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REVIEW

Crystallization of Fats: Influence of Minor Components and Additives

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Abstract Over the years, there has been a steady stream of publications on the influence that minor components and additives have on the physical properties of fat continuous systems. These have been reviewed here. Both indigenous and added components are taken into account. The various materials have been discussed, ranging from partial glycerides and phospholipids to esterified sugars and polyols. Within the publications in this area, the (sub-)micron effects that these minor components have on nucleation, crystal growth, morphology, heat capacity and polymorphic stability have been described and discussed and, sometimes, explained. Similarly, the effects on a macroscopic level, such as visual aspects, melting profiles, post-hardening and rheology have been the subject of research. Although limited compositional information, especially of additives, hinders appropriate discussions of the relevant mechanisms, some generic guidelines as to what type and strength of effect can be expected have been derived. As a general rule, a more significant influence is observed when the acyl group of the minor component (where present) is similar to those present in the fat itself. Additives may have different effects depending on the fat they are added to, their concentration and the temperature, especially with increasing undercooling (which typically reduces the effect of additives).

Keywords Emulsifier · Sorbitan tristearate · Span · Tween · Polyols · Partial glycerides · Phospholipids · Nucleation · Crystal growth · Crystal morphology · Crystal habit · Crystallization inhibitor · Bloom retarding fats · Polymorphism

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Introduction

Fats and oils are important ingredients in many home and personal care (HPC) and food products. They are unique in the way they develop plastic structures in a wide range of products. Their physical state plays an important role in product perception. The structure of fat continuous products especially, provides a characteristic texture: creamy or snappy, smooth or sandy. In HPC products this texture influences appreciation, but may influence the functionality too: release of active ingredients or application itself. In food products, the organoleptic properties (mouth-feel) are determined by the structure as well as melting profile and heat capacity [1]. In liquid oils, minor components may help maintain clarity, or cause clouding. The sensorial aspects are related to melting point, size and shape of the solid fat particles, i.e. fat crystals. They can be influenced both by composition and by processing [2–4].

There have been good reviews of fat crystallization over the last decade, or so [5, 6], but few have reviewed the role played by components other than the principal crystallizing species. This review seeks to redress the situation.

The influence of minor components on the crystallization properties, during processing and/or in the final product has been widely acknowledged for many years [7–10]. Minor components can be present indigenously or be added. Additives are used, and minor components removed, for the influence they have, or are presumed to have, on crystallization, surface gloss, temperature stability, rheology, polymorphic stability, etc. Of course, minor components may also be removed due to their contribution to aftertaste, oxidative instability or just because they are worth more as a separate product; these aspects will not be covered here. In addition, although non-fat solid particles (e.g. sugar, protein, cocoa particles) can have an influence on many of the fat crystallization properties, they are not primarily taken into account in this review. Also the use of minor components as structuring agents in themselves for liquid oils is not discussed as it has already been reviewed recently [11].

There is no firm definition of what concentration makes a component "minor". In practice, it will depend on the concentrations of the "major" components. The result is that, in certain situations, a component at a concentration of 10% may still be considered a minor component. In other situations, minor components will generally account for less than 2 or 3% of the composition, but often far less (<1%). The concentration required to achieve a given effect differs greatly depending on the mechanism by which the component works. Incorporation into the crystal structure is likely to require concentrations in the range of 0.5–5%. If the component's main role is played during nucleation, a concentration <0.1% may already be sufficient to make a significant difference [12]. Those components that act by blocking growing sites on crystal surfaces may be effective at even lower concentrations.

To formulate the right combination of fat, functionality and additive, the additive's mode of action should be known. Likewise, it is worthwhile understanding the mechanisms of nucleation, crystal growth, polymorphic transitions, etc. It is important to realize that products tend to be in a kinetically frozen state rather than in thermodynamic equilibrium. The fact that many minor components influence the kinetics, rather than the equilibrium situation, will make a difference to the final product.

This review will focus on those components that have been investigated for their influence on fats in fat-continuous systems. An overview of the components of interest will be provided, as well as the effects observed and the possible mechanisms by which they work. The vast majority of published research has been empirical in nature, with the result that much less is known than may have been anticipated. The effect of emulsifiers, specifically, on fat crystallization in emulsions is well covered by Garti and Yano [13] and will receive limited attention here as it is a large enough topic on its own.

Minor Components

The next two sections will describe the minor components themselves: both those indigenous to fats and those that are added. Subsequent sections will detail the effects on crystallization of specific minor components. A summary of minor components that have been studied, including in which fat, are given in Table 1, along with reference to the appropriate publications.

Indigenous Minor Components

The principal minor lipid components that are indigenous to oils and fats are free fatty acids (FFA), monoacylglycerols (MAG), diacylglycerols (DAG) and phospholipids (lecithin) [14]. Within a fat, certain classes of triacylglycerols (TAG), when present at low levels, also might be considered as minor components. Non-lipid minor components can include various minerals, metal ions, proteins and foreign particles. However, these non-lipid components are usually removed or reduced during refining of the oil [15].

The composition of FFA, MAG and DAG reflects the overall fatty acid composition of the fat. Concentrations of FFA, DAG and MAG can vary greatly between fats and even between different batches of the same fat. If fats are fractionated, the partial glycerides and FFA may concentrate in one of the fractions, and this can vary between dry and wet (solvent) fractionation [16]. A high level of FFA, in itself, is considered a sign of poor quality (indicating a degree of hydrolysis); thus, FFA is reduced to <0.1% during refining. MAG are usually removed during refining [17], but DAG remain unchanged. Thus, a low DAG level in the crude oil is usually desired.

Lecithin (a class of phospholipid) is structurally similar to DAG, except that the third glycerol hydroxyl group is esterified with a phosphate group (which, itself, can be linked to a variety of molecules, such as choline, ethanolamine, inositol, or serine). Phospholipids vary greatly in their interaction with fat. Lecithin is found in many vegetable oils at varying levels, and is mainly commercially obtained from soybean oil and sunflower oil [18]. This concentrated lecithin is used as an emulsifier in both food and non-food applications. As such, it is frequently added to oils other than its native source. Although not entirely correct, the words "lecithin" and "phospholipid" are often used interchangeably. In reality, lecithin is a mixture of phospholipids, such as phosphatidylinositol (PI), lysophosphatidylcholine (LPC) and phosphatidylcholine (PC).

Table 1 Minor components and the fats in which they have been studied, according to the references indicated

	Cocoa butter[a]	Milk fat	Lauric fats[b]	Palm oil	Sunflower oil	Fatty acids	Pure TAG[c]	Other[d]
FFA	[26, 29, 121]		[24, 28]	[25, 30]			[27, 31]	
MAG	[26, 29, 32, 35, 74, 121]	[36, 73]	[31, 34, 101]	[25, 34, 66, 122, 123]	[122, 123]		[3, 27, 35, 70, 95, 97, 106, 112, 119, 124, 125]	[34, 57, 72, 113, 122, 123, 126, 127]
DAG	[26, 29, 32, 33, 37, 74, 121]	[36, 63, 73, 92, 105]	[24]	[16, 30, 56, 61, 128–132]			[27, 70, 93, 95, 106, 112, 133]	[57, 90, 113, 126, 134, 135]
TAG	[26, 29, 38, 51, 59, 60, 62, 75, 82, 86, 87, 121, 136]	[137–139]		[66, 140]			[141]	[57, 65]
Phospholipids	[21, 58, 60, 74]	[1, 142, 143]	[24, 31]	[71, 100, 122, 144]	[64, 100, 122, 145]		[119, 124, 125]	[19, 20, 122, 123, 127, 146]
STS & other Span®	[35, 83, 96]		[34]	[34, 111, 144]			[4, 35, 94, 95, 102, 133, 147–150]	[34, 126, 127, 151]
SMS/Span® 60	[3, 10, 35, 77, 83, 85]			[111]		[3, 110, 152, 153]	[3, 4, 35, 89, 96, 98, 102, 147–150, 154]	[3, 127, 151]
Tween®	[3, 83]	[99]				[3, 153]	[3, 102, 149, 150]	[127]
Sucrose esters		[52–55, 108, 155, 156]	[28]	[111]			[93, 95]	[157–160]
Other	[10, 35, 60, 74, 78–80, 84, 88, 161]	[48, 105, 108, 161]	[31, 34]	[30, 34, 162]	[12, 163]	[153]	[3, 4, 102, 106, 119, 124, 125, 147–150, 154]	[34, 40, 50, 57, 127, 164]

Natural fat, a fraction or a derivative (e.g. hydrogenated)

[a] Cocoa butter and/or chocolate

[b] Palm kernel and coconut oil

[c] Pure TAG or combinations of pure TAG with natural fats

[d] Including fat blends, sal, canola oil, normal rapeseed oil, soy bean oil, margarine, whale and beef tallow

Since different lecithins can have varying phospholipid composition, they may have different effects on the crystallization properties of fats.

The effect the various phospholipids have on crystallization, for example, can vary [19–21]. PI and LPC, in particular, seem to slow down the crystallization of cocoa butter but PC might accelerate crystallization.

Phytosterols can be present in oils in widely varying concentrations and composition, and may be used analytically as a fingerprint to identify the oil. In certain cases, the sterols are isolated in order to be used elsewhere as a food ingredient, e.g. as a means to reduce blood cholesterol levels. Although they have been studied as structuring agents in oil [22], they have not been studied or used in relation to modifying the crystallization properties of oils and fats.

Waxes, strictly speaking, are esters of long chain fatty acids with long chain primary alcohols [23]. They are present in many oils (e.g. sunflower oil) but, where present at significant levels, are often removed by winterization in order to prevent the oil becoming cloudy at low temperatures.

To a certain extent, oxidized glycerides may be considered as minor components. However, oxidized material is generally considered simply to be an indicator of poor quality. They are usually removed during refining but can be present through subsequent mishandling of the oil.

Additives

Any of the indigenous minor components, described above, could be used as additives. However, in practice, this is not generally the case. Phytosterols are neither used nor studied as additives to influence crystallization properties of fats. FFA have been studied [24–31], but this mainly to identify their role as unwanted minor components, since they have a negative effect on taste and stability. Although MAG and DAG are usually removed, they may be deliberately added to oils and fats [26, 31–37]. If this is the case, their fatty acid composition may or may not reflect that of the original fat.

Specific triacylglycerols may be used as additives. The TAG may be indigenous to the fat (in which case it is enriched by the addition) or alien to the specific fat. For example in cocoa butter, the indigenous 1,3-distearoyl-2-oleoylglycerol (StOSt) content may be increased, or the foreign 1,3-dibehenoyl-2-oleoylglycerol (BOB) might be added [38]. In this review, additives used to enrich the concentration of indigenous material will only be included when the concentration is small enough (say <5%) to consider it a minor component both before and after addition.

Many other additives are derived from lipids, such as citric acid esters and propylene glycol esters [39]. Esters of fatty acids with all kinds of sugars result, for example, in sorbitan tristearate (STS), sorbitan monostearate (SMS), sucrose esters and many others. Sorbitan esters may be ethoxylated too. The majority of these are emulsifiers, but have the potential to alter crystallization in a non-emulsion system. Non-lipid additives include proteins (e.g. sodium caseinate, whey protein isolate, and milk protein), sodium dodecyl sulfate and xanthan gum.

Table 2 shows an overview of potential additives, including some trade names.

Outside the food and HPC area, research on additives has focused on issues like reducing the cloud point of biodiesel, perhaps using esters of branched alcohols such as isopropyl or 2-butyl [40, 41]. Although the results can be

Table 2 Examples of some additive brand names and types

Abbreviation/trade name	Description
3G1S®	Triglycerol monostearate
Acidan®, CAE	Citric acid ester
DATA esters, DATE(M)	Diacetyl tartaric acid esters (of monoglycerides)
GLP	Lactic acid esters/glycerol lactopalmitate
GMO	Glycerol monooleate
GMS	Glycerol monostearate
P-170, S-170	Sucrose esters
PGE	Polyglycerol esters
PGMS	Propylene glycol monostearate
SAE	Succinic acid esters
Span® 20, 40, 60/SMS	Sorbitan monolaurate, monopalmitate, monostearate
Span 65®/STS/Crill® 36/Durtan®	Sorbitan tristearate
Span® 80, 85	Sorbitan monooleate, trioleate
Tween® 20, 40, etc.	Ethoxylated sorbitan esters

very interesting, the additives are not generally food grade and will not be reviewed here.

A specific problem related to published research on additives is the use of trade names to describe the material investigated. Many studies are based upon commercially available additives. Taking sorbitan tristearate, as an example, in reality it is composed of mono- di-, tri- and tetra-esters, of palmitic, stearic and other fatty acids, with sorbitan, sorbitol and isosorbide [42–45]. FFA has been found to be present in concentrations from near zero to almost 20%. Thus, STS is a mix of many different components. In addition, for most of these components, there are many possible positional isomers, multiplying the true number of components in the product. Of commercial STS, possibly only 1–3% will be the true tri-ester of stearic acid with sorbitan (of which there are ten positional isomers). The same is true of polysorbate emulsifiers—Tween®—which are composed of a complex mixture of oligomers [46]. In such mixtures, each of the individual components could have a distinct effect on the crystallization properties of fats. The variability in composition between suppliers, and even batches, of the same material means that it can be difficult to compare effects across different studies.

Moving away from pure fat alone to full recipe products (e.g. from cocoa butter to chocolate) many other ingredients come into the picture. Some of them will play a role, while others will not. Those ingredients that will dissolve in the fat phase (e.g. lecithin) will be considered an additive in the scope of this review. The others (mainly solid particles like sugar crystals) will not be addressed in this review. However, that certainly does not mean that they don't influence the crystallization properties of the fat phase (see, for example, [47]).

Note that not all additives are accepted for use in foods in all countries. In some cases, use of a specific additive is accepted in only a few countries (e.g. BOB in Japan).

In some studies, waxes have been added to a fat in an endeavor to influence crystallization [48] but this is uncommon. Others have looked at wax to structure liquid oils [49], although this application will not be considered here.

Effects

In this section, the reported effects of additives and indigenous minor components are reviewed. Note that due to the compositional uncertainty of some additives (see above), the reported effects will be mentioned, in general, without any further comments. In a limited number of cases only is discussion of the observations useful. Overall, the effects reported mainly demonstrate what is possible to achieve in term of modifying the crystallization properties of fats. To deduce how to obtain a specific effect in a specific application is not trivial. In each case, the right additive must be found either by trial and error or by dedicated research.

A few words of caution are necessary. Note that other components (further additive, solid particles, etc.) or a different application may completely alter the effect of the original additive. Similarly, note that the same additive may have a different effect at different concentrations (e.g. the effect of dioleoylglycerol on the crystal growth of coconut oil [24]), at different degrees of undercooling or even in the presence or absence of agitation [50]. Further, note that the same component may have a different effect in a different fat. Additionally, in emulsion systems, due to the surface active nature of many minor components, the effect can be quite dissimilar to that in the bulk fat.

Addition of crystalline material at some point during the processing in order to influence crystallization (i.e. seeding) will not be covered in this review on minor components.

Crystallization: Nucleation

One of the most interesting effects of minor components is that on crystallization. A minor component can affect either nucleation or growth or both. In the latter case, the effect on each is not necessarily the same. Some components stimulate nucleation, whilst retarding growth, or vice versa, others stimulate or retard both. The effects measured with respect to nucleation are: alteration of nucleation time, shift of nucleation temperature, and change in the number and nature of the nuclei formed.

In many investigations, the first thermal effect during the crystallization process is considered the start of nucleation. However, in DSC thermograms, for example, a minor component may affect the initial, minor peak, whilst the later crystallization peak (representing the bulk of crystallization) may not be affected. Such an observation in the cooling curve is often accompanied by an increased trailing shoulder in the heating (melting) curve [51]. This is often reported as an influence on the nucleation of the fat. In fact, what is observed are two separate events: firstly the nucleation and crystal growth of a high-melting fraction of the fat and, secondly, the nucleation and growth of the bulk of the fat. In such cases, it is probably better to conclude that the minor component did not influence nucleation, unless it is crystallization of the minor fraction that is of interest. In certain systems, the first crystallization event corresponds to that of an unstable polymorphic form, which subsequently transforms into a more stable form, followed by continued growth of this second polymorph. This is true of palm oil, which crystallizes into the α form, transforms into β' and crystallizes further in that form. In this system, predominantly unsaturated MAG (from

sunflower oil) do not impact the nucleation of crystals but more saturated MAG (derived from palm oil itself) promote nucleation [25].

In milk fat—sunflower oil blends, palmitic and stearic sucrose ester with HLB = 1 (principally di-, tri- and polyester) delay nucleation [52] and lead to a decreased crystal size with a narrower size distribution, although a palmitic sucrose ester with HLB = 16 (greater proportion of monoester) does not alter the crystal size or the distribution. This is true in a similar system incorporating the high-melting fraction of milk fat [53–55].

A substantial part of research regarding the influence on nucleation is based on the investigation of the initial crystals, also referred to as seeds [26, 32, 56–61]. This assumes that the specific components influencing nucleation will be over-represented in the seeds. Again, this might influence only the initial crystallization event or affect crystallization of the bulk of the fat as well. In cocoa butter nucleation, trisaturated TAG and phospholipids are vastly over-represented in the seeds [60]. However, increasing their concentration by adding additional trisaturated TAG does not influence the main crystallization [26, 32]. Loisel et al. [32] found that addition of extra tristearoylglycerol increases only the small initial DSC crystallization peak, making it appear earlier and bigger. It does not affect the main crystallization step of chocolate, the onset, or the speed of the main crystallization. Unlike tristearoylglycerol, distearoylglycerol and stearic acid do not influence the initial crystallization. Looking into the detail of the nucleation process, it appears that some phospholipids, especially PI and LPC seem to slow down crystallization, while PC concentrations might be related to faster crystallization [59, 60]. There is no correlation found between nucleation times and either the original cocoa butter or the seed crystal total phospholipid concentrations.

Cebula and Smith [62] studied trisaturated TAG and native DAG in a cocoa butter equivalent. Increasing levels (from about 1 up to 5%) increases the degree of crystallization in the early stages and raises the temperature of nucleation. This could be the result of the DAG and the trisaturated TAG precipitating first and then nucleating further TAG material. In a similar approach, Wright et al. [63] removed the polar components from milk fat and then added back the DAG. They found that the drop melting point and equilibrium solid fat content (SFC) do not change but that the onset of crystallization is delayed at low undercooling. In addition, it appears that the milk fat DAG alter the growth kinetics, as revealed by the Avrami exponent. Wähnelt, Meusel and Tülsner [33], found that adding DAG (1,2-dipalmitoylglycerol, 1,3-dipalmitoylglycerol, 1,2-dioleoylglycerol, 1,3-dioleoylglycerol) does not influence cocoa butter nucleation, but that trioleoylglycerol and tripalmitoylglycerol does. However, it is likely that the initial crystallization peak, comprising the high melting fraction only, was considered.

Gordon and Rahman [24] showed that bleaching and deodorizing dramatically reduces induction times of coconut oil crystallization. Bleaching removes phosphorus (i.e. phospholipids) and deodorization removes FFA. The biggest effect is seen on complete removal of the phosphorus; the initial reduction by 75% (degumming) has only a small effect. The nucleation of refined coconut oil at 15 °C is most delayed by lauric and oleic acids (compared to palmitic acids), and more so at higher concentrations. The effect of palmitic acid is much less and also less affected by the concentration. The effect of DAG is much weaker than that of fatty acids. 5% dilauroylglycerol extends the crystallization onset from 8 to 11.5 min and 10% extends it even further, to 19 min. Dipalmitoylglycerol does not appear to affect the nucleation. Added phosphatidylcholine delays the onset of crystallization at 0.25% and even more at 0.5%. At lower temperatures, the effects are smaller, perhaps demonstrating the significance of the greater undercooling. It is possible that the delaying effects could be related to different activation energies: control (no acids added) 87 kJ/mol, 2.5 or 5% lauric acid 174 and 203 kJ/mol; 2.5 or 5% oleic acid 178 and 184 kJ/mol; 2.5 or 5% palmitic 95 and 105 kJ/mol.

Herrera observed a delay in the crystallization of partly hydrogenated sunflower oil after adding 0.01–0.1% sucrose esters (P-170, mp 58 °C ex Mitsubishi-Kasei Food Corp) [12]. Rivarola, Añón and Calvelo [64] found that phospholipids do not influence the nucleation step of wax crystallization in sunflower seed oil. The crystal size is halved by adding 300 ppm phospholipids. Reddy and Prabhakar found that removing TAG containing 9,10-dihydroxystearic acid from sal fat lowers nucleation temperature [65].

Tripalmitoylglycerol reportedly increases the crystallization speed of palm oil [66] and causes the formation of β crystals rather than β'. However, given that palm oil itself formed around 10% solid at the crystallization temperature (25 °C) and the levels of addition of tripalmitoylglycerol were about 6 and 11%, similar to the indigenous level of tripalmitoylglycerol, much of the reported increase in crystallization is due to crystallization of the tripalmitoylglycerol itself. Similarly, this could also account for the observation of a strong β peak by X-ray diffraction.

Waxes are usually higher melting components in a fat, and this is true even when they are sourced from sunflower oil. However, they are apparently sufficiently similar to provide nuclei in milk fat [48], reducing the induction time as measured by isothermal DSC at levels of 0.25 and 0.5%.

Crystallization: Crystal Growth

The second stage of crystallization, after nucleation, is crystal growth, which may also be influenced by minor components. Smith and Povey [27] investigated the effect of partial glycerides on trilauroylglycerol crystallization in 1–5% (w/w) concentrations. The growth rate appears to be promoted by FFA and inhibited by DAG, in particular by the 1,3 isomer. Dimyristoylglycerol reduces the growth rate by a third, dilauroylglycerol by two-thirds. Often, additives do not affect the crystal growth mechanisms (e.g. spiral growth), merely the overall growth rate (although this may affect different crystal faces to different degrees, especially where the mechanism differs on each face) [67–69]. The effect of the additive is greatest when the chain length is that of the fat; with the effect decreasing rapidly with shorter chains, and decreasing moderately with longer chain lengths. Although not discussed in the paper, the figures show that monocaproylglycerol results in big trilauroylglycerol crystals, while 1,3-dicaproylglycerol results in much smaller crystals. This suggest an influence on the nucleation stage (more nuclei with similar overall growth equals smaller crystals), rather than the growth stage.

In a similar study, Smith, Cebula and Povey investigated the effect of lauric based molecules on trilauroylglycerol crystallization [70]. Monolauroylglycerol and lauric acid increase the crystal growth rate of trilauroylglycerol, but decrease the facet and crystal size. Dilauroylglycerol isomers significantly reduce growth rate. Crystal morphology is altered and the relative stability of the meta-stable phases is increased. Growth rate is lower for samples containing 1,3-dilauroylglycerol than for samples with 1,2-dilauroylglycerol. The effect is attributed to the varying sizes and shapes of the additive molecules disturbing the regular build of the crystal lattice in different ways.

Phospholipids have been shown to have a marked effect on crystal habit (size and shape) of TAG, the magnitude of the effect dependent on the specific phospholipid added [71]. 0.2% of phosphatidyl ethanolamine increases the size of palm oil spherulites and renders them more dense. Phospholipids reduce the growth rate of the fastest growing faces of pure trilauroylglycerol [71], which is consistent with the development of denser spherulites.

In the presence of phospholipids the concentration of wax remaining in sunflower seed oil is greater than that present following crystallization without phospholipids. The crystal size halves on adding 300 ppm phospholipids [64].

Gordon and Rahman [24] quantified the effect of minor components on the crystallization of coconut oil. Fatty acids reduce the solidification rate at 15 °C, proportionate with the concentration. The effect of oleic acid is comparable to that of lauric acid, and both are more effective than palmitic acid. At lower temperatures, the effects are smaller, probably due to the dominance of undercooling factor. Dilauroylglycerol slows crystal growth only at 10%. Dioleoylglycerol speeds up growth (at 5%) or retards it (at 10%). Phosphatidylcholine largely reduces crystal growth, more so at 0.5% than at 0.25%. Removing phosphorus by bleaching increases the crystal growth rate. Removal of FFA by deodorization increases the crystal growth rate even further. In agreement with this, Chaleepa et al. [28] found that lauric acid (at a level of 15%) in coconut oil delays the onset of crystallization, and reduces its rate. Lauric sucrose ester (L-195) was found to have a similar effect but at a level of only 1%. Stearic sucrose ester (S-170) at the same level of 1% delays crystallization even more effectively. Both lauric acid and L-195 lead to fewer, larger spherulitic crystals. However, with the former additive the crystals have a dense core with a lighter, feathery outer layer, while with the latter additive, the crystals are smooth.

DAG retard the crystal growth of shea nut oil [40]. DAG slows down the velocity of growth of a cocoa butter replacer [32]. Saturated MAG accelerate the crystal growth of partially hydrogenated soybean oil [72], partially hydrogenated palm kernel oil [34, 72] and partially hydrogenated soybean + palm oil [34].

Foubert et al. [73] showed that the influence of DAG and MAG on the crystallization of milk fat is dependent on the acyl groups present in the additives, as well as on their solubility in the liquid oil. Where the acyl chain was stearic, nucleation is enhanced at lower temperatures, while, at higher temperatures, they do not impact the nucleation but do influence the crystal growth. Where the acyl chain is oleic, there is no influence on nucleation rate but the crystal growth rate increases.

In chocolate crystallization, addition of extra tristearoylglycerol increases only the small initial step of crystallization (causing it to occur earlier and to be larger), but not the main crystallization step. Distearoylglycerol and stearic acid slow down the main crystallization step [32].

The work of Tietz and Hartel [74] illustrates the fact that, in terms of the desired or observed effect, there is often an optimum level of additive or minor component. They removed the minor lipids from milk fat and then added them back at twice the natural level. The milk fat was added to cocoa butter at a level of 10%. Longer nucleation times, slower crystallization and faster bloom development are observed for milk fat with no minor components or double minor components. Fortuitously, it seems, the natural level of milk fat minor components is the optimum.

Polymorphism and Melting Profiles

The more complex aspects of the crystallization properties of oils and fats arise from their polymorphism. Melting temperatures, heat capacities, network formation and phase transformations are all related to the various crystalline structures fats can adopt. By stabilizing a certain phase, transitions into another phase—often accompanied by product deterioration like fat bloom in chocolate or sandiness in spreads—may be delayed or even prevented. Polymorphism can be difficult to control fully, for which reason the industry has been looking for ways to improve the situation. Use of additives or removal of specific minor components has been the logical approach.

At levels of 1%, monopalmitoylglycerol and monobehenoylglycerol both reduce the induction time and accelerate crystal growth of palm oil [66], and lead to the formation of more β polymorph. Despite the conclusions of this paper, application of this finding to chocolate (i.e. cocoa butter) to avoid or ease tempering, is unlikely.

Cocoa butter (and chocolate) polymorphism can be influenced by means of additives. It is probably the application that has been investigated the most [3, 21, 26, 29, 32, 33, 58, 75–81]. In particular the prevention of fat bloom has been targeted [10, 38, 74, 82–88]. The conclusions from such studies should be approached with great care, since DSC often is used as the sole means of identification of polymorphs, which is not an unambiguous method. On occasion, a closer study of the details presented, can lead to conclusions different to those of the authors. Although visual or instrumental assessment of the change in the whiteness of the surface is unambiguous, the change may not be due to a polymorphic change but to a recrystallization. In such cases, X-ray diffraction can help to establish which factor(s) are implicated.

STS (Span® 65) is reported to decrease and broaden the melting point of the β_V of cocoa butter, with increasing concentrations. Additionally, STS retards the formation of cocoa butter β_{VI} from β_V but promotes most other transformations, including from the β' forms to β_V. On a temperature program that would fully transform β_V to β_{VI}, 5% of either sorbitan monostearate (Span® 60) or sorbitan monopalmitate (Span® 40) retains 50% or more of the cocoa butter in the β_V form. STS, however, maintains all the cocoa butter in the β_V polymorph. A blend of lipophilic and hydrophilic emulsifiers (such as Tween® and Span®) is apparently more effective than either alone (at 5%) [3, 10, 83, 85, 89]. A blend of Span® 60 and Tween® 60 improves bloom resistance of chocolate, although the mechanism behind is not explained [83]. Distearoylglycerol and stearic acid retard the polymorphic transition after the second, major, crystallization step in chocolate crystallization. DAG retard polymorphic transitions in CBE on heating [32, 62, 83, 89]. A high melting fraction of milk fat increases the bloom stability of chocolate [86].

In palm oil, the nucleation of the α polymorph is promoted by MAG from palm oil itself, but not by the (more unsaturated) MAG from sunflower oil. However, both types of MAG accelerate the transformation from the α to the β' polymorph [25].

Saturated MAG (mono-myristoylglycerol, palmitoylglycerol, stearoylglycerol and behenoylglycerol) influence (mainly decreasing) the melting points of hydrogenated soybean oil, palm kernel oil, beef tallow and whale oil [72]. Unspecified MAG (with respect to composition) lower the melting points of partially hydrogenated palm kernel oil and partially hydrogenated soybean + palm oil [34].

DAG (from lard) retard the β' to β transformation in a low-erucic acid (partially hydrogenated) rapeseed oil-based margarine. The β-phase is clearly seen after 4 weeks in the absence of DAG. It takes 8.5 weeks with 0.5% DAG and 44 weeks with 5% DAG. The effectiveness of the DAG depends on the position of the acyl chains. The sn-1,2 form delays the β' to β transition more than the sn-1,3 isomer [90, 91]. This difference in the influence of positional isomers is also observed in milk fat [92]. Only the 1,2 isomer increases the nucleation activation free energy barrier and so delays crystallization.

Other emulsifiers having a stabilizing effect on a specific polymorph, or slowing transformation rates are sucrose esters. Addition of 0.01–0.1% sucrose esters to partially hydrogenated sunflower oil delays the β' to β transition [12]. A similar observation is made with pure tristearoylglycerol, with stearic acid sucrose ester slowing both the α to β and β' to β transition [93].

For research purposes, the use of pure TAG instead of natural fats has advantages. The system is better characterized and effects on specific TAG may be singled out. Several studies, thus, take this approach. Krog examined the effect of a range of additives on tripalmitoylglycerol [39]. He found that STS and citric acid esters stabilize the α phase of tripalmitoylglycerol more than the other additives. Of these, only propylene glycol esters stabilize α to any degree, but the other additives have no effect on polymorphic changes in the TAG. When mixed with trisaturated TAG of shorter fatty acids (C_{14}, C_{12}), none of the additives tested show any influence on the crystal structure. In a study of the effect of STS on the phase behavior of tristearoylglycerol, tri-elaidoylglycerol and tri-oleoylglycerol, Elisabettini et al. [94, 95] found that the influence of 5% STS differs according to the way the α to β' transition takes place. It delays transformations below the β form and disturbs the transversal packing of tri-elaidoylglycerol and, especially, of tristearoylglycerol, which are TAG showing a melt-mediated α to β' transition. In the case of tri-oleoylglycerol, the solid state α to β' transition does not allow

an appropriate insertion of STS into the TAG structure. However, in both Elisabettini's and Krog's studies, the observed differences of activity might be better explained as being the result of more or less similarity between the fatty acids of the additive and of the TAG investigated.

The α to β transition of monoacid TAG is also affected by SMS [96]. The α to β′ or β transformation in quenched (rapidly cooled from the melt) tristearoylglycerol, or a 90:10 blend of tristearoylglycerol and tripalmitoylglycerol, upon heating at 10 °C/min is prevented by 10% SMS. However, whilst heating at 5 or 2 °C/min, it reduces the α to β′ transition and prevents the β′ to β transition. Both tripalmitoylglycerol and the emulsifier have a kinetic effect on the polymorphic transformation of tristearoylglycerol, but neither affects the thermodynamic stability of the individual polymorphs [97]. SMS in liquid 1,3-distearoyl-2-oleoylglycerol significantly retards the α to γ_{po} transition. The γ_{po} to pseudo-β′ transition is not slowed. SMS behaves as a conventional impurity, causing a reduction in the melting temperatures of each polymorph [98].

Miscellaneous Effects

Addition of 0.1% Tween® 60 or 0.1% glycerol to a mixture of high melting fraction of milk fat with trioleoylglycerol increases the yield force at 5 °C [99]. However, higher levels of addition cause a reduction in yield force. Peculiarly, Tween® 60 and glycerol have opposite effects on the induction time for crystallization.

Lecithin (4%) in hydrogenated sunflower oil causes a slightly higher peak in the DSC cooling curve, and has a similar, but smaller effect, on refined palm oil, but no effect on coconut oil (copra butter). On the SFC curve, slight differences can be observed. However, in the presence of water (84/16 fat/water) the effect of lecithin is much bigger, retarding crystallization [100].

The difference in emulsifier action depending on the application is clearly seen in a study on the effects of emulsifiers on protein-fat interaction in ice cream mix during ageing [101]. Ageing a water continuous mix, containing hydrogenated coconut oil, skimmed-milk powder, sucrose and stabilizer, for 30 min at 5 °C, results in a SFC of 55% in the absence of emulsifiers. In the presence of 0.2% (on emulsion, or 2% on fat phase) mono-oleoylglycerol (GMO), the SFC is 65% and, in the presence of 0.2% mono-stearoylglycerol (GMS), is 75%. This effect is not seen in the fat alone. The different influences of emulsifiers in bulk fat and in the emulsified state indicate that the effect on fat crystallization is due to action at the interface. The mean fat globule diameter is 1 μm. Emulsifiers also affect the desorption of protein from the fat globules into the water phase. The speed and amount of desorption is least in the control, greater in the presence of GMS and greatest in the presence of GMO. The presence of emulsifiers results in stable agglomerates of fat globules, in contrast to the control. Again, GMO has a stronger effect than GMS [101].

Emulsifiers (up to 10%) can affect the heat capacity of mono-acid trisaturated TAG, apparently without influencing the crystal lattice. The effect of emulsifier is strongly dependent on the transformation conditions. 10 wt% of solid emulsifiers (Span® 60/65) gradually increase the heat capacity (C_p) of β tristearoylglycerol, at temperatures close to the melting point, from the point where the slope of the C_p line changes. The C_p of α tristearoylglycerol is not affected. Acidan® and 3G1S® increase the C_p of α and β across all temperature ranges, parallel to the C_p of pure tristearoylglycerol [4, 102].

MAG stimulates post-hardening (post-processing crystallization) of hydrogenated soybean oil, palm kernel oil, beef tallow and whale oil [72]. However, in water MAG forms surface-active crystals at the water/oil interface, when the concentration of MAG exceeded its solubility, lowering the interfacial tension [103]. In emulsified systems, smaller milk fat globules lead to lower nucleation rates, due to the presence of fewer heterogeneous nuclei per droplet. Micelles of MAG and possibly DAG are proposed to increase nucleation rate; removal of these partial glycerides considerably lowers the nucleation rate, while addition of GMS increases it [104].

Somewhat surprisingly, while the minor polar components of milk fat affected its crystallization, the mechanical properties and microstructure remained unchanged, being influenced far more by the temperature [105].

Mechanisms

In order to know which components should be added or removed, to achieve the specific requirements for a given application, an understanding of the relevant mechanisms is essential, as well as of the processes of nucleation, crystal growth and polymorphic change. In some publications, mechanisms for the effects are proposed. However, in none of these is the component of interest adequately analyzed, and often a proper analysis of the fat phase is absent. Given that different components within a single additive could have quite different effects, such proposed mechanisms are at best debatable. Some researchers openly admit that the mechanisms are not clear [83]. Figure 1 gives a summary of the ways in which additives may function.

In many cases, the component acts either as a promoter or as an inhibitor of the nucleation and/or growth processes. This being the case, the component will not affect the total amount of solid phase when the system has reached equilibrium. However, it can influence the rate at which this equilibrium is attained [106].

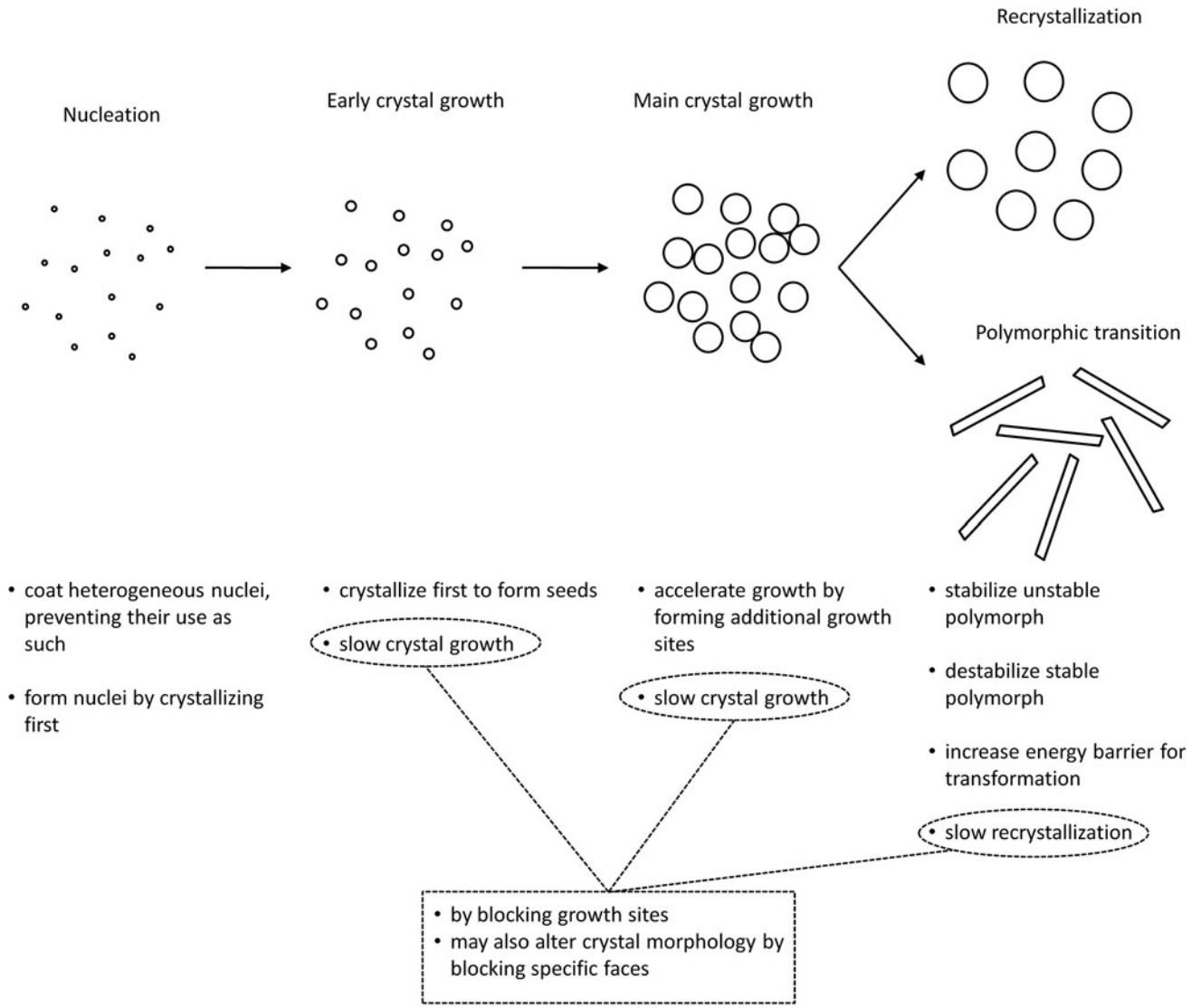

Fig. 1 Modes of action of additives

There are two cases in which the component will influence the final amount of solids: firstly, by changing the equilibrium conditions (e.g. via incorporation of the additive into the solid phase or, by stabilizing the liquid phase) or, secondly, by the fact that a kinetically stable situation may be achieved, rather than true thermodynamic equilibrium. Since minor components frequently influence the kinetics, they may very well, in practice, influence the final SFC. Such a kinetic effect is likely to occur when the influence of the component is dependent upon heating and/or cooling rates [102].

The two cases described above can occur together. Schlichter et al. [102] describe emulsifiers that are incorporated into pure monoacid trisaturated TAG. They do not influence the crystal lattice, but they do affect the heat capacity. The effect of the emulsifier is strongly dependent on the transformation conditions. The kinetic effect of the additive on the solid–solid transformation is found to be strictly associated with the structure of its hydrophilic moiety. A model of molecular incorporation is proposed, which describes the arrangement of the surfactant molecules parallel to the TAG chains, leading to the formation of vacancies in the structure. The effect of on polymorphic transformations is explained by the additive's capacity to create hydrogen bonds with the neighboring TAG.

Nucleation and Growth

Nucleation is the development of small solid particles exceeding the critical size. Below this size, clusters of molecules re-dissolve rather than grow, while above this size, they will grow further. From a minor component

perspective, nucleation can be influenced by providing heterogeneous nucleation sites [13], stabilizing the developing nuclei, or affecting the driving force, e.g. by changing the solubility of the other components, reducing the surface tension etc. They may also increase secondary nucleation by adsorbing at growth sites, leading to crystal defects and weaker crystals that may break at that point [107]. Where the nucleation rate is reduced, this may be due to shielding of the heterogeneous nuclei present by the minor component or additive, rendering them less suitable as initiators of crystallization [107].

In the case of high melting fractions of milk fat, polyglycerol esters increase the nucleation rate, but sucrose esters decrease it [108]. Given their molecular structures, this is perhaps not unexpected. However, it is important to keep in mind that many techniques which promise to measure nucleation rate do not do so directly. In this case, the technique depends on nuclei growing into crystals that achieve detectable sizes—i.e. both nucleation and early growth are involved.

One proposed nucleation mechanism involves minor components in the early stages. Complex lipids with surface-active properties in combination with high-melting (saturated) lipids form the initial crystals. The main TAG components are then incorporated in order of decreasing melting point [58–60]. Nucleation and crystal growth through such a mechanism should imply an influence from surface active and/or high melting components. However, it seems that the first and second crystallization stages (DSC peaks) are quite independent in many fats. The first crystallization stage frequently involves fully saturated TAG, while the second stage is often the crystallization of partly unsaturated (usually monounsaturated) TAG. Nuclei principally composed of highly saturated TAG do not necessarily provide a good growing basis for a partly unsaturated fat. It is, therefore, no surprise that increased levels of trisaturated TAG, and certain DAG, increase the degree of crystallization in the early stages, and also raise the temperature at which nucleation occurs. However, faster nucleation does not imply faster crystal growth. The best crystal growth conditions are attained when there is a great deal of similarity between the existing nuclei and main part of the fat; this should be in terms of chain length, saturation, and type and position of unsaturation (*cis*/*trans*).

The growth process from pure solutions gives an insight into the potential growth process in actual fat blends. Fat crystals appear to grow via a spiral dislocation mechanism [109], from solvent or the melt. In the presence of Span® 60 the mechanism is the same, but the absolute growth rate is considerably decreased. This is explained by an adsorption of the emulsifier at kink sites [110]. DAG may interfere with the interface structure in this way, and prevent further molecules from joining the crystal [27]. Phospholipids may also partially adsorb to the crystal surface. The more of the crystal surface that is covered, the greater is further growth of crystals hindered [64]. Additionally, minor components might influence nucleation and growth by having a preference for a particular type of crystal lattice. DAG may be of interest in this respect, since the 1,2 isomer might better be accommodated in orthorhombic crystals, while 1,3 might prefer triclinic crystals [90].

It appears that the maximum influence is observed when the acyl group(s) of the additive are similar (or identical) to those of the crystallizing TAG [27, 111, 112]. Naturally, there is some influence from the polar group of the additive. However, the requirement for an additive to have an effect on crystallization is that it should be sufficiently similar to the crystallizing species that it can join the crystal matrix—at least at the growth site. The additive's specific influence will depend on whether its molecules are completely included into the matrix by overgrowth of the crystallizing species, or whether the structural dissimilarity is such that further crystallization is blocked. By acting at growth sites specifically (Fig. 2), only very small amounts of additive or impurity may be necessary to observe a large effect [68]. Similarly, by acting at growth sites on certain crystal faces, the morphology of the crystals will be altered [68].

Frequently, it is found that the minor component or additive has less influence at greater degrees of undercooling [63, 113]. Due to the dissimilarity of the additive molecule to the TAG structure, it may be less likely to adsorb at a growth site than the TAG molecules themselves. At low undercooling, this is not a significant difference and, once there, the additive blocks further growth, However, at higher undercooling, growth rates are high and the additive has much less opportunity to adsorb at the growth site [114].

Sangwal gives a clear description of the way in which impurities affect crystal growth kinetics [67]; although not specifically directed at fats, many of the concepts are

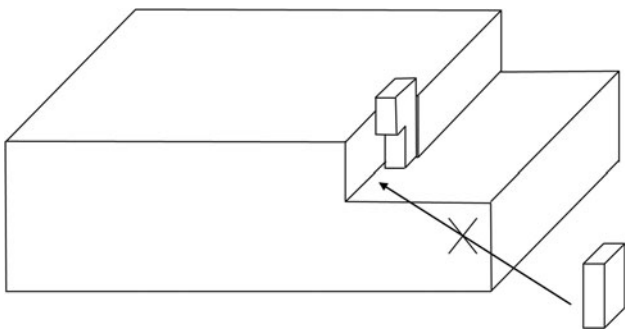

Fig. 2 Schematic representation of the blocking of growth site by an additive

applicable to such systems and usefully supplement this review.

Polymorphic Transitions and Stability

For additives utilized to influence phase transitions (e.g., to retard or enhance post-hardening or fat bloom) it is of great importance to know whether the transition involved is solid-state, or melt/solvent mediated, since this determines, to a substantial extent, the way in which the transition can be influenced. For example, crystal habit modifiers might influence solid-state transitions, while other types of additives could influence transitions that occur via a liquid phase. The former must be incorporated in the crystals properly during crystallization, while the latter should perform better when present in the liquid fraction of the fat. This principle can also be used the other way around: if an additive is known to increase the liquid fraction of a fat, transitions accelerated by this emulsifier are likely to be liquid/solvent mediated. In many publications, however, the arguments towards either are never convincing.

In any system where solid and liquid fat are present (i.e. most natural fats, and blends used in foods), there is a dynamic exchange of molecules between the two phases [115]. This permits recrystallization, which may simply be Ostwald ripening, or a fractionation of TAG, or may involve a polymorphic change as well. Partial acylglycerols have been shown to slow this process of exchange in tripalmitoylglycerol [112]; as anticipated, palmitic partial acylglycerols are the most effective.

STS was found to retard the cocoa butter β_V to β_{VI} transformation [83, 89]. This is proposed to be a solid state transition, delayed due to STS increasing the liquid fraction of β_V. The same increased liquid fraction would promote a β' to β_V transformation, although it is not immediately obvious that a slight increase of liquid would greatly influence the latter transition. Garti [83] proposed an alternative explanation along similar lines, that a solid-state transition (like β_V to β_{VI}), which requires a slight movement of molecules, would be hindered by the rigidity of the STS-type additive. However, it could be that the β_V to β_{VI} transformation proceeds via the liquid phase, in which case STS could act as a crystal poison at the growth sites of the growing β_{VI} crystals. Indeed, a small amount of liquid (hazelnut oil) added to cocoa butter accelerated the β_V to β_{VI} transformation [116]. To test this hypothesis, more structural information about β_V and β_{VI} crystal packing, and their differences, is required to support the liquid mediated transformation. Recent publication of the structures of the two β forms, calculated from synchrotron powder patterns, would seem to indicate that the transition could not be solid state [117, 118].

An alternative interpretation of the STS data would be that incorporation into the crystal stabilizes the β_V structure. A lower energy of the β_V structure would increase the driving force for the β'_{IV} to β_V transition, while it would retard the β_V to β_{VI} transformation, just as has been observed, and irrespective of the type of transformation. Unfortunately, there is no further evidence of such incorporation, nor of its effect on the crystal energy, so the latter hypothesis is not proven either.

The pure TAG studies of Elisabettini et al. [94] point in the same direction; the influence of 5% STS differs according to the way the α to β' transition takes place. It delays the transformations below the β form and disturbs the transversal packing of tri-elaidoylglycerol and especially of tristearoylglycerol, which are TAG showing a melt-mediated α to β' transition. In the case of tri-oleoylglycerol, the apparently solid state α to β' transition does not allow an appropriate insertion of STS into the TAG crystal structure. However, the differences in behavior might also be related to more or less similarity between the fatty acids of TAG and emulsifier. Obstruction of transformation from α to a denser polymorph due to steric hindrance by an incorporated bulky emulsifier has been reported for stearic acid crystals as well [110].

Other Mechanisms

Tween® 60 added to a mixture of the high melting fraction of milk fat with trioleoylglycerol leads to the formation of smaller crystallites, due to its impact on the nucleation stage [99]. These smaller crystals give rise to an increased yield force. However, although glycerol has a similar impact on the yield force, it has an opposite effect on nucleation (induction time), leading to larger crystallites. Litwinenko et al. [99] speculated that the influence of glycerol must be attributed to increases in the crystal-melt interfacial tension, without indicating how this might occur.

In fat/sugar mixtures, saturated MAG in amounts over the solubility limit tend to precipitate as a network between fat or sugar crystals, which causes bulky sediments and results in better stability against oiling out [119]. The emulsifiers adsorb more strongly to sugar crystals than to fat crystals and form tightly packed monolayers with hydrocarbon chains directed to the oil.

The change in heat capacity of β tristearoylglycerol in the presence of emulsifiers [4] is explained as the result of mixed crystals. Three dimensional melting involves the whole crystal network disintegrating into the liquid phase. However, the authors of this study, on the heat capacity change, appeal to the concept of two dimensional melting, illustrated by Brinkman et al. [120]. This proposes that the relative stability of a crystal is nonetheless maintained

while thermal fluctuations give rise to dislocations and disorder in the crystal, allowing a gradual breakdown of the crystal network.

Additive Design

Predicting the effectiveness and specific influence of an additive in a fat is extraordinarily difficult from first principles. Some have taken a theoretical approach to move towards a rational design process. Thus, consideration is made of the specific types and location of growth sites and the effect, on crystallization and morphology, of blocking each of these [69]. This is simply the first step in a rational approach and much further work is necessary to cover the complete process. Currently, it is far better to explore the literature for something from which to modify and develop a new additive [114]. It is worth keeping in mind the general guideline, found throughout many publications, that similarity with the TAG molecular structure and affinity with the crystal matrix is a good starting point [27, 112, 114].

Conclusion

Over the years a steady stream of published research on minor components and additives has disclosed many effects on microscopic phenomena such as nucleation, crystal growth and morphology, as well as macroscopic effects such as post-hardening, rheology and visual aspects. The majority of research is of an empirical and descriptive nature. In a limited number of studies, underlying mechanisms are proposed, but these are not always properly supported by the experimental results. However, by combining the information gained out of a multitude of studies, a number of generic guidelines can be derived as to what to expect from minor components, be they indigenous or added.

The effect of minor components on crystallization, from nucleation to crystal growth and polymorphic phase behavior, is strongly dependent on the similarity between the bulk fat and the minor components themselves. The greater the similarity, the stronger is the effect, especially where this similarity is in terms of the acyl chain characteristics, such as length and number of double bonds. A high similarity allows integration into the crystal matrix and/or adhesion onto a crystal growth site. In addition, this explains why one additive may have different effects in different fats.

The degree of undercooling strongly influences the effect of minor components: increasing undercooling reduces the effect of the minor component. This may very well relate to different activation energies at different levels of undercooling as has been demonstrated in some specific cases.

The concentration at which a minor component influences the physical properties of the bulk fat varies greatly with the mechanism involved. Poisoning of growth sites, limiting crystal growth or changing morphology may be achieved at concentrations well below 0.1% w/w. However, to operate as heterogeneous nuclei, the concentrations typically have to be significantly higher. Note that since some components can play different roles, the concentration at which it is present may determine the dominant effect.

The general guidelines and the cumulative research should provide a good starting point for tailor made additives with dedicated functionality. The recent studies on interaction between additive and crystal growth sites are a clear indicator of developments in this direction. However, a number of shortcomings in the literature must be taken into account. One of the most significant of these is that the additives studied are commonly referred to by their trade name, despite the fact that—from brand to brand or even batch to batch—the precise composition might vary, and appropriate analytical data of the additive is rarely provided.

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