Value Added Bakery Fat Products From Low Cost Raw Material By Using Chemical Interesterification

[1]Subodh Ghule, [2]Dr.G.A.Usmani
[1]Student, [2]Professor
[1]University Institute of Chemical Technology,
[1]North Maharashtra University, Jalgaon, India

Abstract : Chemical interesterification between super stearin and palm kernel olein blends were reported to show various degrees of plasticity, which were suitable for commercial margarines and shortenings. The chemically interesterified blends at ratios 70:30 and 80:20 of super stearin and palm kernel olein were shown to be suitable melting point and solid fat content for shortening applications with good plasticity and spreadability. The resultant chemically interesterified blends showed lower slip melting points and solid fat content, while having desirable very fine spherulitic β′ crystals. The interesterified blends exhibited smoothness, with good aeration and creaming properties well suited for the production of vanaspati, margarine, shortening, non-temper-type confectionery fats, and fats for whipped creams. Chemical interesterification is a safe, easy and cost effective alternative method to hydrogenation. With the advanced technology cheap raw material such as super stearin can be optimize for the fat products formulation. The Chemical interesterification process is much more flexible in modifying oils & fats as well as time saving and environment friendly.

Index Terms **- Interesterification, Chemical Interesterification, Super Stearin, Palm Kernel Olein.**

I. INTRODUCTION

Interesterification consists of a rearrangement of fatty acid between two triglycerides, which can consequently lead to changes in the different physical and functional characteristics of the interesterified fat. The distribution of the fatty acids on the glycerol molecule is thus modified, although the fatty acid composition of the fat is retained. Chemical interesterification involves the use of chemicals as a catalyst such as alkali metals (sodium, potassium and their alloys) and their corresponding hydroxides and alkoxides to accelerate the redistribution of the fatty acids.

Interesterification is one of the processes used to modify the physico-chemical characteristics of oils and fats. Interesterification is an acyl-rearrangement reaction on the glycerol molecule. On the other hand, hydrogenation involves addition of hydrogen to the double bonds of unsaturated fatty acids. Due to health implications of trans fatty acids, which are formed during hydrogenation, the industry needs to find alternatives to hydrogenated fats. So interesterified fats, with particular reference to interesterified palm products, as alternatives to hydrogenation can be used for health conscious people (Nor and Noor, 2005).

Two types of interesterification are available, i.e. chemical and enzymatic. Interesterification produces a complete positional randomization of acyl groups in triacylglycerol, by using chemical catalysts. Enzymatic interesterification uses lipases as catalyst. Each type of interesterification possesses advantages and disadvantages. The random or chemical interesterification is the most applied interesterification modification process of oils and fats as it is simpler, cheaper and easier to carry out compared to directed or enzymatic interesterification (Sreenivasan, 1976).

Interesterification helps to stabilize the fats and to increase the amounts of crystals which are needed for a smooth texture and functional properties, and products are free from trans fatty acids. A softer product with a lower melting point and without phase separation can be produced by Interesterification.

Interesterification as such or used in combination with dry fractionation has received increasing interest lately as an alternative to partial hydrogenation [1] for the production of ‘‘low trans’’ hard fat suitable for shortenings, stick or tub-type margarines and confectionary fat production [2].In this context, super stearin, a hard fraction obtained by palm oil dry fractionation, is a suitable alternative. It is added to improve tolerance to high temperatures, and for crystal morphology and stability [3]. However, blending with soft oils (like palm kernel olein, sunflower, soybean or rapeseed) remains necessary in order to impart plasticity to the final interesterified product [4]. A wide range of consumer table margarines and spreads, bakery margarines and frying shortenings can be formulated by mixing interesterified blends and native oils in adequate proportions [5].

The solid fat content (SFC) profile is critical in the evaluation of suitability for shortening or margarine formulation: the values of SFC at 10˚C, SFC at 20˚C and SFC at 35˚C are important as related to the rheological behaviour of fats at storage, packaging and utilization of bakery margarines, respectively [5]. The SFC at 10˚C will determine the hardness of the final product at refrigerator conditions. SFC at 10˚C and SFC at 20˚C are important parameters for determining the feasibility of the use of a

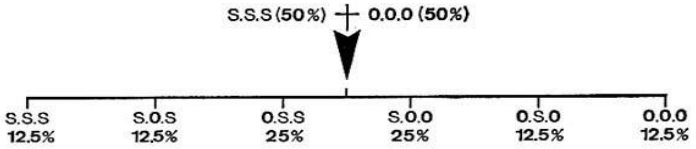
blend in the production of bakery margarines [6]. The SFC at 35˚C is particularly important in margarine manufacture, since it is related to the extent of melting in the mouth. In interesterified blends, this parameter must be as low as possible to prevent a sandy and coarse texture of the margarine [5].

Interesterification can be conducted chemically or enzymatically. Chemical interesterification (CIE) is usually random and produces complete positional randomization of the acyl groups on the glycerol backbone [7]. Depending from enzyme regioselectivity, enzymatic interesterification (EIE) can be random or specific. Intermediate specificity can also be obtained simply by adjusting the residence time of the enzymatic process. Nevertheless, a full conversion seems to be preferred: Zhang et al. [8] observed that margarine storage stability increases with an increasing conversion degree of the interesterified blend. Random interesterification (CIE or EIE) is mainly used for the production of commodity fats with the main purposes to modify the overall melting properties, to increase compatibility within the solid phase (not achievable by simple blending) and to enhance plasticity of the final product.

Interesterification is used to:

- Change the overall melting profile (usually to smoothen the solid fat content) or the melting point of the mixture (usually a decrease)
- Improve the compatibility of the different triglycerides in the solid state
- Improve the plasticity of the resulting solid by changing the (re)crystallization properties
- Combine the properties of mixed oils and fats
- Blends of soft oils with hard fats to a desired functionality and consistency
- To produced good quality of confectionery fats
- By combining IE and other modification processes, many products such as shortenings, margarines, and vegetable ghee with low trans fat or no trans fat at all can be formulated.

The figure below shows how several randomized heterogeneous triglycerides obtained by interesterification of a mixture of tristearine (SSS) and triolein (OOO).



The build up of triglycerides with determined structure is realized through the use of enzymes (lipases, esterases) as transferases in 3 types of reactions :

1. transesterification : exchange of carbonyl groups between esters
2. Acidolyse : exchange of carbonyl group between esters and carboxylic acids (fatty acids)
3. Alcoholyse : exchange of alcohol between esters and alcohols.

Acidolysis is the most commonly used process to enrich vegetable oils in one component (linoleic, oleic or eicosapentaenoic acid).

II. EXPERIMENTAL METHOD

Materials

Refined, bleached, and deodorized super stearin (S.St.) [melting point (MP) 58°C, iodine value 26.16] was obtained from Palm Fractionation Plant of AAK Kamani pvt. Ltd. RBD palm kernel olein [melting point (MP) 28°C, iodine value 22.04] was obtained from Palm Kernel Oil Fractionation Plant of AAK Kamani pvt. Ltd. Sodium methoxide ($NaOCH_3$) a catalyst for the chemical interesterification reaction was purchased from the Chem tech Ltd. Phosphoric Acid (H_3PO_4) for the catalyst inactivation was purchased from the Chem tech Ltd.

Laboratory-Scale Batch Chemical Interesterification (CIE)

The fat blend (100 g) was dried while stirring under vacuum for 60 min at 120°C. After lowering the temperature to 90°C, 0.1% sodium methoxide (powder dissolved in oil) was added as the catalyst. Interesterification was conducted under a vacuum at 90°C for 30 min after the appearance of the characteristic dark 'brownish' color. After completion of the reaction, the vacuum was broken and a 1.5 times of sodium methoxide the phosphoric acid added to inactivate the catalyst, while the mixture was stirred for a further 15 min. Filtration was carried out to remove soap formed by the reaction. Post-bleaching was performed with 0.75% of activated bleaching earth (Tonsil 210 FF) under vacuum for 30 min at 90°C. Filtration was done over a preheated Buchner filter.Deodorization was done at 240°C with 30 min retention time.

Analytical Determinations

Determination of Iodine Value

The iodine value (IV) was determined by the Wijs method according to the AOCS Official recommended method Cd 1b-87 [21].

Determination of Melting Point

Open-tube Capillary-Slip Method

The clear melting point of before and after interesterified blends determined according to ISI Handbook of Food Analysis (Part XIII) – 1984 , page 68/IS : 548 (Part 1) – 1964, Methods of Sampling and test for Oils and Fats page 33, AOCS Official Method Cc 3-25 – Slip melting point - AOCS Standard Open Tube Melting Point.

Determination of Solid Fat Content

The solid fat content (SFC) was analyzed using low field pulsed Nuclear Magnetic Resonance (p-NMR) with a Bruker Minispec mq 20 (Bruker, Germany), according to the standard IUPAC method 2.150 [22]. Serial methods, with and without tempering, were applied.

Determination of Fatty Acid Composition

Preparation of fatty acid methyl esters was done according to the AOCS Official Method Ce 2-66 (alternate method for fats and oils with acid value 2) [21]. GC determination was based on the AOCS Official Method Ce 1e-91 [21]. The FAME were separated on a 6890N gas chromatograph from shimadzu scientific instruments, equipped with a flame ionization detector and a BPX 70 capillary column (60 m length 9 0.10 mm internal diameter) (Supelco, Bellefonte, PN, USA). Initial column- temperature was set at 60 _C and increased at a rate of 10 _C/min to 150 _C, then further to 175 _C at 5 _C/min and held isothermally for 45 min at 175 _C. Injector and detector were maintained at 250 _C. Helium was used as the carrier gas, flowing at 0.3 mL/min. The flow rates of hydrogen and air were, respectively, 30 and 400 mL/min. The injection volume was 0.5 lL in hexane.

III. RESULT AND DISCUSSION

In order to utilize the by-product of the palm fractionation plant we were taken the super stearin having IV 26.16 and MP 58 and also taken the palm Kernel olein having IV 22.04 and MP 28. Makes the blends of them having composition of super stearin : Palm kernel olein about 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80,10:90, 0:100 and did the lab Scale chemical Interesterification of the blends using sodium methoxide as a catalyst. We have checked the Iodine value, Fatty acid composition, melting point and solid fat content of the before and after chemically interesterified blends.

We found that iodine value and fatty acid composition are same of before and after chemically interesterified blends but melting point and solid fat content of the after interesterified blends are lower than the corresponding before interesterified blends. These two parameters clear slip melting point and solid fat content are the evolution parameters of degree of Interesterification.

By doing the chemical interesterification hard blends are getting converted to soft blends that are matches the specification of shortening, margarine and vanaspati for the bakery products.

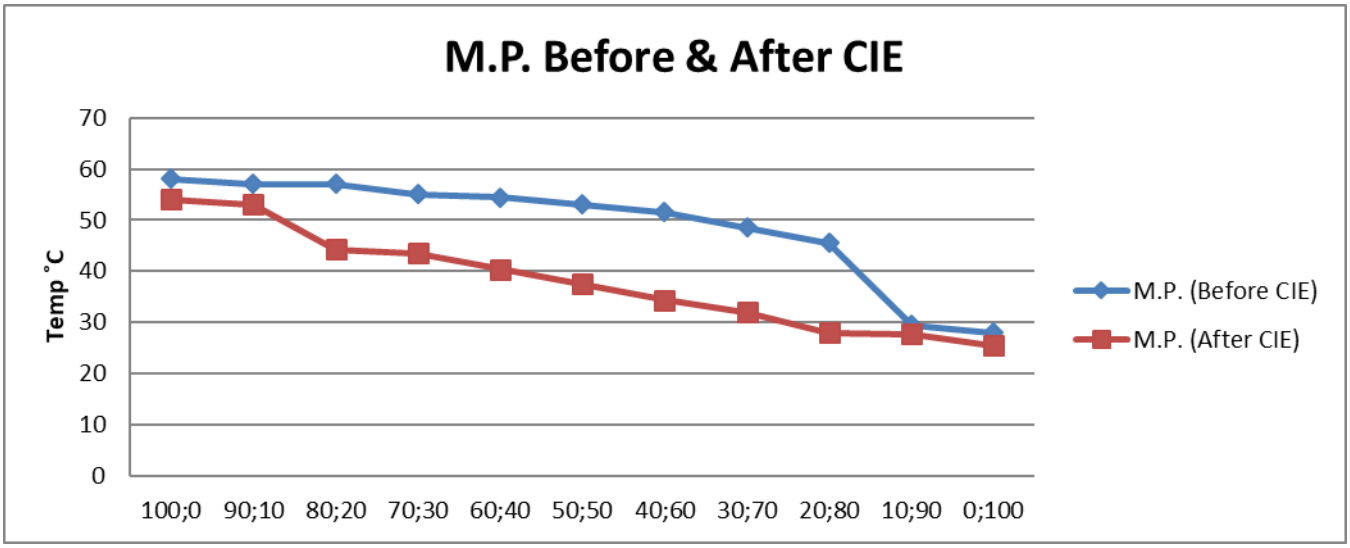
Below is the systematic data of the before and after chemically interesterified blends which includes melting point, solid fat content, iodine value and fatty acid composition.

Super Stearin	**100%**		**90%**		**80%**		**70%**		**60%**		**50%**		**40%**		**30%**		**20%**		**10%**		**0%**	
PKOlein	**0%**		**10%**		**20%**		**30%**		**40%**		**50%**		**60%**		**70%**		**80%**		**90%**		**100%**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
M.P.	58	54	57.5	53	57	44.3	55	43.5	54.5	40.4	53	37.5	51.5	34.4	48.5	32	45.5	28	29.5	27.7	28	25.5
SFC																						
20 °C	82.79	77.13	75.96	73.32	68.42	62.47	61.47	58.31	54.16	54.4	47.48	49.1	41.54	39.87	37.43	32.07	32.37	26.55	32.15	19.36	21.72	11.45
25 °C	76.73	68.28	69.71	62.19	61.28	51.93	54.2	44.57	45.78	40.69	38.71	34.31	30.81	24.78	23.97	15.75	16.39	10.62	10.88	3.91	0.12	0.11
30 °C	72.02	60.04	65.06	51.92	55.45	40.55	49.14	33.25	41.32	27.75	34.05	22.31	26.08	11.63	19.61	4.42	12.43	0.49	6.56	0.29	0.05	0
35 °C	65.37	47.94	56.66	38.17	48.99	28.87	43.04	18.05	36.21	16.04	29.63	9.44	22.73	2.3	15.9	0.14	10.51	0.44	3.92	0.07	0	0
40 °C	58.63	39.4	52.18	31.28	42.44	15.44	37.59	10.67	31.4	5.19	24.96	0	18.52	0	13.45	0	7.92	0.11	1.52	0	0	0
I.V.	26.16		25.63		25.27		24.83		24.44		24.01		23.62		23.25		22.86		22.42		22.04	
FAC																						
Caproic	0		0		0		0		0		0		0		0		0		0		0.26	

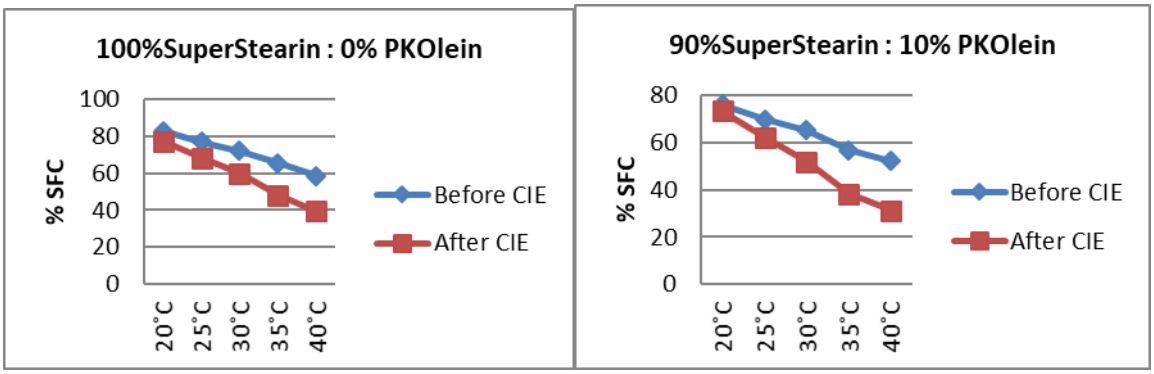
Caprylic	0	0.17	0.62	0.96	1.55	1.85	2.34	2.49	2.99	3.6	4.63
Capric	0	0.2	0.62	0.93	1.33	1.72	2.14	2.38	2.76	3.14	3.83
Lauric	0.16	4.15	9.39	13.33	18.72	22.28	27.39	30.99	35.35	40.93	45.99
Myristic	1.02	2.14	3.52	4.53	5.85	6.86	8.44	9.41	10.87	12.14	13.02
Palmitic	72.66	67.2	59.01	54.32	47.35	41.14	34.6	28.42	22.26	15.2	8.35
Stearic	5.13	4.92	4.82	4.27	3.9	3.84	3.44	3.77	3.45	4.75	2.38
Oleic	17.34	17.63	18.27	18.26	18.11	18.74	18.4	19.03	19.19	17.44	18.71
Linoleic	3.34	3.36	3.42	3.23	3.06	3.31	3.02	3.37	2.99	2.68	2.79
Arachidic	0.18	0.17	0.22	0.13	0.1	0.16	0.13	0.1	0.09	0.08	0
Linolenic	0	0	0	0	0	0	0	0	0	0	0

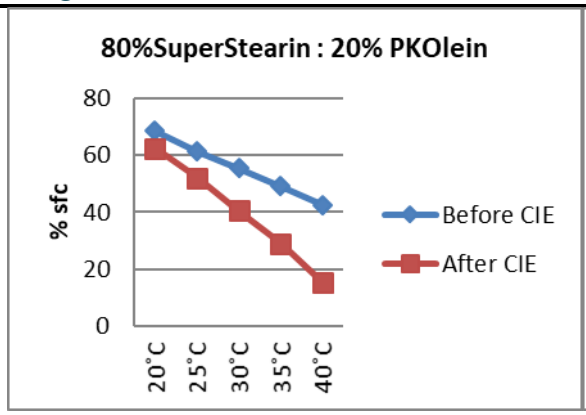
SAFA	79.15	78.95	78.2	78.47	78.8	77.84	78.48	77.56	77.77	79.84	78.46
MUFA	17.34	17.63	18.27	18.26	18.11	18.74	18.4	19.03	19.19	17.44	18.71
PUFA	3.34	3.36	3.42	3.23	3.06	3.31	3.02	3.37	2.99	2.68	2.79

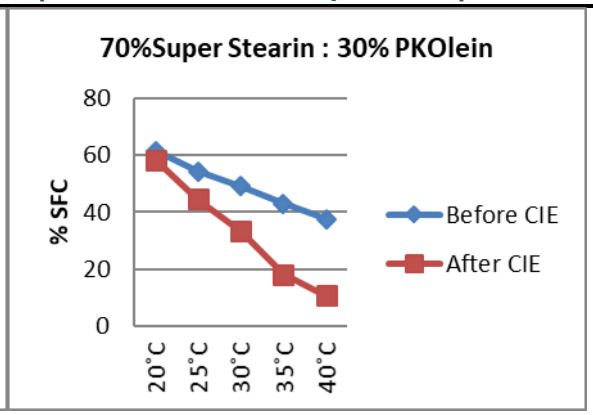
Graphical representation of melting point of before and after chemical interesterification.

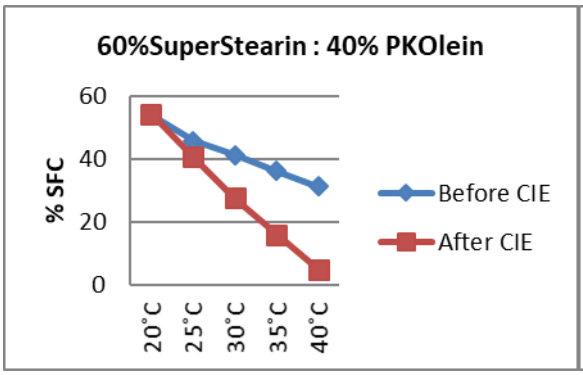


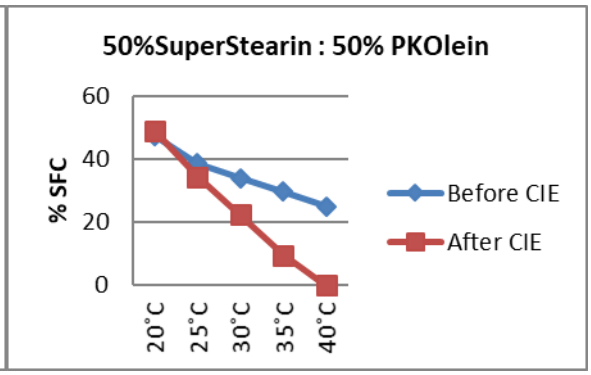
Graphical representation of solid fat content of before and after chemical interesterification.

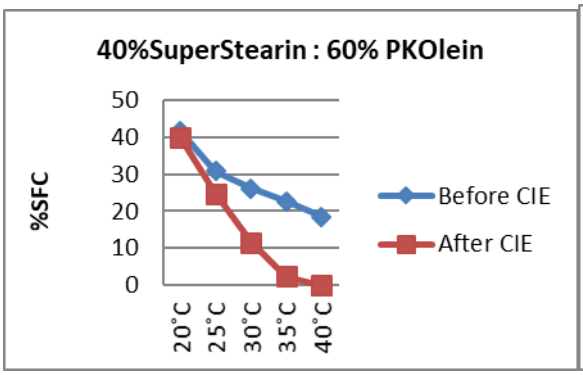


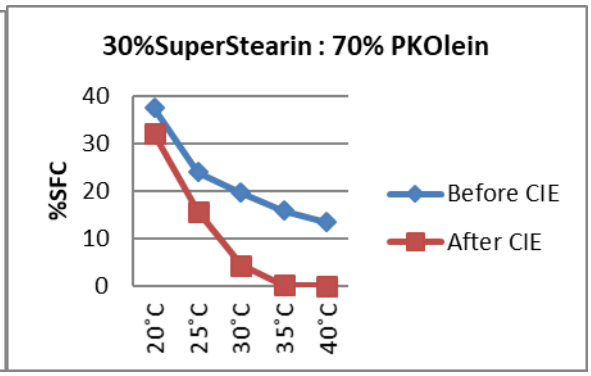

80%SuperStearin : 20% PKOlein
% sfc
80
60
40
20
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE

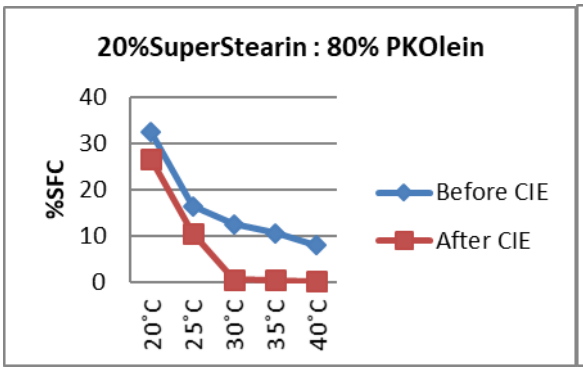

70%Super Stearin : 30% PKOlein
% SFC
80
60
40
20
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE

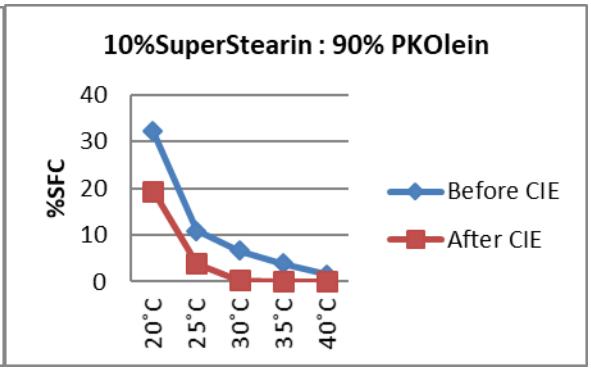

60%SuperStearin : 40% PKOlein
% SFC
60
40
20
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE

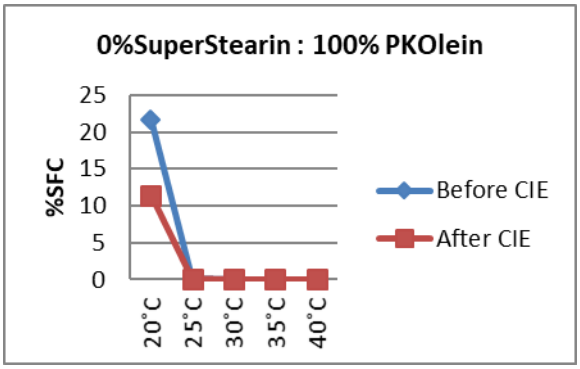

50%SuperStearin : 50% PKOlein
% SFC
60
40
20
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE


40%SuperStearin : 60% PKOlein
%SFC
50
40
30
20
10
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE


30%SuperStearin : 70% PKOlein
%SFC
40
30
20
10
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE


20%SuperStearin : 80% PKOlein
%SFC
40
30
20
10
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE


10%SuperStearin : 90% PKOlein
%SFC
40
30
20
10
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE


0%SuperStearin : 100% PKOlein
%SFC
25
20
15
10
5
0
20°C
25°C
30°C
35°C
40°C
Before CIE
After CIE

IV. CONCLUSION

Super stearin the by-product of the palm oil fractionation plant having iodine value 26.16 and melting point 58˚C and the palm kernel olein from the palm kernel oil fractionation plant having iodine value 22.04 and melting point 28˚C by blending them in different proportion and by doing the chemical interesterification the blends gets modified which are useful for the shortening, margarine and vanaspati for the bakery products.

From the series of chemically interesterified blends, the 70% super stearin : 30% palm kernel olein and 80% super stearin : 20% palm kernel olein found the suitable melting point and solid fat content for the shortening, margarine and vanaspati for the bakery products and having the good bakery products application results.

REFERENCES

1. ISI Handbook of Food Analysis (Part XIII)-1984 Page 67/ IUPAC 2.201(1979) /IS: 548 (Part 1) – 1964, Methods of Sampling and Test for Oils and Fats/ ISO 660:1996 Determination of acid value and acidity.

2. IUPAC 2.301 , 2.302 (1979)/FAO Manuals of Food quality Control 14/8 , pages 274 – 281/AOAC 17th ed^{n}, 2000 Official method 969.33 and 969.22 Fatty acids in oils and fats Preparation of methyl esters/Gas chromatographic method.

3. ISI Handbook of Food Analysis (Part XIII) – 1984 , page 68/IS : 548 (Part 1) – 1964, Methods of Sampling and test for Oils and Fats page 33, AOCS Official Method Cc 3-25 – Slip melting point - AOCS Standard Open Tube Melting Point.

4. AOAC 17th ed^{n}, 2000, Official method 920. 159 – Iodine absorption number of oils and fats / ISI Handbook of Food Analysis (Part XIII) – 1984 page 76).

5. AOCS Official Method Cd 1b-87: Iodine value of fats and oils: Cyclohexane AOCS Official Method Cd 1D-92: Iodine value of fats and oils: Cyclohexane Acetic acid method.

6. Raquel Costales-Rodrı´guez, Ve´ronique Gibon, Roland Verhe, Wim De Greyt (2009) Chemical and Enzymatic Interesterification of a Blend of Palm Stearin: Soybean Oil for Low trans - Margarine Formulation, Journal of Oil & Fat Industries,Volume 86(7):681–697.

7. Rai Muhammad Amir, Muhammad Asim Shabbir, Moazzam Rafiq Khan, Shahzad Hussain(2012), Interesterification of fats and oils-A Review, Pakistan Journal Food Science, 22(3), 2012: 143-153.

8. Amir R M, Shabbir M A, Khan M R and Hussain S (2012). Interesterification of fats and oils – a review. Pak. J. Food Sci., 22(3): 143-153.

9. Augstin, M A and Versteeg, C (2006). Milk fat: physical, chemical and enzymatic modification. Advanced Dairy Chemistry (Fox, P F and Mc- Sweeney, P L H eds.). Volume 2 Lipids. 3rd ed. Springer Science+Business Media, New York.

10. Lee, Y; Tang, T and Lai, O M (2012). Health benefits, enzymatic production, and application of medium- and long-chain triacylglycerol (MLCT) in food industries: a review. Journal of Food Science, 77: 137– 144.

11. Ghosh S, Bhattacharyya DK (1997) Utilization of high-melting palm stearin in lipase-catalyzed interesterification with liquid oils. Journal of American Oil Chemist Society, 74:589–592.

12. Noor Lida, H M D; Sundram, K and Noraini, I (2007). Effects of chemical interesterificationon the triacylglycerol and solid fat content profile of palm stearin, sunflower oil and palm kernel olein blends. European Journal of Lipid Science and Technology, 109:147-156.

13. Linsen Liua, and Dan Lampertb (1999). Monitoring Chemical Interesterification, Journal of the American Oil Chemists' Society 76(7):783-787.

14. Hiroaki Konishi, William E. Neff and Timothy L. Mounts, (1993) Chemical Interesterification with Regioselectivity for Edible 0ils, Journal of American Oil Chemist Society, Volume 70(4):411–415.

15. G. A. Usmani and H. V. Patil (2010), Lipase catalysed interesterification for the production of oleochemicals from non traditional oils, Rasayan Journal of Chemistry, Vol.3(2): 354-358.

16. Noor Lida, H M D; Sundram, K and Noraini, I (2006). DSC study on the melting properties of palm oil, sunflower oil and palm kernel olein blends before and after chemical interesterification. Journal of American Oil Chemist Society, 83(8): 739-745.