

## Review article

**Food applications of *trans* fatty acid substitutes**

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**Summary** The review outlines the increasing need to reduce *trans* fatty acids, and addresses the functionality issues of various *trans* free solutions through discussion of hydrogenation, interesterification, and fractionation, and their influence on fat crystallisation and solid fat content. Caution is urged not to focus solely on physio-chemical aspects, but to approach *trans* free designing for specific food applications from a multidisciplinary angle. Examples of specific applications; margarines, shortenings and frying oils are given. The review also offers a glimpse into what the future *trans* free trends may hold.

**Keywords** Blending, crystallisation, fractionation, hydrogenation, interesterification, *trans* fatty acids.

**Introduction**

Suspicion exists suggesting adverse health effects from the use of *trans* fatty acids in foods and their subsequent intake. However, there is no indication that cessation of *trans* fatty acid use would negatively impact health – au contraire! Similarly, ceasing to use industrially produced *trans* fatty acids should not impair the quality of food. Recommendations from the Danish Nutrition Council (Stender & Dyreberg, 2003) say (a) that industrially produced *trans* fatty acids should not be used in food and (b) that the use of industrially produced *trans* fatty acids in food should be phased out as soon as possible. At the time of writing, the World Health Organization (WHO) has recommended that governments around the world phase out partially hydrogenated oils if *trans*-fat labelling alone does not spur significant reductions. The recommendation was put forth by the WHO in a proposed action plan for its food standards rulemaking body, the Codex Alimentarius Commission (Codex) entitled, 'Request for comments on draft action plan for implementation of the global strategy on diet, physical activity and health' (Fletcher, 2006).

The increasing pressure to remove *trans* fatty acids from food products, indeed even to remove the term 'hydrogenated' from the food label; coupled with the drive to supply products with much lower saturated fat contents has become a global high-profile topic. Food producers are faced with the difficulty to not only satisfy the nutritional demands, but also create *trans*-free

options, which concomitantly deliver acceptable functional performance – be that physiological, textural or other technical perspectives.

The aim of this review is to explore how practical applications of *trans*-free solutions are currently being successfully implemented, provide insight into realistic future possibilities, and to deliver marketable food products.

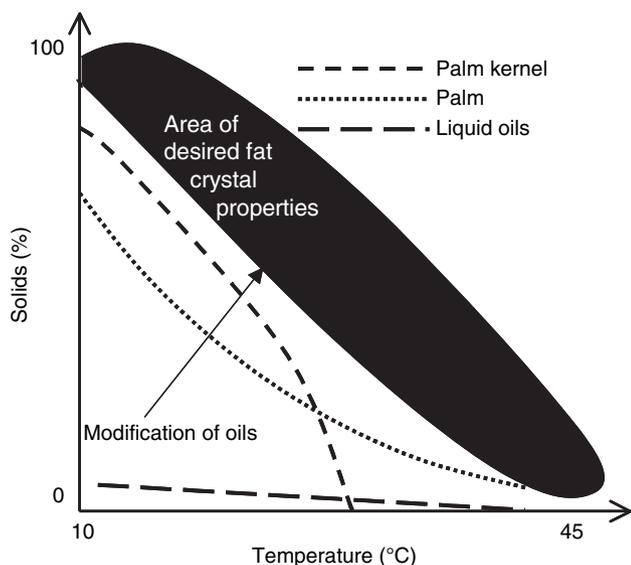
**Functionally *trans*-free – the issues**

Successful replacement of *trans* fatty acids is not easily achieved by simply removing the *trans* isomer, because of a host of beneficial functional characteristics that are readily attributable to *trans* fatty acids. As previously stated, the presence of *trans* isomers influence melting behaviour, textural properties and oxidative stability. Production of fat blends that are either low in *trans* or regarded as *trans*-free therefore requires modification of the base natural fats or oils; this can be achieved by various techniques: hydrogenation (partial or full), interesterification, and fractionation (Morin, 2006).

**Hydrogenation**

Hydrogenation, by dint of saturating some double bonds and converting others to the *trans* configuration is already an apt technique to provide fats, which can impart firmness to margarines (Kok *et al.*, 1999), and plasticity and emulsion stability to shortenings (Reddy & Jeyarani, 2001).

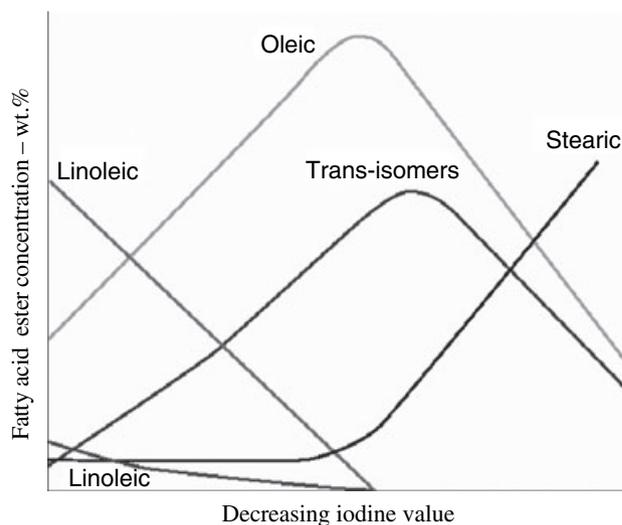
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**Figure 1** Desired solid phase lines for hardstocks (green area) compared to naturally occurring oils and fats (adapted from van Duijn *et al.*, 2006).

Hydrogenation of oils and fats has been used since the beginning of the 20th century to produce hardstocks from a great number of oils – mainly liquid oils. Hydrogenation involves the addition of hydrogen atoms across the unsaturated double bonds of the particular triglycerides. Depending on the ‘natural’ occurring starting point of unsaturation of the said oil, the degree of hydrogenation will result in a more saturated fat having a higher melting point than the starting material. The fundamental importance of this aspect cannot be overemphasised, because it enables the production of solid and semi-solid fats. These then provide structure, texture and hardness to the food product, lubrication, and in terms of emulsion stability – can provide specific crystallisation behaviour, necessary for continuous fat phase dispersions/emulsions. The extent and degree of satisfying these criteria are, as stated, dependent on the amount of solid fat, size, shape and synergistic interactions of the crystals. Today, in view of the limitation of solidifying ‘natural’ liquid oils to structural hardstocks, we are able to utilise other naturally occurring hardstock components, i.e. from palm oil. (Heller, 2005) This is shown schematically in Fig. 1. It is easy to see the degree of modification required to the liquid oil to obtain the desired solid fat structure that for instance could be used for margarine or shortening production.

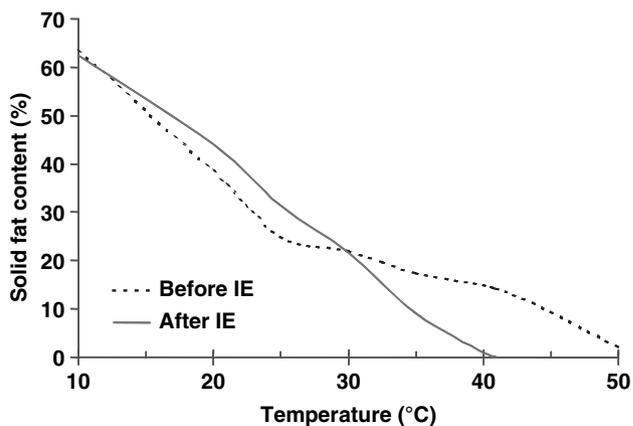
The degree of hydrogenation influences the degree of saturation (Fig. 2) and hence solid fat content (SFC); however, this aspect must be balanced so as to account for the level of *trans* isomer formation.



**Figure 2** Degree of *trans* isomer according to fatty acid saturation as a function of iodine value.

### Interesterification

Interesterification has been developed as an alternative to hydrogenation, with the specific aim of eliminating the formation of *trans* fatty acids (Özay *et al.*, 1998). The process rearranges the distribution of the fatty acids either chemically or enzymatically, within and between the triglycerides, thus the fatty acid distribution is altered, but the fatty acid composition remains unchanged – this rearrangement can be done either in a random or controlled manner (Yusoff & Dian, 1995). The technique is effective and can be used to produce fat products for spreads that are soft and spreadable and also *trans*-free (Özay *et al.*, 1998).



**Figure 3** A blend of 60% palm stearin/40% palm kernel before and after interesterification.

Interesterification is nothing new, having been around for some time, and the basic principles were first documented in 1969 (Fondu & Willems, 1969). The patent claims a PUFA margarine ‘free from hydrogenated hard fat’. The last and most general claim is,

Process for the preparation of a margarine fat ... which comprises interesterifying a mixture of unhardened fats comprising a coconut fat, a palm fat and a constituent with at least 60% fatty acids of a chain length of at least 16 carbon atoms, and blending the interesterified mixture with 25–90% of a liquid fat with at least 40% of polyunsaturated acids ....

An example of this is shown in Fig. 3, where a mixture of palm stearin and palm kernel are interesterified.

### Fractionation

The controlled crystallisation of a triacylglycerol can result in the separation of a solid phase (stearin) and a liquid phase (olein), and these in turn can be further fractionated (van Duijn *et al.*, 2006). If fat is melted and cooled slowly to below its melting point, the triglycer-

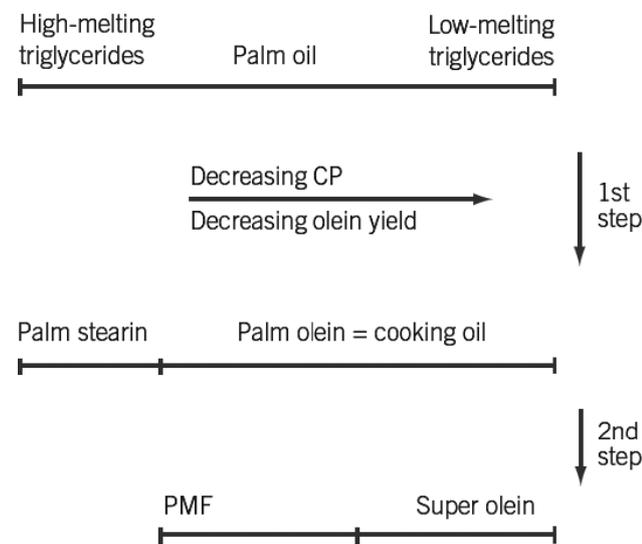


Figure 4 Fractionation principles of palm oil.

Table 1 Typical fatty acid compositions of palm, palm kernel and their fractions as established by gas-liquid chromatography

	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18.0</sub>	C <sub>18.1</sub>	C <sub>18.2</sub>	IV range
Palm oil	–	1.0	44.4	4.1	39.3	10.0	50–55
Palm oil (olein)	–	1.0	39.8	4.4	42.5	11.2	56 min
Palm oil (stearin)	–	1.5	55.8	4.8	29.6	7.2	48 max
Palm kernel oil	48.2	16.2	8.4	2.5	15.3	2.3	14–19
Palm kernel (olein)	42.6	12.4	8.4	2.5	22.3	3.4	25–31
Palm kernel (stearin)	55.2	19.9	8.1	3.3	6.9	0.8	6–9

ides with a higher melting point than the tempering temperature will eventually form crystalline material, which can be relatively easily filtered off from the liquid part. Today, the most important oil in terms of fractionation is palm because it has a unique fat profile that can be broken down into individual fractions and sub-fractions thereof. The first fraction gives palm stearin and olein, the second fraction palm mid fraction and super olein. With today’s modern fractionation techniques it is possible to fractionate individual palm fractions into very precise sub-fractions to achieve very specific solid fat curves and melting points. The principle of fractionation is shown in Fig. 4, and the major fatty acid components of these fractions are shown in Table 1.

Palm oil is an excellent natural candidate for fractionation and fat blending (see Design and control of the fat blend) due to it containing not only a significant portion of high melting triglycerides, but also tending to crystallise in the favoured β’ configuration (Lida & Ali, 1998; Sundram, 2005). However, to maximise the potential of palm oil as a blending source it is occasionally necessary to fractionate the palm oil (Jeyarani & Reddy, 2003). This can be done in one of two ways, either dry fractionation or solvent fractionation. Under dry conditions the palm oil is heated and then cooled to a given temperature under agitation such that the partially crystallised mass can be filtered off under vacuum to give the palm stearin. The remaining liquid fraction gives the palm olein. The process under solvent conditions is similar albeit that the palm oil is first dissolved in a solvent and then the process proceeds as above. Subsequent removal of solvent is done under vacuum.

### Singular or multidisciplinary approach?

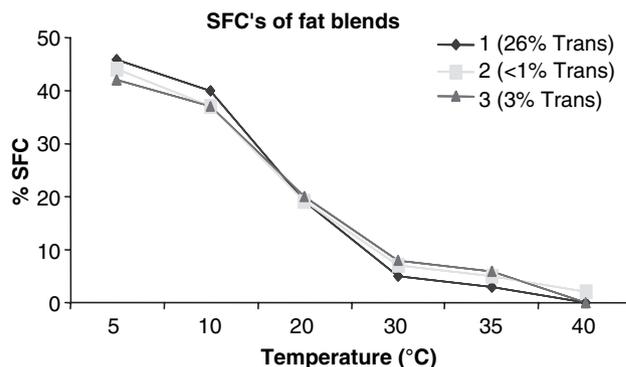
The above modification techniques have been shown to offer the chance to minimise and control the *trans* content of oil blends, and can be used to successfully formulate *trans*-free hardstocks. However, the combination of these techniques, leads to a greater variety of hardstocks with a wider range of physical properties such as solid fat phase and melting point behaviour. This is particularly important for fats where they are expected to have specific performance. Addressing the functionality issues of replacing *trans* fatty acids, SFC, and crystalline elements are the main physical success criteria of a *trans*-free solution. Therefore, to effectively solve the challenge, performance phenomena such as creaming, crystallisation and emulsification also need to be considered. Thus, to exclusively focus purely on the physico-chemical aspects but neglecting the fat’s required functional role within the final application is likely to lead to serious and significant developmental problems.

**Table 2** Three commercial shortening blends of similar SFC at the working temperature of 20 °C but with quite different degrees of saturation and *trans* content (inter blend = 60% Pst/40% PK)

Fat blend	1	2	3
Palm oil	20	40	35
Rapeseed oil	30	30	40
hPO_mp43			25
Inter blend		30	
hSB_mp35	50		
SFC % (Bruker pNMR)			
5 °C	46	44	42
10 °C	40	37	37
20 °C	19	19	20
30 °C	5	7	8
35 °C	3	5	6
40 °C	0	2	0
Melting point ( °C)	33.6	41.5	37.8
Nutrition%	1	2	3
sats.	24	42	34
monos.	38	42	47
polys.	12	15	16
% <i>Trans</i> acid content	26	<1	3

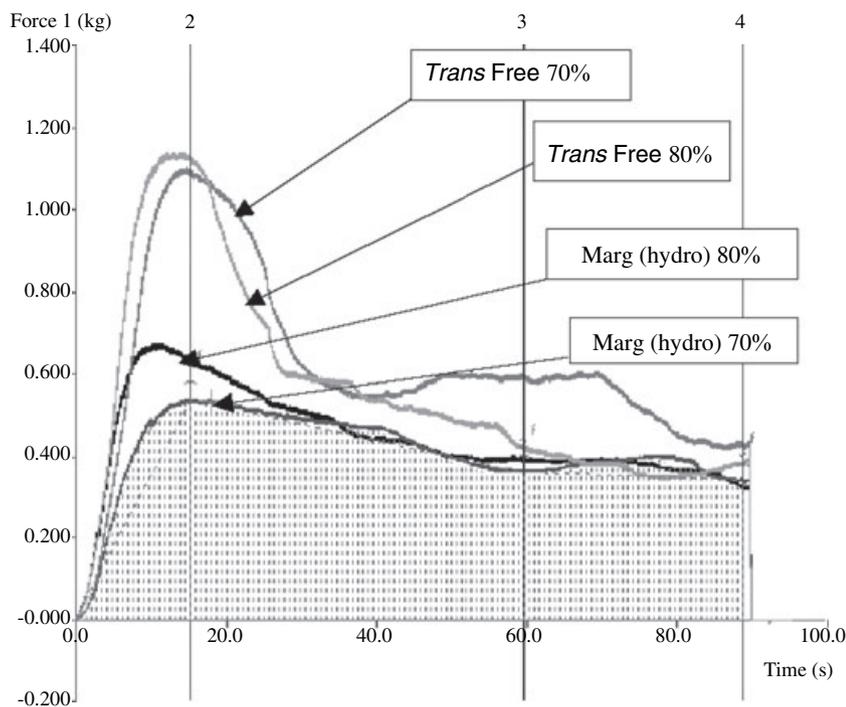
The dangers of addressing SFC in isolation when considering the degree of saturation or indeed *trans* fatty acid content of commercial fat blends are highlighted by Table 2 and graphically demonstrated in Fig. 5.

Attempts to match the physical properties of a commercial fat blend to a specific application are often based on solid fat profile, melting point and textural



**Figure 5** SFC content as a function of temperature for the three commercial fat blends given in Table 2.

qualities, whereby the commercial fat blend's plastic range might be expected to be within a given tolerance. While Table 2 and Fig. 5 clearly show that similar SFC can be achieved, while simultaneously achieving a low *trans* fatty acid content, pursuing this philosophy is potentially flawed, and could lead to inadequate functionality of the given commercial fat blend in the final application. Inadequate functionality can be symptomatic of excessive focus on physical character as it may lead to significant post-crystallisation. This all suggests that control over the crystalline issue needs to be accounted for because if only focussing on the physical like-for-like criteria, for example an oil blend



**Figure 6** Texture analysis of a low *trans* margarine compared to a margarine containing partially hydrogenated hardstocks.

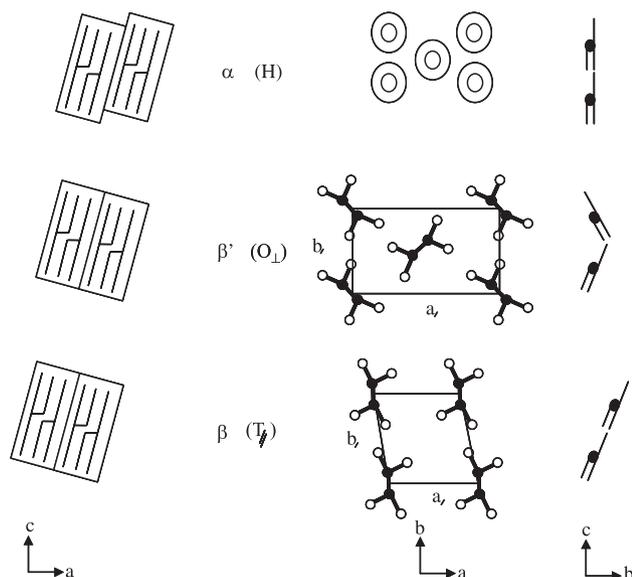


Figure 7 The three projections of  $\alpha$ ,  $\beta'$  and  $\beta$  crystal forms (with permission from Leatherhead Food International, UK).

might be particularly high in palm content, it is well documented (Ueno *et al.*, 2006; Bell *et al.*, 2007) that the post-crystallisation phenomenon is likely to cause textural problems in products containing palm. Figure 6 shows such effects through the measurement of hardness of a *trans*-free margarine formulated with palm oil components compared to a margarine having similar SFC, and containing partially hydrogenated hardstocks. It can be seen that where the pump speed during processing is either increased or decreased (70% and 80%) there is a direct effect on the textural property of the margarine.

The *trans*-free margarines are formulated with palm oil components, the *trans* (hydro) margarines have similar SFC but are formulated with partially hydrogenated hardstocks.

This suggests that more intensive crystallisation and kneading by a reduction in pump speed and hence longer process residence times, may bring the textural property of a *trans*-free product closer to a *trans* containing analogue.

Crystalline issues within fats and fat/oil blends are basically governed by three polymorphic forms in which the fat crystals can exist, and these have important and significant impact on the fat's final functionality within the individual application.

The three basic polymorphic crystal forms are,  $\alpha$ ,  $\beta'$ , and  $\beta$  (Young & Wassell, 2007) and are schematically given in Fig. 7.

For many applications the most desirable polymorph is the  $\beta'$  form, but this is by no means exclusive. For some applications, e.g. liquid shortenings and chocolate, the  $\beta$  form can be regarded as the most desirable. The

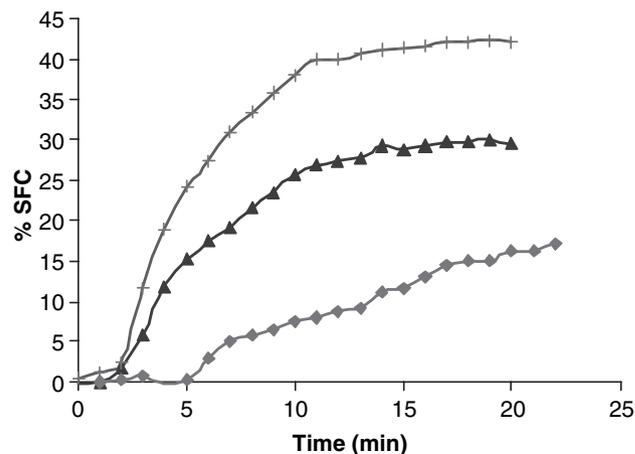
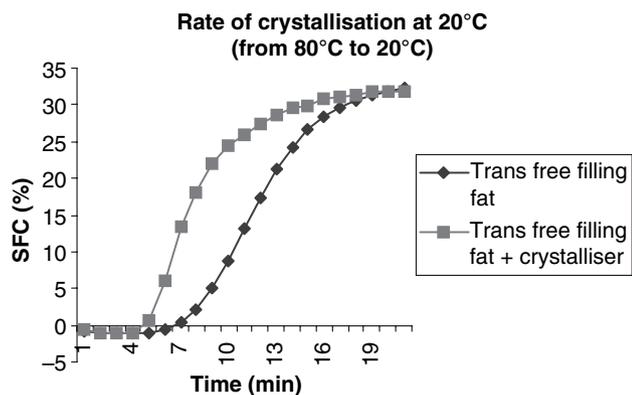


Figure 8 Rate of crystallisation for three different fat blends which have similar SFC, while measured under static conditions using Bruker p-nuclear magnetic resonance.

general desirability of the  $\beta'$  form is based on this polymorph having a small crystal size giving a fine packing quality, a large surface area and a greater oil-holding capacity. The occurrence of the  $\beta'$  polymorph can be highly influenced by the presence of, the type of, and amount of fats present, where their natural polymorph is  $\beta'$ . The presence of a percentage of *trans* isomer also affects the fat crystallisation kinetics, where it can aid the formation and drive the crystal form towards the  $\beta'$  form even though the natural tendency is towards the  $\beta$  form. Therefore, replacing the *trans* isomer may require that another kinetic mechanism is present to drive polymorphism towards the preferred form. Thus, simply decreasing the *trans* fats could negatively impact the functionality unless care and attention is taken to crystal form details (Mayamol *et al.*, 2004).

The need to improve the rate of crystallisation is highlighted in Fig. 8, which shows three different fat blends having similar SFC profiles but quite different crystallisation kinetics.

Improving the rate of crystallisation of *trans*-free fat blends can be highly beneficial, allowing the fats to reach a specific SFC, often within certain limitations of the process. This issue is fundamentally critical, because where a given fat blend is not optimally crystallised during manufacture, e.g. of margarine, then 'uncontrolled' post-crystal changes will occur. Therefore, simply selecting a portfolio of oil blends and expecting these to run on 'standard' process conditions is not always a guarantee of success. In some cases manufacturers have been running long established oil blend formulae on old 'trustworthy' processes and equipment for many years. However, being forced, because of increasing *trans* awareness to make a switch to alter-



**Figure 9** Rate of crystallisation on a *trans*-free filling fat with and without additional crystal promoter.

native oil formula's with similar SFC profiles, but quite different crystallisation properties, can be complicated and troublesome, especially when attempting to maintain economically viable production rates. If the plant operator's scope to compensate within the process, i.e. increase supercooling, etc. is exhausted, then other strategies will have to be sought out and adopted.

One alternative strategy can be the addition of 1–2% fully/highly saturated triglyceride. The addition of a small proportion of fully hardened triglyceride is an inexpensive and often effective approach to induce the onset of nucleation within a given set of process conditions. While this approach may help to some degree, it is unlikely to counter and solve processing and crystallisation issues entirely.

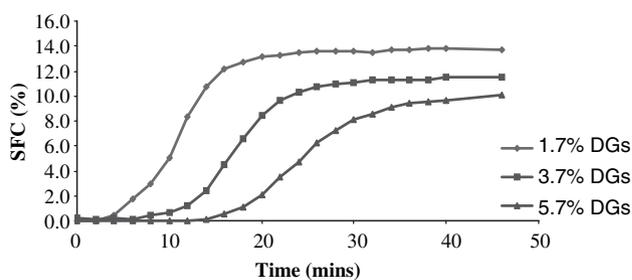
Upgrade or increasing capacity of an existing process, i.e. adding more scraped surface heat exchanger units can also be investigated. However, to focus on the crystallisation issues from an ingredient angle, one could begin to use emulsifiers as crystal promoters. The effect of such crystalliser technology can be seen in Fig. 9. The graph shows the effect on SFC of a *trans*-free fat, i.e. <1% *trans* vs. the same *trans*-free fat with added crystalliser.

The fats were melted and held at 90 °C for 1 h before cooling. The first reading was taken at 80 °C and thereafter every minute for 20 min. The sample was kept in a water bath at 20 °C during the experiment. The rate of crystallisation was measured with a low field-pulsed nuclear magnetic resonance spectroscopy. The time taken to reach an SFC of 25% in the sample with crystalliser was 9 min as opposed to 14 min for the sample without crystalliser, a time saving of some 64%. Here, the crystalliser, an emulsifier based on similar technology as referred to by Cerdeira *et al.* (2005), acts as a source of heteronuclei, accelerating nucleation – and hence the rate of crystallisation. This technology itself was based on reports that the longer the hydro-

phobic chain the greater the effect on the crystallisation kinetics (Sakamoto *et al.*, 2004). Polyglycerol behenic ester has a long hydrophobic chain, which can positively affect nucleation. It has been demonstrated that even at low concentration, when polyglycerol behenic esters were added to palm oil; they acted as a driving force promoting the crystallisation of the  $\beta'$  polymorph, and prevented formation of granular crystals (Sakamoto *et al.*, 2003). They further went on to report that the palm oil crystals were not only smaller but there were significantly more of them as determined by polarised light microscopy. This suggests that use of these polyglycerol behenic esters may set up favourable antagonistic processes where the promotion of the  $\beta'$  polymorph proceeds at the expense of the  $\beta$  polymorph, i.e. one emulsifier two functions.

Control over the rate of crystallisation can of course be governed by the concentration of the added crystalliser, but Kristensen & Wassell (2006) have shown that other techniques can be similarly effective with palm oil. The increasing use of palm oil to solve the *trans*-free problem places further pressure to gain control over the crystallisation as it is accepted that the presence of diglycerides (DG) slows the crystallisation process and changes the melting behaviour (Siew & Ng, 1990; Siew, 2002). This slowing of the crystallisation process leads to post-hardening during storage of palm-based margarines. By gaining control over the DG content of palm oil Kristensen & Wassell (2006) showed that not only control but also improvement over the crystallisation rate was possible. Figure 10 shows the effect of adding DG back into the palm oil under controlled conditions.

The DG was first separated, and then added back such that the concentrations achieved were 1.7%, 3.7% and 5.7%. The results show that the lower the DG concentration the faster the rate of crystallisation, which in turn has other process implications of shorter inductions times and higher SFCs compared to samples where the DG content has been ignored. These results overall demonstrate that control of the crystallisation rate can be gained by either varying the concentration of



**Figure 10** Crystallisation curve of palm oil with varying amounts of DGs (1.7%, 3.7% and 5.7% DGs); crystallisation temperature 25 °C. NB: The reference product contains 5.7% DGs.

the crystalliser or by accounting for the DG content giving rise to the possibility of tailoring the crystallisation process of a specific fat blend for a given application.

Concentrating exclusively on the fat phase, where we are only concerned with reducing *trans* fatty acids does not address the problems of total saturates or the presence of partially hydrogenated fats. Addition of a water phase, creating an emulsion, automatically reduces the fat content into the final application, can redress the balance of total saturates and *trans* fatty acids. However, to effectively pursue this course requires balanced emulsifier technology and the possible use of thickeners, and possibly subsequent redesign of the final food product may be necessary.

Historically, oil blends were often formulated as either summer or winter blends according to seasonal variation. In Europe in particular, this is rarely practised. Oil blends have become ‘softer’ and therefore where there is still scope – a strategy that can be used, is to reformulate a given fat blend such that it has a lower SFC profile. Simultaneously it is then possible to achieve a fat blend with lower saturates and even the absence of hydrogenated hardstocks. This particular approach must be carefully thought out bearing in mind local climatic conditions.

Irrespective of the strategy followed, careful choice of the fat type or fat blend can ensure that functionality is maintained, and in some cases improved, but this must be carefully balanced. Of course the new oils or fat sources must be at least as cheap if not cheaper than the existing materials. Over and above the oils or the fat blends, the combination of emulsifiers are also important as their interaction and influence on the fat components can change the crystallisation kinetics and adjust texture (Cerqueira *et al.*, 2006), leading back to the favoured advocacy of the multidisciplinary approach.

**Design and control of the fat blend**

*Trans*-free fat blends can be constructed by blending oils (high oleic and low linolenic) with fully hardened oils (soya, cottonseed or palm), or indeed where the entire blend has been randomised through interesterification. Such blends are given in Tables 3 and 4 as quoted by Orthofer (2005).

Blending vegetable oil types from different sources is an efficient alternative to hydrogenated vegetable oils (Sahasranamam, 2005; Cerqueira *et al.*, 2006), and still provides the appropriate physico-chemical properties and nutritional requirements demanded. The additional benefit of this technique is that no chemical modification is necessary and therefore the fat blend conforms to the modern consumer-driven trend of ‘all things natural’ (Jeyarani & Reddy, 2003). Such fat blends can also be rich in polyunsaturated fatty acids as well as being *trans*-

**Table 3** Solid fat content profiles for high-oleic, low-linolenic (HOLL) canola blended with increasing amounts of fully hydrogenated oil (Orthofer, 2005)

Blend (% hardfat)	% solids at the following temperatures					
	10 °C	21 °C	27 °C	33 °C	38 °C	40 °C
Soy hardfat						
10	11.5	10.2	9.7	8.4	7.7	7.0
20	22.5	20.9	19.5	17.6	16.1	15.6
30	33.2	31.9	29.6	27.5	25.4	24.7
Cottonseed hardfat						
10	11.3	10.3	9.3	7.9	7.0	6.8
20	21.6	20.8	19.2	17.4	15.6	14.9
30	32.3	31.4	29.6	27.3	25.1	24.1
Palm hardfat						
10	10.9	9.7	8.3	6.9	5.6	4.9
20	21.9	19.8	18.2	16.0	13.9	12.8
30	31.3	30.3	28.5	25.9	23.2	21.9

**Table 4** Solid fat content profiles of interesterified high-oleic, low-linolenic (HOLL) canola blended with increasing amounts of fully hydrogenated oil (Orthofer, 2005)

Blend (% hardfat)	% solids at the following temperatures					
	10 °C	21 °C	27 °C	33 °C	38 °C	40 °C
Soy hardfat						
10	1.4	0.6	0.1	0	0	0
20	5.4	4.5	2.6	0.9	0.2	0
30	12.7	12.6	10.7	4.8	2.4	2.0
Cottonseed hardfat						
10	5.1	2.0	1.4	0.6	0.4	0.1
20	5.9	4.3	2.2	0.6	0.1	0
30	11.4	11.1	8.9	3.9	1.8	1.0
Palm hardfat						
10	7.9	5.8	5.0	3.6	2.3	1.3
20	19.7	17.3	15.9	13.6	10.8	9.7
30	29.7	25.9	23.7	19.9	16.2	14.5

**Table 5** Preparation of interesterified hardstocks, which are then further blended with liquid oil to obtain desired melting behaviour, all blending amounts are given in percentage terms

Component	1	2	3	4	5	6	7
Palm stearin (soft)	60				60	40	
Palm stearin (m.p. 50 °C)			70				
Palm stearin (m.p. 54.4 °C)							50
Palm oil				75			
Palm olein		75					
Palm kernel oil		25					50
Fully hydrogenated soybean oil				25			
Liquid oil <sup>a</sup>	20		30				
Palm kernel olein	20				40	60	

<sup>a</sup>Liquid oils can be sunflower, rapeseed and soybean oils.

**Table 6** Manipulation of fat blends for table spreads to industrial margarine or shortening

	TF	TF	TF	TF	TF	TF
Fat type						
Interesterified hardstock*	25	20	25	30	25	30
Palm oil		20	25	30	50	50
Liquid oil	75	60	50	40	25	20
SFC values						
5 °C	16	24	31	38	46	52
10 °C	13	20	26	32	39	46
20 °C	6	11	14	18	21	24
30 °C	3	5	6	7	8	10
35 °C	2	3	4	4	4	5
40 °C	0	1	1	2	2	2
Slip melting point °C	29.4	31.5	32.8	34.3	36.3	36.6

\*60% palm stearin /40% palm kernel.

free (Cerqueira *et al.*, 2003). Examples of suitable *trans*-free oil blend precursors are given in Table 5 (Berger & Idris, 2005). Often these are found by trial and error, and manipulation with the oil blend is made until a suitable SFC or melting profile is found as shown in Table 6, which refers to a preparation of interesterified hardstocks, which are then further blended with liquid oil to obtain desired melting behaviours.

Different applications demand different fat blends and in designing a specific fat blend the individual requirements must be addressed. *Trans*-free options are commercially available in the form of a blend of tailored emulsifiers and oil blends (Doucet, 2004; Miller, 2006) where they meet demands for shelf-life, processing and distribution requirements.

These *trans*-free options are available for a wide range of products covering, snacks, cakes, breads, tortillas, nutrition bars, cookies and breakfast cereals. *Trans*-free oil blends are also routinely designed for margarines, where they impart structure and texture (Kok *et al.*,

1999), and shortenings where they provide firmness and contribute to crumb structure (Idris *et al.*, 1989; Wassell, 2006). Examples of a range of suitable *trans*-free fat blends are shown in Table 7.

### Fat/oil blends for margarines

#### Table margarines

*Trans*-free oil/fat blends for margarines can be designed by simple blending, which may encompass combination of fractions which can either be fully hydrogenated or not with liquid oil and/or interesterified oils which again may contain fully hydrogenated hardstocks. A  $\beta'$  tending fat/oil source is a huge benefit for margarine applications and therefore one of the oils of choice is palm oil (Özay *et al.*, 1998; Berger & Idris, 2005). In addition to its  $\beta'$  tendency palm oil has a natural semisolid consistency, useful to margarine applications, but one, which can also be hardened further by random interesterification without the subsequent formation of *trans* fatty acid. Palm oil is however a complex mixture of triglycerides, with respect to the carbon chain length. By combining different amounts of palm stearin or palm olein the SFC can be optimised to the benefit of the application in hand, and today with more complex fractionation techniques specific mid-fractions may be used because they can provide for precise SFC profiles. The SFC therefore has important implications for the overall melting characteristics of margarines and spreads at various temperatures. This is particularly important for low fat spreads. At low temperatures, i.e. 4–10 °C the value of the SFC will lead to an indication of spreadability when the product is removed straight from the fridge. Here, SFC values should not exceed 32% at 10 °C (Lida & Ali, 1998). Higher temperatures – around room temperature of 20–22 °C – determine

**Table 7** A range of *trans*-free formulations for table spread to industrial pastry margarine

	Interesterified blend	Spread fat blend	Industrial shortening/ margarine fat blend	Croissant fat blend	Puff pastry fat blend	Puff pastry fat for hot climate
SFC values of fat blend (IUPAC method)	55% palm stearin 45% palm kernel oil	60% rapeseed oil 40% interesterified	40% palm 35% rapeseed oil 20% interesterified 5% FH palm	52% palm 35% palm stearin 13% rapeseed oil	15% palm 55% palm stearin 20% rapeseed oil 10% interesterified	20% palm 70% Palm stearin 10% rapeseed oil
5 °C	77%	23%	42%	60%	60%	68%
10 °C	73%	19%	34%	53%	55%	64%
20 °C	47%	10%	19%	35%	40%	48%
30 °C	18%	5%	7%	19%	25%	32%
35 °C	7%	1%	3%	14%	17%	24%
40 °C	0.5%	0	1%	9%	13%	19%
Slip melting point °C (AOCS Cc 3–25 method)	36 °C	31 °C	34 °C	40 °C	46 °C	52 °C

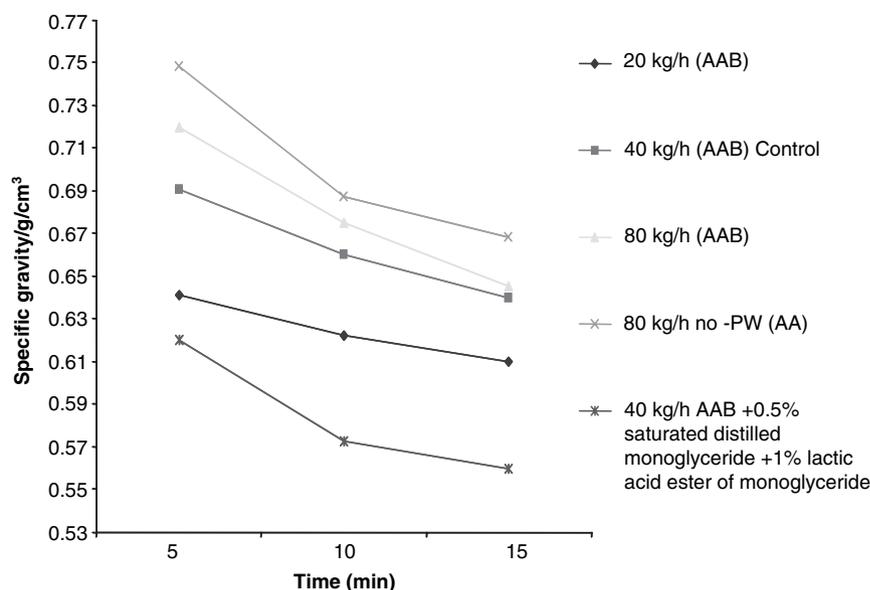
the product stability and resistance to oil exudation at table-top conditions, and the SFC should be at least 10%. Finally the SFC at around 35–37 °C provides data on the thickness and mouth feel characteristics as well as flavour release, and should be around 1–3%.

One of the main issues to consider here is that the resulting blend accounts for the necessary SFC conditions according to the local climatic and distribution chain conditions demanded by margarine applications, be they retail or industrial margarine (Yusoff *et al.*, 1998).

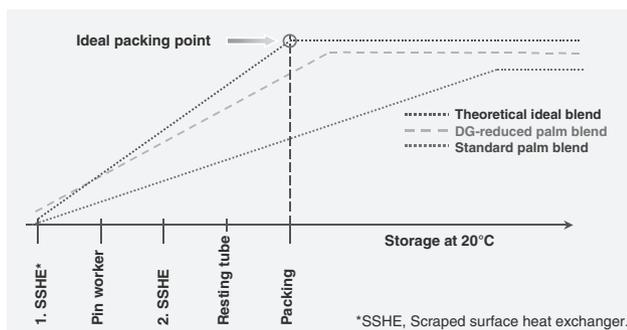
A typical *trans*-free fat blend for a table margarine could look like palm stearin, palm kernel olein and sunflower seed oil in the ratios of 60:20:20, respectively (Yusoff & Dian, 1995), or alternatively a blend of palm oil, palm olein and canola oil in the ratio 57:23:20 would suffice (Yusoff *et al.*, 1998). In order to improve the melting properties of the margarine, and thereby the texture, palm oil can be interesterified with fats containing shorter chain fatty acids such as palm kernel oil. The effect here is to lower the melting point such that the margarine melts quicker. Equally palm olein could be used to good effect. The list could essentially go on with different combinations or different blends equally fulfilling the requirements demanded by table margarine. The key is to create a blend that has the correct SFC profile, melting profile, and crystallisation process such that texturally the fat blend gives the optimal structure and sensory properties characteristic of table margarine.

### Industrial margarine

Moving on to the next class of margarine, industrial margarine, the requirements here call for a firmer margarine and therefore a fat blend with a higher SFC at a given temperature. This similarly results in higher melting points compared to table margarine. The firmer texture of industrial margarines, which are used for cakes and/or creams can be obtained simply by direct blending of palm oil and its fractions – generally without the need for further liquid oils. Here we may be looking at fat blends consisting of 40% palm olein, 10% palm stearin, and 50% rapeseed oil; or 45% palm oil, 40% palm olein, 7% palm stearin, 3% palm kernel oil, 5% sunflower oil (Yusoff *et al.*, 1998). As well as simply creating another *trans*-free blend for the application in hand, it is worth examining the consequences of the blend. Take for example the two quoted above, both are *trans*-free and successful, so the criteria have been fulfilled. It is recognised that palm kernel oil, because of its short chain lauric content, is excellent for industrial type margarines due to it enhancing creaming properties of the margarine and influencing fat crystallisation properties (Yusoff & Dian, 1995). Similarly, to maintain the beneficial effects of palm kernel oil, its use could be extended by interesterification. While it is recognised that certain modifications can be made to an oil blend to improve its application in cakes, creams and fillings, it is often the case that emulsifiers must be used to enhance their performance. Furthermore, it is also the case that once the fat blend and emulsifier system has been chosen then the preferred system will require optimisation



**Figure 11** Creaming performance of an industrial margarine produced on a Gerstenberg Schröder pilot plant. A units (700 r.p.m.) refer to scrape surface heat exchangers and the B unit refers to pinworker (250 r.p.m.).



**Figure 12** Principal crystallisation profile in processing equipment illustrating the consequences on DGs in fat blends.

through processing demonstrated in Fig. 11 for creaming performance by the reduction in specific gravity.

### Puff pastry margarine

For puff pastry margarine the SFC is significantly higher in order to confer the required plasticity to the margarine, and as such higher percentages of palm stearin are used in the *trans*-free blends. The direct blending of palm oils with liquid oils is necessary to give the functionality required but the levels of palm products can range from 80% to 100%, such that typical formulations may look like 10% palm oil/90% palm stearin; or 80% palm stearin/20% palm kernel oil; or 80% palm stearin/20% soybean oil (Yusoff *et al.*, 1998). Manufacturers of industrial pastry margarine, if utilising large amounts palm oil products, should give due consideration to the inhabiting nature of diglycerides on crystallisation. Hence, plant capacities may need to compensate with longer residence times and potentially more super cooling. This is schematically shown in Fig. 12 (Kristensen & Wassell, 2006). The ideal plant set-up will force the product to be fully crystallised by the end of the processing line. However, certain limitations exist and therefore an absolute optimal situation rarely exists. Thus post-hardening, to some degree, will occur. The challenge is to minimise this effect during production.

The net effect of this with more working and longer residence time is the ability to produce pastry margarines, which are successful replacements for the former products where partially hydrogenated oils were used. Understanding this approach to processing is critical to avoid post-textural problems, which, as stated earlier, are often encountered when simple exchanging of the oil blend takes place without concomitant thought for processing conditions. Furthermore the plastic range of pastry margarines can be additionally enhanced by the inclusion of emulsifiers. Addition of lecithin at low concentrations is often able to extend the plasticity of

the pastry; however, due to issues of GMO, and proof of identity/traceability, many producers are considering additions of polyglycerol esters, which are able to achieve smaller water droplet size distribution, thereby increasing plasticity. Another issue in the manufacture of pastry margarines, particularly where there is a high utilisation of palm products, is crystallisation. In this case it has been found that the synergistic effects of both a crystal-promoting agent based on a combination of behenic monoglyceride and polyglycerol ester are finding applicational uses (Food Navigator 2006).

Another approach to tackling the *trans* fatty acid content and where there is a need to lower the saturates, apart from lowering the SFC, could be the incorporation of a larger water phase whereby the emulsion can be designed to act as an efficient laminating medium. However, where a larger water phase is present within the emulsion, during baking of the puff pastry product it might be the case where a longer baking cycle is required to compensate for the additional moisture to evaporate. Depending on the volume of the water phase introduced to the emulsion it is suggested that the utilisation of low fat technology could also be used, thereby allowing for emulsifiers such as polyglycerol polyricinoleate, which can often only be used in fat products of 41% fat or less. Another argument here is why not simply add less laminating fat? The answer simply is because it is often necessary to have a given volume of laminating medium in order to successfully achieve the desired technical effect.

### Fat/oil blends for shortenings

Fats and oils added to breads, cakes and similar baked goods are often referred to as shortenings that contribute to tenderness, improve volume gain of bread dough, enhance texture, crumb structure and shelf-life of the products (Aini & Maimon, 1996; Podmore, 2002; Wassell, 2006). In order to produce a satisfactory shortening, one has to pay specific attention to the crystal structure (Reddy & Jeyarani, 2001), and similarly the consistency of the shortening will depend on the ratio of solid to liquid fat present at different temperatures. Palm oil, again because of its naturally  $\beta'$  tending nature, is favoured for shortening applications, such that it can impart stability to the emulsion, smooth consistency and provide good aeration properties.

The function of semi-solid fats, termed plastic fats, is influenced by the ratio of liquid to solid (Telloke, 1983) in the lipid phase, and the crystal packing arrangement developed during processing. The crystal form, size and shape must be balanced with careful blending, as it is critical for the final application in bakery products. The function of fats in bakery application is well studied (Hartnett & Thalheimer, 1979; Tamstorf *et al.*, 1986; O'Brien, 1998). While the traditional baking methods

have been modified, the requirements for the functional properties of fats remain. Creaming and emulsifying capacity are of paramount importance – creaming because of its contribution to the baked volume, and emulsification because it controls the moisture and liquid take-up. These functions are critical in applications such as cake batter systems, where emulsifiers are finding increased use in the demands for improved performance (Podmore, 1996).

Designing a shortening for a specific bakery application, or product, is a challenge. *Trans* fats, in certain applications, offer desirable physical and functional attributes. Often, a shortening is expected to perform in a range of products, and meet varied demands in manufacture, and given its particular plastic range, it may be expected to perform within certain critical tolerances. Conversely, the same shortening may be expected to satisfy a number of different applications. Therefore, removal of *trans* fats tends to minimise this range of versatility. This point, coupled with the preference to reduce total saturates, generates further complexity.

Shortenings designed for cakes must create a stable emulsion such that it can withstand the rigours of the baking process combined with favourable creaming properties. Cake shortenings have been known to contain 100% of palm oil products (Yusoff & Dian, 1995), although other oil components may also be blended, e.g. rice bran oil (Mayamol *et al.*, 2004). Reddy & Jeyarani (2001) reported that effective *trans*-free shortening can be produced from more exotic oils derived from mango kernels, which showed similar crystallisation and melting characteristics to those of the commercially available hydrogenated shortenings.

Good creaming properties, or creaming power, is related to the amount of air that can be incorporated into the fat/sugar mix of the cake or cream during aeration (Idris *et al.*, 1989).

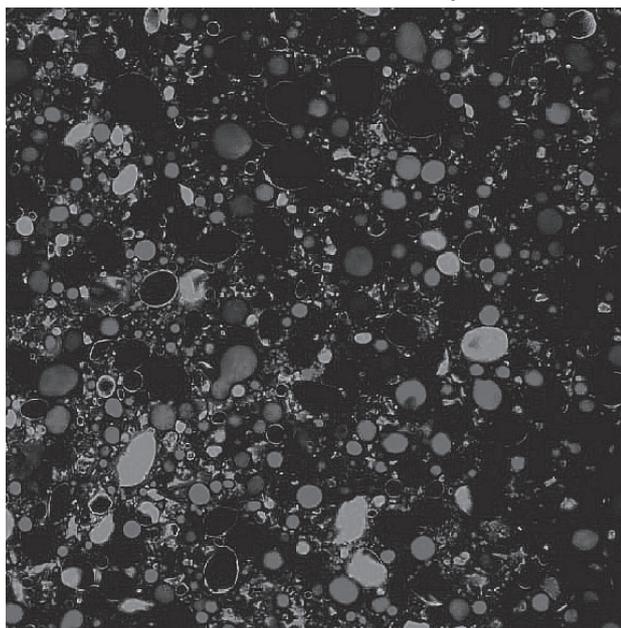
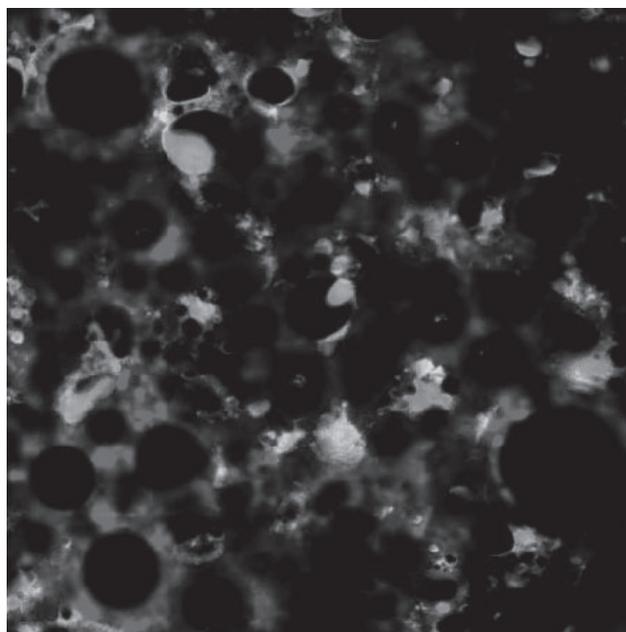
Highly emulsified shortenings with good creaming properties can still be achieved even when the SFC at 20°C is ranging between 15% and 20%. The addition of 5–10% triglyceride enriched in lauric (C<sub>12</sub>) will also enhance creaming performance. Good shortenings consist primarily of  $\beta'$  tending crystals (Idris *et al.*, 1989), and are able to tangentially orientate at the air/fat or fat/moisture interface. In turn, crystal size is related to the content of palmitic acid (C<sub>16</sub>) in the fat blend, and as palm oil and its products are particularly rich in C<sub>16</sub>, they are stable in the  $\beta'$  form. Cottonseed oil is also high (22%) in palmitic acid and therefore also  $\beta'$  stable, but other frequently used fats; soybean oil, low erucic acid rape (LEAR) oil have lower palmitic contents – 10% and 4%, respectively (Idris *et al.*, 1989), and are therefore stable in the  $\beta$  form. However, these latter oils can be blended into palm and cottonseed oils to create the flexibility that is often called for in melting

profiles and SFC values to optimise the shortening performance. Creaming tests showed that the best performances were gained with the palm oil products and the cottonseed oils, whereas when baking performance was tested, better cake volumes were obtained with the  $\beta$  tending LEAR and soybean oils. Hence, for these particular oils a combination might be required to obtain optimal cake functionality.

Bell *et al.* (2007) described the effects of shear where they showed that the rheological changes of a plastic shortening can be related to the size and number of spherulites that determine the space occupied in the matrix by the crystals. They also said that the extent of structuring of a given semi-plastic shortening is also heavily dependent not only on the dynamic shearing conditions during crystallisation but also on the triacylglycerol composition. These authors also show that a higher SFC leads to a higher value of the elastic modulus ( $G'$ ), and of course the nature of this is affected by the liquid-to-solid ratio, crystal size, packing, shape and polymorphism. As stated above, it could also be the case that a shortening might be formulated with a softer SFC profile to achieve a particular lower level of saturates. In doing so the shortening may also act as a carrier system and therefore synergy between the fat blend quality and emulsifier selection exists.

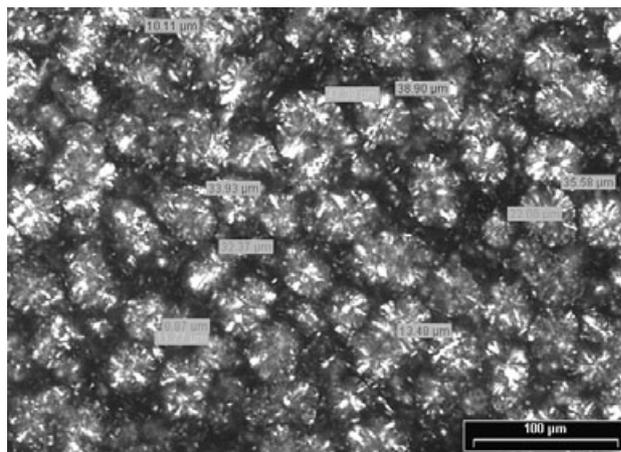
Shortenings are made in a number of formats, but are typically used in the plastic form, often described as 'traditional'. Where boxed plastic fats are not used, pumpable shortenings have found good application because their SFCs tend to be closer to those of the traditional boxed shortenings, and have general versatility for 'all purpose' applications (Wilson, 2003).

Wassell (2006) addressed the option of liquid shortenings, and described how these liquid oils are often found to be unsuitable for cakes, as addition of liquid oils gives low volume, open grain and poor structure. However, reducing the total level of fat and using the correct types of hydrophilic and lipophilic emulsifiers, high-quality cakes can be produced with a liquid shortening instead of the once traditional solid, 'boxed' shortenings. Figure 13 shows that a sufficient concentration of  $\alpha$ -tending emulsifier such as Propylene Glycol Mono Stearate (PGMS) combined with a fully saturated monoglyceride in liquid oil is able to maintain a physical film around the oil droplets. Another approach could be to use a lower concentration of the same or similar emulsifier system in a liquid shortening, and by liquid shortening we mean there is a significant proportion of hardstocks to the liquid oil. The use of  $\alpha$ -stable emulsifier gels is another method to achieve stable aeration and emulsion structure when using liquid oils. Areas other than specifically cakes where emulsified liquid shortenings or non-emulsified liquid oil and  $\alpha$  gels may be used include doughnuts, cookies, pies and muffins (Wassell, 2006).

**8% PGMS + 2% mono-di within liquid oil**Sp Vol : 3,25 cm<sup>3</sup>/g**4% PGMS + 1% Mono-di within liquid shortening**Sp Vol: 3,46 cm<sup>3</sup>/g

**Figure 13** Effect of emulsifier concentration in a liquid oil compared to a liquid shortening in a cake batter system at the same concentration (12.5%).

Wassell (2006) goes on to describe the manufacture of such liquid shortenings, where, in general, they consist of relatively small and stable amounts of the  $\beta$  tending



**Figure 14** Non-emulsified liquid shortening as visualised using polarised light microscopy.

phase, as opposed to the  $\beta'$  phase that was evident in the solid shortenings. A typical formulation then for a liquid shortening will consist of a hard fat source and possibly emulsifiers. An anticrystalliser, such as sorbitan tristearate might be used, although similar effects could be achieved with sucrose polyesters of lauric acid (Yuki *et al.*, 1990), polyglycerol esters and lecithins. The use of sucrose esters has been shown to inhibit and delay rates of crystallisation (Herrera & Marquez-Rocha, 1996; Cerdeira *et al.*, 2006). The role of the anticrystalliser here is to delay or hinder the crystallisation process of the fats during the slow cooling and slow agitation steps, such that the shortening maintains its fluid state for extended periods. During this whole production step the incorporation of air should be kept to a minimum to avoid any undue increases in viscosity. The actual raw materials for such shortenings can take the form of liquid oil (e.g. rapeseed, soybean oil, sunflower oil) and a hardstock consisting of combinations of palm oil, interesterified palm stearin and interesterified palm kernel oils. The liquid to solid size and shape as described earlier is shown in Fig. 14.

In Fig. 14 we are clearly able to see the crystal-to-crystal flocculation, where it may be assumed that London–van der Waal's forces maintain the network structure.

In India, and many other Middle East and South Asian countries, hydrogenated fats have been used to make a product known as vanaspati, which is consumed as an alternative to ghee (anhydrous butter fat). For nutritional reasons there has obviously been interest in substituting hydrogenated fats to produce *trans*-free vanaspati. This has been achieved by randomisation of a saturated fatty acid or oil fraction such as palm oil or palm stearin. The liquid oil content coming from soybean oil, sunflower, rapeseed and even rice bran oil

(Majumdar & Bhattacharyya, 1986; Ray & Bhattacharyya, 1996; Jeyarani & Reddy, 2003; Mayamol *et al.*, 2004). Vanaspati is often required to have a granular (grainy) structure; these characteristics in structure are important in countries such as India, Pakistan, Bangladesh and certain Middle Eastern countries; however, a smoother texture is required in Malaysia. *Trans*-free vanaspati can be successfully produced based on direct blending of palm and its fractions and a liquid fraction possibly coming from palm kernel as described by Nor Aini *et al.* (1999).

Orthofer (2005) reported the use of high oleic low linolenic (HOLL) acid oils from canola (rapeseed), sunflower and peanut oils. The HOLL canola oil is easily blended or interesterified and can be used to produce shortenings for the bakery industry as well as other, e.g. margarines and frying, applications. The typical breakdown of the HOLL oil is 3.6% palmitic acid, 2% stearic acid, 73% oleic acid, 15% linoleic acid, < 3% linolenic acid and 0.7% arachidic acid. Therefore, the shortenings for baking will require blending with harder fats, but for frying applications the HOLL oil will perform well.

#### Fat/oil blends for frying applications

The definition of a perfect frying oil is that it must have high oxidative stability, a healthy composition, i.e. be low in saturates and low in *trans* fats, and finally produce high quality foods (Orthofer, 2005). Traditionally frying shortenings were high in saturates, solid and had a degree of hydrogenation to minimise the oxidative processes (O'Brien, 1998). Liquid shortenings for this application were first introduced in the 1950s where the stability of the then shortening was dependent on the addition of dimethylpolysiloxane as an anti-foaming agent that also hindered oxidation and polymerisation, doubling the frying lifetime of the oils, and without the need for hydrogenation.

Today palm oil is a prime candidate for the frying application due to its moderate and small contents of linoleic and linolenic acids respectively. It naturally has a high resistance to oxidation due to its high content of palmitic acid and can either be used as palm oil itself, or indeed is blended with other palm forms (Yusoff & Dian, 1995). Blends of palm oil, palm olein and sunflower oil have also shown good performance and frying results in tests with potato crisps and French fries (Berger & Idris, 2005). The HOLL oil mentioned above can also be used as a successful candidate for frying where less viscosity build up is present after frying due to less polymerisation, less change in viscosity and less peroxide development (Orthofer, 2005). Frying results gained using HOLL oil were similar, or superior, to partially hydrogenated rapeseed oil, high oleic sunflower oil and palm oil. The HOLL oil equally developed less

free fatty acids, had greater oxidative stability, and in general the results demonstrated that HOLL oil possesses greater frying stability compared with partially hydrogenated oils. The results gained were almost equivalent to those obtained with high oleic sunflower oil shortenings containing up to 80% oleic acid.

#### The future

The issue of *trans* reduction is more than simply removal of *trans* fatty acids, but in some instances it is complicated by the emotive necessity to also remove the hydrogenated edible oil even if any of the components of the oil blend are fully hydrogenated (van Duijn *et al.*, 2006). Furthermore, governmental bodies, nutritionists and medical personnel exert powerful legislation and lobbying to find and create alternative products with ever increasing demands to achieve a lower degree of total saturates. The knock on effect is that edible oil manufacturers have to supply fats, which are able to satisfy these requirements, and are driven to hunt down more and more exotic and novel sources of raw materials.

Furthering the potential use of exotic oils, recent communication from the Advisory Committee on Novel Foods and Processes (2006) reports a novel food application under article 4(1) of regulation (EC) 258/97 for the authorisation of *Allanblackia* seed oil. The use of such would be, for the manufacture of edible spreads and creams, to replace current edible oils such as palm oil and palm kernel oil. The advisory committee further reports: that *Allanblackia* contains approximately 45–58% stearic and 41–51% oleic acid, along with other fatty acids commonly found in the diet and is solid at room temperature, thus conforming to the principles outlined in Fig. 1. *Allanblackia* is unique in the fact that it contains high levels of stearic-oleic-stearic

**Table 8** Specifications for *Allanblackia* seed oil

Lauric acid (C 12:0)	<1%
Myristic acid (C 14:0)	<1%
Palmitic acid (C 16:0)	<2%
Palmitoleic acid (C16:1)	<1%
Stearic acid (C18:0)	45–58%
Oleic acid (C18:1)	40–51%
Linoleic (C18:1)	<1%
$\gamma$ -Linoleic acid (C18:3)	<1%
Arachidic (C20:0)	<1%
Free fatty acids	Max 0.1%
<i>Trans</i> fatty acids	Max 0.5%
Peroxide value	Max 0.8% mEq kg <sup>-1</sup>
Iodine value	<46 g/100g
Unsaponifiable matter	Max 0.1%
Saponifiable value oil	185–198 mgKOH g <sup>-1</sup>

(SOS) and stearic-oleic-oleic (SOO). Table 8 shows the specification for *Allanblackia* seed oil.

A recent patent (Wester, 2006) discusses a range of approaches to solving nutritional and texturing issues of fat blends. It neatly describes and presents background to prior art and concludes with a description of the use of combinations of stanol and sterol fatty acid esters or their blends, and is quoted as forming crystal networks with similar properties as those of conventional hardstock triglycerides. The use of phytosterols and organogels is also shown to offer structure and textural properties in edible oil mixtures (Bot & Agterof, 2006; Wright & Marangoni, 2006)

An alternative to provide the texture often required in *trans*-free solutions can be addressed by the use of wax technology (Shigemi, 2006). The production of plastic oil composition, which can be used for bread improvers and confectionery is obtained using combinations of palm stearin or palm stearin and palm oil together with a wax. Here, the wax in question is beeswax, and it can be speculated that the future of this 'lipocolloid'-like component is set to grow.

The authors also speculate that the current increase in the use of biotechnology will lead to the increased use of enzymatic technology that will come to the fore in the future. This is highly likely to open up new and exciting possibilities in the region of making and modifying new lipid structuring materials, inherently free from *trans* fatty acids.

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