Chocolate tempering

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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.







Kevin Smith

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!

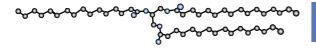
Without tempering, the chocolate can be 'warm' in the mouth. Correctly tempered, the chocolate will produce a pleasant cooling sensation in the mouth.

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

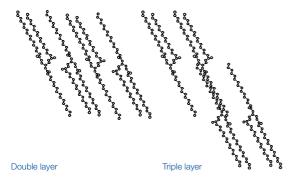
Cocoa Butter Polymorphism

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.

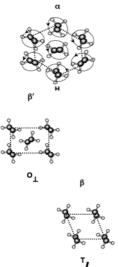


If the look down on the end of the fatty acid chains, we see what distinguishes the three basic polymorphs of fats. Polymorphic forms are generally identified as α , β ' and β , in order of increasing stability and melting point (Figure 3).

Figure 1 Triglyceride molecule

Figure 2 Double and Triple layer packing

Figure 3 α , β' and β Crystal structures



Chocolate tempering

The **a** 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.

Table 1Polymorphism of POP, POS, SOS

POP	POS	SOS		
α	α	α		
Y		Y		
δ	δ			
β'2				
β' ₁	β'	β'		
β2		β2		
β,	β	β ₁		

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 4 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 b 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 β 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 β 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-a, Form II as a, Forms III & IV as β ' and Forms V & VI as β . However, cocoa butter polymorphs have been designated in a great variety of ways as you can see in Table 2.

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, γ (or sub-a), a, a continuous range of β' (incorporating those previously identified as Forms III & IV) and two β forms. In addition, they proposed that the melting point of the sub-a or γ form has rarely been measured correctly due to the extremely rapid transformation of this polymorph into the a form and that the melting point usually attributed to the a form (II) is likely to be due to β' 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 β 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 β .

If fully molten cocca butter is cooled quickly to low temperatures (say below 0°C), the sub- α form crystallises. Cooled to slightly higher

Figure 4 X-ray diffraction patterns for POP, POS and SOS



Figure 5 Speculative structure of SOS

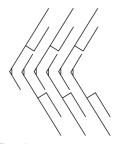
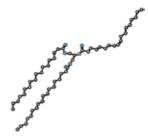


Figure 6 Actual structure of β-2 SOS from Peschar et. al., J. Phys. Chem. B 2004, 108, 15450-15453



Veack	Veack	Duck	Wille & Lutton	Larsson	Witzel & Becker	Love-gren et al.	Hern- qvist	Van Malssen et al.
1951	1960	1964	1966	1966	1969	1976	1988	1999
γ	γ	Y	I	β'2		VI	sub-a	γ
α	α	α	11	α	α	V	α	α
			Ш	mixed	β' ₁	IV	β' ₂	β' range
β"	β'	β"	IV	β' ₁	β' ₂		β' ₁	
β	β	β'	V	β2	pre-β	II	β	β-V
		β	VI	β,	β	I	β	β-VI

Table 2Cocoa butter polymorphs

Chocolate tempering

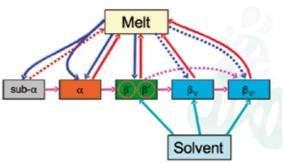
temperatures, crystallisation may begin in the sub-**a** form but will convert to the **a** form during crystallisation. The **a** polymorph will also form if the temperature of the sub-**a** form is raised. It is also possible to form **a** direct from the melt without sub-**a** if the temperature is 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 ' us 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_v form, which will go on, in time, to produce the β_v polymorph. The β_v 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.



Phase transformation scheme

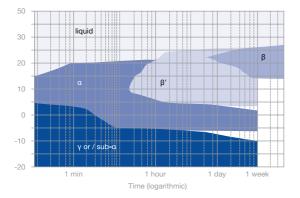


For completeness, it should be noted that both β' and β forms can be crystallised from solvent.

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- α form is not seen because it transforms into α 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 **a** area below 0°C does not indicate only **a** present, but that some **a** is detected in addition to the sub-**a** initially present. Similarly, it doesn't mean that no sub-**a** is present.





Van Malssen, et al. J Am Oil Chem Soc 1999 76 669-676 Van Malssen, et al. J Am Oil Chem Soc 1996 73 1209-1215

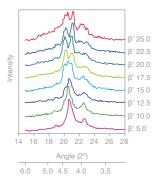
Note, also, that the crystallisation here is static - no stirring, no shear.

From this diagram it is clear that although the sub-**a** form crystallises at 4°C, within 1 minute, it has begun to transform into a. At 10°C, the **a** form crystallises, but begins to transform into **β**' 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 **a** form crystallises. Rather crystallisation is directly into the **β**' form. Note that, within the four weeks of this series of experiments, nothing crystallises above 26°C and no **β** form crystallises from the melt, but only comes from transformation from the **β**'. 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 β' polymorphs. Figure 9 shows the x-ray diffraction patterns for a series of β' 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 β' forms.

Figure 9 β' Phase range

Van Malssen, et al. J Am Oil Chem Soc 1999 76 669-676 Van Malssen, et al. J Am Oil Chem Soc 1996 73 1209-1215



Polymorph	Wille & Lutton	Huyghebaert & Hendrickx	Dimick & Davis	Riiner	Van Malssen et al.	
sub-a (l)	17.3	14.9-16.1	13.1	2	-5 to +5	
a (II)	23.3	17.0-23.2	17.7	16	17-22	
β' (III)	25.5	22.8-27.1	22.4	25	20-27	
β' (IV)	27.5	25.1-27.4	26.4		20-21	
β-V	33.8	31.3-33.2	30.7	32	29-34	
β-VI	36.3	33.8-36.0	33.8		20.04	

Table 3Cocoa butter melting points

Chocolate tempering

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 Riiner, 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 a 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.

Figure 10 Electron micrograph of 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 $\beta_{\rm v}$ 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.

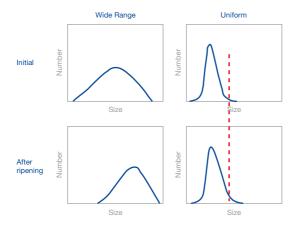


Figure 11 Crystal size

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 fooling and low temperatures (compared to the β_{v} 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 of 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.

Chocolate tempering

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.

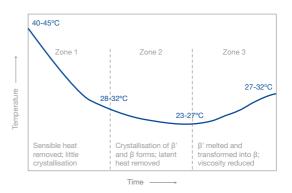
Finally, it is worth mentioning that systems have been patented were seed material (as a powder or fluidised in some way or even by recirculation of tempered chocolate) is fed into a continuous chocolate flow to produce suitably tempered material.

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.

10

Figure 12 Continuous tempering



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.

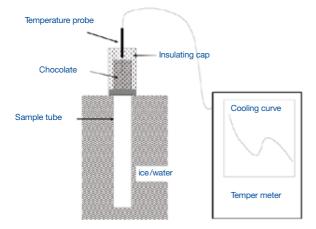
How do these curve shapes arise?

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.

Chocolate tempering

11



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.

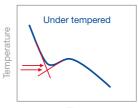
If there are a greater number of seed crystals present, we see a slight change in the crystallisation. Nevertheless, this small change is enough to change the shape of the curve and we see the plateau of a well tempered chocolate.

f 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.

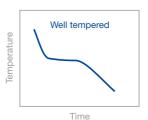
Thus, the precise desired shape of temper curve is a matter of preference. There are no step changes between under temper, well tempered and over tempered. Rather, there is a smooth evolution between such states. The desired temper state depends on the tempering equipment used, the application (depositing,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





Time

Figure 14 Temper curves



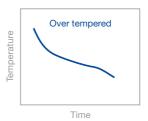
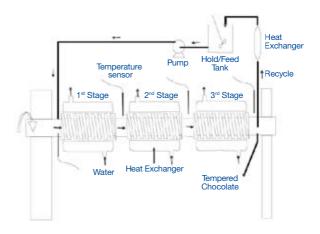


Figure 15 Model Temper Unit



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.

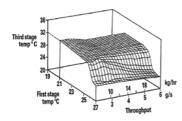
In the experiments I shall describe, we kept the screw speed constant. We also fixed the second stage temperature to be 1.5°C lower than the first stage. This reduced the number of variables. We then set the first stage temperature and throughput and searched for the third stage temperature that would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

Figure 16 'Dark' chocolate

Chocolate tempering



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 coccoa 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.



