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ABSTRACT

The present study is concerned with the development of the miscella interesterification process to produce edible plastic fat products from sunflower oil admixed with some selected vegetable oils.

Conditions have been established for the miscella (oil inhexane) interesterification process which enable us to make plastic fats of desired melting points and dilatation characteristics from sunflower oil blended with certain other vegetable oils as binary and ternary mixtures. The products can be used as new kinds of Vanaspati (unhydrogenated type) and margarine fats having variable polyunsaturated fatty acids (PUFA) content and without trans-unsaturated fatty acids (TUFA) which have been demonstrated to have adverse nutritional and bio-chemical effects.

INTRODUCTION

Sunflower oil is a major edible oil in many countries of the world. It is expected to be also a major edible oil in India. The use of sunflower oil as a cooking oil and also as a component of margarine after selective hydrogenation and by interesterification is well known. However, even today, research is being continued for better utilization of sunflower oil by process developments such as miscella refining, hydrogenation and interesterification.

The present paper is concerned with the development of the miscella interesterification process for the purpose of obtaining plastic fats to be used as substitutes of hydrogenated vanaspati and also as margarine fats in various types of margarine from sunflower oil when mixed with some selective vegetable oils and oil fractions. The miscella interesterification process has been investigated in view of the certain advantages observed earlier from this laboratory (Chakrabarty and Bhattacharyya, 1968, 1972) in the interesterifica-tion reactions of fats and oils in solvent system and also because the refining of sunflower oil in the miscella state is gaining importance (Adhikari and Bhattacharyya, 1980). In the present study, sunflower oil in different proportions

with other oils as binary and or ternary mixture have been interesterified. The binary mixtures contain palm oil, palm stearin and sal. The ternary mixtures include palm and sal as

well as palm stearin and sal. It may be stated here that the combinations of the blend interesterified in the present work do not appear to have been studied earlier by other workers. The course of interesterification reactions of random and directed types was followed by examination of melting slip points and dilatations.

MATERIALS AND METHODS

The purified oils (acid value of about 0.05 and peroxide free) were blended in various proportions. The interesterification reaction of the different sunflower blends was carried out by using sodium methoxide catalyst in presence of n-hexane as the solvent according to the method reported from the laboratory (Chakrabarty and Bhattacharyya, 1968, 1972). The initial randomisation reaction was carried out by continuous stirring for half an hour with 0.4% sodium methoxide catalyst (30% Nao Me in anhydrous methanol). Thereafter, the products were subjected to various low temperatures for different lengths of time to complete the directed interchange. The catalyst was destroyed with dilute phosphoric acid and the excess acid removed by washing with distilled water. The solvent was distilled off and the product was finally isolated by drying on heating under vacuum.

Product was examined for slip point and dilation. The slip points of the prepared fats were determined after proper stabilization at $0 \pm 1^{\circ}$ C for 24 hrs.

Methyl esters of the oil under investigation were prepared by the method of Ludy, Barford, Barb and Magidman. The fatty acid compositions were determined by Gas Liquid Chromatography.

The dilation studies were carried out on some selected samples, melting at $35 - 42^{\circ}$ C, according to a standard procedure. The solid fat index values (ml/kg) were calculated from dilation values.

RESULTS

The fatty acid composition of the oils investigated is shown in Table 1. The melting slip points and solid fat index of the various interesterified sunflower oil blends are included in Tables 2, 3, 4 and 5.

Table 1. Fatty acid composition of the oils.

Oil	Fatty Acid Composition, % (W/W)						
	C14:0	C16:0	C18:0	C18:1	C18:2	C20:0	C18:3
Sunflower	_	8.1	4.1	42.4	45.4	_	
Sal		6.9	41.5	38.4	3.2	10.0	
Palm	1.7	44.0	6.4	38.1	9.6	0.1	
Palm Stearin	2.2	55.7	5.4	28.2	8.4	_	_

Table 2. Interesterification of binary mixtures of sunflower oil with other oil.

Oil Mixture	Randomised	Direc	Slip	
		Temperature (°C \pm 1°C)	Time (hr.)	point °C
Sunflower + Palm (30:70)	Randomised	—		37
Sunflower + Palm (70:30)	-do-	5	24	37
Sunflower + Palm $(50:50)$	-do-	5	24	39
Sunflower $+$ Palm (40:60)	-do-	5	2	35.5
Sunflower $+$ Palm (40:60)	do	5 + 10	0.5 + 0.5	35
Sunflower + Palm (40:60)	-do-	5 + 15	0.5 + 0.5	37
Sunflower + Palm (40:60)	-do-	5 + 10	1 + 0.5	36
Sunflower + Palm Stearin $(30:70)$	-do-	_		42
Sunflower + Palm Stearin $(70:30)$	-do-	5	24	37
Sunflower + Palm Stearin $(40:60)$	do	_		36
Sunflower + Palm Stearin $(40:60)$	-do-	5	1	37.5
Sunflower + Palm Stearin $(40:60)$	-do-	5	2	39.5
Sunflower + Palm Stearin $(40:60)$	do	5 + 10	0.5 + 0.5	37
Sunflower + Palm Stearin (40.60)	-do-	5 + 15	0.5 + 0.5	37
Sunflower + Palm Stearin $(40:60)$	-do-	5 + 10	0.5 + 1	39.5
Sunflower + Palm Stearin (40:60)	-do-	10	2	37
Sunflower + Palm Stearin (40:60)	do	15	2	36.5
Sunflower + Palm Stearin $(50:50)$	-do-	5	2 2 2	36
Sunflower + Palm Stearin (50:50) Sunflower + Palm Stearin (50:50)	do do	$5 + 10 \\ 5 + 15$	3 + 3 3 + 3	35 35
		5 + 15 5 + 15	3 + 3 2 + 4	33 36
Sunflower + Palm Stearin (50:50) Sunflower + Palm Stearin (50:50)	do do	5 + 15 5	2 + 4 24	30 41
Sunflower + Sal $(50:50)$	-do-	5	24 24	41
Sumower - Sar (SU.SU)	-u0-	5	24	42

Table 3. Interesterification of ternary mixtures of sunflower oil with other oils.

Oil mixture	Randomised	Direc	Slip	
		$ \overset{\text{Temperature}}{^{\circ}\text{C}} \pm 1^{\circ}\text{C} $	Time (hr.)	Point [°] C
Sunflower $+$ Sal $+$ Palm (40:20:40)	Randomised	5 + 15	2 + 2	37
Sunflower + Sal + Palm $(40:20:40)$	-do	5 + 15	2 + 4	37.5
Sunflower + Sal + Palm $(40:30:30)$	do	5 + 15	2 + 4	35
Sunflower + Sal + Palm $(40:40:20)$	do	5 + 15	2 + 4	42
Sunflower + Sal + Palm Stearin $(40:30:30)$	-do-	5	6	40
Sunflower + Sal + Palm Stearin $(40:30:30)$	-do-	5 + 15	2 + 4	38
Sunflower + Sal + Palm Stearin $(40:30:30)$	-do	5 + 15	2 + 2	37
Sunflower + Sal + Palm Stearin $(40:20:40)$	-do-			35
Sunflower + Sal + Palm Stearin $(40:20:40)$	-do-	5	4	37
Sunflower + Sal + Palm Stearin $(40:20:40)$	-do	5 + 15	0.5 + 0.5	36.5
Sunflower + Sal + Palm Stearin (40:40:20)	-do-	5 + 15	1 + 1	37

Table 4. Solidfat index of some interesterified fat products from binary systems.

Fat Product	Slip point	Solid Fat Index (ml/kg)
	°C	15°C 20°C 25°C 30°C 35°C 40°C
Sunflower + Palm (70:30) D.I. $5 \pm 1^{\circ}$ C/24 hr.	37	8.0 7.3 5.6 4.6 3.1 1.1
Sunflower + Palm (40:60) D.I. $5 \pm 1^{\circ}C/2$ hr.	35.5	15.1 13.0 10.8 8.6 5.7 1.1
Sunflower + Palm (40:60) D.I. $5 \pm 1^{\circ}$ C/0.5 hr. + 10 $\pm 1^{\circ}$ C/0.5 hr.	35	13.4 11.5 9.0 7.8 5.5 2.0
Sunflower + Palm (40:60) D.I. $5 \pm 1^{\circ}$ C/0.5 hr. + 15 ± 1°C/0.5 hr.	37	13.3 11.2 9.0 7.6 5.4 1.5
Sunflower + Palm (50:50) D.I. $5 \pm 1^{\circ}C/24$ hr.	39	11.9 11.1 9.9 9.0 6.5 2.3
Sunflower + Palm Stearin (70:30) D.I. $5 \pm 1^{\circ}C/24$ hr.	37	9.0 8.3 6.9 6.3 3.5 1.1
Sunflower + Palm Stearin (40:60) (Randomise)	36	16.1 12.3 9.9 8.4 6.2 1.7
Sunflower + Palm Stearin (40:60) D.I. $5 \pm 1^{\circ}$ C/0.5 hr. + 10 $\pm 1^{\circ}$ C/1 hr.	39.5	16.3 15.2 13.7 12.4 8.4 3.4
Sunflower + Palm Stearin (40:60) D.I. $5 \pm 1^{\circ}$ C/0.5 hr. + $10 \pm 1^{\circ}$ C/0.5 hr.	37	15.9 14.7 13.3 11.5 7.6 2.2
Sunflower + Palm Stearin (40:60) D.I. $5 \pm 1^{\circ}$ C/1 hr.	37.5	16.1 14.7 13.4 11.7 8.0 3.0
Sunflower + Palm Stearin (40:60) D.I. $5 \pm 1^{\circ}$ C/0.5 hr. + 15 ± 1°C/0.5 hr.	37	15.7 14.3 13.0 11.0 7.3 2.2
Sunflower + Palm Stearin (40:60) D.I. 15 \pm 1°C/2 hr.	36.5	15.5 14.0 12.8 10.8 7.0 2.0
Sunflower + Palm Stearin (60:40) D.I. $5 \pm 1^{\circ}$ C/24 hr.	40.5	13.8 12.1 10.5 9.2 6.7 2.7
Sunflower + Palm Stearin (50:50) D.I. $5 \pm 1^{\circ}$ C/6 hr.	36	15.0 13.0 10.5 8.2 5.0 3.5
Sunflower + Palm Stearin (50:50) D.I. $5 \pm 1^{\circ}C/2$ hr. + $15 \pm 1^{\circ}C/4$ hr.	36	15.5 13.5 11.0 8.5 5.8 2.8
Sunflower + Palm Stearin (50:50) D.I. $5 \pm 1^{\circ}C/3$ hr. $+ 10 \pm 1^{\circ}C/3$ hr.	35	15.4 13.2 10.9 8.1 5.3 2.1
Sunflower + Sal (50:50) D.I. $5 \pm 1^{\circ}C/24$ hr.	42	13.9 11.7 10.6 8.9 6.9 4.1

Table 5. Solid fat index of some interesterified fat products from ternary systems.

Fat products	Slip Point	Solid Fat Index (ml/kg)
	°C	15°C 20°C 25°C 30°C 35°C 40°C
Sunflower + Sal + Palm (40:20:40) D.I. $5 \pm 1^{\circ}C/2$ hr. $+ 15 \pm 1^{\circ}C/2$ hr.	37	15.6 12.4 9.5 6.4 1.8 -
Sunflower + Sal + Palm (40:30:30) D.I. $5 \pm 1^{\circ}C/2$ hr. $+ 15 \pm 1^{\circ}C/4$ hr.	35	16.7 14.3 11.6 8.5 4.0 1.5
Sunflower + Sal + Palm (40:20:40) D.I. $5 \pm 1^{\circ}C/2$ hr. $+ 15 \pm 1^{\circ}C/4$ hr.	37.5	16.3 13.9 11.1 7.8 3.6 1.2
Sunflower + Sal + Palm (40:40:20) D.I. $5 \pm 1^{\circ}C/2$ hr. + $15 \pm 1^{\circ}C/4$ hr.	42	16.7 15.0 11.9 9.0 4.7 2.1
Sunflower + Sal + Palm Stearin (40:30:30) D.I. $5 \pm 1^{\circ}$ C/2 hr.		
$+ 15 \pm 1^{\circ}$ C/4 hr.	38	19.1 15.8 13.3 9.7 4.7 1.9
Sunflower + Sal + Palm Stearin (40:20:40) (Randomise)	35	18.6 14.2 10.4 7.5 4.0 0.5
Sunflower + Sal + Palm Stearin (40:20:40) D.I. $5 \pm 1^{\circ}$ C/0.5 hr.		,
$+ 15 \pm 1^{\circ}$ C/0.5 hr.	36.5	18.5 14.0 10.6 7.0 3.3 —
Sunflower + Sal + Palm Stearin (40:30:30) D.I. $5 \pm 1^{\circ}C/2$ hr.		
$+ 15 \pm 1^{\circ}$ C/2 hr.	37	17.6 14.7 11.7 8.5 3.7 1.1
Sunflower + Sal + Palm Stearin (40:40:20) D.I. $5 \pm 1^{\circ}$ C/1 hr.		
$+15 \pm 1^{\circ}$ C/1 hr.	37	17.3 13.4 10.0 6.6 2.8 0.86
Sunflower + Sal + Palm Stearin (40:20:40) D.I. $5 \pm 1^{\circ}$ C/4 hr.	37	19.1 15.8 12.6 8.4 3.7 0.27
Sunflower + Sal + Palm Stearin (60:30:10) D.I. $5 \pm 1^{\circ}$ C/24 hr.	42	14.0 12.8 11.5 9.4 7.0 3.7

DISCUSSION

The primary objective of the study is to obtain plastic fats of melting slip points ranging from $35^{\circ}C - 42^{\circ}C$ for use as Vanaspati and margarine like fats. It will appear from the tables that the melting ranges and the dilatation characteristics depend on the composition of sunflower oil blend as in some cases, simple randomisation in hexane and in many cases subsequent directed types of interesterification reactions at different low temperatures are required to get higher melting range characteristics.

Products having slip points $35^{\circ}C - 42^{\circ}C$ are obtained by simple randomisation of mixtures of sunflower oil and palm (30:70) as well as sunflower and palm stearin (40:60). Sunflower oil when blended with 30 parts of palm oil needs 24 hrs. directed interchange at $5 \pm 1^{\circ}$ C to obtain a product of 37°C. By reducing the percentage of sunflower oil by 20 percent, a product of slip point of 39°C is obtained by directed reaction at 5 ± 1 °C for 24 hrs. However, when the percentage of palm oil is increased to 60% in sunflower oil, it becomes possible to obtain a plastic fat of slip point 35.5° C by directed reaction at $5 \pm 1^{\circ}$ C for 2 hrs. If this combination is kept at $5 \pm 1^{\circ}$ C for 1 hr. and then at $10 \pm 1^{\circ}$ C or $15 \pm 1^{\circ}$ C for 0.5 to 1 hr., it becomes possible to get a product of slip point from $35^{\circ}C - 37^{\circ}C$. When palm stearin is used in place of palm oil in the same proportion (sunflower:palm stearin = 40: 60), a product of slip point of 36°C is obtained by simple randomisation. When the sunflower oil is blended with less palm stearin (e.g. 50:50), products of slip points $35^{\circ}C - 36^{\circ}C$ are obtained by directed reaction at $5 \pm 1^{\circ}C$ for 6 hrs. or at $5 \pm 1^{\circ}C$ for 3 hrs. and then at $10 \pm 1^{\circ}$ C or $15 \pm 1^{\circ}$ C for 3 hrs. The blending of sunflower with 50 parts by weight of sal fat needs directed interchange for 24 hrs. at $5 \pm 1^{\circ}$ C to get a product of slip point 42°C. In the ternary system (e.g. sunflower + sal + palm = 40:20:40) a product of slip point of 37.5°C has been obtained by directed reaction at 5 ± 1 °C for 2 hrs. and at $15 \pm$ 1°C for another 4 hrs. When the percentage of sal is increased from 20% to 40%, the slip point of the product becomes 42°C at the same condition. But when palm stearin is used in place of palm, reverse reaction occurs. In the presence of 20% sal (e.g. sunflower + sal + palm stearin = 40:20:40) only randomisation reaction is sufficient to yield a product of slip point of 35°C. However, when the blend contains 40% sal (e.g. sunflower +

sal + palm stearin = 40:40:20), a product of slip point of 37° C can be obtained when directed first at $5 \pm 1^{\circ}$ C for 1 hr. and then at $15 \pm 1^{\circ}$ C for another 1 hr.

The solid fat index values (calculated from dilatometry studies) for various interesterified fat products shows certain significant features. Fat products having similar slip point may have different S.F.I. values (e.g. sunflower + palm 40:60 and sunflower + palm stearin 40:60) which can be explained from saturated-unsaturated fatty acid ratios. The sunflower and palm mixtures has a saturated/unsaturated acid ratio 0.57 where as for sunflower and palm stearin mixture, the ratio is 0.75. This accounts for the high S.F.I. values in the latter case.

From the foregoing results, it will appear that appropriate conditions for miscella interesterification process have been established which can convert sunflower oil in the form of certain binary and ternary mixtures into plastic fat products of melting slip points of $35^{\circ}C - 42^{\circ}C$ and having low S.F.I. at temperatures between $20^{\circ}C - 35^{\circ}C$ which are close to many samples of natural ghee and margarines. It is, therefore, possible to extend the utilization of sunflower oil in making plastic fat products like new kinds of vanaspati which will be more similar to natural ghee and also margarine fats that can be used in different commercial types of margarine products. The special features of these fats are that they do not contain any transisomer, but contain on the other hand, essential fatty acids like linoleic acid in varying proportions.

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