Articles and Lectures

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At Loders Croklaan, we continuously strive to be at the forefront of technical developments and innovations in the field of oils and fats. This involves developing innovative products, improving processes, researching new areas, deepening knowledge and increasing expertise – all in order to create added value for our customers.

The innovative power of Loders Croklaan is widely acknowledged in the industry and in the scientific community. We hold many patents (279 so far in the field of palm oil alone, with more applied for), and some of our brand names – Coberine, for instance – have become so influential that they are often seen as generic terms. Our researchers regularly publish seminal papers in peer-reviewed scientific journals, present their findings at international conferences, and make their work accessible to a wider public in popular scientific articles in the trade press.

Now, in this booklet, we are pleased to present a short review of our major R&D achievements in 2006. Such achievements are only possible when you are fortunate enough to have the right partners to work with, both on the theoretical and the applied level. I would therefore like to take this opportunity to thank colleagues at the renowned research institutes and universities in various countries with whom we collaborate, and to thank our customers for taking us at our word when we say “Let’s create together” – because by doing so, they help us to maximise the value we can add to their business.

| Dr Loek Favre | Director, Product management & Processing |
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The wide range of different melting triglycerides in palm oil makes it highly versatile. Its versatility is increased when these different triglycerides are separated from each other. This can be achieved by solvent fractionation of the oil.

Introduction
Food manufacturers on both sides of the Atlantic are under increasing pressure to remove trans fatty acids and hydrogenated fats from their products. While there are a number of alternatives potentially available to them there is, nevertheless, usually a need for those alternatives to be able to provide structure and stability to the end product. That generally means having some solid fat present. If this solid fat cannot be produced by hydrogenation because the consumer has been “taught” by the popular media to equate this on a label to the presence of trans fats then oils naturally rich in solid triglycerides must be used. The most readily available of these oils is palm oil.

Palm oil is probably the most flexible of vegetable oils in terms of its triglyceride composition and hence its functionality. It contains triglycerides that are liquid at room temperature, triglycerides that melt sharply at about body temperature and triglycerides that are even higher melting. In order to make the best use of each of these groups of triglycerides it is necessary to fractionate palm oil. While dry fractionation can and, indeed, often is used for this process a better, ‘cleaner’ separation is achieved by solvent fractionation.

A number of solvents have historically been used for this process but the most common ones are acetone and hexane. The fractions obtained
from these two solvents do differ however, mainly in the distribution of partial glycerides across the fractions. Because, as indicated, there are three broad groups of triglycerides in palm oil it is possible to separate the oil into three fractions – a liquid fraction (oleine), a solid fraction (stearine or ‘top’-fraction) and a middle-melting fraction (‘mid’-fraction). This means that a two-stage fractionation process is needed.

Clearly this can be carried out in two ways. Either the oleine fraction can be removed in the first stage and then the mid and top fractions separated in the second stage, or the top fraction separated in the first stage and then the oleine and mid fractions separated in the second stage. There are good reasons for operating in the first way rather than the second. This is because then the presence of high-melting triglycerides helps nucleation in both fractionation stages, whereas, in the second way, these are removed prior to the second stage of fractionation.

The main ‘solid’ triglycerides in palm oil are POP (Palmitate-Oleate-Palmitate - representative of the middle-melting triglycerides) and PPP (Palmitate-Palmitate-Palmitate -representative of the high-melting triglycerides). Although the actual amounts are subject to natural variations typical levels were reported as long ago as the early 1980s to be 30.5% POP and 4.6% PPP.

To understand better the solvent fractionation of palm oil, model systems of both pure POP and PPP as well as mixtures/blends of the two triglycerides have been evaluated. Such studies are considered to be useful in determining the crystallization behavior of the components of palm oil. Acetone was used as the fractionation solvent.

One of the most critical phases in fractionation is nucleation and it is considered that the width of the metastable zone is of great importance in its influence on this process. This topic was extensively reviewed by J.W. Mullin of University College London, United Kingdom in his classic text “Crystallisation” that was published in 2001 as a fourth edition.

**Metastable Zone**

What exactly is the metastable zone? We have given more detailed examination elsewhere, but essentially it is the degree of undercooling ($\Delta T_{\text{max}}$). This is best explained with reference to Figure 1. This diagram shows the changes in temperature of a pure triglyceride (e.g. POP) in acetone as it is first cooled to allow it to crystallize and then re-heated to allow it to re-dissolve. In a pure triglyceride such as POP the degree of undercooling is the difference between the cloud point, $T_c$, (where the first signs of nucleation are observed), and the clear point, $T_{cp}$. These two points can be determined in a model system by measuring the turbidity of the system or its degree of transmittance. When the triglyceride is cooled down the cloud point is first detected at the temperature at which the transmittance is reduced. Conversely, the clear point is the temperature at which the transmittance returns to its
The metastable zone

The metastable zone is the initial value when the system is reheated. The difference between these two temperatures is the degree of undercooling or the ‘metastable zone’.

The growth temperature, $T_g$, is the temperature at which the crystal growth exotherm commences. In a pure system such as POP the cloud point and the growth temperature are coincident (as is shown in Figure 1); in a mixed system such as POP-PPP, the growth temperature will be lower than the cloud point. If the triglyceride/solvent system is then re-heated after crystallization has occurred, the crystals will begin to re-dissolve. The temperature at which they have completely dissolved is the clear point, $T_{cp}$. The difference between $T_c$ and $T_{cp}$ is called the ‘metastable zone’.

Crystallization of the pure triglycerides and blends

A range of concentrations of POP,PPP and their blends in dry acetone were prepared and held, with stirring, at 0°C for 20 minutes prior to crystallization. The solutions were cooled at rates of between 1°C/h and 180°C/h using a temperature programmer and values for $T_c$ and $T_g$ were measured by means of turbidimetry of the solution. The systems were then re-heated at 30°C/h to measure the clear point ($T_{cp}$). Additionally some systems were studied by ‘crash cooling’ with a cooling rate of about 1000°C/h.

The solubility of both POP and PPP were measured by determining the clear point of each concentration. The solubility lines shown in Figures 2a (POP) and 2b (PPP) are calculated from these data using the equation noted by Timms. Also shown in these Figures are the supersaturation curves (at cooling rates of 12°C/h, 18°C/h and 180°C/h) of POP (Fig. 2a) and PPP (Fig. 2b).

Using the measurements of cloud point and clear point we can calculate the width of the metastable zone for a range of cooling rates and triglyceride concentrations. Examples of these are shown in Figure 3a (for POP) and Figure 3b (for PPP).
In the case of POP, the width of the metastable zone ($\Delta T_{\text{max}}$) varied from about 13°C to about 17°C as the cooling rate increased and is relatively insensitive to cooling rate. With PPP, however, the width of the metastable zone varied from about 13°C to about 19°C at lower PPP concentrations but from about 9°C to about 1°C at higher PPP concentrations and shows a greater dependence on cooling rates. The greater dependency of PPP on concentration can also be seen from the supersaturation curves in Figure 2b which are not as parallel to the solubility curve as they are for POP.

Some differences between POP and PPP were seen in terms of the appearance of an exotherm after the cloud point had been reached. POP showed such an exotherm (as seen in Figure 1) whereas PPP did not. This is undoubtedly due to the differences in crystallizable material in both cases (this being higher for POP than for PPP).

The growth exotherm of the blends commences when the bulk of the POP crystallizes; growth and nucleation are effectively coincidental with pure POP, i.e. $T_c \approx T_g$. The presence of PPP, however, delays the growth exotherm by about 5°C.
The information obtained suggests that the nucleation process is not particularly sensitive to cooling rate and that for the cooling rates used very high concentration supersaturations are necessary before there is any appreciable nucleation. Lower cooling rates, however, should be used to prevent POP and PPP from co-crystallizing, particularly at higher levels of PPP.

Crystal Size and Crystal Habit
The size and habit of crystals produced during solvent fractionation are of importance in terms of ease of ‘washing’ of the crystals on a filter belt. The easier crystals are to wash the easier it is to remove entrained oleine. Electron microscopy of the POP and PPP crystals helps to give some indication of the shape and size of the crystals and hence of how easy (or not) it will be to wash out entrained material.

The POP crystals were essentially spherulitic (β-3) – Figure 4. Programmed cooling gave a slightly more open texture than did crash cooling which might help to improve the ease of washing.
At a concentration of 3.8g/100g solution the spherulites were about 50 to 75µm in diameter. Reducing the concentration to 0.5g/100g also reduced the crystal diameter to 25 to 50µm.

In contrast, PPP gave flat, plate-like crystals (β-2) – Figure 5. At a cooling rate of 12°C/h crystals of about 30 x 6µm were produced whereas at a cooling rate of 18°C/h the crystals were close to 15 x 10µm. Crash cooling tended to produce amorphous clusters of up to about 50µm in diameter (Figure 5). Both polymorphs are produced with β-3 predominating when PPP is added to POP, but more β-2 crystals are present after programmed cooling than after crash cooling suggesting that the slower the cooling rate the greater the likelihood of a PPP-like phase being produced.

### Summary

In our current low-trans or even trans-free world the use of palm fractions is becoming increasingly important. In order to be able to optimally fractionate palm oil a knowledge of the crystallization behavior of the main solid components is critical. In general terms these can be equated to POP and PPP as being representative of these solid components. A study of each of these individually gives us important fundamental information about how these triglycerides crystallize. Information of this kind is of great relevance in whichever order the fractionation is carried out. It is probably most common to remove the oleine fraction first and then, in a second stage, to separate the POP-rich fraction from the PPP-rich fraction. For such systems information on the crystallization characteristics of a mixed POP-PPP system is important, especially for the first stage of crystallization in which a POP-rich phase crystallizes in the presence on PPP.

### References


Chocolate tempering

[originally presented at the Confectionery Manufacturing Expo, Brussels, Belgium, June 2006]

Tempering is a critical part of chocolate production. A well-tempered chocolate will have a good gloss and snap together with a long shelf-life. Understanding the physical processes that take place during tempering is fundamental to understanding the process itself.

Overview

In this lecture I am going to cover the process of chocolate tempering. I will discuss the polymorphism of cocoa butter, the theory of tempering – including tempering machines, the measurement of temper and finally talk about some model tempering unit studies we have carried out. Of necessity, part of what I talk about will be well known to some of you but I hope nevertheless there will be much of interest.

But, firstly, we must answer the question “Why temper?”

Even before the polymorphic nature of cocoa butter was fully understood, chocolate producers realised the necessity of tempering.

Without tempering, a chocolate becomes dull and is susceptible to fat bloom. Correctly tempered, the chocolate is glossy and bloom resistant.

Without tempering, it is difficult to demould the chocolate, and there is a greater probability of mould marks on the surface. Correctly tempered, the chocolate contracts and demoulds easily.

Without tempering, the chocolate is soft. Correctly tempered, it is hard and has a satisfying snap!
Without tempering, the chocolate can be ‘warm’ in the mouth. Correctly tempered, the chocolate will produce a pleasant cooling sensation in the mouth.

Finally, correctly tempered chocolate will release the cocoa flavour in the optimum manner.

**Cocoa Butter Polymorphism**

Depending on the process conditions used, cocoa butter can be crystallized into different crystal forms, each of which possess a distinct melting point and density. The phenomenon of different molecular packing in such crystals is called polymorphism. All fats demonstrate some degree of polymorphism. To understand the polymorphism of cocoa butter, we will look first at the fat polymorphism in general.

Figure 1 shows a triglyceride molecule showing three fatty acids attached to a glycerol backbone. The three positions on the glycerol are not equivalent. Note that there are two outer positions and one centre position. Changing the position of the fatty acids on the glycerol can significantly change the properties of the triglyceride.

Such molecules can pack together in two basic ways (Figure 2). These are termed ‘double layer’ and ‘triple layer’ packing – depending on the number of fatty acid chains between one crystal layer and the next. These are what are called the long spacings.

If the look down on the end of the fatty acid chains, we see what distinguishes the three basic polymorphs of fats. Polymorphic forms are generally identified as α, β’ and β, in order of increasing stability and melting point (Figure 3).
The α form has a hexagonal arrangement of the fatty acid chains and the orientations of the carbon ‘zig-zag’ are random. The β’ form has an orthorhombic arrangement of fatty acid chains. In this form the chains are perpendicular to adjacent chains. In the β form, the chains are arranged in a triclinic pattern and are parallel to each other.

Triglycerides that are similar, display similar structure. For example, if we consider the saturated mono-acid triglycerides we find that the crystal structure of tri-C10, tri-C12 and tri-C16 are identical in every way except for the chain lengths. This is an important observation that we will come back to.

Polymorphs differ in structure, as we have seen, but also in other properties. They have different melting points, different melting enthalpies and different densities. They also have different stabilities.

Crystal forms with low melting point are less stable and tend to transform into more stable forms, with higher melting points. The speed with which polymorphic changes occur depends on the relative stability of the crystal forms and the temperatures which they experience. Similarly, the specific polymorph that will crystallise depends on the process conditions used. Generally, faster cooling to lower temperatures favours the formation of the least stable polymorphs, although these may well transform into those of higher stability when the temperature is raised.

The polymorphism of a fat depends very much on its composition, and cocoa butter is no exception.

Cocoa butter is mainly composed of triglycerides. Of these, three predominate, accounting for up to 90% of all triglycerides present. These three are POP (~20%), POS (~38%) and SOS (~28%), where P=palmitic, O=oleic and S=stearic and where the position of the letter denotes the position of the fatty acid on the glycerol. – in each of these case, oleic acid occupies the centre position.

The properties of cocoa butter are determined by these three triglycerides, so we will look at their polymorphism now.

In Table 1 we see that a relatively simple triglyceride like POP has up to seven distinct polymorphs, while SOS and POS have fewer. Although the melting point of a triglyceride is a good indicator of the polymorphic form present, the only unambiguous way to identify the polymorph is by using x-ray diffraction. Using this technique, each polymorph shows a unique pattern.

In Figure we see the patterns for the β’ and β forms of POP. Note that the β’ forms have two main peaks while the β forms have one main peak with a group of lesser peaks. This type of pattern is seen for POS and SOS as well. As we shall see, cocoa butter is very similar.
Until very recently, the actual crystal structure for the \( \beta \) form of SOS (and also POP, POS and cocoa butter) was not known. Speculative structures were published and Figure 5 is one such structure. The kink in the chain here is due to the double bond in the oleic acid chain.

However, in 2004, the group at the University of Amsterdam, sponsored by IOI Loders Croklaan, determined the structure of the \( \beta_2 \) form of SOS. As you can see, it has quite a different structure to those proposed (Figure 6).

Let’s move on to look at cocoa butter. As I’ve already noted, the polymorphism of cocoa butter is similar to that of its major triglycerides – POP, POS and SOS. Here it is evident that the \( \beta \) forms of cocoa butter have similar x-ray patterns to those of POP and SOS especially.

Since the 1950s, there has been much debate in the literature about the number of polymorphic forms of cocoa butter. General agreement has settled on six forms, using the nomenclature of Wille & Lutton, i.e. the Roman numerals I through VI, with form VI being the most stable and having the highest melting point. Following Chapman’s notation for fat polymorphs, Form I is identified as being sub-\( \alpha \), Form II as \( \alpha \), Forms III & IV as \( \beta’ \) and Forms V & VI as \( \beta \). However, cocoa butter polymorphs have been designated in a great variety of ways as you can see in Table 1.

In 1999, the paper of Van Malssen et al. proposed that earlier work may have been mistaken in terms of number of forms and their melting points. They identified only five forms, \( \gamma \) (or sub-\( \alpha \)), \( \alpha \), a continuous range of \( \beta’ \) (incorporating those previously identified as Forms III & IV) and two \( \beta \) forms. In addition, they proposed that the melting point of the sub-\( \alpha \) or \( \gamma \) form has rarely been measured correctly due to the extremely rapid transformation of this polymorph into the \( \alpha \) form and that the melting point usually attributed to the \( \alpha \) form (II) is likely to be due to \( \beta’ \) that was formed during the preparation for the measurement or during the measurement itself.

Whatever the true situation, it is fair to say that cocoa butter polymorphism is complex! Chocolate that is composed of unstable (or mixtures of) polymorphs, has a tendency to undergo physical changes associated with the transitions of the unstable forms into a more stable form. These physical changes are likely to affect adversely the appearance and/or texture of the chocolate. Thus, it is necessary to obtain cocoa butter in a stable \( \beta \) form for maximum stability and shelf-life.

Figure 7 presents the scheme for the transformation of cocoa butter polymorphs. Here I have used the standard nomenclature for fat polymorphs, with the addition of V and VI as subscripts to \( \beta \).

If fully molten cocoa butter is cooled quickly to low temperatures (say below 0°C), the sub-\( \alpha \) form crystallises. Cooled to slightly higher
temperatures, crystallisation may begin in the sub-α form but will convert to the α form during crystallisation. The α polymorph will also form if the temperature of the sub-α form is raised. It is also possible to form α directly from the melt without sub-α if the temperature is above about 5°C.

If the α form is warmed, it will transform into the β′ form, which can also form by direct crystallisation from the melt, if the temperature is above about 20°C. In Figure 7 β′ is shown as a range of forms rather than as two polymorphs – Forms III and IV. I will explain why, shortly.

Warming the β′ form results in a transformation into the β\textsubscript{VI} form, which will go on, in time, to produce the β\textsubscript{VI} polymorph. The β\textsubscript{VI} polymorph can, in certain circumstances, form directly from the β′ form. The β forms do not generally crystallise directly from the melt except when seeded.

For completeness, it should be noted that both β′ and β forms can be crystallised from solvent.

Finally, all polymorphs will melt directly to the liquid phase, although the heating rate should be high enough, in the case of the less stable forms,
to melt before transformation occurs into another polymorph. In practice, the melting of the sub-\( \alpha \) form is not seen because it transforms into \( \alpha \) extremely easily.

Figure 8 summarises the isothermal crystallisation of cocoa butter. Fully melted cocoa butter was cooled to the temperature indicated on the y-axis and simply held at this temperature whilst monitoring the polymorphic form. The time at which a polymorphic form was first observed is plotted. Thus, the purple \( \alpha \) area below 0°C does not indicate only \( \alpha \) present, but that some \( \alpha \) is detected in addition to the sub-\( \alpha \) initially present. Similarly, it doesn’t mean that no sub-\( \alpha \) is present.

Note, also, that the crystallisation here is static – no stirring, no shear.

From this diagram it is clear that although the sub-\( \alpha \) form crystallises at 4°C, within 1 minute, it has begun to transform into \( \alpha \). At 10°C, the \( \alpha \) form crystallises, but begins to transform into \( \beta' \) after about 15 minutes. At temperatures above 15°C crystallisation does not begin immediately but after a shorter or longer period of time, depending on the temperature. At temperatures above 21°C no \( \alpha \) form crystallises. Rather crystallisation is directly into the \( \beta' \) form. Note that, within the four weeks of this series of experiments, nothing crystallises above 26°C and no \( \beta \) form crystallises from the melt, but only comes from transformation from the \( \beta' \). To re-iterate, this work was performed statically. Stirring or shearing accelerates crystallisation and polymorphic transformation.

I mentioned that I would return to the question of \( \beta' \) polymorphs. Figure 9 shows the x-ray diffraction patterns for a series of \( \beta' \) forms crystallised isothermally at different temperatures, as indicated. There is a clear progression through the patterns. However, although it appears to be the case, the intermediate patterns do not indicate a mixture of two specific \( \beta' \) forms.
Table 3
Cocoa butter melting points

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Wille &amp; Lutton</th>
<th>Huyghebaert &amp; Hendrickx</th>
<th>Dimick &amp; Davis</th>
<th>Rilner</th>
<th>Van Malssen et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>sub-α (I)</td>
<td>17.3</td>
<td>14.9-16.1</td>
<td>13.1</td>
<td>2</td>
<td>-5 to +5</td>
</tr>
<tr>
<td>α (II)</td>
<td>23.3</td>
<td>17.0-23.2</td>
<td>17.7</td>
<td>16</td>
<td>17-22</td>
</tr>
<tr>
<td>β′ (III)</td>
<td>25.5</td>
<td>22.8-27.1</td>
<td>22.4</td>
<td>25</td>
<td>20-27</td>
</tr>
<tr>
<td>β′ (IV)</td>
<td>27.5</td>
<td>25.1-27.4</td>
<td>26.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-V</td>
<td>33.8</td>
<td>31.3-33.2</td>
<td>30.7</td>
<td>32</td>
<td>29-34</td>
</tr>
<tr>
<td>β-VI</td>
<td>36.3</td>
<td>33.8-36.0</td>
<td>33.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the same way, there is a continuous variation in melting profile – here measured using x-ray diffraction. Each β′ shows a distinct melting profile. The conclusion is that cocoa butter exhibits a continuous range of β′ polymorphs, of which the forms previously identified as Forms III and IV are two examples.

Table 3 compares the melting points determined for cocoa butter polymorphs over the decades. Bear in mind that a certain variability is expected since the origin of the cocoa butters examined differs.

The interesting observation is that Van Malssen et al. confirm the melting point of the sub-α form (Form I) as determined by Rilner, and this is much lower than found by other workers. The reason for this appears to be that the sub-α form transforms extremely rapidly into the α form. Other workers, therefore, measured the melting point of the α form when trying to obtain that of the sub-α.

Similarly, it is possible that the melting point previously measured for the α form is actually that of the lower end of the β′ range. Melting points of Forms III and IV thus represent examples of the β′ phase range.

Tempering Theory and Machines
The avoidance of fat bloom such as is shown in Figure 10 is one of the principal reasons for tempering.

According to Edward Seguine in a lecture at the PMCA, the purpose of tempering is to produce “the largest number…of the smallest possible crystals…of the right crystalline form.” Although close, I would say that the purpose of tempering is to produce sufficient, uniform β seed crystals to ensure that the temper state is stable and that subsequent crystallisation of the whole of the chocolate mass occurs into the stable crystalline form. Properly tempered chocolate is important for qualities such as mould release (contraction), hardness, snap, mouthfeel, flavour release, gloss and resistance to fat bloom.
If molten chocolate is cooled to 32°C (or, at least, above the melting point of the β’ form but below that of the β form), crystallisation will start to occur into the β₀ polymorph. However, this will take a very, very long time - months. Since this is impractical, tempering processes have been established to generate β seed crystals more rapidly.

However, we want more than just stable crystal seeds. We want small crystals of uniform size.

Small, uniform crystals lead to a more stable state of temper. They are less susceptible to Ostwald ripening.

Figure 11 shows a wide crystal size distribution. After a time, ripening of the crystals occurs – larger crystals grow even larger and small crystals disappear. The result is that the average crystal size increases significantly, while the number of crystals decreases.

If the size distribution is narrower, less ripening takes place and the number and size of the crystals remains more or less the same.

The final chocolate will be glossier, if the seeds are small (and many), since the small average crystal size will lead to a finer structure in the chocolate.

The viscosity of the chocolate will also be lower with uniform small crystals.

In order to obtain small uniform crystals, it is desirable to crystallise relatively rapidly to produce much of the nuclei together. This requires relatively fast foiling and low temperatures (compared to the β₀ melting point). Naturally, as I mentioned earlier, this will give rise to unstable polymorphs. Thus, these must be transformed into the more stable β crystal form. This is what happens in tempering.
What tempering methods are there?

Firstly, chocolate can be tempered manually, using what is termed “slab tempering” or “tabliering.” Of course, this is on a small scale.

Secondly, chocolate may have stable crystal seeds added to it.

Thirdly, so-called automatic tempering equipment may be used, which may operate in a either a batch or continuous process.

Slab tempering is a very traditional method. It involves melting the chocolate at 40-45°C, removing about 1/3 – 2/3 of a batch of molten chocolate to a cool marble slab and spreading it back and forth until it cools, crystallises a little and thickens. The partly crystalline chocolate (which will contain mainly unstable, but also some stable polymorphs) is returned to, and mixed into, the remaining molten chocolate. During this mixing, unstable polymorphs will either melt or be transformed into stable ones, leaving stable seed crystals in the chocolate. At this point the state of temper would be checked, and the bowl may be warmed slightly to slow any further thickening of the chocolate. If the chocolate is not sufficiently tempered, a further amount may be spread on the slab briefly.

Tempering is controlled by the amount of chocolate removed to the slab and by the time it spends on the slab.

In a simple batch operation, molten chocolate at 40-45°C is cooled to a temperature above that of the unstable polymorphs (the precise temperature depends on the origin of the cocoa butter and the presence of milk fat). Powdered or flaked chocolate (or even fat itself), which is already in the stable β form, is added and the mixture is stirred while holding at this temperature until temper has been attained, when it may be warmed slightly to arrest further crystallisation and maintain the tempered state longer.

This tempering is controlled by the holding temperature, amount of seeds added and the time allowed for further seeds to develop.

In another batch operation, which may be automated, molten chocolate at 40-45°C is cooled, while stirring, to a temperature below which β’ forms will crystallise (again dependent on cocoa butter origin and milk fat level). This induces crystallisation to occur into both β’ and β forms. Once a sufficient amount of solid has formed (which may represent less than 10% of the fat phase), the temperature is increased above (or near to) the β’ melting point. It is held isothermally for a time so that the unstable forms will melt or transform, and so that further crystallisation may take place into the stable polymorph, until temper is achieved. Again, the temperature may be raised a little more to arrest further crystallisation.
Control parameters here are the temperatures selected for crystallisation and later transformation and the time allowed for crystallisation and transformation.

Many types of continuous tempering equipment exist and, although there are differences in the precise mode of operation, they follow a common regime. Molten chocolate is passed through a series of scraped surface heat exchangers, where shear (sometimes high shear) is applied. Shear aids the formation of stable solid by increasing nucleation rate, breaking up crystals to generate further seeds, ensuring a good heat and mass transfer, encouraging the transformation of unstable crystals, and uniformly distributing the seeds through the mass. However, the shear must be carefully applied. Shear imparts energy to the system and will add heat. If the shear rate is too high, this heat can melt the seeds crystals as they form.

As a general rule, the chocolate is cooled in the initial heat exchanger(s), cooled a little further in the intermediate exchangers during which crystallisation occurs into a mixture of polymorphs, and finally re-heated in last stage(s) to transform the unstable polymorphs into the stable β seed crystals.

The important control parameters here are the temperatures of the heat exchangers and the flow rate or throughput.

The continuous tempering process is illustrated in Figure 12. In zone 1, the sensible heat is removed from the chocolate, thus lowering the temperature. Little or no crystallisation occurs in this zone. In zone 2, a little more sensible heat is removed, and a lot of latent heat of crystallisation. In this zone, the bulk of the crystallisation occurs into both stable and unstable forms. During the final zone, 3, the temperature of the chocolate is raised to melt/transform the unstable crystals leaving only stable, β, seed crystals. The rise in temperature also leads to a reduction in the viscosity of the chocolate, which helps in the later enrobing or moulding processes. The specific temperatures involved are very dependent on the composition of the chocolate. Milk and white chocolates will require lower temperatures than dark chocolate. Some continuous tempering equipment has a final “maturing” zone where the stable seed crystals can mature.

Finally, it is worth mentioning that systems have been patented were seed material (as a powder or fluidised in some way or even by recirculation of tempered chocolate) is fed into a continuous chocolate flow to produce suitably tempered material.

**Measurement of temper**

Aside from the experienced eye (or mouth, or finger!), the degree of temper is usually measured using a temper meter. But it should be noted that it doesn’t measure the quality of temper as such – that is specific to a given application. It measures a simple cooling curve.
Figure 12
Continuous tempering

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-45°C</td>
<td>Zone 1</td>
<td>Sensible heat removed; little crystallisation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28-32°C</td>
<td>Zone 2</td>
<td>Crystallisation of β' and β forms; latent heat removed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23-27°C</td>
<td>Zone 3</td>
<td>β' melted and transformed into β; viscosity reduced</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, it is a reproducible means to measure the state of seed development and thus can be used to maintain a particular desired level in production.

There are a number of varieties of such instruments but they all operate in a similar way. Figure 13 shows a schematic of typical temper meter components. A sample of the chocolate is placed into the upper part of a metal (e.g. copper) tube whose base is cooled by an ice water bath. The temperature is recorded as a function of time using a thermistor and the resulting curve is diagnostic of the degree of temper in the chocolate.

What is important in a temper curve? Generally, one or more of three parameters are assessed. Firstly, the initial slope of the cooling curve. Secondly, the slope following the point of inflection. And, thirdly, the actual point of inflection itself. This latter is either found by the intersection of the extrapolated slopes or defined as the temperature at the minimum. The maximum temperature achieved during the crystallisation may also be recorded.

As chocolate approaches temper it will yield different cooling curves as shown in Figure 14.

How do these curve shapes arise?

Let’s look more closely at our system. We have a portion of chocolate in the top of a copper tube. This tube is cooled by the ice water and in turn cools the chocolate. This causes the chocolate to crystallise.

When a material crystallises, heat is generally given out, which causes a deviation from the cooling profile expected in a non-crystallising system. The particular deviation manifested is indicative of the progress towards proper temper.
If we first consider a non-crystallising system, we see that the temperature falls smoothly. The curvature is because the that cooling rate due to the ice depends on the difference in temperature between the ice and the chocolate. Clearly, as the chocolate cools, the difference decreases and therefore so does the amount of cooling.

So what happens if the chocolate crystallises to some degree? Now, we not only have the cooling due to the ice but we have the heat generated by the crystallising chocolate. These work against each other and in this case the crystallisation heat is enough to overcome the cooling and we see a rise in the temperature (which is why we see the cooling due to the ice vary as well). This is evidently an under tempered situation.

If there are a greater number of seed crystals present, we see a slight change in the crystallisation. Nevertheless, this small change is enough to change the shape of the curve and we see the plateau of a well tempered chocolate.

If even more seeds exist, the crystallisation is again altered and we see the curve shape typical of an over tempered chocolate.

The curves of under, well and over tempered chocolates are clearly not distinct situations. The number of seeds can vary continuously so that under temper blurs into good temper then into over temper.

Thus, the precise desired shape of temper curve is a matter of preference. There are no step changes between under temper, well tempered and over tempered. Rather, there is a smooth evolution between such states. The desired temper state depends on the tempering equipment used, the application (depositing, enrobing, dipping) and on the subsequent cooling. Thus the best state of temper must be determined by each manufacturer.
Now I want to look at a model tempering unit we have studied (Figure 15).

This model tempering unit can give useful indications of the important parameters to control during the process. The work was carried out for IOI Loders Croklaan.

The aim in tempering is to obtain a chocolate that will crystallise into the stable form, but that will maintain this condition for as long as possible. As noted previously, this is achieved in tempering machines by cooling in two zones and reheating in the third. Thus we studied a three stage tempering unit.

The schematic shows the three stages. The temperature of each is independently controlled, as is the rate of turn of the screw and the throughput of the chocolate.

In the experiments I shall describe, we kept the screw speed constant. We also fixed the second stage temperature to be 1.5°C lower than the first stage. This reduced the number of variables. We then set the first stage temperature and throughput and searched for the third stage temperature that would yield a well tempered chocolate.

The chocolate we used contained 5% milk fat as a percentage of the fat phase. What we found was that we could obtain a “well tempered” chocolate with a variety of conditions. In fact, any point on the surface shown in Figure 16 represents well tempered chocolate. The area above the curve (i.e. higher third stage temperature) represents the region of under tempered chocolate, while that beneath the surface is over tempered.

It is apparent that decreasing temperatures in the 1st (and 2nd) stages requires an increase in temperature of the 3rd stage in order to maintain
well tempered chocolate. This occurs because a greater amount of solid is formed in the initial stages and a higher temperature is required to melt or transform this into stable crystals in the final stage.

Similarly, if the throughput is decreased, the longer time in the first stages permits greater amounts of crystallisation to take place, requiring higher temperatures in the final stage.

If the temperatures in the first two stages are increased, a point is reached where insufficient crystals can form and the final stage temperature must be drastically reduced. Ultimately, it is not possible to produce a tempered chocolate at all. This is where the plateaux falls off. Clearly, operating near the edge of the plateau would not be desirable. Thus, normal operational conditions should be away from this edge.

In the same way, we looked at a chocolate containing 25% milk fat (Figure 17). Clearly, and as we would expect, the temperatures are lower for the higher level of milk fat. In fact, the whole surface is shifted downwards in temperature for both first and third stage temperature.

Thus, there is not a single way to set up a tempering machine to lead to tempered chocolate. Rather, there is a collection of such conditions. However, although the chocolate may yield a well tempered curve by the temper meter, the conditions are not all equally desirable.

A similar surface probably exists for each tempering machine and an understanding of the extent and shape of this surface would enable the optimum settings for the machine to be selected (e.g. to avoid operating on the edge of the plateau).

Summary
To summarise, tempering is demanded by the complex polymorphism of cocoa butter and the desire for a shelf-stable, high quality chocolate product.

Most tempering machines have a cooling zone followed by a heating zone. Seed crystals, both stable and unstable, are formed in the earlier stages while the unstable seeds are either melted or transformed into stable seeds in the final stages.

The specific tempering conditions required will depend on the cocoa butter used, the type of product being made and the subsequent processing.

The cooling curve obtained via a temper meter provides a simple, robust but indirect means of determining the quantity of seed crystals and can be used to ensure a consistent quality of chocolate product.

Finally, correct temper will yield a product that is glossy, has a good snap, cool mouthfeel, good flavour profile and storage stability.
Effects of Trisaturated Triglycerides on Chocolate Rheology

[originally presented at the Euro Fed Lipid Congress, Madrid, October 2006]

The various fats used in chocolate can all contain different levels of trisaturated triglycerides. Since these can crystallise out early in the tempering process they can, in some instances, have an effect on the rheology of the chocolate.

Introduction

The 2003 EU Regulations for Chocolate Products have, for the first time, permitted the use of non-cocoa vegetable fats in chocolate throughout Europe. In doing so, however, a number of restrictions were placed on where these vegetable fats can be sourced from and what processes they are allowed to undergo.

Six basic source oils are permitted – palm oil, shea oil, illipe butter, sal oil, kokum gurgi and mango kernel oil. Of these six oils four of them (palm, shea, sal and mango kernel) usually have to undergo some form of fractionation process to concentrate the SOS type of triglyceride necessary for equivalence to cocoa butter. Palm oil is further complicated in that it contains a significant quantity of trisaturated triglycerides which also have to be removed.

To be equivalent to cocoa butter a CBE needs to have a concentration of total SOS triglycerides similar to that found in cocoa butter. In total, cocoa butter typically contains about 80% of these triglycerides. This level is also found in illipe and kokum – but not in the other four oils. By fractionation, the SOS levels can be increased to levels similar to those found in cocoa butter (Table 1).

This is achieved by taking stearines from shea, sal and mango kernel.
With palm oil, however, the situation is somewhat different.

The triglycerides in palm oil can be divided into three main groups:
- **Trisaturated triglycerides** – triglycerides with no double bonds
- **Monounsaturated triglycerides** – triglycerides with only one double bond
- **‘Poly’-unsaturated triglycerides** – triglycerides with more than one double bond (NB these may be from two or three oleic acid groups or from truly polyunsaturated fatty acids)

Typical levels for each group quoted by Jurriens (1) are shown in Table 2.

If we were to simply take a stearine fraction from palm oil as with the other base oils and assume we got a perfect split between the SSS/SOS triglycerides and the rest then the levels of trisaturated triglycerides in those stearine fractions would be 14.8% from the West African oil and 18.3% from the South-East Asian oil. These levels are far too high to be acceptable in a CBE and so palm oil is fractionated a second time to remove as much of these trisaturated triglycerides as possible.

### Current Chocolate Industry practice

Despite its speciality nature, bulk chocolate is traded as a commodity and, as such, needs to conform to certain specified parameters to ensure batch-to-batch consistency.

One of the parameters usually specified for chocolate is its viscosity. Clearly this is of great importance to the end users of the chocolate because if there is too great a variability in the flow properties of the chocolate they purchase and receive this will have a major influence on aspects such as temperability and particularly on the pickup weight of enrobed coatings.
It is common practice in the chocolate industry to measure viscosity on chocolate at 0°C and these measurements form the basis of many delivery contracts. From the point of view of the fat phase, however, this temperature is far from optimal. There are two reasons for this. Firstly, it does not necessarily exclude crystal memory effects. Crystal memory is a phenomenon whereby fat crystals can apparently melt yet retain some form even when in the liquid phase which can affect how they recrystallise when cooled down again. Taking a solid chocolate and warming it up to 40°C is not always enough to destroy its crystal memory. To ensure such destruction would require heating to 50°C.

A more important issue associated with measuring the flow properties at 0°C, however, is that this takes no account of how the chocolate will flow at temper. It may be assumed that a chocolate with a higher viscosity at 0°C will also have a higher viscosity at temper but this is by no means always the case because there may be some triglycerides present in the chocolate that would be in a liquid state at 0°C yet would have crystallised before temper and therefore able to contribute to an increased viscosity at temper. Trisaturated triglycerides are an example of such a system.

If we consider the fats generally used in chocolate, cocoa butter and CBEs can contain low levels of these types of triglyceride but, because of its saturated fatty acid content and fatty acid distribution, milk fat can contain higher levels. Since the melting points of many of these triglycerides are above 0°C their presence would be expected to affect the viscosity of the chocolate at this temperature. This is not necessarily the case, however.

### Chocolate studies

In all our studies we used a standard basic chocolate recipe:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa butter</td>
<td>23%</td>
</tr>
<tr>
<td>Cocoa powder (10/12)</td>
<td>20%</td>
</tr>
<tr>
<td>Sugar</td>
<td>52%</td>
</tr>
<tr>
<td>Added fat</td>
<td>5%</td>
</tr>
<tr>
<td>Plus lecithin</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

The 5% added fat fell into three main groups:

1. Cocoa butter with 0%, 3% and 6% added tristearin. These blends would therefore add 0%, 0.15% and 0.3% tristearin to the chocolate itself.
2. CBE made from (a) conventional palm fraction (such as that used in the manufacture of Coberine™), (b) conventional palm fraction plus an extra 3% of fully hardened palm oil
3. Butterfat and butter stearine

Each chocolate was batch tempered at 30°C in a batch kettle with seeding. This means that a small amount of polymorphically stable cocoa butter seeds were added to the chocolate once it had cooled down to 30°C. Temper was considered to have been reached when a plateau was achieved during a tempermeter measurement. Once temper had been reached the flow properties of the chocolate were measured on the tempered chocolate at 30°C.

The temperature of the chocolate was then raised to 50°C to melt out all the crystals and erase any crystal memory and the flow properties
were again measured. Finally the temperature was reduced to 40°C and the flow properties again measured. The 40°C and 50°C measurements were made in this order to ensure no crystal memory effects on the 40°C readings.

**Addition of tristearin to cocoa butter**

Looking firstly at ‘ease of tempering’ we can see from Figure 1a that increasing the level of trisaturated triglyceride markedly increases the time taken to achieve temper. Even though the trisaturated triglycerides will start to crystallise out first as the chocolate is cooled and stirred to temper it, they do not act as ‘seeds’ for the SOS triglycerides to grow on. Indeed, the contrary is so, they seem to inhibit the nucleation and growth of the main cocoa butter triglycerides.

Not only was the tempering time significantly lengthened by the addition of SSS, the viscosity of the tempered chocolate was so high as to be impossible to measure it. This is in contrast to the viscosities measured at 40°C (Figure 1b) which were either similar to or even lower than that measured on the cocoa butter chocolate itself. This then indicates the possible pitfalls of measuring viscosities on untempered chocolate. As expected, the viscosities at 50°C are lower still.

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**Figure 1**
Cocoa butter with added SSS

a) Tempering Time

b) Viscosity
When we come to look at Yield Value (Figure 1c) we see a similar effect. The rheology of the chocolates with added SSS at temper was such that neither viscosity nor yield values could be measured. They were clearly much higher than observed with cocoa butter, yet at 40°C and at 50°C the yield values of all the samples were fairly similar.

When we come to look at CBEs with different levels of trisaturated triglycerides we again see differences moving from normal (i.e. those found in CBEs produced by Loders Croklaan) to high levels of SSS. The high-SSS levels were achieved by deliberately adding 3% fully hydrogenated palm oil to the CBE.

As far as tempering times (Figure 2a) are concerned the time for the high-SSS CBE is considerably longer than for the other two samples, again demonstrating that these glycerides do not act as temper seeds.

Looking now at the viscosities (Figure 2b) of the chocolates at temper, we find very similar values for the control and normal-SSS CBE but a viscosity about 30% higher with the high-SSS CBE implying that above a certain level of SSS, viscosity at temper will significantly increase.
Since the viscosities of the chocolates at 40°C and 50°C are all very similar to each other such an effect would not have been predicted by simply measuring the flow properties of the untempered chocolates.

When we look at the Yield Values (Figure 2c) we find, interestingly, that the yield value at temper of the normal-SSS CBE chocolate is about half of those of the cocoa butter control and of the high-SSS CBE chocolates. Indeed the yield values at temper of the normal-SSS sample is not much higher than those measured at 40°C and 50°C.

Butterfat and Butterfat Stearine
The trends of increasing time to achieve temper with increasing trisaturated triglyceride levels are also seen in the butterfat systems (Figure 3a). It should be remembered that, although we are used to seeing butterfat as a component of chocolate, it is by no means a fat which is compatible with cocoa butter. Apart from its lower melting profile and therefore softening effect it is also rich in saturated fatty acids which means that it is, in turn, rich in trisaturated triglycerides. When butterfat is fractionated these higher melting triglycerides become more concentrated in the stearine. It comes as no surprise, therefore, to find that the tempering time increases when cocoa butter...
is replace by butterfat and increases further when butterfat stearine takes its place.

What is perhaps more surprising is that these increased levels of trisaturated triglycerides do not contribute to the same degree of increase in viscosity (Figure 3b) as was found when SSS was added to either cocoa butter or a CBE.

Where we see a big difference, however, is in the Yield Value (Figure 3c). The replacement of 5% cocoa butter with 5% butterfat gives very little change in either viscosity or yield value whether this is measured at temper, at 40°C or at 50°C. When cocoa butter is replaced by butterfat stearine, however, even though the viscosity at temper is only slightly increased the yield value doubles. This effect on flow could have large consequences if the chocolate is to be used in moulding applications where a low yield value is usually required (2).
Viscosity and Yield Value Ratios

All of these rheological results can be condensed down numerically by calculating the ratios of the viscosities at 40°C and 50°C to that at temper, and making the same calculations using the yield value data.

Looking first at viscosity (Table 4), it is quite normal for the viscosity of tempered chocolate to be twice that measured at 40°C and three times that measured at 50°C. When the trisaturated triglyceride level increases, however, these viscosity increases are even higher being typically 2.5-3 times higher at temper than when measured at 40°C and 4-4.5 times higher at temper than when measured at 50°C.

<table>
<thead>
<tr>
<th>Added fat</th>
<th>$V_{temper}$/V$_{40}$</th>
<th>$V_{temper}$/V$_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa butter</td>
<td>1.75</td>
<td>3.35</td>
</tr>
<tr>
<td>Normal-SSS CBE</td>
<td>1.95</td>
<td>3.13</td>
</tr>
<tr>
<td>High-SSS CBE</td>
<td>2.69</td>
<td>4.43</td>
</tr>
<tr>
<td>Butterfat</td>
<td>2.18</td>
<td>3.29</td>
</tr>
<tr>
<td>Butterfat stearine</td>
<td>2.88</td>
<td>4.31</td>
</tr>
</tbody>
</table>

With a typical cocoa butter chocolate we also see the same ratio in terms of yield value (Table 5), i.e. twice as high at temper compared with 40°C and three times as high at temper compared with 50°C.

<table>
<thead>
<tr>
<th>Added fat</th>
<th>$\gamma_{v,temper}$/V$_{40}$</th>
<th>$\gamma_{v,temper}$/V$_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoa butter</td>
<td>2.11</td>
<td>2.94</td>
</tr>
<tr>
<td>Normal-SSS CBE</td>
<td>1.73</td>
<td>1.59</td>
</tr>
<tr>
<td>High-SSS CBE</td>
<td>2.34</td>
<td>2.18</td>
</tr>
<tr>
<td>Butterfat</td>
<td>1.93</td>
<td>2.92</td>
</tr>
<tr>
<td>Butterfat stearine</td>
<td>5.87</td>
<td>6.09</td>
</tr>
</tbody>
</table>
When a CBE is used, however, this ratio decreases significantly. A CBE with a ‘normal’ level of SSS will show only a ratio of about 1.5, and this is irrespective of whether the yield value at temper is compared with measurements at 40°C or at 50°C. Even deliberately adding hardened palm oil to increase the trisaturated triglyceride level only increased the ratio to that found with cocoa butter.

Using butterfat in the recipe gave no change in yield value ratios compared with those found for the control chocolate. Using butterfat stearine, however, showed a very large increase in the ratio from 2 or 3 with the cocoa butter control chocolate to 6 when butterfat stearine was included in the composition.

**Summary**

To summarise, therefore, elevated levels of trisaturated triglycerides, because they crystallise out without contributing to temper of chocolate, can cause undue increases in both viscosity and yield value at temper.

Neither of these increases is predicted from the normal chocolate industry standard method of measuring rheological properties of chocolate at 40°C.

The use of a cocoa butter equivalent with a normal level of trisaturated triglycerides gives viscosity increases from 40°C or 50°C to temper similar to those found with cocoa butter but a much reduced change in yield value making this type of chocolate of particular use in some enrobing or hollow moulding applications.

**References**


Introduction

Before looking at what might be considered to be correct cooling conditions it is necessary to define exactly what it is that is going to be cooled. Ambient confectionery coatings can be divided into four types.

1. Chocolates within the scope of the 2003 EU Chocolate Regulations which contain up to 5% cocoa butter equivalent or CBE
2. Coatings outside the scope of the 2003 EU Chocolate Regulations which contain CBE-type vegetable fats but at a level much higher than 5%. These are called ‘supercoatings’
3. Coatings whose main fat is a partially hydrogenated and
fractionated non-lauric fat. These will be called non-lauric CBR coatings.

4. Coatings whose main fat is a fraction of palm kernel oil. These will be called lauric CBS coatings.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Typical coating recipes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Milk chocolate</td>
</tr>
<tr>
<td>Cocoa mass</td>
<td>20.0</td>
</tr>
<tr>
<td>Cocoa butter</td>
<td>12.0</td>
</tr>
<tr>
<td>Cocoa powder 10/12</td>
<td></td>
</tr>
<tr>
<td>Full cream milk powder</td>
<td>20.0</td>
</tr>
<tr>
<td>Skimmed milk powder</td>
<td></td>
</tr>
<tr>
<td>Sugar</td>
<td>43.0</td>
</tr>
<tr>
<td>CBE</td>
<td>5.0</td>
</tr>
<tr>
<td>Non-lauric CBR</td>
<td></td>
</tr>
<tr>
<td>Lauric CBS</td>
<td></td>
</tr>
</tbody>
</table>

In formulation terms the recipes of each of these coatings typically differ as shown in Table 1.

The differences then are:
1. All of the added cocoa butter in chocolate is replaced by CBE in the supercoating. Apart from that the formulations are identical.
2. Non-lauric CBRs have a limited tolerance to cocoa butter which allows a small amount of cocoa mass to be used meaning that the non-lauric CBR comprises about 80% of the total fat phase.
3. Lauric CBS fats have effectively no tolerance to cocoa butter and so the only cocoa component allowed is a low fat cocoa powder which means that about 95% of the fat phase of such coatings is made up of the lauric CBS.

Because of their close similarity, chocolate containing CBEs and supercoatings can be considered together. But, first, we need to look at what happens to any coating when it goes through a cooling tunnel.

Cruickshank (2006) has defined the functions of cooling as:
- To remove specific and latent heat
- To contract the chocolate such that it releases cleanly from the mould
- To produce a stable and attractive product

The cooling tunnel conditions are of paramount importance in carrying out these functions.
Without, at this stage, getting into the details of cooling tunnel temperature profiles, many are set to have higher temperatures at the entry and exit points than they do in the middle where there is a minimum temperature (see Figure 1). The actual temperature settings depend, to a large extent, on the type of coating. At the point of deposition – moulding or enrobing – the coating contains very little solid fat.

From the point of deposition to the point of entering the cooling tunnel, the coating will generally cool slightly and will therefore show a small increase in solid fat content. During the time in the cooling tunnel, the rate of solidification increases as the temperature of the coating decreases. The rate of temperature decrease is large at first but then slows down as the temperature of the coating approaches the air temperature in the tunnel. Towards the exit of the tunnel with the rise in air temperature there may also be a slight rise in product temperature and a slowing down of the crystallisation rate.

Cooling tunnel profiles

The temperature profile of a cooling tunnel is dependent upon the type of coating being passed through the tunnel. Generally used tunnel profiles fall into two types:

- Those in which the temperatures in the entry and exit zones are higher than the temperature in the middle zones of the tunnel
- Those in which the entry and middle zones are quite cold but which have a higher temperature exit zone

The first type of profile is generally used for what we might call polymorphic systems, those that need to be tempered before cooling. In other words, chocolate and supercoatings. The second type is more generally used for the two kinds of compound coating, although the first type of profile can also be used for non-lauric compounds.

When coatings are crystallised then the solid fat content at the cooling temperature may be considered to be the ‘target’ level for equilibrium during cooling (Figure 1). This level is, however, not always achieved either because crystallisation is slow or because further post-crystallisation and post-hardening occurs on storage. Despite this, it is still possible to achieve an equilibrium solid fat level during cooling. What is important is that (a) this equilibrium should be attained in a fairly short time to maximise cooling tunnel throughput and (b) the equilibrium solid fat content should be high enough for the coating to be dry to the touch and able to be immediately wrapped on exiting the tunnel.
In the first part of the tunnel the coating cools down by removal of specific heat but only minimal crystallisation occurs. The bulk of the crystallisation takes place in the central zone of the tunnel when the temperature needs to be cold enough to not only remove specific heat but also latent heat of crystallisation. In some ways it would be more efficient to have the temperature in zone 3 as low as in zone 2 to allow products to pass through the tunnel more quickly but there is a major problem in having the exit temperature too low.

This is the problem of condensation on the surface of the product. If the exit temperature is below the dew point in the environment close to the tunnel exit then humidity from the atmosphere will condense on the coating surface.

At the very least this will cause unsightly drying marks. Worse effects can be the formation of sugar bloom as some of the sugar in the coating firstly dissolves in the condensed droplets of water and then recrystallises on the surface as the water evaporates. Another potential problem of such condensation can occur with lauric coatings where there is a risk of hydrolysis of the fat phase occurring giving soapy off-flavours.

**CBEs and supercoatings**

Polymorphic coatings, based on either cocoa butter (with or without vegetable fat where this is permitted in chocolate) or on cocoa butter equivalents in supercoatings, both require tempering. Tempering ensures that there are sufficient polymorphically stable crystal seeds present at the point at which the coating enters the tunnel to ensure that the bulk of the coating also crystallises in this same polymorphically-stable form. The crystal form which is required after tempering is the beta-form or Form V.

Even though the coating may be well-tempered and contain enough stable crystals to seed the bulk crystallisation, if the tunnel temperature is set too low then it is still possible to produce unstable crystals alongside the more stable ones as the product passes through the
tunnel. The end result is a softer product and potentially a more unstable product in terms of possible fat bloom formation.

To show this a cocoa butter fat phase and a supercoating fat phase were tempered and cooled for 60 minutes at average temperatures of 22.5°C, 15°C and 0°C. The solid fat content of cocoa butter is lower after having been cooled at 0°C which is consistent with some unstable crystals having been formed.

The effect is also seen, perhaps to a slightly greater extent, with the supercoating fat phase (Figure 2). In general, therefore, for both chocolate and supercoatings, a tunnel entry temperature of about 15°C would be recommended. In the centre of the tunnel the temperature can be reduced to as low as 8°C, although if tunnel length and throughput time permits a temperature of about 10°C is to be preferred. The exit temperature should, as already mentioned, be above the dew point and typically about 15°C.

**Figure 2**
Effect of cooling temperature on supercoating crystallisation

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**Compound coatings**

Moving on now to compound coatings – it is always recommended that lauric coatings undergo the type of shock cooling in the tunnel which involves a very low entry temperature, typically about 8°C, although it is even possible to go as low as 6°C.

When we get to non-lauric coatings advice tends to vary with some recommendations being to shock-cool in the same way as lauric coatings are cooled and others being to follow the more ‘gentle’ type of cooling given to chocolate and supercoatings. This would imply that non-lauric compound coatings are highly flexible in the way in which they should be cooled.

To examine that, a typical non-lauric coating was cooled through a variety of cooling tunnel temperature regimes. The coatings were stored at 15°C, 20°C and 25°C for 3 months and gloss was measured using a glossmeter after 3 months.
After 3 months we see clear distinctions between both cooling tunnel temperature profiles and storage temperature. Firstly, the higher the storage temperature the lower is the gloss (Figure 3). Secondly, a cooling tunnel temperature profile with zone 1 and zone 3 temperatures of 12°C and a zone 2 temperature of 8-10°C is clearly preferable in terms of gloss.

Figure 3
Effect of cooling conditions on gloss of non-lauric coatings (after 3 months)

One of the main issues these days with non-lauric compounds is nothing to do with cooling conditions but is that they are based on partially hydrogenated vegetable oils and therefore contain trans fatty acids. This means that, in many instances, they are being replaced by either chocolate or supercoating or by lauric compounds. To look at the effect of changing from a trans-containing non-lauric compound to a trans-free lauric compound, Loders Croklaan has sponsored some work at the University of Ghent (Foubert et al, 2006).

Comparing the rates of crystallisation of these two types of coating fat by DSC it was found that the lauric fat crystallised much more quickly than the non-lauric fat. Equilibrium was reached in shorter times and at higher temperatures with the lauric fat.

Much lower temperatures are needed with the non-lauric fat to achieve the same speed of crystallisation. In many ways, this is contrary to any advice that might be given about relative cooling temperatures for the two types of fat where a lower tunnel temperature would generally be advised for laurics. These results would suggest that although that is what is advised, the lauric fats do not actually need such deep cooling because they crystallise quickly anyway.

But reaching equilibrium alone is not the only factor to take into account. The solid fat content at that equilibrium is also of critical importance. The lauric fat, for example, reaches an equilibrium of sorts at 30°C within 30 minutes but the solid fat content at that temperature would be far too low to allow the product to be satisfactorily wrapped.
Because crystal size and structure is linked to crystallisation rate it is therefore no surprise to find that these too are temperature-dependent. Comparing the two types of fat microscopically we can see that, whilst the number of crystals of the non-lauric fat decreases as crystallisation temperature increase there is little effect on crystal size (Figure 4). With the lauric fat, however, crystals formed at higher temperatures such as 30°C are much bigger. As gloss is related to crystal size this could well explain why shock cooling is needed to get a good gloss on a lauric coating.

Interesting things happen to these coatings on storage (Figure 5). Firstly, although it would be expected that irrespective of the cooling temperature used an equilibrium of sorts would result on storage, we find that coatings cooled at 10°C (that is the dotted lines) are harder after 1 day and 1 week storage at 0°C than coatings cooled at 15°C. Setting aside aspects such as gloss and cooling tunnel throughput this factor alone would be enough to suggest that these coatings should be cooled at as low a temperature as possible rather than be cooled more gently.
Secondly, we also see an apparent reduction in hardness on storage which is contrary to what might be usually expected in terms of coatings post-hardening when stored. There is no decrease in the amount of crystallisation nor is there a change in polymorphism to account for this decrease. The only explanation, therefore, is that a change in crystal structure is occurring.

It is generally well known that lauric based coatings have excellent hardness and snap whereas non-lauric coatings tend to be softer and more malleable making them ideal for cuttable cake coatings, for example. These differences were seen here with the hardness of the lauric coating crystallised at 10°C being almost twice that of the non-lauric coating crystallised at the same temperature. What is more surprising is that no such differences were seen between the two fats cooled under the same conditions. This could be a result of the shorter chain triglycerides in the lauric fat being able to form a tighter, firmer network and that this results in a higher hardness.

Summary
So, taking all these things into account, what temperature profiles are best for each type of coating?

Starting at the end first (Figure 6) – the exit temperature from the tunnel must always be above the dew point whatever type of coating is going through the tunnel. What happens before that is dependent on the type of coating being used.

With chocolate and supercoating there should be a fairly high entry temperature with a minimum in the middle zones of the tunnel. This ensures that all the fat crystallizes in the same stable V form that is present in the tempered coating.
With lauric coatings the entry temperature and middle zone of the tunnel should be quite low, typically about 6-8°C. This is not to speed up cooling because laurics crystallize quite fast anyway. It is to ensure that small fat crystals are produced to enhance the gloss of the coating.

Conflicting advice is often given for non-laurics but on the basis of the work on gloss retention described here, a recommended profile would be to have an entry temperature of about 12°C – between that of chocolate and laurics and a middle zone temperature of about 8-10°C, again between that of chocolate and laurics. This then provides a good compromise between crystallization speed and good gloss on storage.

References


Introduction
Oil migration has been, and indeed still is, a major problem in some composite foods. It is prevalent in any composite food in which two components each having a different continuous fat phase are in contact. An example of such a product is the chocolate coated fat-based centre in which there can be in terchange between coating and filling fats. We can extend this to coated and cream-filled biscuit products in which there are not only coating and filling fats but also dough fats. In a completely different type of application, oils can migrate into batters and breadcrings and into potatoes during frying.

This phenomenon is often referred to as ‘fat migration’ but it is, strictly speaking, the oil phase which migrates if we distinguish between oils as liquids and fats as solids – hence the use of the term ‘oil migration’.

In this article we will review what might be termed the ‘basics’ of oil migration. By this we mean its mechanism, ways of detecting and ways of quantifying oil migration.

Effects of oil migration
Oil migration can have a number of effects on a product, most of which can be considered to be ‘adverse’ effects. In a chocolate-coated centre, filling fat will migrate out of the centre into the chocolate. This both

Migration of oils between fillings and coatings can have a major impact on the quality of a confectionary product, particularly in terms of the hardness and bloom resistance of the coating. In this, the first part of a multi-part series of articles on oil migration, we look at the basic effects of oil migration, the interactions between fats, methods of detecting and quantifying the extent of oil migration and the mechanism by which it occurs.
increases the hardness of the filling and the softness of the coating as the soft oils move from one phase to the other. The result is not only a loss of textural differences between the two parts of the product but also a product that becomes increasingly difficult to handle as the chocolate softens. The more liquid oil there is in the centre fat phase the greater is the problem both in terms of speed of migration and its effects on the product.

Such migration is often accompanied by the formation of fat bloom on the chocolate as the migrating oils make it easier for the cocoa butter in the chocolate to undergo the kind of polymorphic change that results in bloom.

Whilst bloom formation is not an issue in fried products, changes in texture are. Undue migration of frying oils into batters can result in a loss of crispness of the batter and an increase in sogginess of the whole product (Simoneau et al, 1993).

**Interactions between fats**

Essentially we have two types of interaction when one fat migrates into another – dilution and eutectic formation. Migrating oils are by definition softer than the fats they are migrating into and therefore there will be softening of the receptor fat phase purely because of dilution by a more liquid oil. This can be seen clearly when a very liquid fraction of palm oil is blended with a more solid fraction (Figure 1). This kind of softening will occur when, for example, nut oil from a praline centre migrates into a chocolate coating.

Eutectic softening occurs when the migrating centre fat is ‘incompatible’ with the coating fat. The interactions of the two fat phases result in the formation of eutectics with solid fat contents lower than those found in the individual fats. An example of this is the migration of a lauric fat centre such as hardened coconut oil into a cocoa butter chocolate (Figure 2).
Methods of Detection

A wide range of methods of detecting oil migration have been described in the literature and the choice often depends on what kind of system is being studied and the degree of similarity that exists between the various fat phases.

The ‘Washer Test’

Talbot (1996) developed a simple method for contacting coatings and fillings in a reproducible way. This involved moulding the filling composition within a steel washer of fixed dimensions and then fixing to the top of this a similar washer which contained tempered chocolate. These systems were then stored at various temperatures and the texture and content of the chocolate measured at various time intervals to evaluate both the effects and extent of migration. The method has the benefit of considerable flexibility in that by using different numbers and thicknesses of washers different filling:coating ratios can be used, the effects of barrier layers evaluated and samples of reproducible thicknesses taken for analysis. The test also formed the basis of some of the magnetic resonance imaging work carried out by Couzens and Wille (1997).

Texture Analysis

Since one of the main problems associated with oil migration is the textural change that occurs measuring such changes has been one of the main methods of detecting and determining its effects. Often texture analysers are used to determine the force needed to crack, compress or penetrate the phase being most affected by migration. When the affected phase is a chocolate coating simple penetrometry measurements are often sufficient to determine effects.

Fatty Acid Methyl Ester (FAME) and Triglyceride Gas Chromatography

Providing the migrating oil is sufficiently different in its composition from the receptor fat phase GC can often be used to follow the rate of migration. This can be easily done by triglyceride carbon number GC.
in systems such as that shown in Figure 2 in which a fat high in C34-C38 triglycerides is migrating into chocolate which is rich in C50-C54 triglycerides. Where the migrating and receptor fats have similar carbon number distributions measurement of migration rates can often be made using FAME GC. An example of this would be when peanut oil migrates into chocolate – linoleic acid in the peanut oil can be used as a marker.

**Spectroscopy**

Although electron spin resonance has been used (Tabouret, 1987) as a means of detecting fat migration a more commonly used spectroscopic method is magnetic resonance imaging (MRI). This has usually been carried out as a 2-dimensional technique (Couzens and Wille (1997)) but 3-D imaging of products (Miquel et al, 1998) can give useful information about the structure of products and any preferred directions of migration.

**Image analysis**

A novel way of following oil migration is to use a nile red stain within the migrating phase and monitor the progress of this stain into cocoa butter using a flatbed scanner linked to image analysis software (Marty, 2005).

**Quantification**

Detection, in itself, is of little use if this cannot be quantified. It is often useful to try to condense down the measurements made on a migrating system into a single figure that can then give an indication, at least, of the overall extent of migration. In an attempt to generate such an indication the concept of the Specific Migration Index (SMI) was developed (Talbot, unpublished):

\[
SMI = \frac{\sum_{i=1}^{i=n} \text{Abs}(x_{ci} - x_{si})}{\sum_{i=1}^{i=n} \text{Abs}(x_{ci} - x_{fi})} = \frac{MI}{MI_{total}}
\]

where \(x_c\) is the amount of a particular fatty acid or carbon number group in the original coating, \(x_f\) is the amount in the original filling and \(x_s\) is the amount in the coating after migration.

The following example can be used to demonstrate the measurement of SMI.
Solvent fractionation of palm oil

Table 1
Example of determining extent of migration

<table>
<thead>
<tr>
<th></th>
<th>C48</th>
<th>C50</th>
<th>C52</th>
<th>C54</th>
<th>C56</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original coating</td>
<td>2.0</td>
<td>18.6</td>
<td>43.6</td>
<td>33.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Original filling</td>
<td>4.0</td>
<td>30.1</td>
<td>24.3</td>
<td>39.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Sample coating after migration</td>
<td>2.1</td>
<td>21.7</td>
<td>34.3</td>
<td>39.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Absolute difference between coating and filling</td>
<td>2.0</td>
<td>11.5</td>
<td>19.3</td>
<td>6.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Absolute difference between coating and sample</td>
<td>0.1</td>
<td>3.1</td>
<td>9.3</td>
<td>5.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The total of absolute differences between the original coating and the sample after migration is termed the MI – in this case this has a value of 18.5. The total of absolute differences between the original coating and the original filling is termed the MItotal – in this case this has a value of 39.1. MI expressed as a percentage of MItotal is the specific migration index, SMI – in this case 47%.

Talbot (1989) also used a slightly different relationship to calculate the extent of migration which can be simplified to:

\[
\text{Degree of migration} = \frac{\text{CN}_S - \text{CN}_{CTG}}{\text{CN}_{FIL} - \text{CN}_{CTG}}
\]

where CN indicates the value of a specific carbon number and the subscripts S, CTG and FIL indicate parameters relating to sample, coating and filling respectively. From this the degree of migration for each individual carbon number can be calculated. Using the data in Table 1 and calculating the mean value for XFIL over the range of carbon numbers we find a degree of migration of 42%.

Mechanism of Migration

Once we have methods of detection and quantification we can then start to define mechanisms which will fit with the results we find experimentally.

Oil migration has long been thought to be governed by the diffusion process and, to a large extent, the rate of migration can be defined by the following equation from Ziegleder (1997):

\[
\frac{m_t}{m_s} = \frac{\sqrt{D* t}}{d}
\]

In which \(m_t\) is the amount of oil which has migrated from the filling after time \(t\); \(m_s\) is the amount of oil which has migrated after saturation; \(D\) is the diffusion coefficient; \(d\) is the thickness of the chocolate and \(t\) is the storage time. This equation means that the rate of oil migration is fastest in the initial stages of storage levelling out with time to reach an
equilibrium. This equilibrium will change to a different level if the storage temperature increases.

This equation relates the extent of oil migration to the square root of storage time. The linear nature of this relationship can be seen by converting data from Miquel et al (2001) into a suitable graphical form (Figure 3). Miquel et al stored a filling containing hazelnut oil and sugar in contact with a tempered dark chocolate and measured the degree of movement of hazelnut oil into the chocolate by MRI.

![Figure 3](image)

**Figure 3**
Concentration of hazelnut oil migrating from filling to chocolate

Source: adapted from Miquel et al – Food Res.Int. 34 (2001) 773-781

Couzens and Wille (1997) and Guiheneuf et al (1997) demonstrated by MRI that in a model system in which a filling phase was stored in contact with a chocolate phase, liquid oil from the filling initially diffused through the chocolate but then moved towards the surface of the chocolate as a ‘front’. After 14 days at 28°C the intensity of the liquid oil signal from the NMR was uniformly distributed throughout the chocolate layer but after 84 days it showed a maximum at the chocolate surface and a minimum at the filling/chocolate interface. This is contrary to what would be expected as a result of normal diffusion.

This observation has led some workers (Aguilera et al, 2004) to question whether the mechanism for oil migration actually is a diffusion process. A similar relationship between extent of migration and the square root of time would result from a capillary flow mechanism. Such a mechanism could better explain the observation of hazelnut oil migrating as a front. Further support for capillary flow as the mechanism for oil migration results from the microscopic detection of interparticle pores and crevices in chocolate which would allow capillary action to occur (Khan et al, 2003).

**Summary**

As in many areas of food science our knowledge of the causes, mechanisms and solutions to oil migration continues to expand. Ten to twenty years ago it was considered by most people working in the
area to be a diffusion controlled process. Now it looks possible that capillary flow could also be playing a role. Whilst some studies suggest the migration of oil to produce a 'front' this is not the case in other studies, suggesting that the real mechanism is a combination of diffusion and capillary flow with the dominating mechanism being dependent on other factors such as recipe, temperature etc.

References


Khan RS, Hodge SM, Rousseau D (2003) – ‘Morphology of surface pores in milk chocolate’ – AOCS Annual Meeting and Expo, 4-7 May, Kansas City, USA


Oil Migration: Minimisation of Extent and Effects


Introduction
Oil migration has been, and indeed still is, a major problem in some composite foods. It is prevalent in any composite food in which two components each having a different continuous fat phase are in contact. In a previous, related, article we reviewed what we might call the ‘basics’ of oil migration – its effects, how we can detect and quantify it and the latest ideas on what the mechanism is.

In this article, we will focus on two further aspects of oil migration: what are the factors important in oil migration and how we can use our knowledge of these to suggest ways of minimising both the extent of oil migration and the effects it has. As with the previous article we will review and use information published over past 15 years or so as our guide.

Factors affecting oil migration
If we know what things affect oil migration we are then well on the way to suggesting possible solutions. Ziegleder (1997, 1999) details a number of factors which will affect the rate of migration of, for example, a filling fat into a coating fat.

Factors which influence particularly the diffusion coefficient, D
A number of factors related to both chocolate and filling will have an influence on the diffusion coefficient (see the previous article for a
definition of diffusion coefficient). Those that are not discussed
elsewhere include:
• Percentage of fat in the chocolate
• Solid fat content of the chocolate fat phase
• Viscosity of the chocolate
• Interactions between the oil phase and the non-fat particles
• Percentage of liquid oil in the filling
• Mobility of this liquid oil phase

Chocolate thickness
The thicker the chocolate the more readily it can absorb migrating
filling fats before its texture becomes unacceptable.

Ratio of filling:chocolate
To some extent this is linked to chocolate thickness. The lower the
filling:chocolate ratio the less filling fat there is available to migrate and
the more chocolate there is to accommodate it.

Product geometry
Even at given filling:chocolate ratios and given weights some product
geometries allow a thicker chocolate coating. For example a
hemispherical product would have a thicker chocolate coating than a
cylindrical one.

Storage temperature
The higher the storage temperature, the higher the liquid oil contents
of both filling and chocolate and the faster will be the rate of migration.
Not only will the rate of migration be quicker but the degree to which
the fats will migrate will also be higher. For example, a palm kernel oil
based filling stored in contact with a cocoa butter based chocolate
showed the following degrees of migration after 56 days storage
(Talbot and Bennett, unpublished work):

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Migration</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>11%</td>
</tr>
<tr>
<td>25°C</td>
<td>46%</td>
</tr>
<tr>
<td>30°C</td>
<td>55%</td>
</tr>
</tbody>
</table>

Ali et al (2001) stored a filling based on palm mid-fraction and
desiccated coconut adjacent to a dark cocoa butter-based chocolate.
The chocolate itself had an initial hardness of 3.5kg force. After 8
weeks storage at 18°C the hardness had decreased to about 2.8kg
force. After 8 weeks storage at 30°C, however, a significant decrease
in hardness down to about 0.5kg force was observed due to migration
of the filling into the chocolate and to the eutectic effects of such
migration.

Miquel et al (2001) found that migration from a hazelnut oil filling into
dark chocolate reached saturation after 3 weeks at 28°C but took
about 6 months at 23°C to reach saturation. Even after a year at 20°C
this point had not been reached.
Formulation
It has long been thought that harder chocolate shells produced by using either hard cocoa butters, cocoa butter improvers or low levels of milk fat are more resistant to migration from fillings. However, Ziegleder (1999) has shown that softer milk chocolates have almost the same diffusion rate as harder dark chocolates even though the liquid oil content in the milk chocolate is some 2½ times greater than in dark chocolate. The reason given for this apparently unusual behaviour is that the non-fat milk particles in the chocolate are more porous and therefore more able to absorb much of this extra liquid oil phase leaving only about 2% of the liquid oil in the chocolate in a ‘free’ state irrespective of whether this is a milk or a dark chocolate.

Contrary to this observation Choi et al (2005) compared three chocolates containing 0%, 3.57% and 10% milk fat and found a significant difference between them, with the chocolate containing 10% milk fat suffering more from migration from a peanut butter paste at 30°C than did the chocolates with lower levels of milk fat.

Ways to reduce oil migration
It is fine to be able to detect and quantify oil migration and to suggest the things which will have an effect on it but the all-important question is ‘how do we prevent it?’ Since, in a practical sense, it is very difficult to completely prevent oil migration a better question would be ‘how do we minimise the extent and effects of oil migration?’ In this section we will look at various suggestions and ideas that either emanate from the factors defined above or which have been made in the literature.

Compatible filling and coating fats phases
This approach (Talbot, 1989) does not stop oil migration but it ensures that, when it occurs, any softening will be due solely to dilution of the coating fat with liquid oils from the filling rather than any extra softening occurring because of eutectic formation between the coating and migrating oils.

Barrier layers between the coating and filling
Although when initially suggested (Talbot, 1989) the proposal was to use a thin layer of a high-solid fat content fat between the coating and filling it is possible to use other materials in this way to act as barriers against fat migration. For example, some products incorporate wafers as part of their product structure which, as well as adding sensory and textural differences to the product also act as an oil migration barrier. Barriers based on shellac or on hydrocolloids can also be used in this way.

Structuring fats
These are high-melting fats which are added to the main filling (or migrating) fat. On cooling, they crystallise in such a way as to form a network structure within the filling that acts as an internal barrier and thus slows down migration (Talbot, 1989).
Optimisation of product structure and design
Taking some of Ziegleder’s (1997, 1999) factors which affect the rate of oil migration we can clearly turn these around and use them to suggest ways of minimising oil migration. Some of these will be difficult to modify (chocolate fat content and melting profile) whilst others (product geometry, ratio of filling to chocolate) may well be defined by the design of the product – although in the design of a new product these are factors which the product developer should bear in mind.

Reduced storage temperatures
Some factors, of course, may only be partially under the control of the manufacturer. An example of this is the storage temperature. This can be well-controlled by the manufacturer, relatively well-controlled by the retailer (especially by the larger multiples), but, by the time the consumer buys the product control is generally lost and the product can then often undergo large fluctuations in storage temperature. As the rate of oil migration is fastest in the early stages of migration it does not take long at an elevated temperature for a significant degree of migration to have occurred.

Use of absorbent non-fat solids within the chocolate
An interesting observation from Ziegleder (1999) is that the porosity of non-fat milk solids can affect the amount of free liquid oil in the chocolate and hence affect the degree of migration. This would suggest that the inclusion of skimmed milk powder even into plain chocolate would improve its resistance to migration by including the non-fat solids to improve absorption without the softer fat being present to increase the amount of liquid oil phase. Although Ziegleder only looked at this effect in the chocolate, it would also be interesting to evaluate the effects of such non-fat solids when included in the filling phase.

Optimised particle size distribution in the chocolate
A further possibility which is dependent more upon the non-fat particles than on the fat phases themselves is based on optimising the particle size distribution. Chocolate manufacturers aim to reduce the particle size of chocolate to less than about 25 microns so as to make the particles then undetectable on the palate. If all of the particles are of a uniform size then there will be gaps or voids between them through which the liquid oil can migrate more easily. If, however, the particle size distribution of the chocolate is such that it also contains some much smaller particles that are able to fill these voids then it is possible that this would help to reduce the rate of oil migration. Choi et al (2005) found that a chocolate with a high particle size (60 microns) was more quickly affected by oil migration from peanut butter than was a chocolate with a smaller (45 micron) particle size. The overall extent of migration was similar in both cases. Both of these particle sizes are, however, much larger than would normally be found in a high-quality chocolate.
Control of particle aggregation in the filling
Alander et al (1994) have suggested that having a particle concentration close to the critical volume fraction of the filling is a further way of reducing oil migration. This can be achieved by aggregation of the solid particles within the filling. This, in turn, is best achieved by the use of β'-stable filling fats. They also show that the addition of lecithin to fillings increases the rate of oil migration because the surfactant effect breaks up sugar aggregates. On the other hand, Choi et al (2005) have not seen a difference between chocolates containing no emulsifiers and chocolates containing up to 0.5% of a lecithin/PGPR mix in terms of their being affected by oil migration from a peanut butter phase in contact with them.

Optimised temper state in the chocolate
Miquel et al (2001) evaluated the migration of hazelnut oil into chocolates which had been tempered to different degrees. They found that a ‘low’-temper (or slightly undertempered) chocolate was able to ‘receive’ more hazelnut oil due to migration than did a ‘high’-temper (or slightly overtempered) chocolate. This may be due to the lower-temper chocolate having a looser packing of crystals (Talbot 1999). Miquel and co-workers also found that an even lower degree of hazelnut oil inclusion was found in the chocolate if the chocolate was given a post-crystallisation treatment involving storage for 24 hours at 30°C followed by 24 hours at 4°C. During the storage at 30°C about 4% hazelnut oil migrated into the chocolate but the subsequent 4°C storage period stabilised the chocolate such that the saturation concentration of hazelnut oil in the chocolate was lowered to about 12% w/w (compared with about 16% w/w with the ‘low’-temper chocolate). They also found that whilst the diffusion coefficients were similar for the ‘high’ and ‘low’ temper chocolates it was lower for the chocolate which had undergone this post-crystallisation regime.

Summary
As in many areas of food science our knowledge of the causes, mechanisms and solutions to oil migration continues to expand. Ten to twenty years ago solutions were limited to suggestions of improving compatibility between coatings and fillings, using barrier layers or structuring fats. Whilst these are still today very valid ways of trying to reduce oil migration our understanding of the factors which affect such migration has increased allowing us to now suggest a number of other possibilities, many of which involve changes and optimisation of the chocolate rather than changes to the filling.

It is also clear that our knowledge of the whole phenomenon is by no means complete and is still growing. This means exciting possibilities for the future in terms of potentially new ways to solve the problem of oil migration.
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Introduction
The correct choice of oil for frying is important for two reasons. Firstly, the oil is used as the heat transfer medium during frying and must be able to withstand not only frying temperatures but also have a high enough stability to allow it to be used repeatedly. Secondly, products being fried will take up some of the oil and therefore the oil needs not only to have a high oxidative stability during the life of the product but also to be both palatable and nutritious.

During frying a range of reactions occur within the oil – oxidation, polymerisation, darkening and hydrolysis are some of the more important of these. Each of these has an effect on the ‘fry-life’ of the oil. In addition, components in the food being fried can also have an effect on the end quality of the oil.

It is important, therefore that oils used for frying should have a high oxidative stability and good nutritional characteristics.

Types of oils
The oils preferred for frying have changed considerably over the years and reflect flavour preferences, nutritional requirements, oil stability and economics. For example, animal fats have now been widely replaced by vegetable oils. This change has been mainly on the grounds of

Increased Industrial Use of Palm Oleine


Over the years, as nutritional thinking has changed, frying oils have moved from animal fats to partially hydrogenated vegetable oils to, nowadays, non-hydrogenated vegetable oils. Avoiding rancidity is a key requirement in frying and palm oleine, with its higher oxidative stability compared with many other non-hydrogenated alternatives, is being increasingly used for this purpose.

Geoff Talbot, Imro ‘t Zand
nutritional requirements, animal fats being rich in saturated fat, despite the good flavour they impart to the food. Semi-solid fats, or frying shortenings, are however still sometimes used to prevent an oily texture being formed in products such as french fries and doughnuts.

Partially hydrogenated vegetable oils were once widely used in industrial frying because of their high oxidative stability. Over the past few years the use of such oils has decreased significantly because of the effects of trans fatty acids in such oils on cardiovascular health. They were initially replaced by oils such as rapeseed oil and soyabean oil but the oxidative stability of these oils is quite low, especially when being used repeatedly at frying temperatures and so, more and more, the oil of choice for industrial frying is palm oil based.

**Oxidative and Hydrolytic Stability**

One of the main stability issues with frying oils is indeed that of oxidative stability. This is more pronounced as manufacturers also move away from partially hydrogenated fats in favour of oils rich in cis-unsaturates. Such oils have a lower oxidative stability than fats richer in saturates or trans-unsaturates.

Antioxidants naturally present in the oil can, of course, help. Natural antioxidants such as tocopherols and tocotrienols are especially useful in prolonging the fry-life of oils, -tocopherols and tocotrienols being particularly good at inhibiting oxidation. Oils containing naturally high levels of these components are corn oil, cottonseed oil, soyabean oil and palm oil.

As many foods which are fried contain significant quantities of water, this can have two adverse effects. Firstly, when the food is added to the hot oil, there can be a tendency for the oil to foam as the high temperature causes the water to flash off. This foaming increases the surface area of the oil thus increasing the risk of oxidation. Secondly at such high temperatures the water in the food can interact with oil causing hydrolysis. This is a breakdown of the triglyceride molecules in the oil which releases free fatty acids. As the free fatty acids in the

![Figure 1](image)

*Figure 1*  
Effect of free fatty acid on smoke point  
from Weiss (1983) quoted by Kochhar (2001)
oil build up (Figure 1), the smoke point of the oil decreases to such a point that it is considered a hazard (Weiss, 1983 quoted in Kochhar, 2001).

Palm oil and Palm oleine

It has already been mentioned that, increasingly, the oil of choice for industrial frying is palm oil based. This may be palm oil itself but there is a general preference for the use of palm oleine, the low-melting fraction of palm oil. The reasons for this are two-fold. Firstly the melting point of palm oleine (15-25°C) is much lower than that of palm oil (about 38°C) making it much easier to handle and secondly the degree of unsaturation in palm oleine is higher than that in palm oil giving it better nutritional characteristics. This means that there is a slight trade-off in oxidative stability but the stability of palm oleine is still much higher than that of other liquid oils such as rapeseed oil (Table 1).

Improvements to frying oils

The main improvements that can be made to frying oils are in their oxidative stability. As well as the antioxidants naturally present in oils it is permissible under certain circumstances to add either natural or synthetic antioxidants to frying oils. It is important to check legislation, however, before doing this as regulations vary from country to country.

With the trend away from synthetic food additives to more natural equivalents there is an increasing move towards the use of ‘natural’ antioxidants such as herb extracts. Rosemary and sage extracts are particularly beneficial in this with rosemary being found to be more effective than the synthetic antioxidant BHT in prolonging the life of snacks fried in palm oleine (Che Man and Tan, 1999).
triglycerides which oxidised during frying (Figure 2). Typical levels of use are 2 ppm of silicone.

**Summary**

The optimal frying oil should be non-hydrogenated (for nutritional reasons), oxidatively stable (for fry-life reasons) and contain a limited amount of linoleic acid. Palm oil and, especially, palm oleine fulfil all of these requirements. Their fry-life can be extended further by the use of low levels of silicones to reduce foaming and the generation of oxidised triglycerides and by the addition of natural antioxidants such as rosemary extract.

**References**


Effect of trans fatty acids

There are two main types of cholesterol in our blood – HDL cholesterol and LDL cholesterol. Because excess HDL cholesterol is carried to the liver and then excreted it is considered to be ‘good’ cholesterol. LDL cholesterol, on the other hand, remains in the blood plasma and can start to produce plaques in the arterial wall. For this reason, LDL-cholesterol is seen as being ‘bad’ for our health (Figure 1).

Studies (e.g. ref. 1) have shown that trans fatty acids raise the level of LDL cholesterol and lower the level of HDL cholesterol thus resulting in double detrimental effects.
Trans fatty acids are found naturally in dairy products such as butter and cheese but are also produced during the partial hydrogenation of vegetable oils. These types of oils are gradually being replaced by more ‘healthy’ alternatives.

**Why have oils been hydrogenated?**

There are two main reasons why oils have been hydrogenated:
- Oxidative stability
- Structure and solid fat content

Trans fatty acids are not only more stable than their corresponding cis counterparts they also have higher melting points so enabling easier production of products needing structure and some solid fat.

Examples of such products are confectionery coatings and fillings, biscuits, toffees, analogues of dairy products such as butter, cream and toppings.

**Options to retain structure**

In all of these applications some solid fat is needed. If this solid fat cannot be obtained from fats containing trans fatty acids it must be obtained from fats containing saturated fatty acids. So, where do we get such fats from?

Natural sources of saturates
- Palm kernel oil
- Palm oil
- Cocoa butter
- Shea butter

Processed source of saturates
- Interesterified blend of fully hydrogenated C18-rich oil with non-hydrogenated C18-rich oil
Saturates from natural sources are lauric acid (palm kernel oil), palmitic acid (palm oil), stearic acid (cocoa butter and shea butter). Only stearic acid is obtained from the processed source.

The question we need to answer then is:
Are some saturates better for us than others?

**Biochemical markers of cardiovascular disease (CVD)**
Although HDL and LDL cholesterol levels are, in themselves, important, ‘the ratio of total to HDL cholesterol is considered more important than the total or lipoprotein cholesterol concentrations in estimating risk’

A second important marker of CVD is the level of plasma fibrinogen, the central protein in the blood coagulation system.

**Effect of fatty acids on total:HDL cholesterol - Mensink study**
Mensink et al carried out a meta-analysis of 60 controlled trials in which 1% of dietary energy from carbohydrate was replaced in turn by 1% of dietary energy from different fatty acids. The effects on the total:HDL cholesterol ratio was determined (see Figure 2).

The total:HDL cholesterol ratio is increased by trans fatty acids, lowered by cis-unsaturates and unaffected by saturates. Saturates in general, therefore, show some neutrality in this respect. Individual saturates, however, have slightly different effects.
Lauric acid lowers the total:HDL cholesterol ratio to a similar extent to that seen with cis-monounsaturates. Looking at the other three saturated fatty acids, there is considerable overlap showing that, statistically speaking, no real difference in behaviour was seen.

**Effect of fatty acids on total:HDL cholesterol - Judd study**

Judd et al replaced not just 1% of dietary energy from carbohydrate but 8% of dietary energy from carbohydrate with the following fatty acid sources:

- **Cis-C18:1** – oleic acid (OL)
- **Trans-C18:1** – elaidic acid (TFA)
- 1:1 **trans-C18:1:stearic acid** (TFA/STE)
- **Stearic acid** (STE)
- A blend of lauric, myristic and palmitic acid containing 83% palmitic acid (LMP)

The effects on the total:HDL cholesterol level were determined:

---

**Figure 3**
The diet rich in palmitic acid (LMP) was not statistically different from the carbohydrate-rich control (CHO) or the diet rich in oleic acid (OL). The diet rich in stearic acid, though, gave a significantly higher ratio of total:HDL cholesterol.

**Effect of fatty acids on plasma fibrinogen**

Baer et al. carried out a similar diet comparison to that described above and examined its effect on plasma fibrinogen. It was found that the diet enriched in stearic acid resulted in higher fibrinogen levels than did any of the other diets except the mixed trans/stearic acid diet. It was estimated that the change in fibrinogen after the stearic acid diet could increase the risk of myocardial infarction by 7%.

<table>
<thead>
<tr>
<th>Source</th>
<th>Lauric</th>
<th>Palmitic</th>
<th>Stearic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm kernel oil</td>
<td>Palm oil</td>
<td>Cocoa butter</td>
<td>Interesterified, fully hydrogenated liquid oils</td>
</tr>
<tr>
<td>Coconut oil</td>
<td></td>
<td>Shea butter</td>
<td></td>
</tr>
<tr>
<td>Processing</td>
<td>Refining</td>
<td>Refining</td>
<td>Refining</td>
</tr>
<tr>
<td>Fractionation</td>
<td>Fractionation</td>
<td>Fractionation</td>
<td>Hydrogenation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Interesterification</td>
</tr>
<tr>
<td>Labelling</td>
<td>Vegetable oil</td>
<td>Vegetable oil</td>
<td>Vegetable oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrogenated vegetable oil</td>
</tr>
<tr>
<td>HDL cholesterol</td>
<td>Increases considerably</td>
<td>Increases slightly</td>
<td>No significant increase</td>
</tr>
<tr>
<td>Total:HDL cholesterol</td>
<td>Decreases</td>
<td>Neutral</td>
<td>Neutral (Mensink)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Increases (Judd)</td>
</tr>
<tr>
<td>Fibrinogen</td>
<td>Not studied</td>
<td>Neutral</td>
<td>Increases significantly</td>
</tr>
</tbody>
</table>
Advantages and disadvantages of individual saturates

Lauric acid
Found naturally in palm kernel oil and coconut oil. Lowered total:HDL cholesterol ratio more than other saturates in Mensink study. High levels of saturates in naturally occurring sources could mean that total saturates increase when they are used as trans fatty acid replacers.

Palmitic acid
Found naturally in palm oil. Judd found a lower ratio of total:HDL cholesterol in a palmitic-rich diet compared with a stearic-rich diet.

Stearic acid
Found naturally in cocoa butter and shea butter – but both of these are expensive and specialist fats.

Most likely source (in significant industrial quantities) would be to fully hydrogenate an oil rich in C18 unsaturates, blend it with the unhydrogenated oil and interesterify. This route has consumer issues in that the oil still needs to be labelled ‘hydrogenated’ and it goes through two processing stages, one at least of which is chemically-catalysed.

From a nutritional point of view Judd and Baer showed that a diet rich in stearic acid increased the total:HDL cholesterol ratio and plasma fibrinogen levels both adverse markers of cardiovascular disease risk.
Over the past few decades we have seen a large increase in obesity (Figure 1) leading to deaths from coronary heart disease, strokes, different forms of cancers and diabetes. It could be argued that fats in general have played their part in this because they all have essentially the same calorific content and therefore excessive consumption will lead to the same levels of obesity irrespective of the type of oil consumed. In terms of their effects on chronic diseases, however, we cannot treat all oils as being the same because oils from different sources will have different effects, particularly on the biochemistry of digestion and metabolism. The end result of these different effects will be to potentially accelerate or delay the onset of some of these diseases.

As cv fatty acids take an increasingly higher profile because of nutritional concerns and labelling requirements we need to ask whether there are any healthy alternatives to these fats. In many cases replacement is by saturated fatty acids because of the need to maintain structure in the product. But should these saturated alternatives be lauric-rich, palmitic-rich or stearic-rich? This lecture looks at the effects of these acids on the biochemical markers of cardiovascular disease.

Are there any healthy alternatives to trans fats?
Over the past few years, trans fats have come under increasing scrutiny in terms of their effects on health in general and on cardiovascular disease in particular.

It is now well known that there are two major types of cholesterol in our blood – LDL-cholesterol and HDL-cholesterol. Excess cholesterol which is being carried by HD lipoproteins goes to the liver from where it is excreted; excess cholesterol which is being carried by LD lipoproteins remains in the blood plasma and can start to produce plaques in the arterial walls. For this reason, LDL-cholesterol is seen as being “bad” for our health.

If we compare the relative effects which cis and trans fatty acids have on these types of cholesterol, we can see that, whilst cis fatty acids lower LDL cholesterol and raise HDL cholesterol, trans fatty acids do exactly the opposite, raising the ‘bad’ cholesterol and lowering the ‘good’ cholesterol (Figure 2). These are the reasons why labelling regulations have been introduced in the USA this year, why Denmark has put constraints on the levels of trans in foods, and why so many manufacturers are trying to find alternatives to trans.

To come back to the title of my talk – are there any healthy alternatives to trans? To answer that we need to look at what the alternatives are. Essentially there are three:

- Replace with non-fat solids
- Replace with cis-unsaturates
- Replace with saturates

The first option not only reduces trans but reduces total fat as well but may well have such a large effect on functionality that it cannot be considered a universal solution. The second option is attractive from a health point of view but highly problematic from a product functionality aspect.

Figure 1: Increase in obesity (Source: The Independent (UK), 16 Dec 2005)

Figure 2: Effect of cis and trans fatty acids on blood cholesterol (based on data from ref. 1)
Solvent fractionation of palm oil

Are there any healthy alternatives to trans fats?

Acid  | Cocoa butter oil | Coconut oil | Cottonseed oil | Palm oil | Palm kernel oil | Shea butter
--- | --- | --- | --- | --- | --- | ---
C8:0 |  | 12.2 |  | 8.3 |  | 
C10:0 | 8.0 |  |  | 7.3 |  | 
C12:0 | 48.8 |  | 0.2 | 49.5 |  | 
C14:0 | 0.1 | 14.8 | 0.8 | 1.0 | 13.9 | 
C16:0 | 26.0 | 6.9 | 27.3 | 45.0 | 6.8 | 3.3 |
C18:0 | 34.4 | 2.0 | 2.0 | 4.6 | 2.7 | 44.3 |
C18:1 | 34.8 | 4.5 | 18.3 | 37.7 | 9.9 | 45.6 |
C18:2 | 3.0 | 1.4 | 50.5 | 10.6 | 1.1 | 5.5 |
Others | 1.7 | 1.4 | 1.1 | 0.6 | 8.8 | 

Table 1
Typical fatty acid compositions of saturate-rich oils

Table 2
Fatty acid compositions of palm oil and human breast milk fat

Within the normal range of vegetable oils there are very few which contain any significant levels of saturates without needing to be hydrogenated. Those that do are shown in Table 1. The lauric-rich fats, coconut oil and palm kernel oil are highly saturated containing no more than about 10-11% unsaturates. The stearic-rich fats, cocoa butter and shea butter are both expensive fats with specific uses in confectionery. Of the palmitic-rich fats, cottonseed oil is still an essentially liquid oil with functionality limitations, whereas palm oil has a good balance between saturates and unsaturates and has a composition which, in fatty acid terms, is close to that of the first fat many of us consumed – human milk fat (Table 2).

Of the natural oils containing significant levels of saturates, palm oil does then offer some attraction. Indeed, if we stick to natural, unprocessed oils it is probably the only one which offers the benefits of a good balance between saturates and unsaturates at an economic price and without any issues of availability.
It is not, however, the only source of saturates that could be considered because it is possible to start with an oil rich in C18 unsaturated fatty acids such as oleic, linoleic and linolenic acids. Examples of oils of this kind are rapeseed oil, soya bean oil and sunflower oil. The oil is then fully hydrogenated.

This converts all of the C18 unsaturates into C18 saturate, i.e. stearic acid, without the formation of any trans fatty acids. We can see an example of this by looking at what happens if we fully hydrogenate rapeseed oil (Table 3). The end result is a fat containing well over 90% stearic acid.

Before we even start to consider any nutritional effects of the various saturated fatty acids there are, however, two major drawbacks to this approach.

The first is that the oil still needs to be labelled ‘hydrogenated’ with all the negative connotations now being associated with this. Secondly, the oil itself is totally unpalatable having a melting point of about 70°C. This means that it needs to be processed further by blending with softer oils and then undergoing an interesterification process. This can be either chemically- or enzymically-catalysed. So, yet another process step to add to the complexity.

Table 3
Non-hydrogenated and fully hydrogenated rapeseed oil

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Non-hydrogenated</th>
<th>Fully hydrogenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>C18:0</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>C18:1</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>C18:2</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>C18:3</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C20:0</td>
<td>Trace</td>
<td>2</td>
</tr>
<tr>
<td>C20:1</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Interesterification is a randomisation process – chemically-catalysed interesterification completely randomises the fatty acids on the triglyceride molecules. Enzymically-catalysed interesterification generally randomises those in the 1- and 3-positions. This means, that in both cases, a significant amount of the saturated fatty acids will end up in the 2-position of the triglycerides, unlike the distribution in natural vegetable oils where saturates are generally in the 1- and 3-positions.

If, for example, a 1:1 blend of fully hydrogenated rapeseed oil and unhydrogenated rapeseed oil were interesterified then 50% of the triglycerides would contain stearic acid in the 2-position. Using this ratio it makes no difference whether the fats were chemically or enzymically interesterified.

In naturally-occurring vegetable oils there is a general rule of distribution of fatty acids which says that the 2-position is firstly filled with all the available unsaturated fatty acids and then the remaining fatty acids are randomly distributed across the 1- and 3-positions. The effect of this is that it is quite rare to find significant levels of saturated fatty acid in the 2-position in a natural fat. The situation is quite different in an interesterified blend.

This difference could be quite important in the way these fats firstly are digested and then further metabolised. There are conflicting reports in the literature. Some workers suggest that fatty acids in different positions on the triglyceride molecule have different degrees of absorbency during digestion and imply that these differences can then
affect their effects on, for example, the markers of cardiovascular
disease. Other workers have found no difference between interesteri-
fied and non-interesterified oils on these markers – although it has to
be said that these systems were not particularly rich in high-melting
saturates for the reasons of palatability referred to above.

We therefore have a number of possibilities to replace trans – use a
high-lauric fat such as palm kernel oil, use a fat rich in palmitic acid in
the 1- and 3-positions such as palm oil, or fully hydrogenated and
interesterify a C18-rich oil to bring stearic acid into the end product.

The key question is “are some saturates ‘better for you’ than others?”. To try to answer that I will look at some of the biochemical markers
associated with cardiovascular disease.

Firstly cholesterol. It is popularly considered that LDL cholesterol is bad
and promotes CVD, whilst HDL cholesterol is good and helps to protect
against CVD. To a large extent this is true but it is now considered that
the ratio of total cholesterol to HDL cholesterol is more important than
either the total, the LDL or the HDL cholesterol separately in estimating
the risk of CVD.

A second marker that I will look at is plasma fibrinogen. This is the
central protein of the blood coagulation system and high levels of
plasma fibrinogen have been associated with CVD. For example a
review of the literature in this area shows nineteen independent studies
which conclude that fibrinogen is a CVD risk factor.

But, first, cholesterol. Mensink and his co-workers carried out a
statistical study\(^2\) of sixty controlled trials evaluating the effects of fatty
acids classes and of individual saturated fatty acids on blood cholesterol.
In these trials 1% of dietary energy from carbohydrate was replaced by
1% of dietary energy from each type of fatty acid in turn. The effects
on the various types of blood cholesterol and on the all-important ratio
of total:HDL cholesterol were documented and shown in Figure 3.

Figure 3
Effect on blood cholesterol of
isoenergetically replacing CHO
with fatty acid groups
Mensink, Zock, Kester, Katan
Am J Clin Nutr 2003;177:1146 -55
Looking firstly at total cholesterol levels, we can see that saturates and trans both increase the level of these, monounsaturates show a slight reduction whereas polyunsaturates show a much greater reduction. These effects are mirrored almost exactly by the changes in LDL.
Solvent fractionation of palm oil

Are there any healthy alternatives to trans fats?

cholesterol, although in the case of trans the increase in LDL cholesterol is greater than with saturates. When we look at the effects on HDL cholesterol, however, we seen that all of the three fatty acid classes arising from non-hydrogenated fats raise the level of the ‘good’ HDL cholesterol, with saturates raising it slightly more than the unsaturated fatty acids, whereas trans is at best neutral and, in some trials, lowered HDL cholesterol. So, what do we make of this?

At this point it’s useful, I think, to quote from Mensink’s paper about what is important and what isn’t. Mensink in his introduction is quite clear in stating that ‘the ratio of total to HDL cholesterol is considered more important than the total or lipoprotein cholesterol concentrations in estimating risk’.

So, to save time to allow me to talk about various other trials I will concentrate only on the results on the total:HDL cholesterol ratio (Figure).

Firstly, they looked at the effect of fatty acid classes on this ratio. The results show that the ratio of total:HDL cholesterol is increased by trans fatty acids, is unaffected by saturates but is lowered by cis-unsaturates. So, whilst the results from saturates are not as good in terms of reducing CVD risk as those for unsaturates they do, at least, show reasonable neutrality and, based on the total:HDL cholesterol ratio should not increase CVD risk. The results also show that replacing trans by saturates will decrease risk, even if replacing trans by cis-unsaturates would, from a nutritional point of view be better – but, of course, limited by functionality characteristics.

What is of real interest, though, is – from a CVD point of view, would one saturated fatty acid be preferred over the rest?

Mensink also compared lauric, myristic, palmitic and stearic acids in this study (Figure 5). He found that, whilst there were differences in the effects on specific types of blood cholesterol and whilst there are
numerical differences between the mean values for the ratio for each fatty acid, when the 95% confidence intervals are taken into account, there is statistically no difference between any of them, even though lauric acid appears to have slightly more beneficial effect than the other acids. This is because lauric acid was found to raise all the cholesterol levels – total, HDL and LDL - more than the other acids but there was a particularly strong effect on HDL cholesterol which resulted in a lower numerical value for the ratio. I have also included Mensink’s results on monounsaturated fatty acids (essentially oleic acid) on this diagram to show that the lowering effect on the total:HDL cholesterol ratio obtained from lauric acid is at least as much, if not greater, than that achieved from oleic acid. To this we can also add the theories of Dr Mary Enig in her book, ‘Eat Fat, Lose Fat’ in which she promotes the benefits of lauric-rich fats in helping weight loss.

This is important because in many summaries of these types of study, including a report from the World Health Organisation, the conclusion has been that stearic acid is neutral in its effects on cholesterol whilst the other acids are said to show adverse effects.

In his paper, Mensink goes on to say that ‘palm oil is an acceptable alternative for the industry, and, in terms of the effect on total:HDL cholesterol, palm oil is still better than the partially hydrogenated vegetable oils used in the food service industry.’

This view is further supported by Hu and co-workers who assessed the relative risks of coronary heart disease according to quintiles of intakes of individual saturated fatty acids comparing lauric and myristic acids together with palmitic and stearic acids individually (Figure 6).

**Figure 5**
Effect of individual saturates on total:HDL cholesterol ratio
Are there any healthy alternatives to trans fats?

With lauric and myristic acid, relative risk remains constant up to the third quintile and then increases. Palmitic acid shows a slightly reduced risk from the first to second quintile and, as with lauric and myristic acids, increases most from the fourth quintile onwards. Stearic acid, however, shows both the greatest relative risk of all the saturated acids and also has an increasing risk throughout. The conclusion from this work was ‘a distinction between 18:0 (stearic acid) and other saturated fats in dietary advice to reduce CHD risk does not appear to be important’.

Perhaps the most rigorous study, however was carried out by Judd and co-workers (4) in which diets with 8% energy enrichment in

- oleic acid (OL)
- trans 18:1 (TFA)
- 1:1 trans 18:1:stearic acid (TFA/STE)
- stearic acid (STE), and
- a blend of lauric, myristic and palmitic acids in which palmitic acid predominated (LMP)

were compared with one with the same energy enrichment achieved by lowering fat content and increasing carbohydrate content (CHO).

Looking at the ratio of total:HDL cholesterol, the diet rich in lauric/myristic/palmitic was not statistically different from the carbohydrate or oleic acid-rich diets (Figure 7). The diet rich in stearic acid, on the other hand, gave a significantly higher total:HDL cholesterol ratio. Not surprisingly, the diet rich in trans fatty acids gave an even higher ratio. These results give further scientific support to the dietary benefits of palmitic acid compared with stearic acid.
As well as being ‘better’ than the stearic-rich diet in terms of the total: HDL cholesterol ratio, the diet rich in palmitic acid was also better in terms of absolute HDL cholesterol levels. The absolute levels of the ‘good’ HDL cholesterol were higher on the palmitic-rich diet (1.303 + 0.041 mmol/L) than on the stearic-rich diet (1.156 + 0.041 mmol/L).

We’ll leave the effects on cholesterol and look at the effects on fibrinogen. Baer and co-workers used a very similar diet comparison to that of Judd’s which we have just discussed. They came to the following conclusions:

Consumption of the diet enriched in stearic acid resulted in higher concentrations of fibrinogen than did consumption of all other diets except the trans+stearic diet

The change in fibrinogen observed after consumption of the stearic-rich diet compared with the carbohydrate-rich diet could raise the risk of myocardial infarction by 7%

The effect of stearic acid on LDL-cholesterol concentrations is often thought to be ‘neutral’; however, our study showed that stearic acid may increase the risk of cardiovascular disease through mechanisms other than cholesterol concentrations, such as an increase in fibrinogen concentrations

So, we can see further demonstration of the benefits of palmitic acid compared with stearic acid – this time on a completely different CVD risk factor.
Advantages and disadvantages of main saturate-providing fats

So, where does all of this leave us in terms of deciding which is the healthiest option to trans fats in those applications where solidity, structure and therefore a saturated fat is needed? Whilst the answers are not totally clear-cut they do point towards palm oil being the oil of choice.

Why? Let’s just try and summarise.

Lauric acid is found in coconut oil and palm kernel oil. These oils are very rich in total saturates – to such an extent that, in replacing trans fats the final saturates level could well be higher than the starting saturates + trans level. This is something which most manufacturers are keen to avoid. Having said that, we have seen that lauric acid has a very strong lowering effect on the ratio of total:HDL cholesterol levels.

The use of cocoa butter and shea butter as alternatives to trans-containing fats is mainly limited to confectionery coatings. This is because they are both expensive oils with very specific physical characteristics and functionality. It is these characteristics which make them suitable for use in chocolate and in cocoa butter equivalents. These same characteristics, coupled with cost and availability issues, limit their use as wide-spectrum alternatives to trans fats.

This leaves us with a choice between palmitic-rich palm oil and a stearic-rich fat produced by fully hydrogenating an oil rich in C18 unsaturates and then interesterifying this with a more liquid oil. So let’s look more closely at these two alternatives.

Palm oil is a naturally occurring vegetable oil. Because of the high levels of natural tocopherols and tocotrienols which it contains it also possesses a high degree of natural oxidative stability. It contains a wide range of different triglycerides with different melting points, profiles and functionalities. Some of these are very high melting and are suitable for use in stabilizing non-hydrogenated margarines and spreads. Some are very low-melting making them suitable for trans-free frying oils with a good oxidative stability. Some melt around mouth temperature making them suitable for use in a wide range of non-hydrogenated confectionery products. And, of course, we should not forget the oil itself which is functional in biscuits and other bakery products.

To obtain this wide range of fats with their different melting and crystallization functionalities, all that needs to be done is to fractionate the oil – a mild, physical separation process involving no chemical reactions.

To obtain an oil rich in stearic acid, however, we have two choices. One is to base it on cocoa butter or shea butter but, we have just eliminated these oils as possibilities because of cost and availability constraints. The other option is to take an oil rich in C18 unsaturates.
and then fully hydrogenate it to produce a stearic-rich system. Apart from any nutritional or dietary considerations this will produce a fat which needs to be labeled as ‘hydrogenated’ even though it contains no trans fatty acids. The question here is ‘can consumers, with all the information they have been fed by the popular press, distinguish between a hydrogenated fat which contains trans and one which doesn’t?’

Even then hydrogenation needs to be followed by interesterifying the fat with a liquid oil to produce anything like a palatable product. This can be carried out using a chemical catalyst which then means the oil has undergone two chemical processing stages – hydrogenation and interesterification – or it can be enzymically catalysed incurring extra processing costs.

Even if these considerations are set aside we still have to consider that the liquid oil which needs to be used in the whole interesterification process to give palatability will be either rich in linoleic and, possibly, linolenic acid which can adversely affect the overall oxidative stability of the product, or rich in oleic acid which may mean the use of expensive oils such as olive oil or high oleic sunflower oil.

Let’s now try to summarise the dietary information as it relates to the effects of these two fatty acids on CVD.

Judd’s study shows that a diet rich in palmitic acid results in a higher HDL cholesterol level than one rich in stearic acid, whilst there is no significant effect on LDL cholesterol levels. As far as the all-important ratio of total:HDL cholesterol is concerned Judd’s work shows a significantly lower ratio after the palmitic rich diet compared to the stearic rich diet. This would imply that a diet in which the saturates are obtained from palm oil would be ‘better’ in terms of blood cholesterol levels that one based on a fully hydrogenated and interesterified C18 unsaturate system.

Now let’s look at fibrinogen. Stearic acid raises fibrinogen levels more than do other fatty acids, including palmitic acid. Fibrinogen is a cardiovascular disease risk factor.

From this point of view palm oil would be healthier.

Let’s try to summarise things a bit more (Table 4).

Lauric acid, obtained from either palm kernel oil or coconut oil, allows a ‘clean’ label with only fractionation and refining as processes needed to produce alternatives to trans in some applications. Lauric acid considerably increases HDL cholesterol levels and decreases the ratio of total:HDL cholesterol. No studies have been carried on its specific effects on fibrinogen.
Are there any healthy alternatives to trans fats?

Palmitic acid is obtained predominantly from palm oil and also allows a ‘clean’ label of simply ‘vegetable oil’. This is again because only fractionation and refining are needed to produce a range of alternatives for a very wide range of applications. Palmitic acid gives a slight increase in HDL cholesterol levels and is effectively neutral in its effect on total:HDL cholesterol and on fibrinogen activity.

Stearic acid can be obtained from two routes. One of these is from cocoa butter or shea butter both which allow a clean ‘vegetable fat’ labeling but a relatively restricted range of uses as alternatives to trans fats. The other is to take a liquid oil rich in C18 unsaturates and fully hydrogenate it before interesterifying with a more liquid oil. This no longer allows a clean label because although interesterification as a process does not need to be declared, hydrogenation does. Irrespective of where the stearic acid is sourced from its metabolic effects are the same in giving no significant increase in HDL cholesterol levels, a neutral effect on total:HDL cholesterol ratio but a significant increase in fibrinogen levels.

Which of these differences can be considered to be ‘good’ and which ‘bad’?
Even a quick glance at this table now shows that lauric acid is generally a good alternative to trans fats, as is palmitic acid. Stearic acid, however, fares less well in terms of effects on cardiovascular disease markers as well as issues with processing and labeling if it is sourced from an interesterified, fully hydrogenated liquid oil base system.

So where does this leave us? Essentially with lauric and palmitic acids as the preferred saturated alternatives to trans fats. And where can we source these fatty acids from? Fortunately, they are both found in one single fruit – the oil palm.
The fruit of the oil palm is a bit like a peach with a soft fleshy outer portion enclosing a much harder kernel. Palm oil, rich in palmitic acid, is found in the outer fleshy part of the fruit, while palm kernel oil, rich in lauric acid, is, perhaps not surprisingly, found in the kernel.

Taking all these things into account, then, suggests that the oil palm is the source of the healthy alternatives to partially hydrogenated, trans-containing fats. The lauric and palmitic acids found in palm oil, palm kernel oil and their fractions show the most positive effects on the main biochemical markers of cardiovascular disease - and that is before even mentioning the health benefits of some of the more minor components of palm oil such as beta-carotene (important in the formation of Vitamin A which plays a major role in eye health) and tocopherols and tocotrienols (Vitamin E).

References


As bakers are increasingly looking for trans-free alternatives to hydrogenated vegetable oils in shortenings, the SansTrans™ range of products from Loders Croklaan is providing the solution. This lecture looks at the science behind such a choice.

Introduction

In defining what are potentially healthier alternatives to trans in bakery products I would like to consider three aspects. Firstly, what are trans fats and how do they arise? Secondly, what is ‘unhealthy’ about them, and, finally, but perhaps most importantly, how can ‘healthier’ alternatives be produced for use in bakery products.

What are trans fats and how do they arise?

Fatty acids are divided into four main groups – saturates, cis-unsaturates, cis-polyunsaturates and trans. All, apart from saturates, contain carbon-carbon double bonds in the fatty acid chain which can be in either the cis or the trans configuration. In vegetable oils the ‘natural’ form is cis; in some animal fats both forms can occur naturally.

So let’s start by looking at the structure of these acids – firstly saturates. As you can see (Figure 1) all of these saturated fatty acids have straight carbon chains (ignoring the zig-zag along the chain).
When we move to unsaturates, however, we see that where there is a cis double bond in the chain there is also a bend (Figure 2). Cis means that the chains coming out of the double bond are on the same side of the bond as each other. Trans, on the other hand, means that the chains are on opposite sides of the double bond. This results in a structure which is much straighter and more similar to saturates. It is because of this straighter structure that the melting points of trans fatty acids are higher than of the corresponding cis fatty acid.

We can see these effects in Table 1. As the degree of unsaturation increases the melting point decreases, but, where the unsaturation is in the trans form the melting point is much higher than with the corresponding cis fatty acid.

So where do these trans fatty acids come from?
There are three main sources.

Firstly, they are formed naturally by microbial hydrogenation in the rumen of cows and sheep. This means that they are present in butter, milk, cheese and other dairy products as well as in the meat of these animals. Typical levels in butterfat are between 3% and 8%. This means that the consumption of trans fats is not new, although the level of consumption may be.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Name</th>
<th>Abbreviation</th>
<th>M.Pt. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18:0</td>
<td>Stearic</td>
<td>St</td>
<td>70.1</td>
</tr>
<tr>
<td>C18:1 cis</td>
<td>Oleic</td>
<td>O</td>
<td>16.0</td>
</tr>
<tr>
<td>C18:1 trans</td>
<td>Elaidic</td>
<td>E</td>
<td>44.0</td>
</tr>
<tr>
<td>C18:2</td>
<td>Linoleic</td>
<td>Li</td>
<td>-6.5</td>
</tr>
<tr>
<td>C18:3</td>
<td>Linolenic</td>
<td>Ln</td>
<td>-12.8</td>
</tr>
</tbody>
</table>
Secondly, they can be produced when fats are subjected to high temperatures – high in this context being over about 250°C – when some of the cis double bonds can start to isomerise into trans. Long times at lower elevated temperatures, for example, long periods at 180°C in an industrial fryer can also start to produce low levels of trans. Because it is rare for oils to be abused in this way, this is not a major source of trans in the diet.

The process which has been targeted as a means of reducing trans is partial hydrogenation as this has been the most common way of introducing trans into the diet.

Hydrogenation is a process in which an oil is reacted with hydrogen in the presence of a catalyst, usually nickel. Two reactions compete with each other. The first is one in which hydrogen combinations with the carbon atoms on the double bonds producing a saturated single bond. The other is one in which the double bond momentarily breaks and rotates before re-forming in a trans configuration.

Both processes result in a fatty acid with a higher melting point and this has been one of the main reasons why oils have been hydrogenated – to allow fats with a wide range of melting profiles and melting points to be produced. There are other product benefits to be gained from hydrogenation. Trans double bonds have a higher oxidative stability than cis double bonds, a factor important in industrial frying. Hydrogenated fats also impart other benefits such as aeration properties and gloss retention.

For these reasons they have been widely used in a number of applications. In terms of bakery applications their use in dough fats and shortenings is probably the most relevant, although many bakery products also make use of confectionery coatings and fillings.

In terms of intake, the TRANSFAIR study in 1998 showed that across Europe we consumed typically up to 2% of dietary energy from trans fatty acids. In the UK it was slightly less than this at about 1.2-1.3% and this was roughly split 2:1 between trans from hydrogenated oils and trans from dairy products. Since then our consumption of trans from hydrogenated oils has reduced which suggests that trans from natural sources now makes up a bigger proportion of our consumption.

What is ‘unhealthy’ about them?
We turn now to look at what is unhealthy about trans. Essentially, the problem mainly revolves around their effect on blood cholesterol. There are two main types of cholesterol in our blood – that carried by high-density lipoproteins (called ‘HDL cholesterol’) and that carried by low-density lipoproteins (called ‘LDL cholesterol’). We need a certain amount of cholesterol for metabolic purposes but we need to eliminate any excess.
Excess HDL cholesterol is carried to the liver from where it is excreted. Excess LDL cholesterol remains in the blood and is laid down as plaques in the arterial wall. Eventually these can build up and cause cardiovascular disease. This is why HDL cholesterol is generally considered to be ‘good’ cholesterol whilst LDL cholesterol is ‘bad’.

Cis-monounsaturates have a completely different effect on these types of cholesterol than do trans-monounsaturates. Essentially cis raises the ‘good’ HDL cholesterol and lowers the ‘bad’ LDL cholesterol, whilst trans does exactly the opposite – a dietary double whammy!

However, many clinical nutritionists now consider the ratio of total cholesterol to HDL cholesterol to be more important in estimating cardiovascular risk. I’ll come back to this paper later in my talk but, at this point, it’s useful to look at some of the results from Mensink’s work.

If we look at the effect that each fatty acid group has on this ratio (Figure 3) we can see firstly that trans increases this ratio and hence has an adverse effect on cardiovascular disease risk. Monounsaturates and polyunsaturates both reduce the ratio and the risk, while saturates are neutral neither raising nor lowering the ratio.

So, in very bald terms – trans fatty acids are ‘bad’ for us. Saturates are neutral but if it is possible to replace them with nutritionally ‘better’ fatty acids then we should do so. The question also arises as to whether some saturates are better or worse than others – a question I’ll touch on later. Cis-monounsaturates are good, as are cis-polyunsaturates but here we need to ensure a correct balance between omega-3 and omega-6.

**How can ‘healthier’ alternatives be produced for use in bakery products?**

Knowing what the problems are, then, how can we produce ‘healthier’ alternatives to trans for use in bakery products?
Healthier alternatives to trans in bakery products

We could consider replacing trans with non-fat solids. This would have a doubly beneficial effect by also reducing total fat content and hence a reduction in calories. However, this is also often a restricted solution because of functionality constraints.

The simplest way, having seen the effect that each type of fatty acid has on blood cholesterol, is to, say, replace all the trans by cis-unsaturates. The major problem with this is that, as we have seen, the melting point of cis-unsaturates is much lower than that of trans and, in most bakery applications, be they as dough fats, cream fats or coating fats, we need some solid fat to be present.

This then means that some, at least, of the trans fatty acids often need to be replaced by saturates.

Bakery fats are often called ‘shortenings’ because of the ‘short’ texture they give to, for example, pastry. If pastry were to be made from just flour and water the wheat proteins would hydrolyse forming a tough, brittle network of gluten. If we include fat in the whole system then it becomes smeared through the dough when the dough is mixed. These smeared fat droplets protect the surfaces of the flour particles from water which, in turn, interrupts the development of the gluten chains giving a pastry with a much better texture. However, it is not just enough to use any fat for this purpose.

If the fat contains too much solid fat it will not be well distributed through the dough and will still give a hard pastry. If it contains too much liquid oil then the dough becomes soft and unworkable and may well suffer from oil exudation after baking.

So a good bakery fat should have a fairly flat melting profile with enough solid fat to coat the flour particles over the normal working temperature range of about 15-30°C. Figure 4 shows the melting profiles of some typical bakery shortenings. Those with the higher melting points are mainly for use in biscuits and cookies, those with the lower melting points for use in cakes and cake creams.

Figure 4
Melting Profiles of Shortenings

![Melting Profiles of Shortenings](image-url)
The crystal form of the fat is also important. Fats crystallise in three main forms known as \( \alpha \), \( \beta' \) or \( \beta \). While traditional pastry fats such as lard crystallise in the \( \beta \) form it is often considered that a good bakery fat is one which naturally crystallises in the \( \beta' \) form. Indeed, the partially hydrogenated fats which we are seeking to replace crystallise in this form. There are various reasons why the \( \beta' \) form is preferred. Firstly, fats in this form have small crystals which are easy to blend with the dry components of a mix. Secondly \( \beta' \) crystals are very effective at entrapping small air bubbles, a feature which is important for good creaming and lightness of texture.

All of this means that we need to have some solid fat and structure in the bakery fats. Where does this come from?

There are a limited number of natural vegetable oils which contain significant amounts of solid fat at these working temperatures. Ignoring various exotic oils, there are four such oils – coconut oil, palm kernel oil, palm oil and cocoa butter. Coconut oil and palm kernel both have high levels of lauric acid and high levels of saturates in general. Cocoa butter contains both stearic acid and palmitic acid but because of its specific functionality and high price it is unlikely to be used as a trans-free alternative to bakery fats. Palm oil, on the other hand, is rich in palmitic acid, is readily available, and has a good balance between saturates and unsaturates.

It is also very similar in fatty acid terms to nature’s first food for many us – human milk fat (Table 2).

<table>
<thead>
<tr>
<th></th>
<th>C12:0</th>
<th>C14:0</th>
<th>C16:0</th>
<th>C16:1</th>
<th>C18:0</th>
<th>C18:1</th>
<th>C18:2</th>
<th>C18:3</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm oil</td>
<td>0.2</td>
<td>1.0</td>
<td>45.0</td>
<td>0.1</td>
<td>4.6</td>
<td>37.7</td>
<td>10.6</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Human milk fat</td>
<td>3.0</td>
<td>5.8</td>
<td>26.6</td>
<td>5.3</td>
<td>6.7</td>
<td>36.4</td>
<td>11.1</td>
<td>0.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

There is another possibility and that is to take an oil rich in C18 unsaturates such as rapeseed oil, soyabean oil or sunflower oil and fully hydrogenate this to convert all the C18 unsaturates into their fully saturated form – stearic acid. This gives a product which is essentially free of trans.

We can see in Table 3 the effect on fatty acid composition of fully hydrogenating rapeseed oil. Even before we get on to any nutritional implications there are two issues relating to this route. Firstly, the product still needs to be labelled ‘hydrogenated’ with all of the negative connotations associated with this and, secondly, the end product has a melting point of about 70°C. This means that it needs to undergo further processing to get it in a palatable form. This further processing is usually interesterification with the non-hydrogenated oil.
Interesterification can be either chemically-catalysed – yet another chemical process – or enzymically-catalysed. Even when we’ve gone through all of this the highly unsaturated acids in the non-hydrogenated portion of the product can have adverse effects on the overall stability of the fat. It would be so much easier to stick with a palm oil based option instead.

**But is palm oil going to be the healthiest source of saturates?**

**Or are some of the other saturates better?**

To answer that question we’ll look at the effects of saturates on two of the main biochemical markers of cardiovascular disease – the ratio of total:HDL cholesterol and the level of plasma fibrinogen. This is the main protein responsible for blood clotting.

To look first at cholesterol, I’ll show you the results of two studies. The first of these is the Mensink work referred to earlier and is actually a statistical analysis of 60 trials in which 1% of dietary energy from carbohydrate was replaced by 1% of dietary energy from different saturated fatty acids.

Before going into the results I’d just like to remind you of the opinion of Mensink, which is also shared by other clinical nutritionists, that the ratio of total to HDL cholesterol is considered more important than the total or lipoprotein cholesterol concentrations in estimating risk. For that reason I shall concentrate mainly on this ratio (although individual lipoprotein cholesterol concentrations were also measured)

This study showed firstly that lauric acid (C12) reduced the ratio of total:HDL cholesterol to a level similar to that found with monounsaturates (Figure 5). Secondly there was no statistical difference between the effects on this ratio of myristic acid (C14), palmitic acid (C16) or stearic acid (C18).

---

**Table 3**

Fatty acid composition of non-hydrogenated and fully hydrogenated rapeseed oil

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Non-hydrogenated</th>
<th>Fully hydrogenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>C18:0</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>C18:1</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>C18:2</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>C18:3</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C20:0</td>
<td>Trace</td>
<td>2</td>
</tr>
<tr>
<td>C20:1</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 5**

Effect of individual saturates on total:HDL cholesterol
In the discussion part of his paper Mensink says that ‘palm oil is an acceptable alternative for the industry, and, in terms of the effect on total:HDL cholesterol, palm oil is still better than the partially hydrogenated vegetable oils used in the food service industry.’

In the second study carried out by Judd and co-workers the comparison with carbohydrate was not at a level of 1% dietary energy but 8% dietary energy – a much more exacting trial. Amongst other comparisons the trial made was one between oleic acid, stearic acid and a blend of acids in which palmitic predominated.

It is clear from the results (Figure 6) that, at these levels, stearic acid resulted in a significantly higher ratio of total:HDL cholesterol than did the palmitic-rich system.

Although I said that I would concentrate on the total:HDL cholesterol ratio as the most important parameter it is also worth showing the effects of the palmitic-rich and stearic-rich diets on HDL cholesterol levels themselves. At 1.303 + 0.041 mmol/L these are significantly higher with the palmitic-rich diet than with the stearic-rich diet (1.156 + 0.041 mmol/L).

The effects of similar diets on plasma fibrinogen were also studied with the conclusion that the diet enriched in stearic acid gave higher fibrinogen concentrations than the other diets, to such an extent that the risk of a myocardial infarction could increase by 7%.

So, where do our alternatives to trans fit into these results of clinical nutrition trials?

Firstly lauric acid. This lowers the ratio of total:HDL cholesterol more than the other main saturates and lowers it to a level similar to that found with monounsaturates. It is the main fatty acid in coconut and palm kernel oils. The disadvantage with using these oils is that they are very rich in total saturates (of the order of 90%) and so using them to
replace partially hydrogenated oils can result in an end product in which the saturates level is greater than the combination of trans and saturates in the original.

Secondly, stearic acid. Apart from sourcing this from cocoa butter the main way is to fully hydrogenate and then interesterify a C18 rich oil. Here we not only have consumer issues because we are using one, if not two, chemical processing steps and still having to label the product ‘hydrogenated’ but we also have nutritional issues because of the effects of stearic acid on plasma fibrinogen and the blood cholesterol ratio.

Which brings us to palm oil in which the main saturated fatty acid, palmitic acid, has a neutral effect on the total:HDL cholesterol ratio and on fibrinogen levels. Palm oil also has a high natural oxidative stability because of the natural antioxidants present in the oil. It has a good balance between saturates and unsaturates which allows a wide range of fats with different physical and functional characteristics to be produced by fractionation.

Let’s try to summarise things a bit more. Lauric acid, obtained from either palm kernel oil or coconut oil, allows a ‘clean’ label with only fractionation and refining as processes needed to produce alternatives to trans in some applications. Lauric acid considerably increases HDL cholesterol levels and decreases the ratio of total:HDL cholesterol. No studies have been carried on its specific effects on fibrinogen.

Palmitic acid is obtained predominantly from palm oil and also allows a ‘clean’ label of simply ‘vegetable oil’. This is again because only fractionation and refining are needed to produce a range of alternatives for a very wide range of applications. Palmitic acid gives a slight increase in HDL cholesterol levels and is effectively neutral in its effect on total:HDL cholesterol and on fibrinogen activity.

Stearic acid can be obtained from two routes. One of these is from cocoa butter or shea butter both which allow a clean ‘vegetable fat’ labeling but a relatively restricted range of uses as alternatives to trans fats. The other is to take a liquid oil rich in C18 unsaturates and fully hydrogenate it before interesterifying with a more liquid oil. This no longer allows a clean label because although interesterification as a process does not need to be declared, hydrogenation does. Irrespective of where the stearic acid is sourced from its metabolic effects are the same in giving no significant increase in HDL cholesterol levels, a neutral effect on total:HDL cholesterol ratio but a significant increase in fibrinogen levels.

Which of these differences can be considered to be ‘good’ and which ‘bad’? Let’s put a few ticks and crosses on a summary table of these effects (Table 4).
Even a quick glance at this table now shows that lauric acid is generally a good alternative to trans fats with four ticks, as is palmitic acid with three big ticks and two smaller ones. Stearic acid, however, fares less well having only one small tick and a cross in the cardiovascular disease marker boxes as well as two crosses in the processing and labeling boxes if it is sourced from an interesterified, fully hydrogenated liquid oil base system.

All of this, then, brings us back to palm oil. From palm oil we can obtain a range of fractions each with different melting profiles. So I’d like to spend the last few minutes of my talk looking at the use of palm-based fats in bakery products.

You may recall that earlier in my presentation I showed the ideal melting profiles of some bakery shortenings. These were in reality a range of non-hydrogenated, palm-based bakery fats produced and marketed by Loders Croklaan under the brand name SansTrans (Figure 7).

Because these are derived from palm oil they contain a significant amount of palmitic acid which, as we have already seen, compares...
Healthier alternatives to trans in bakery products

<table>
<thead>
<tr>
<th>Product</th>
<th>Type</th>
<th>Application</th>
<th>% SAFA</th>
<th>% MUFA</th>
<th>% PUFA</th>
<th>% TFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SansTrans 45</td>
<td>Hard plastic shortening</td>
<td>Biscuits and crackers</td>
<td>54</td>
<td>37</td>
<td>9</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SansTrans 47</td>
<td>Plastic shortening</td>
<td>All purpose shortening</td>
<td>52</td>
<td>38</td>
<td>10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SansTrans 39</td>
<td>Soft plastic shortening</td>
<td>Cakes, biscuits and fillings</td>
<td>51</td>
<td>40</td>
<td>9</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 5
Nutritional Profiles of SansTrans products

well from a nutritional point of view with other saturates. A further benefit is that it naturally crystallises in the β’ polymorphic form making it very suitable for use in bakery shortenings. While there are an increasing number of products within the SansTrans range, three in particular are suitable for use in bakery products (Table 5).

These are all plastic shortenings ranging in texture from hard to soft. The number after SansTrans indicates the melting point of the fat in degrees Celsius. Because they are non-hydrogenated they all contain less than 1% trans and are a close match to the hydrogenated cake and biscuit shortenings and dough fats that have been used in the bakery industry.

How well do they work?

The American Institute of Baking compared SansTrans 39 and SansTrans 45 with hydrogenated shortenings in a biscuit and yellow cake application (Figure 8). They used their own standard recipes and conditions without any adjustments and compared their scores. The performance was essentially identical between the pairs of fats showing that SansTrans has the same functionality in these bakery products as the hydrogenated fats they were designed to replace.
One of the options I gave earlier for replacing trans was to replace it with a non-fat solid – in other words, to reduce the total fat content of the product. I’d just like to look briefly at this in the context of biscuits and will take a simple jam-filled sandwich biscuit as an example. I chose this because data on the fat breakdown in the product is available in McCance and Widdowson’s Composition of Foods which allows me then to quote it as a generic rather than a specific manufacturer’s product.

In the original the product contains 17.3% fat, 1.38% of which is trans from the partially hydrogenated dough fat. If we replace that fat with palm oil still keeping the fat content the same then we have zero trans and slightly higher saturates and cis-unsaturates. But not all of the palm oil used in the dough fat is functional in this application. By using only the functional parts we may be able to reduce the fat content.

The three parts of palm oil have three different effects in a biscuit dough fat. The low melting fraction gives a soft texture to the biscuit but, on its own, causes oil exudation. The high melting fraction is needed to structure the biscuit and reduce the degree of oil exudation. The middle melting fraction in this application is of limited functionality so removing this could all a reduction in fat of up to about 30%

This now means that we can reduce the total fat content from 17.3% to 12.1% with zero trans and a significant decrease in saturates. Reducing the fat content will have an effect on the texture of the biscuit and so it may also be necessary to include emulsifiers in the recipe to counteract this.

Finally a quick word on coatings and creams.

Partially hydrogenated coating fats have often been used in chocolate flavoured coatings for bakery products because (a) they are easy to cut and (b) they possess a long, glossy shelf-life. The only options to these are to use a palm kernel fraction (which has a high level of saturates), cocoa butter (in other words, real chocolate), or a coating rich in cocoa butter equivalents (and this is where the mid-fraction from palm oil has real functionality). Coatings based on cocoa butter or a CBE both need to be tempered a process which was not necessary with the original hydrogenated coating nor with one based on palm kernel fractions.

Bakery filling creams which were originally based on hydrogenated fats can be replaced by creams based on palm fractions. In doing so, not only is more than 50% trans removed from the cream but the levels of cis-unsaturates are almost doubled.

In summary then, most bakery applications require some solid fat to be present. Palm oil can provide this solid fat from a source that is: trans-free, natural, well-balanced between saturates and unsaturates and with palmitic acid as its main saturated fatty acid. Palm oil is also able to provide a wide range of fats with different melting profiles from the single oil by means of fractionation. This range of fats is best exemplified by the SansTrans™ range of fats.
Effect of nut oil migration on polymorphic transformation in a model system

Abstract

Fat migration in confectionery products can lead to significant deterioration in quality. This occurs not only through loss in texture contrast between chocolate and filling but also through the appearance of fat bloom on the surface of the chocolate. This latter aspect is often, although not exclusively, linked to the transformation of the cocoa butter $\beta_v$ phase into $\beta_w$. In this study, the influence of hazelnut oil on the polymorphic transformation of cocoa butter has been determined, showing that even small additions (1%) of nut oil can have a significant impact on the rate of transformation. Additionally, use of a model system has shown that polymorphic transformation in cocoa butter is linked to the degree of migration of nut oil from a filling. Portions of the cocoa butter close to the filling experience both greater degrees of migration and faster transformation.

Kevin Smith, Fred Cain, Geoff Talbot
Relationship between crystallisation behaviour, microstructure and macroscopic properties in trans containing and trans free coating fats and coatings

Abstract

The objective of this study is to gain further understanding into the relationship between crystallization behavior, microstructure, and macroscopic properties in coating fats. The isothermal crystallization behavior of two coating fats (one trans containing and one trans free) was examined, both as pure fats and in coatings, by DSC and microscopy. Furthermore, the hardness of the samples was examined after cooling in a water bath at two different temperatures and at three different storage times. Both fats seemed to show a $\alpha$-mediated $\beta'$ crystallization at lower temperatures and a direct $\beta'$ crystallization at higher temperatures. The trans free coating fat clearly crystallized faster and in smaller crystals. The hardness was governed not only by the amount of solid fat present in the network but also by the structure of this network. The coating matrix components seem to have a pronounced influence on the microstructure and thus on the macroscopic properties.

*Imogen Foubert, Jeroen Vereecken and Koen Dewettinck are from the Laboratory of Food Technology and Engineering and BIOMATH, Faculty of Bioscience Engineering, Ghent University

This work was funded by Loders Croklaan
Abstract
The crystallisation behaviour of three fat blends comprising a commercial shortening, a blend of fats with a very low trans fatty acid content ("low-trans") and a blend including hardened rapeseed oil with a relatively high trans fatty acid content ("high-trans") was studied. Molten fats were lowered to a temperature of 31°C and stirred for 0, 15, 30, 45 and 60 minutes. Samples were removed and their rheological properties studied, using a controlled stress rheometer, employing a frequency sweep procedure. Effects of the progressive crystallisation at 31°C on the
melting profile of fat samples removed from the stirred vessel and solidified at -20°C were also studied by differential scanning calorimetry (DSC).

The rheological profiles obtained suggested that all of the fats studied had weak viscoelastic “liquid” structures when melted, but these changed to structures perceived by the rheometer as weak viscoelastic “gels” in the early stages of crystallisation (G' (storage modulus) > G" (loss modulus) over most of the measured frequency range). These subsequently developed into weak viscoelastic semi-solids, showing frequency dependent behaviour on further crystallisation. These changes in behaviour were interpreted as changes from a small number of larger crystals “cross-linking” in a liquid matrix to a larger number of smaller crystals packed with a “slip plane” of liquid oil between them.

The rate of crystallisation of the three fats was in the order high trans > low-trans > commercial shortening. Changes in the DSC melting profile due to fractionation of triacylglycerols during the crystallisation at 31°C were evident for all three fats.

*A Bell, M H Gordon and W Jirasubkunakorn are from School of Food Biosciences. The University of Reading

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Solvent fractionation of palm oil

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