. 11 (2):* 13-25.
- Ahmed, I (1984). Significance of palm oil and palm stearin as fatty raw material for soap. *PORIM Occasional Paper No. 13:* 12-22.
- AOAC (1984). Chapter 28.023 – Iodine absorption number Wijs methods. *Official Method of Analysis Iodine.*
- AOAC (2000). Method 965/33: Oils and fats – Preparation of test sample. *Official Method of Analysis.* 17th ed.
- Awang, R; Ahmed, S and Ghazali, R (2001). Properties of sodium soap derived from palm-based dihydroxystearic acid. *J. Oil Palm Res. Vol. 13(2):* 33-38.

- Cavitch, S M (1995). *The Natural Soap Book*. 6th ed. Storey Publishing. 182 pp.
- Dalen, M B and Mamza, P A P (2009). Some physico-chemical properties of prepared metallic soap-driers of aluminium, copper and zinc. *Sc. World J. Vol. 4(3):* 7-9.
- Edoga, M O (2009). Comparison of various fatty acid sources for making soft soap. Part 1: Qualitative analysis. *J. Eng. and Appl. Sci. Vol. 4(2):* 110-113.
- Frank, D G (1984), Reaction of oxygen and unsaturated fatty acids. *J. Amer. Oil Chem. Soc. Vol. 61(2):* 441-447. DOI: 10.1007/BF02678811.
- Gupta, S and Weise, D (1992). *Reigels' Handbook of Industrial Chemistry* (Kent, J A ed.). Van Nostrand Reinhold. p. 1013.
- Habib, A; Kumar, S; Sorowar, Mohd. S; Karmoker, J; Khatun, M S T and Al-Reza, M S (2016). Study on the physicochemical properties of some commercial soaps available in Bangladeshi market. *Int. J. Adv. Res. in Chem. Sc. Vol. 3(6):* 9-12.
- I.S.I. (1984). Part XIII: Methods of sampling and test for oils and fats. *Handbook of Food Analysis*. p. 33-75.
- IUPAC (1979). *FAO Manuals of Food Quality Control*. 17th ed. p. 274-281.
- Koushki, M; Nahidi, M and Cheraghali, F K (2015). Physico-chemical properties, fatty acid profile and nutrition in palm oil. *J. Paramed. Sci. Vol. 6 (3):* 117-134.
- Kuntom, A; Ahmad, I; Kifli, I H and Shariff, Z M (1999). Effects of superfatting agents on cracking phenomena in toilet soap. *J. Surf. and Deter. Vol. 2(3):* 325-329. DOI: 10.1007/s11743-999-0084-5.
- Kuntom, A and Kifli, H (1998). Properties of soaps derived from distilled palm stearin and palm kernel fatty acids. *J. Surf. and Deter. Vol.1 (3):* 329-334.
- Kuntom, A; Kifli, H and Lim, P K (1996). Chemical and physical characteristics of soap made from distilled fatty acids of palm oil and palm kernel oil. *J. Amer. Oil Chem. Soc., Vol. 73:* 105-108. DOI:10.1007/BF02523455.
- Lück, E and Lipinski, G-W V R (2000). Foods, food additives. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA (online: 2002). DOI: 10.1002/14356007.a11_561.
- Maghraby, E EL and Tolba, A (2015). Toilet soap case. *The Mena J. Bus Case Studies*. DOI: 10.5171/2015.636015.
- Mak-Mensah, E and Firempong, C (2011). Chemical characteristics of toilet soap prepared from Neem (*Azadirachta indica* A. Juss) seed oil. *Asian J. Plant Sci. and Res. Vol. 1(4):* 1-7.
- Marikkar, JMN; Lai, O M; Ghazali, HM and Cheman, Y B (2001). Detection of lard and randomized lard as adulterants in refined-bleached-deodorized palm oil by differential scanning calorimetry. *J. Amer. Oil Chem. Soc. Vol. 78(11):* 1113-1119.
- Megson, D; Chandler, S F; George, S S and Bruce, L (1971). Soap toilet bars having improved smear characteristics. Patent US 3,576,749.
- Mishra, D (2013). Preparation of soap using different types of oils and exploring its properties. *E-thesis - 109ch0476*. Department of Chemical Engineering, National Inst. of Tech., India.
- Moulay, S; Chalane, A and Ouad-Feul, Z (2011). Palm stearin in the soap making process. *Natura Montenegrina, Podgorica, Vol. 10(3):* 335-346.
- Ogoshi, T and Miyawaki, Y (1985). Soap and related products: Palm and lauric oil. *J. Amer. Oil Chem. Soc. Vol. 62(2):* 331-335.
- Okolei, PC; Daniel, E C; Onyedika, I C and Ebieladoh, S J (2014). Optimization of a soap production mix using response surface modeling: A case of Niger bar soap manufacturing industry Onitsha, Anambra State, Nigeria. *Int. J. Sci. & Tech. Res. Vol. 3(9):* 346-352.
- Oluwatoyin, S M (2011). Quality of soaps using different oil blends. *J. Microbiol. Biotech. Res. Vol. 1(1):* 29-34.
- Onyango, P V; Oyaro, N; Aloys, O; Linda, M and Wesley, N O (2014). Assessment of the physicochemical properties of selected commercial soaps manufactured and sold in Kenya. *Open J. Appl. Sci. Vol. 4:* 433-440.
- PORIM (1995). *PORIM Technology No. 16:* 20 pp. http://www.palmoilworld.org/about_palmoil.html
- Shahidi, F and Wanasundara, U N (2008). Methods for measuring oxidative rancidity in oils and fats. *Food Lipids: Chemistry, Nutrition and Biotechnology* (Akoh, C C and Min, D B eds.). CRC Press. p. 387-403.
- Tarun, J; Susan, J; Suria, J; Susan, V J and Criton, S (2014). Evaluation of pH of bathing soaps and shampoos for skin and hair care. *Ind. J. Dermatol. Vol. 59:* 442-444.

Warra, A; Hassan, L G; Gunu, S Y and Jega, S A (2010). Process synthesis and properties of soaps prepared from different triacylglycerol sources. *Niger J. Basic and Appl. Sci. Vol. 18(2): 315-321.*

Warra, A; Wawata, I; Gunu, S and Atiku, F (2011). Soap preparation from Soxhlet extracted Nigerian cotton seed oil. *Pelagia Res. Library Vol. 2: 617-623.*