Original Article

Interesterified palm products as alternatives to hydrogenation

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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. This paper discusses some applications of interesterified fats, with particular reference to interesterified palm products, as alternatives to hydrogenation. Some physico-chemical properties of interesterified fats used in shortenings are discussed. With interesterification, more palm stearin can be incorporated in vanaspati. For confectionary fats and infant formulations, enzymatic interesterification has been employed.

Key Words: Interesterification, palm products, palm oil, hydrogenation, margarine

Introduction

Interesterification is one of the four modification processes to alter the physico-chemical characteristics of oils and fats, the others being blending, fractionation and hydrogenation. Interesterification is an acyl-arrangement reaction. Natural oils and fats have a specific distribution of fatty acids. In most oils and fats, the middle, or 2-position, of the triacylglycerol molecules are preferentially occupied by an unsaturated fatty acid, such as linoleic or linolenic acid. During interesterification, the distribution of fatty acids is randomized on the glycerol backbone. This leads to an altered triacylglycerol composition and increased triacylglycerol species. Consequently, this will affect the physical characteristics of the oil or fat, including melting and crystallization.

In hydrogenation, hydrogen is added to the double bonds of unsaturated fatty acids. But in partial hydrogenation, some of the saturated acids are isomerized into *trans* fatty acids from their natural *cis* configuration. In the *cis* configuration, the two carbon moieties are on the same side of the double bond and on opposite sides in the *trans* configuration (Fig. 1). The *cis* configuration is a bent molecule, whereas the *trans* configuration is a straight chain.

Trans fatty acids have similar melting points to those of the corresponding saturated fatty acids and are very important contributors to the functional properties of hydrogenated products. Hydrogenation converts the liquid oil into a semi-solid or solid fat. The margarine firmness is increased by hydrogenation of the base stock due to the formation of saturated and *trans* fatty acids[1], however, *trans* fatty acids are now considered a risk factor for cardiovascular diseases.[2] Due to the health implications, the oils and fats industry is moving towards zero or low *trans* products. For example, in Europe, the levels of *trans* fatty acids in margarine products have been lowered.[3] The industry, therefore, needs to find alternatives to hydrogennated fats. Being naturally semi-solid, palm oil is an obvious choice to replace hydrogenated fats in solid fat food formulations. The industry is now relying more on interesterification to produce low or zero *trans* fats.[4] Liquid

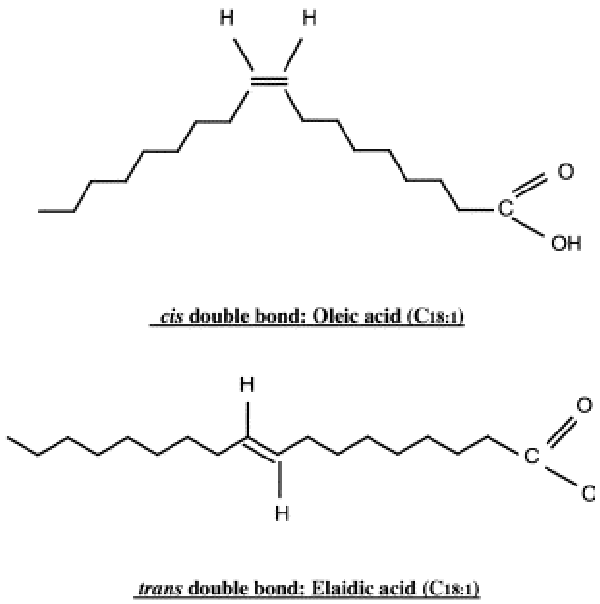

Figure 1. Molecular structure of *cis* and *trans* isomers of C18:1[5] (Reproduced with permission from Elsevier)

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Accepted 30th June 2005

palm products such as palm olein can be interesterified or use in solid fat formulations. Interesterified palm stearin or its inter-esterified blends with other oils or fats can be used in several food applications.

Interesterification

Interesterification was first used in the US in 1940's to improve the poor creaming properties of lard. Unmodified lard is a beta-tending fat, becoming grainy due to the uniform nature of its triglycerides. Most of the palmitic acid in lard is located in the 2-position of the glyceride molecule. In palm oil, the palmitic acid is located in the 1, 3 positions. Interesterification eliminates the graininess in lard as the position of palmitic acid is randomized, resulting in the formation of more desirable beta prime crystals.

Interesterification can be carried out chemically or enzymatically. A chemical, such as sodium methoxide, is used as a catalyst in chemical interesterification which produces complete positional randomization of the acyl groups in the triacylglycerols. On the other hand, enzymatic interesterification uses microbial lipases as the catalyst. Each type of interesterification has its advantages and disadvantages. The advantages of chemical interesterification over the enzymatic reaction include cost recovery and low initial investment as the catalysts are much cheaper than lipases. The process has been around for a long time, with the industrial procedures and equipment available. Enzymatic interesterification is more specific, requires less severe reaction conditions and produces less waste than chemical interesterification. In view of the current concern over *trans* fatty acids, MPOB have been investigating several *trans* fatty acid-free products - shortenings, margarines, vanaspati, ice-cream and confectionaries. For this paper, only selected products will be discussed with work done elsewhere cited.

Table 1 shows the fatty acid compositions of commercial shortenings from five countries compared with two interesterified palm-based shortenings. The levels *of trans* acids is expressed as elaidic acid (C18:1*t*). The shortening from the USA contained the highest *trans* acids at 15.1%, followed by that from Turkey with 11.5% and (closely behind) that from Canada at 11.0%. All these shortenings are based on hydrogenated oils. The South African shortening contained negligible *trans* acids with a fatty acid profile similar to that of the shortening from Malaysia. It is, therefore, likely that it contained high amounts of palm oil products. Malaysian shortenings are usually based on palm oil and palm stearin. Like commercial Malaysian shortenings, the shortening based on interesterified palm olein contained high palmitic and oleic acids [C16:0 and C18:1 (n-9), respectively].

Table 1. Fatty acid composition of shortenings from different countries and shortenings based on interesterified (IE) palm olein (POo) and an interesterified blend of palm stearin (POs) with cottonseed oil (CSO)[a]

Fatty acid (%)	USA	Canada	Turkey	South Africa	Malaysia	IE POo	IE POs:CSO
12:0	0	0	0.8	0.7	0.2	0.2	0
14:0	0.1	0.3	0.9	1.4	1.1	1.1	0
16:0	12.0	16.1	24.8	52.7	45.4	39.9	38.2
16:1	0.1	0.1	0.2	0.1	0.2	0.1	0.1
18:0	11.0	9.9	6.2	4.9	4.6	4.1	4.7
18:1t	15.1	11.0	11.5	0.8	0.1	0	0
18:1(n-9)	40.0	32.7	27.7	29.5	37.0	43.2	27.1
18:2tt,ct	4.0	2.7	0.5	0.2	0.3	0.1	0.2
18:2(n-6)	21.0	22.4	24.7	7.3	10.2	11.0	26.0
18:3(n-3)	1.3	1.5	1.5	0.1	0.3	0	0.1
20:0	0.4	0.5	0.2	0.4	0.4	0	0.5
20:1	0	0.3	0	0.1	0	0	0
22:0	0	0.3	0	0	0	0	0
24:0	0	0.1	0	0	0	0	0
Others	1.7	0.1	0.9	1.7	0	0	0

[a]The fatty acids were analysed as methyl esters using a Hewlett-Packard GC System HP 6890 Model G1530A (Willmington, DE); Column: Fused silica capillary column, 60 m x 0.25 mm, film thickness 0.25 *u*m; Oven temperature: 185°C; Injector temperature: 240°C, Detector temperature: 240°C; Carrier gas: He, 0.8 ml/min. Quantification of the peak was carried out using an integrator built into the system.

It also contained a moderate amount of linoleic acid (C18:2). The shortening based on inter-esterified palm stearin and cottonseed oil contained high palmitic acid and considerable amounts of oleic and linoleic acids.

Applications of interesterification in product formulation

Interesterification is an effective way to increase the slip melting point (SMP) and solid fat content (SFC) of palm olein:tallow blends.[6] After interesterification, there were changes in the triglyceride compositions of the blends (Table 2) - lower C50 and C52 and higher C48 and C54. The creaming performance improved in the interesterified palm olein : tallow blends, as did the baking performance (Table 3).

Beta prime crystals are desirable in margarines and in shortenings for icing and cakes. It is important that the fat crystals are able to remain in beta prime form during storage to maintain the textural quality and functional properties. Studies at MPOB have shown products made from hydrogenated palm oil to be stable in the beta prime form, even after two months from production. Some beta crystals were found in products made from unmodified palm oil after the same storage time, but beta prime crystals still predominated. Beta crystals were predominant in direct blends of palm stearin and sunflower oil. With interesterification, more beta prime crystals were formed in this blend.

Table 2. Slip melting point and triglyceride composition of direct and interesterified (IE) blends of palm olein (POo) and tallow (T)

Sample	POo:T 70:30	IEPOo:T 70:30	POo:T 60:40	IEPOo:T 60:40	Commercial
Slip melting point (°C)					
	33.8	39.7	33.9	35.5	43.8
Triglyceride composition (wt %) by carbon number					
46	0.9	1.9	1.0	1.0	1.9
48	4.6	9.1	5.0	5.6	9.1
50	35.4	27.6	33.6	32.9	20.6
52	41.9	36.0	45.7	44.5	36.4
54	11.9	15.5	14.0	15.0	19.9
56	0.4	0.3	0.5	0.5	0

Table 3. Shortening baking test for blends of palm olein (POo) and tallow (T)

Sample	Specific cake volume (cm^3/g)
POo:T 70:30	2.33
IE POo:T 70:30	2.38
POo:T 60:40	2.46
IE POo:T 60:40	2.49
Commercial	2.30

Margarines and shortenings

The slow crystallizing property of palm oil may lead to a post-hardening in products such as margarine and shortening. Interesterification can ameliorate the problem. Table 4 shows the consistencies of several palm-based shortenings during storage. The shortening made from hydrogenated palm oil was the firmest. For cake making, a softer shortening is preferred (yield value of 200 to 500g/cm^2). The softer shortening acts as a lubricant and aids in the mixing of ingredients. The interesterified palm oil shortening was softer than that made from unmodified palm oil. Similarly, the product based on interesterified palm stearin:sunflower oil was generally softer than the non-interesterified one. The changes in consistency during storage were also minimal in the interesterified products.

Table 4. Consistency measurements[a] of several palm based shortenings

Shortening	PO	HPO	IEPO	POs:SFO	IE POs:SFO
Day					
15	250	1120	190	224	240
30	260	1290	200	441	274
60	300	1370	220	444	365

[a]In terms of yield value (g/cm^2). PO, palm oil; HPO, hydrogenated palm oil; IEPO, interesterified palm oil; POs, palm stearin; SFO, sunflower oil.

Vanaspati

Vanaspati, or vegetable ghee, is a very popular cooking fat in India and Pakistan. In India, vanaspati is made from hydrogenated vegetable oils. The oils commonly used are palm, soybean, rapeseed and cottonseed. Malaysian manufacturers also produce vanaspati, mainly for export to Middle Eastern countries. The Malaysian products are usually from direct blends of palm oil and palm stearin. *Trans* free vanaspati can be produced using palm stearin and other liquid oils either by direct blending or by employing interesterification. Our studies at MPOB have shown that more palm stearin can be incorporated in vanaspati with interesterification.[7] Figure 2 shows the SFC profiles of some of the palm-based vanaspati compared with a commercial hydrogenated vanaspati from India. The vanaspatis based on interesterified palm products had good characteristics, comparable to those in the commercial product. This is proof that interesterified palm products are good alternatives to hydrogenated other oils.

Confectionary products

In confectionary, cocoa butter is an important raw material. Although cocoa butter confers excellent eating qualities, products containing it are subject to bloom, difficult to temper and may melt in hot climates. Furthermore, the inconsistent supply and high price of cocoa butter have encouraged the search for alternatives. These alternatives are fats generally classified into three types, based on their chemical composition and compatibility with cocoa

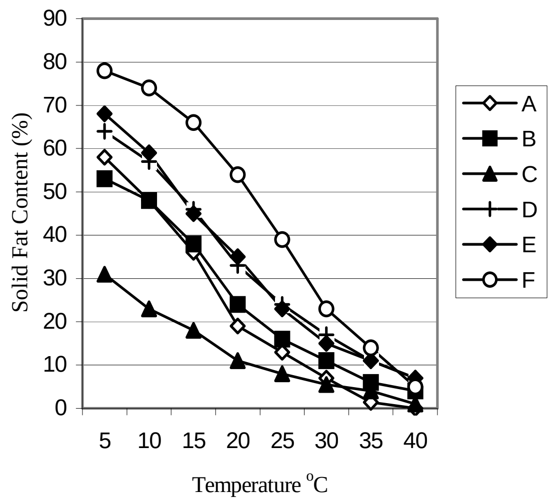

Figure 2. Solid fat content profiles of vanaspati formulations compared to commercial ghee and vanaspati. A = commercial ghee; B = IE PO; C = POs:SBO; D = IE POs:SBO; E = HPO and F = commercial vanaspati

butter. Cocoa butter equivalents (CBE) have chemical and physical properties compatible with those of cocoa butter, and can be used to supplement cocoa butter in confectionery products. Cocoa butter substitutes (CBS) are generally lauric fats incompatible with cocoa butter. Cocoa butter replacers (CBR) are partially compatible with cocoa butter. CBRs are primarily non-lauric fats which have properties in between those of CBEs and CBSs, and are sometimes referred to as non-lauric cocoa butter substitutes. Among these three principal types of alternative fats, CBE is the most and CBS the least expensive. Typically, the substitutes cost only one-third to one-fourth of cocoa butter, making them more economically attractive to consumers.[8]

There are a number of fats suitable for total or partial replacement of cocoa butter. Palm oil is an important source oil in the development of substitutes or equivalents. Undurragaa *et al.*[9] used enzymatic interesterification of palm mid fraction with stearic acid in a solvent free system with a commercially available enzyme to produce CBE. In an earlier study, Chong *et al.*[10] used a solvent-free lipase catalyzed inter-esterification of palm olein with stearic acid, followed by solvent fractionation procedures to produce palm-based cocoa butter-like fat. The yield of cocoa butter-like fat was approximately 25% of the weight of the original palm olein. Table 5 shows the triacylglycerol compositions of a fraction of interesterified palm olein obtained by different solvent fractionation procedures.

Table 5. Composition of a fraction of interesterified palm olein obtained by different solvent fractionation procedures (A, B, C).

Fraction	Triglycerides[a] (%)		
	POP	POS	SOS
F2(A)	15.3	44.1	29.6
F2(B)	16.0	38.7	23.1
F2(C)	13.7	38.5	24.8
Cocoa butter	18.9	41.3	29.7

[a]P, palmitate; S, stearate; O, oleate. (Reproduced with permission from American Oil Chemists' Society).

Infant formula

Another important application of interesterification is infant formula. The fatty acid composition of human milk is often used as the basis for infant formula to create a close semblance to the milk.[11] Human milk fat has triacylglycerols which fatty acid structure, composition and distribution are specific. Its unique characteristics include, firstly, two long-chain polyunsaturated fatty acids (PUFAs) - arachidonic (C20:4, n-6) and docosahexaenoic (C22:6, n-3) - and, secondly, abundance of a saturated fatty acid - palmitic (C16:0) - predominantly at the 2-position of the triacylglycerol.[12]

To obtain a similar fatty acid composition and positional distribution as in human milk fat, oils and fats may be modified by interesterification. Lipid compositions for infant formula, which mimics human milk, as well as the processes for preparation of the compositions by interesterification, either chemical or enzymatic, are described in various international patents. In one, a mixture of lipids containing palm oil enriched with palmitic acid (for example, from palm stearin), a vegetable oil high in linoleic and alpha-linolenic fatty acids, an oil for arachidonic acid and another for docosahexaenoic acid in defined proportions are interesterified to obtain the required fatty acid composition with random distribution of the fatty acid residues between the 1-, 2- and 3- positions of the triacylglycerols. The interesterification can be enzymatic (catalyzed by a non-regiospecific lipase) or chemical. By the reaction, the non-random distribution of fatty acids on the triacylglycerols of the natural lipids is converted to random distribution, with the fatty acids rearranged equally at the three positions. The randomized mixture was then interesterified with a mixture of free fatty acids high in medium chain fatty acids and oleic acid using a 1,3-regiospecific lipase. This step selectively replaces palmitic acid at the 1- and 3- positions with other fatty acids, in particular, with medium chain fatty acids and oleic but not with PUFAs. Many scientists have reported that enzymatic interesterification using 1,3-specific lipase is the most effective way to produce triacylglycerols similar to those found in human milk.[13-17]

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Interesterified palm products as alternatives to hydrogenation
氢化油脂的替代品－酯交换棕榈产品

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酯交换是用于改变油和脂肪理化特性的处理过程之一，是一种甘油分子上的酰基进行重排的反应。而另一方面，氢化作用是指在不饱和脂肪酸的双链上加氢。由于氢化过程中形成的反式脂肪酸对健康的影响，因此食品工业需要找到氢化脂肪的替代品。本文讨论了酯交换脂肪的一些应用，同时作为氢化油脂的替代品，酯交换棕榈油产品在本文中得到详细介绍。本文还讨论了用于制造起酥油的酯交换脂肪的理化性质。酯交换技术使得更多的硬脂酸甘油酯应用于人造黄油的制造中，同时酶催化酯交换技术也已经在糖果专用脂肪和婴儿配方中得到应用。

关键词：酯交换　棕榈产品　棕榈油　氢化作用　人造黄油